

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Research and Development for Health and Environmental Hazard Assessment-Task Order 5. Occupational and Environmental Hazards Associated with the Formulation and Use of White Phosphorus-Felt and Red Phosphorus-Butyl Rubber Screening Smokes		5. TYPE OF REPORT & PERIOD COVERED Final - Task Order 5 4/80 - 2/82
7. AUTHOR(s) J.B. Berkowitz A.J. Colella R.G. Thomas G.S. Young W.J. Lyman R.G. Vranka R.C. Anderson W.D. Steber A.L. Preston		6. PERFORMING ORG. REPORT NUMBER ADL 83744
9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. Acorn Park Cambridge, MA 02140		8. CONTRACT OR GRANT NUMBER(s) DAMD17-79-C-9139
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Medical Research and Development Command Fort Detrick, Frederick, MD 21701		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62777A.3E162777A846.00.019
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) U.S. Army Medical Bioengineering Research and Development Laboratory Fort Detrick, Frederick, MD 21701		12. REPORT DATE March, 1981
		13. NUMBER OF PAGES 176
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Approved for public release; distribution unlimited.		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Screening Smokes	Red Phosphorus-butyl rubber	Hazard Assessment
White Phosphorus	Production	Environmental Hazards
Red Phosphorus	Use	Exposure Assessment
White Phosphorus-Felt	Health Hazards	Toxicology
		Physical/Chemical Properties
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>This report is an assessment of potential health hazards associated with the production and use of white phosphorus-felt and red phosphorus-butyl rubber smoke munitions. Production and use information on the smoke munitions was collected through literature reviews, interviews, field visits, and model development in the following areas: 2 life cycle of the smoke compounds; 2 physical/chemical properties of raw materials and combustion products; 2 routes of environmental contamination; 2 exposure scenarios to workers, community and</p>		

field personnel; ~~by~~ human and wildlife toxicology, and ~~of~~ hazard assessment. The report concludes that the hazard associated with production of smoke munitions presents minimal risk to occupational health and safety, and the surrounding environment. Soldiers in the battlefield can be exposed to smoke concentrations above that noted for acute human effects. This risk is lowered by proper use of respiratory equipment. Future research from the perspective of hazard assessment should address characterization of smoke emissions, evaluations of exposure, and utilization of protective measures. ←

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RESEARCH AND DEVELOPMENT FOR HEALTH
AND ENVIRONMENTAL HAZARD ASSESSMENT

Task Order 5

OCCUPATIONAL AND ENVIRONMENTAL HAZARDS ASSOCIATED
WITH THE FORMULATION AND USE OF WHITE PHOSPHORUS-FELT
AND RED PHOSPHORUS-BUTYL RUBBER SCREENING SMOKES

Final Report

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US Army Medical Research and Development Command
Fort Detrick, Frederick, MD 21701

Contract No. DAMD17-79-C-9139

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FOREWORD

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1.0 EXECUTIVE SUMMARY

1.1 Introduction

On September 26, 1980, the Office of the Deputy Chief of Staff for Doctrine issued the U.S. Army Operational Concept for the Employment of Smoke and for Smoke Countermeasures (TRADOC pamphlet 525-3) which acknowledges that "U.S. Army Forces must be prepared to employ smoke and fight effectively in a smoke environment." Furthermore, the concept pamphlet describes tactics and techniques for the employment of smoke and for countermeasures against enemy smoke. The official promotion of a smoke concept has been preceded by a considerable amount of research involving production efficiency, effectiveness of obscuration, and potential harmful effects. The U.S. Army Medical Research and Development Command at Fort Detrick, Maryland, has been particularly concerned with the hazards of screening smokes and requested Arthur D. Little, Inc., to conduct a study of "Occupational and Environmental Hazards Associated with the Formulation and Use of White Phosphorus-Felt and Red Phosphorus-Butyl Rubber Screening Smokes." The study involved literature reviews, interviews and site visits with an ultimate objective of developing an assessment of the potential hazards associated with the manufacture and use of these particular smokes for the workforce, troops, the general community, and the environment. The following sections describe the results of this study and the assessment of hazards associated with the manufacture and use of these particular screening smokes.

1.2 The Life Cycle for Production and Use of Screening Smokes

The life cycle of white phosphorus-felt (WP-F) and red phosphorus-butyl rubber (RP-BR) smoke materiel includes the following phases:

- (1) blending of components to specified formulations
- (2) production of smoke materiel (projectiles, pots, and grenades)
- (3) quality assurance testing
- (4) packing of materiel for storage/shipment
- (5) transportation/storage of materiel
- (6) deployment of materiel in training/field use
- (7) demilitarization/disposal

The population exposed, the chemicals of concern, the nature of exposure, and the probability of exposure differ markedly in each phase of the life cycle. In phases (1) and (2) production workers might be exposed to individual components of formulations, and the combinations of components for 8-10 hours/day, five days a week. Also in phases (1) and (2), components, combinations of components, and/or transformation products might be released to the environment via stack emissions, wastewater effluents, and

residues for disposal from production lines and pollution control equipment. In phases (3), (4), and (5), exposure would be limited to relatively rare accidental events. In phase (6), troops might be exposed to a combustion aerosol which comprises the screening smoke. Dispersion, deposition, and fall-out of the aerosol components, and physical/chemical transformation of those components in the atmosphere, hydrosphere, lithosphere and biosphere create the potential for widespread environmental exposure. Phase (7) (demilitarization/disposal) has the potential for both workers and environmental exposure to formulations, combustion products, and transformation products, depending upon procedures employed.

1.3 Physical/Chemical Properties of Raw Materials and Combustion Products

The major raw materials and combustion products are characterized in Table 1. The actual chemical composition of screening smokes is a current topic of investigation by A. Snelson and coworkers at IIT Research Institute under Contract No. DAMD 17-78-C-8085 in the case of white phosphorous-felt, and by R. Holmberg and associates at Oak Ridge National Laboratory for red phosphorous-butyl rubber. The results of these studies, both supported by the US Army Medical Research and Development Command, will be used to reassess the findings of this report and to plan inhalation toxicity studies of the phosphorus smokes.

1.4 Routes of Environmental Contamination

Potential routes of environmental contamination resulting from production operations include:

- Workplace air
- Stack emissions
- Land/water deposition of air emissions
- Wastewater discharge
- Solid waste discharge

During field use combustion products will be airborne and eventually will deposit on land or water. Residual formulation may also be dispersed into the environment. Except for field use, pollution controls limit the extent of environmental contamination. On the other hand, control failure can result in high levels of contamination.

1.5 Exposure Scenarios

In order to develop a better understanding of the types, levels, and routes of potential exposure, scenarios are presented for specific segments of the WP-F and RP-BR life cycles which, in general, are considered to consist of two distinct phases: (1) production of smoke screen munitions and related demilitarization and disposal activities, and (2) use of smoke screens under training and battlefield conditions.

TABLE I PHYSICAL/CHEMICAL PROPERTIES OF RAW MAT

MATERIAL (reference)	APPEARANCE	PROCESS INTRODUCTION POINT	MELTING POINT	BOILING POINT	DENSITY	AUTOIGNITION TEMPERATURE	CRITICAL TEMPERATURE	CRITICAL PRESSURE	HEAT CAPACITY (cal/mol deg)	HEAT OF FUSION (cal/mol)	CO (M)
White Phosphorus P_4	Colorless to yellow waxy solid	Raw material	44.1°C	280.5°C	1.828 g/cm ³	30°C (moist air)	695°C	82.2 atm	22.18 at 25°C 22.73 at 44.1°C	600 ± 3 per mole of P_4	72
Red Phosphorus	Red-brown powder	Raw material	sublimes at 416°C		2.34 g/cm ³	260°C in air	589°C	43.1 atm	5.1 at 25°C /mole P		
Methylene Chloride CH_2Cl_2	Colorless liquid	Raw material	-95°C	40°C	1.3266 g/cm ³	624 -622°C	237°C	60 atm	24.5 at 15°- 45°C	1100	
Phosphorus Pentoxide P_4O_{10}	White crystal	Combustion product	420°C (sublimes at 360°C 1 atm)		2.3 g/cm ³				50.6 at 25°C	8200	
Phosphorus Trioxide P_4O_6	Colorless liquid	Combustion product	23.8°C	175.4°C	2.135 g/cm ³				34.4 at 25°C 41.2 at 127°C		
Orthophos- phoric Acid H_3PO_4	Colorless crystalline solid	Combustion product	42.35°C	261°C	1.8741 g/cm ³				25.3 at 25°C		
Phosphorus Acid $H_2(HPO_3)$	Deliquescent colorless	Combustion product	70.1°C		1.65 g/cm ³					3070	
Polyphos- phoric Acid 2-6		Combustion product									
Phosphine PH_3	Colorless liquid	Combustion product	-133.8°C	-87.8°C			51°C	64 atm	8.9 at 25°C	270	

PHYSICAL PROPERTIES OF RAW MATERIALS AND COMBUSTION PRODUCTS

PHYSICAL PROPERTY	HEAT CAPACITY (cal/mol deg)	HEAT OF FUSION (cal/mol)	HEAT OF COMBUSTION (kcal/mol)	VAPOR PRESSURE (mm Hg)	HEAT OF SUBLIMATION (kcal/mole)	SOLUBILITY	ENVIRONMENTAL TRANSFORMATIONS	ENVIRONMENTAL FATES
atm	22.18 at 25°C 22.73 at 44.1°C	600 ± 3 per mole of P ₄	710.2±1.0	1 at 76.6°C	13.4 per mole of P ₄	Slightly soluble in hot H ₂ O 2.5 g/l ² EtOH 10 g/l ether 25 g/l CHCl ₃ 125 g/l carbon disulfide	$4P + 5O_2 \xrightarrow{\text{Combustion}} P_4O_{10}$ $P_4O_{10} \xrightarrow[\text{Moisture}]{\text{Atmospheric}} 4H_3PO_4$ $4P + 3O_2 \xrightarrow{\text{Combustion}} P_4O_6$ $P_4O_6 \xrightarrow[\text{Moisture}]{\text{Atmospheric}} 4H_3PO_3$ PH ₃ (trace)	P ₄ - Hazardous waste landfill Aquatic and soil Fate is oxidation to phosphates via lower oxides
atm	5.1 at 25°C /mole P		703.2±.5			Very slightly soluble in H ₂ O Insoluble in most organic solvents	See white phosphorus transformations	
atm	24.5 at 15°-45°C	1100	144.5	436 at 25°C		Slightly sol. in H ₂ O Sol. in EtOH Sol. in ether	Will react with atmospheric radicals to form phosgene, CO, etc.	Photochemical decomposition
	50.6 at 25°C	8200			22.7	Hydrolysis	Reacts with atmospheric moisture to form oxyacids of phosphorus	Aquatic and soil deposition of phosphates and lower oxides
	34.4 at 25°C 41.2 at 127°C					Hydrolysis	$P_4O_6 \xrightarrow[\text{vapor}]{H_2O} 4H_3PO_3$	Forms H ₃ PO ₄ , PH ₃ , phosphites
	25.3 at 25°C					All proportions	pk ₁ =2.15, pk ₂ =7.1 pk ₃ = 12.4 phosphates	Land and water deposition, calcium, iron and aluminum phosphate salt formation
		3070				All proportions	pk ₁ = 1.8 $4H_2(HPO_3) \xrightarrow[250-275^\circ C]{\Delta} 3H_3PO_4 + PH_3$ phosphite & phosphate salt formation	Land and water deposition, oxidation (slow) to phosphates, possible production of phosphine
							Will form phosphates	Land and water deposition, conversion to phosphate
atm	8.9 at 25°C	270				Sparsingly soluble	Oxidized to form oxyacids of phosphorus	Oxidized or dissociated

A scenario for production was developed, based upon observations of the facilities at the Pine Bluff Arsenal, to describe the fill, close, and packout (dry fill) operation and, specifically, the loading of burster casings into filled canisters. The scenario addresses a series of hypothetical circumstances which could lead to skin contact with white phosphorus. The production scenario also addresses exposure to flora/fauna and exposures related to the pollution control/waste facility. A major focus for RP-BR scenarios in the circumstances which could lead to inhalation of methylene chloride vapors.

Scenario development for training and field use was more complex because of the variability of applications and conditions. Specific scenarios address: (1) small cloud generation using the L8A1 vehicle-mounted grenade, (2) one-time deployment of WP-F smoke with mortars or rockets to screen a large area, and (3) sustained coverage of a large area using WP-F deployed by field artillery. These scenarios describe the circumstances of deployment, the subsequent dispersal of smoke, and their relationship to human or flora/fauna exposures. In general, the scenarios demonstrate that smoke deployment will result in extremely high airborne concentrations over a very limited area. While there are no empirical data which can describe the spatial relationship between troops and smoke screens, the scenarios suggest that the confluence of troops and high smoke concentrations is unlikely. Appendices to Section 3 describe the dispersion models utilized in scenario development and the particle size distribution of smoke clouds.

1.6 Toxicology of WP-F and RP-BR Smokes

A detailed review of the toxic effects of white and red phosphorus and other smoke formulation ingredients is provided in Section 4. In general, it is noted that one would expect a concentration range for any toxic effect rather than a sharp cut-off point between effect and no-effect. For most species tested, it appears that the critical concentration measured as an LC_{50} is about $2,000 \text{ mg/m}^3$. Human exposures at concentrations between 100 and 700 mg/m^3 for less than 15 minutes are associated with reversible pulmonary symptoms and mucous membrane irritation. A longer duration of exposure at these lower concentrations may be associated with more serious effects. Unfortunately, there is no model by which the data on known health effects can be extrapolated to predict safe and unsafe exposure levels and periods. Furthermore, potential effects will vary depending upon the composition of the smoke which, in turn, depends upon weather conditions, particularly humidity.

Other toxic chemicals used in the production of WP-F or RP-BR smokes include methylene chloride, which is used in compounding RP-BR and is associated with depression of the central nervous system, irritation of the eyes and upper respiratory tract, pulmonary edema, and blood carboxy-hemoglobin formation. It has been studied for carcinogenic effects, but no long-term carcinogenicity data are currently available.

1.7 Hazard Assessment

The objective of any hazard assessment is to identify hazards and to quantify risks. The major limitation for the hazard assessment process is the lack of a comprehensive data base, and this limitation is particularly acute for assessing the hazards of the future manufacture and use of WP-F and RP-BR smokes.

The hazard assessment addresses the two major phases of the smoke life-cycle (production and use) individually. The results of the assessment indicate that the production of WP-F and RP-BR screening smokes can be conducted with minimal risk to occupational safety and health and the surrounding environment. Pine Bluff Arsenal has established safe operating procedures, including requirements for the use of personal protective equipment. In case of exposure, emergency eye wash and whole body drenching tubs are available. To prevent the development of chronic disease from long-term low-level phosphorus exposure, the Arsenal conducts a dental health surveillance program. In addition, the planned conversion to enclosed dry line operations will reduce emissions from production operations.

By reducing process water utilization, the dry line also reduces the potential for environmental impacts. More importantly, the development of a zero discharge pollution control system will eliminate the problems previously associated with process emissions.

Industrial hygiene, medical surveillance, and pollution control programs are vital aspects of WP-F and RP-BR production and, when strictly enforced, serve to control a variety of potential hazards.

The deployment of WP-F and RP-BR screening smokes in training or testing field activities presents some hazards which, to a large extent, can be controlled with proper planning and utilization of protective equipment. Community risks can be eliminated by locating training sites in isolated areas. Community risks are not expected to be severe, especially if the distance downwind from the deployment site to the site of any potential community exposure is greater than 300m. As noted in Table 2 and as described in Section 5, susceptible members of the community (e.g., persons with chronic pulmonary disease or asthma) may suffer symptoms of irritation at distances of about 5,000m downwind from the deployment site, and this distance should be considered as a minimum separation between smoke training areas and susceptible residential populations. In wartime, community exposure cannot be well controlled; however, the hazards of screening smokes are negligible in comparison with other hazards of war.

If deployment is concentrated on a small area, environmental impacts are likely; however, they are reversible as shown by the recovery of the area surrounding the production facility at Pine Bluff.

TABLE 2
COMMUNITY EXPOSURE ESTIMATES

<u>Distance Downwind From Deployment</u>	<u>Maximum Concentrations (P₂O₅) ($\mu\text{g}/\text{m}^3$)</u>	<u>Health Effects</u>
100 m	1.46×10^5	Intolerable concentra- tion = $10^6 \mu\text{g}/\text{m}^3$ Minimum harassing concen- tration, masks mandatory = $7 \times 10^5 \mu\text{g}/\text{m}^3$
200 m	6.98×10^4	
300 m	4.36×10^4	Lowest toxic concentra- tion = $10^5 \mu\text{g}/\text{m}^3$
400 m	3.06×10^4	
500 m	2.26×10^4	
600 m	1.84×10^4	
700 m	1.51×10^4	
800 m	1.26×10^4	
900 m	1.10×10^4	
1000 m	9.42×10^3	
5000 m	9.63×10^2	Phosphoric Acid TLV = $10^3 \mu\text{g}/\text{m}^3$

Phosphorus smoke concentrations necessary to maintain an effective screen are greater than those which have been reported to cause death in some laboratory animals and acute effects in man. Thus, if it is assumed that troops may be exposed to such concentrations in training or during tests, the major factors that must be considered in estimating hazard are the availability, effectiveness, and proper use of respiratory protection. The US Army Medical Research and Development Command is currently sponsoring research on the health effects of phosphorus smokes in order to obtain more quantitative information than is now available on the toxic response to current battlefield smokes. These data can be used to more precisely define the hazard and to define the necessary level of protection to be provided to the troops by the respiratory protective device.

1.8 Discussion

The scope of work for this project required the collection of information for an initial estimate of the occupational and environmental hazards posed by the manufacture and use of WP-F and RP-BR screening smokes. Information was collected from a variety of sources including published literature, on-going research conducted by U.S. Army personnel and contractors, and site visits to Aberdeen Proving Ground and the Pine Bluff Arsenal. In addition, models were developed to characterize the environmental fates of the products of smoke deployment. All of this information was reviewed and served as a foundation for developing exposure scenarios and, subsequently, assessment of hazards.

The major problem associated with this logical series of tasks, and a persistent theme throughout the report, is the lack of a comprehensive precise data base.

From the perspective of hazard assessment, there are three basic areas where additional data are needed:

- (1) Characterization of emissions,
- (2) Evaluation of exposures, and
- (3) Utilization of protective measures.

On-going research at the Illinois Institute of Technology Research Institute (IITRI) is focusing on the identification of the products of screening smoke combustion. To date, little work has been conducted to evaluate exposures either in the occupational setting or in the field. During the information collection phase of the study only two industrial hygiene surveys at Pine Bluff Arsenal were identified. No attempts to measure personal exposure in the field were identified. Industrial hygiene sampling techniques should be applied to measure both worker and troop exposure.

Identification and evaluation of hazards should be followed by controls both for the protection of workers and troops and for the protection of the environment.

2.0 LIFE CYCLE DESCRIPTION

2.1 Introduction

The life cycle of WP-F and RP-BR smoke materiel includes the following phases:

- (1) blending of components to specified formulations
- (2) production of smoke materiel (projectiles, pots, and grenades)
- (3) quality assurance testing
- (4) packing of materiel for storage/shipment
- (5) transportation/storage of materiel
- (6) deployment of materiel in training/field use
- (7) demilitarization/disposal

This chapter describes the various phases of the life-cycle, with particular emphasis on potential points of human and environmental exposure to smoke materiel components, formulations, combustion products, and transformation products.

The population exposed, the chemicals of concern, the nature of exposure, and the probability of exposure differ markedly in each phase of the life cycle. In phases (1) and (2) production workers might be exposed to individual components of formulations, and to combinations of components for 8-10 hours/day, five days a week. In phase (2) production workers may also be exposed to combustion products of white phosphorus, especially during the washdown of the dry-filled canisters after filling and inertial sealing of the canister cap. Also in phases (1) and (2), components, combinations of components, and/or transformation products might be released to the environment via stack emissions, wastewater effluents, and residues for disposal from production lines and pollution control equipment. In phases (3), (4), and (5), exposure would be limited to relatively rare accidental events. In phase (6), troops might be exposed to a combustion aerosol which comprises the screening smoke. Dispersion, deposition, and fall-out of the aerosol components, and physical/chemical transformation of those components in the atmosphere, hydrosphere, lithosphere and biosphere create the potential for widespread environmental exposure. Phase (7) (demilitarization/disposal) has the potential for both workers and environmental exposure to formulations, combustion products, and transformation products, depending upon procedures employed.

2.2 Production

The production of white phosphorus-felt screening smokes will probably be limited to the production facilities at the Pine Bluff Arsenal in Pine

Bluff, Arkansas. Plans to develop a production line for red phosphorus-butyl rubber screening smokes have been postponed because funds have not been appropriated. For the next few years, RP-BR will be supplied from production facilities in Great Britain. For the purposes of this report, the description of RP-BR production will be based upon available program plans.

2.2.1 Formulation Process

The traditional process in use at Pine Bluff Arsenal since World War II for formulating and manufacturing white phosphorus screening smokes has been a dip fill or wet line process whereby shells are conveyed on wheeled pallets into a tank containing molten white phosphorus covered by a layer of phosphy water to prevent oxidation of the phosphorus (Figure 1). When the shells are submerged in the tank, the air in each munition is displaced, first by water and then by WP. After leaving the tank, excess WP is manually aspirated to the required filling level and a burster is inserted to close the shell. Since the outside surfaces of the shells are contaminated with WP, they must be cleaned with water sprays and detergent prior to painting, marking, zoning, and leak-testing. This process is rather labor-intensive, requiring thirty-two (32) employees when filling 8000-105 mm munitions per eight-hour shift for the operating three lines. Most of the labor requirements are related to material handling rather than working directly on the production line.

The major problem with this process is frequent spillage of WP, contamination of line equipment and munitions, and employee exposure to WP and P_2O_5 fumes. These shortcomings are related to extensive levels of air and water emissions and to occupational safety and health hazards associated with such an open system. The advantages and disadvantages of the wet fill are shown in Table 3.

In order to reduce the problems related to pollution and worker safety and health, and presumably to increase production efficiency, a dry fill process has been developed in which the munition is filled directly with WP through a nozzle in an inert gas cabinet. (Figure 2). This system reduces spills, emissions, and contamination of the process line. Spills are controlled by the use of a volumetric filling system which delivers premeasured volumes of WP to the nozzle reservoir (Figure 3). In 1976 during a trial run of 105 mm munitions, 5,000 shells were filled with a high degree of accuracy. It was reported that air pollution was negligible and water pollution was reduced by more than 95%. During the trial, labor requirements were reduced from 32 to 12, of which 8 were material handlers. The 105 mm canisters were filled at a rate of 24/min. Dry fill operations are listed in Table 4.

A significant feature of the filling process is the use of an enclosed cabinet (7' x 3' x 12') on the conveyor which is supplied by an inert gas generator. The purging and filling operations occur automatically as munitions are conveyed inside the cabinet. The Phase II plans of the

BLDG. 34-110 DIP FILL PROCESS

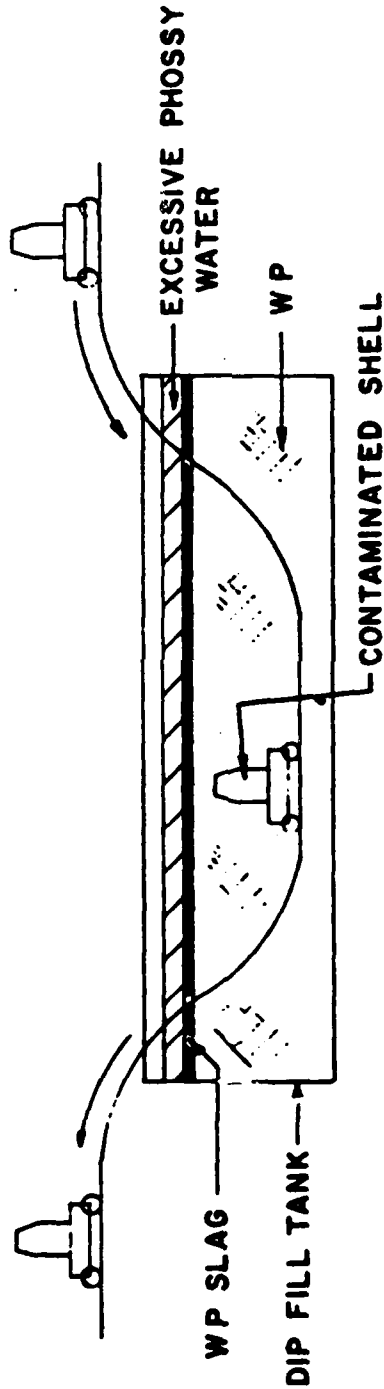


FIGURE 1. Dip Fill (Wet Fill) Process

Source: Stewart and McKinney (1977).

TABLE 3

ADVANTAGES AND DISADVANTAGES OF WET FILLING

ADVANTAGES OF WET FILL:

1. Unsophisticated equipment
2. Low first cost
3. Adequate production record

DISADVANTAGES OF WET FILL

1. Grossly contaminated production line equipment
2. Unacceptable quantities of heavily contaminated air and water--does not meet EPA standards
3. Cannot meet OSHA requirements for personnel safety
4. Large manpower requirements
5. Contaminated munitions which require cleaning and repainting
6. Less accuracy on filling requirements
7. Heavy maintenance requirements and excessive downtime.

Source: Stewart and McKinney (1977).

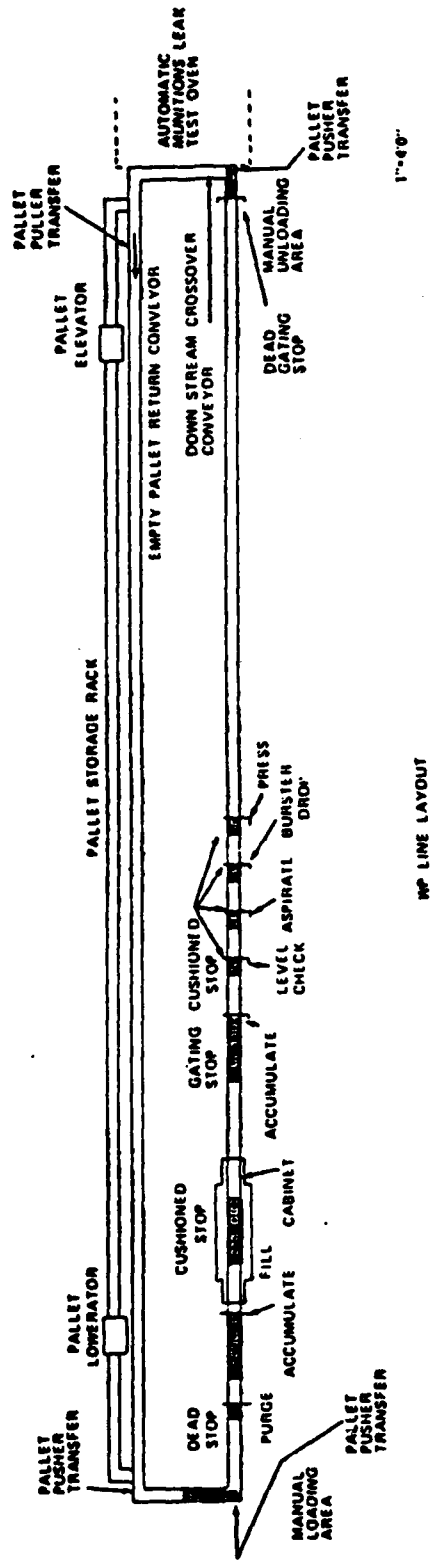


FIGURE 2. WP Dry Filling Line Layout

Source: U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD

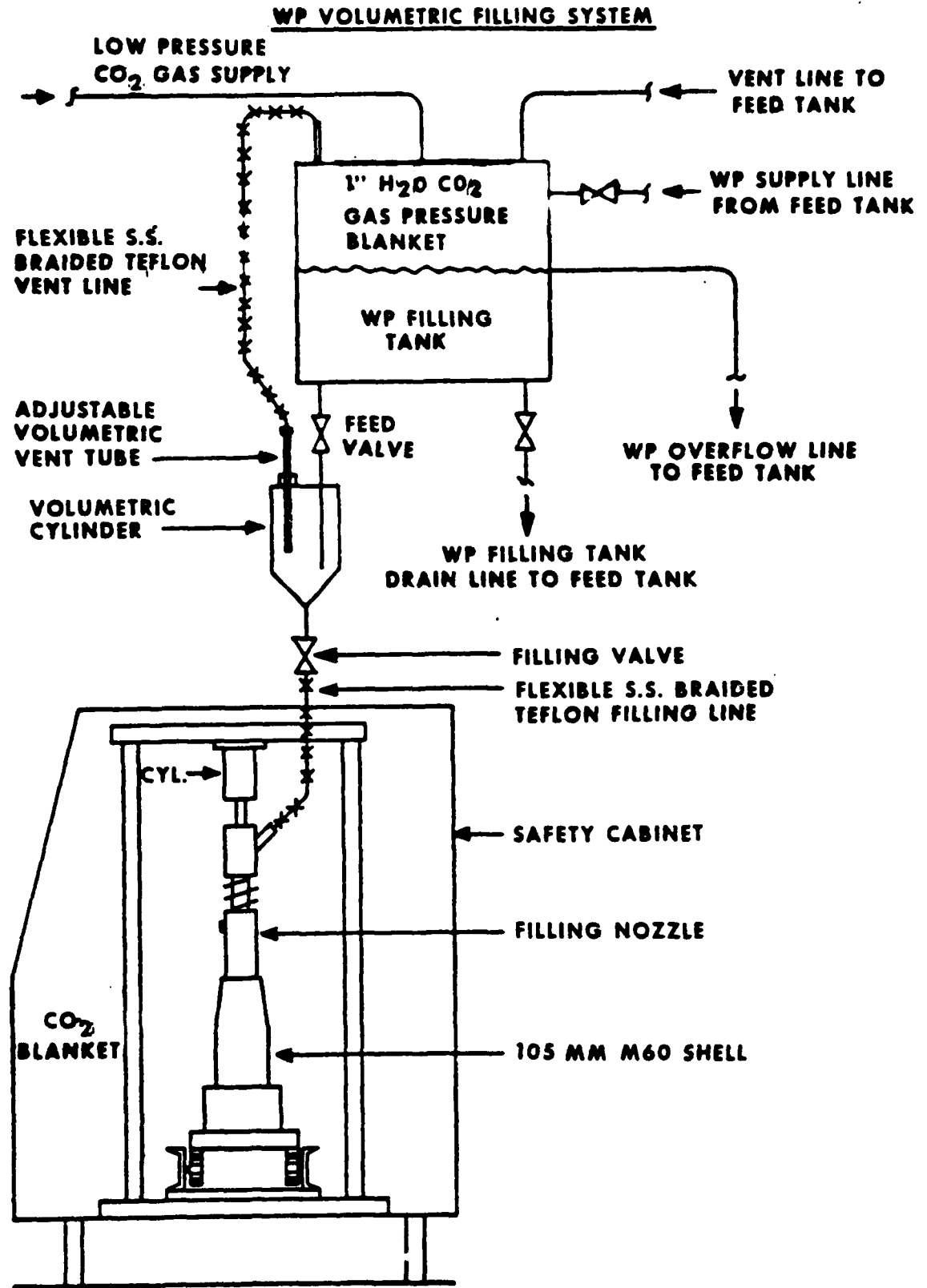


FIGURE 3

Source: Stewart and McKinney (1977).

TABLE 4.

DRY FILL LINE 3: FILL, CLOSE AND PACKOUT

<u>Operation No.</u>	<u>Operations</u>
1	Transfer cartridge from empty storage
2	Start-up procedure: Inert gas generator and WP transfer into filling and storage tanks
3	Prepare empty bodies for filling
4	Transfer bodies to filling line
5	Degrease cartridges
6	Place bodies on filling conveyor
7	Operate and monitor Work Center "D"
8	Start-up procedure: WP Filling Line No. 3
9	Cabinet opening procedure
10	Operate and monitor Work Center "D"
11	Operate and monitor Work Center "C"
12	Load burster casing into filled munitions
13	Press burster casing
14	Unload filled munitions
15	Place cardboard sleeves over cartridges and load cartridge to oven pallets
16	Leakage test of cartridges in oven
17	Inspect cartridge, insert shipping plug and load shipping pallets
18	Close and strap pallets
19	Shut down procedure

Source: Pine Bluff Arsenal Operating Directives

dry fill project call for expansion of the line for a capacity of 8,000 munitions per 8-hour shift. Munitions which will be filled on this line include 60 or 81 mm mortars, 2.75-inch rockets, and 105 mm artillery projectiles. At present, WP production at Pine Bluff consists of 3 wet lines and 1 dry line (Figure 4). Long-range plans call for complete conversion to dry lines, but that may not occur for 10 years. In the meantime, substantial efforts have been made to control the levels of air and water pollution from the wet lines.

Red phosphorus grenades are currently produced in Great Britain. RP-BR is formulated in 200-pound batches. The process involves adding 18% of methylene chloride to the ground-up butyl rubber to form a syrup mixture which is mixed with red phosphorus. The resulting 95% RP, 5% BR composition is dried in outdoor drying ovens and is chopped into 60g plugs. Each grenade is loaded with 360g (six plugs) of the RP-BR mixture.

According to officials at Pine Bluff Arsenal, RP-BR munitions production is tentatively scheduled to begin in 1985. The planned production facility will be located in a renovated 10,000 sq ft building. Exxon 365 (butyl rubber) will be supplied in small bales which will be processed by a guillotine chopper and grinder. Processed BR will be plasticized with RP in an enclosed kneader-extruder using methylene chloride as the solvent. Extruded granules will be transferred on trays to an outdoor drying oven to evaporate the excess solvent. Six 60g batches of granules will be pressed to form a 360g pellet which will be inserted into a rubber sleeve, which in turn will be inserted into the L8A1 grenade.

2.2.2 Controls and Personal Protection

While some ventilation is provided on the WP-F wet line process, the primary strategy for protecting workers is the use of personal protective equipment and the provision of showers and plunge tanks. Employees on the production line are required to wear flame-proof coveralls and a cap, safety shoes, cotton underwear and socks, a Graylite safety apron to 3" below boot tops, a flashmask (face shield) and rubber gloves. The Pine Bluff Arsenal safety protocol for the WP filling plant includes detailed first-aid recommendations. The plant is equipped with several plunge tanks and flood-type showers which are available for use in case of WP burns.

Medical surveillance, particularly comprehensive dental examination, is an important control procedure. Each employee in WP production is examined biannually and banned from work if any of the following conditions are discovered: large carious lesions, badly broken-down teeth, or active

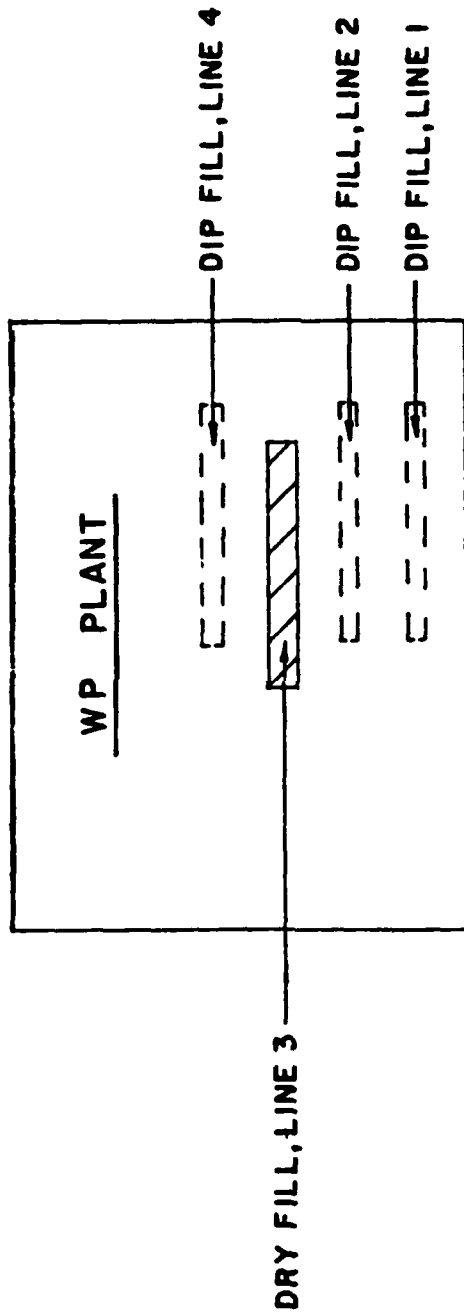


FIGURE 4. WP Plant Layout

Source: Stewart and McKinney (1977).

periodontal disease. Evidence of a need for more routine dental work is followed and can lead to suspension from work if the problems (e.g., caries, scaling and cleaning) are not treated.

The provision of enclosed booths on the dry line is an important engineering control. However, because of the potential hazard, dry line employees are also required to wear the full range of protective equipment.

Information concerning controls for the RP-BR process is limited, particularly control of methylene chloride vapors. The kneader-extruder is a closed process but collection of granules on trays could allow considerable vapor emissions. Unless ventilation controls are provided, standard industrial hygiene practice dictates that respiratory protection should be worn if airborne levels approach the NIOSH proposed OSHA permissible exposure limit of 75 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 500 ppm averaged over a 15-minute period. Since the toxic effects of methylene chloride may be enhanced by carbon monoxide, this compound should also be carefully controlled in RP-BR operations.

2.2.3 Points of Potential Human and Environmental Exposure

2.2.3.1 Air Emissions

The present white phosphorus wet line operation generates air emissions of phosphorus compounds. In order to remove fumes from the work place, 20,000 cfm of P₂O₅-contaminated air is scrubbed and vented through three stacks, two of which are 100 feet and the other 27 feet high. These Venturi scrubbers remove 95% of the P₂O₅. (Permit - Arkansas Department of Pollution Control and Ecology 7/28/78.)

White phosphorus dry line emissions are not known, although fugitive emission of phosphorus containing fumes is likely. The dry line process should have significantly lower emissions.

The most significant air emission during red phosphorus production is methylene chloride. Planned control strategy (Permit Application - Arkansas Department of Pollution Control and Ecology - 5/10/79) consists of a 50-foot high stack for venting commercial grade methylene chloride from the RP-BR drying oven. Ninety percent of the methylene chloride will be removed by charcoal adsorbers with steam regeneration. Two adsorbers will be available, one to be used while the other is being regenerated. Forty-seven lb/hr of methylene chloride and 185 lb/hr of steam are condensed, stored, hauled, and incinerated. Five lb/hr of methylene chloride will escape to the atmosphere. The system will operate six hours or less per day, five days a week, year round, indicating

that as much as 7800 lb/yr of methylene chloride could be emitted. Two hundred fifty pounds of methylene chloride is used per 1000 pounds of product, resulting in an emission of 25 lb/1000 pounds of product. The 5 lb/hr emission rate has been calculated to result in ambient air concentrations of much less than the 160 $\mu\text{g}/\text{m}^3$ (.25 ppm) volatile hydrocarbon standard at the boundary of the Arsenal, which is 4000 feet from the proposed emission point. The standard would be exceeded only at emission levels greater than 36.3 lb/hr.

2.2.3.2 Water Discharges

Scrubber and munition rinse water (phossey water) are used in the WP-F production process. This water is treated and recycled so the system is closed. The scrubber water is neutralized and sent to a steam evaporator; the condensed water is reused in the scrubbing system. Approximately five gallons per minute of makeup water is added to the scrubber system. Approximately 5000 gallons per eight hour shift of phossey water, which contains phosphorus, phosphoric acid, and phosphates, is treated with ozone. The phosphorus is oxidized to P_2O_5 which is vented to the scrubbing system. The ozonated water is then reused to rinse contaminated munitions as they leave the wet line.

Minimal amounts of water are used in the dry line system. Phossey water can be ozonated and recycled as in the wet process.

The conversion to all dry production will scale down the water treatment needs but the basic treatment system will probably remain the same.

No information is currently available concerning water discharged from the red phosphorus process. If any water is used, it is possible that it may be contaminated with phosphorus compounds similar to those found in the white phosphorus processes, as well as methylene chloride. White phosphorus is highly toxic to aquatic organisms and to humans exposed by ingestion; red phosphorus is less toxic to humans. Information was not available regarding the toxicity of red phosphorus to aquatic species.

2.2.3.3 Solid Discharges

There are two sources of solid waste for WP-F production--still bottoms from the molten phosphorus tanks and slags from the scrubbing operation and subsequent white phosphorus platform recovery. The solids from the scrubbing operation in white phosphorus-felt production are processed to recover phosphorus.

The ashes which will contain metals and possibly some phosphorus compounds are quenched with water. Quenching could possibly produce some phosphine from the reaction of metal phosphides and water. The ashes will be presently stored on site and subsequently landfilled when a hazardous waste landfill becomes operable in 1984 at Pine Bluff.

Proper containment in the landfill will minimize environmental effects of the disposed solids. Possible escape paths to either water or soil systems are leachate or run-off. Metals could be incorporated into the aqueous phase and then concentrated in biological systems.

The residual is currently stored in drums. The residual probably contains P_4 , phosphates, and carbonates. A fluidized bed incinerator unit is expected on line in the near future in which the scrubber slag will be burned. Ashes will be quenched with water and then buried in a hazardous waste landfill which is scheduled to be operating in 1984. Still bottoms from the wet and dry lines are also currently stored in drums at Pine Bluff. Still bottoms probably contain P_4 in small amounts and other phosphates. This waste will be disposed in the tentatively planned waste landfill at Pine Bluff.

The total generation of solid waste is 100 pounds per operating day. This includes the still bottoms and the scrubber system waste solids. Any waste containing P_4 would be considered hazardous under RCRA and would have to be disposed in accordance with their regulations. Conversion to all dry line production will reduce the scale of this problem but not eliminate it. The same handling procedure is planned for the still bottoms of phosphorus holding tanks.

2.2.3.4 Summary

The environmental releases of pollutants from WP-F (wet line) and RP-BR production are summarized in Figures 5 and 6. Releases from WP-F dry line production are much less than for wet line. Air emissions are negligible. Contaminated wastewater is 95% the volume generated by the wet line. Still bottoms are treated in the same manner for both production lines.

2.3 Field Use

Smokes have a variety of applications in modern military tactics and can be generally classified as obscuration, screening, or identification smokes. An important role of smoke is to degrade the effectiveness of modern weapon systems which rely upon sophisticated electro-optical acquisition and guidance systems. For example, obscuration smoke may be delivered on an enemy antitank guided missile (ATGM) position to prevent it from acquiring targets. Obscuration smokes may also be used against an attacking armored force to cause it to vary its speed or direction. Screening smokes, on the other hand, are employed in areas of friendly troop operations or between friendly troops and the enemy to conceal ground maneuvers or to create false impressions of movements. Identification smokes are employed to identify targets and positions or can be used for communications.

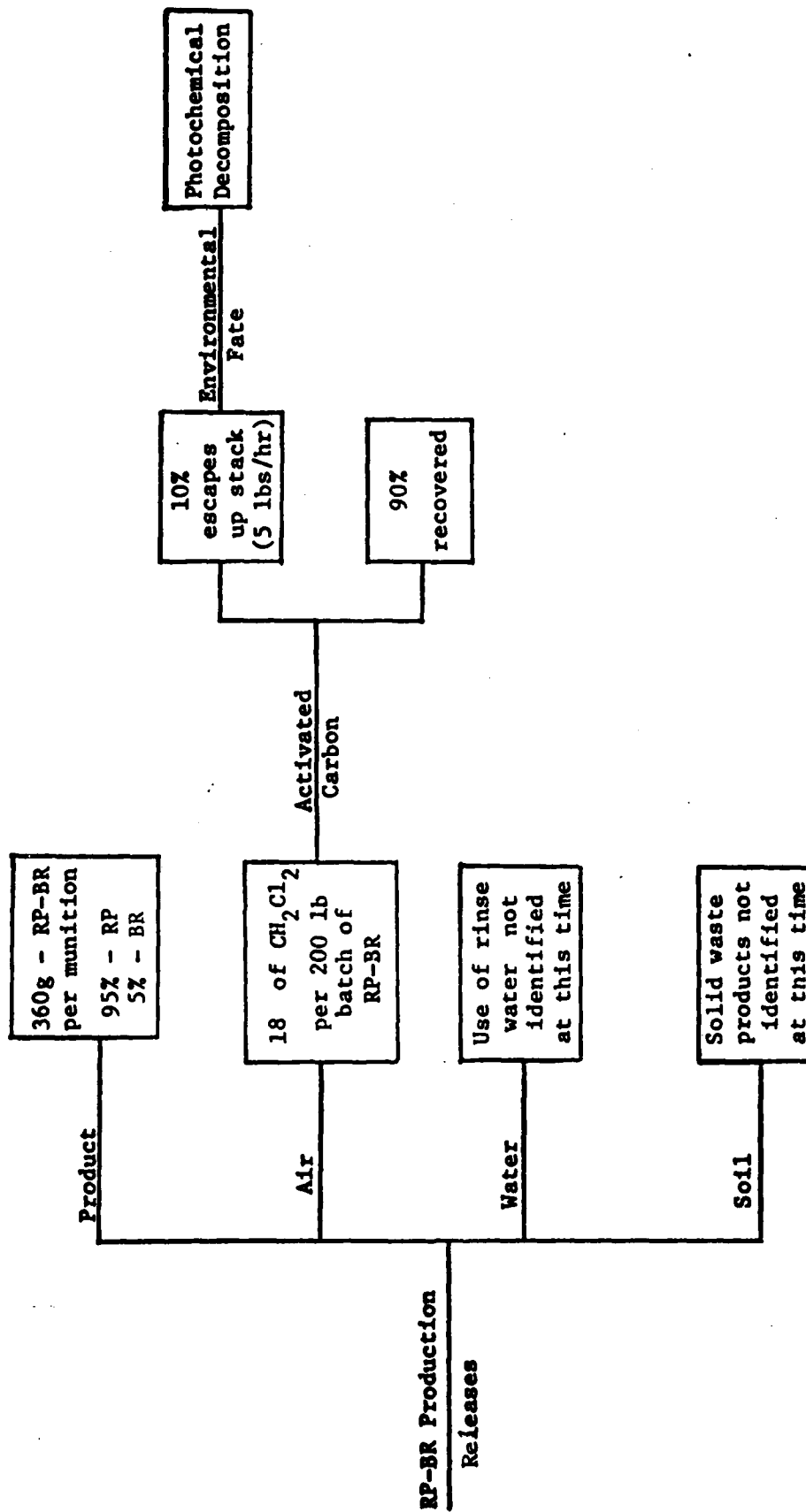


FIGURE 6
PRODUCTION SCENARIO RP-BR

While the general uses and tactics of battlefield smokes are relatively straightforward, there appears to be an endless variety of specific scenarios for deployment depending upon factors such as location, meteorological conditions, numbers and types of friendly and enemy troops and equipment, tactical considerations such as attack, retreat, flanking movement and deceptive movements. Two Army publications; "Small Unit Operations" and "Concept: Smoke, a Combat Multiplier," provide excellent scenarios for smoke use, but, because of the variability of battlefield operations, no scenarios can be construed to represent "typical" conditions. On the other hand, they do provide sufficient information for the purposes of developing hazard assessments.

Our present understanding is that white phosphorus-felt will be deployed by field artillery, while red phosphorus-butyl rubber will be deployed from tank-mounted grenade launchers. It is anticipated that these smokes will eventually be used in mortars, smoke pots and other systems. The following section provides a general discussion of various deployment procedures.

2.3.1 Deployment Procedures

There are 5 basic systems for producing smoke: (1) Field artillery cannons, (2) Mortars, (3) Smoke pots, (4) Smoke grenades, and (5) Vehicle smoke grenade launcher. Field artillery are used to deliver 155 mm and 105 mm smoke on distant targets. Normally, the use of artillery requires careful planning and, because of the long range, does not represent a direct hazard to friendly troops. Mortars (81 mm and 4.2 inch) can deliver a high volume of smoke at mid-ranges in a specific area and also require some planning prior to deployment. Smoke pots produce large volumes of smoke for extended periods of time. Pots are emplaced by hand or can be dropped from vehicles or helicopters and can be ignited manually or by remote electronic signal. At present, smoke pots are limited to the hexachloroethane and fog oil types. White smoke grenades are used to cover or screen individual vehicles while colored smoke grenades are used to mark or spot specific locations. Sometimes they are used as diversionary smokes. The average soldier can throw a grenade 30 to 35 meters. Grenades such as the L8A1 can also be launched from vehicles such as tanks or armored reconnaissance vehicles. They are designed for emergency evasive maneuvers and can generate smoke rapidly to conceal or screen individual vehicles from the enemy.

Present plans call for the use of white phosphorus (in a matrix of either felt or fiberglass) in 155mm artillery rounds and 2.75 inch rockets, and red phosphorus in the L8A1 vehicle-launched grenades and probably in the 81mm mortar. The use of phosphorus in other munitions is not certain. Smoke pots and white smoke grenades may use phosphorus, but colored smoke grenades almost certainly will not.

While the techniques for the tactical deployment of smokes are numerous, some basic techniques can be described (Table 5).

TABLE 5

EXAMPLES OF TACTICAL SMOKE DEPLOYMENT

Offensive Tactics

- Blind enemy observers with artillery and mortars
- Obscure vehicles from enemy direct fire with grenades
- Conceal a bypass with artillery and mortars
- Screen an assault with smoke pots
- Cover a breaching operation with all deployment types

Defensive Tactics

- Slow the advance of attacking forces with artillery and mortars
- Separate and isolate attacking echelons with mortars
- Force enemy infantry to dismount from mechanized vehicles with artillery and mortars
- Cover movement with smoke pots
- Expose enemy helicopters with artillery and mortars

Smoke Countermeasures

- Use artillery and mortar countersmoke to blind enemy defenders
- Use enemy smoke to cover a defensive maneuver
- Use close air support aircraft and attack helicopters to fly above enemy smoke and attack.

2.4 Demilitarization/Disposal

Munitions which are retired or outdated are processed to recover phosphorus. The munition shell, which will still be contaminated with P_4 , is incinerated in the fluidized bed incinerator at Pine Bluff which will be operable in the near future. The residual P_4 will yield combustion products of oxy-acids of phosphorus, phosphates, phosphites, and possibly trace amounts of phosphine.

3.0 EXPOSURE SCENARIO

3.1 Introduction

Chapter 2 described the points of potential human and environmental exposure during the life cycle from production, through use, to disposal of smoke materiel. This chapter first describes the nature of the potential exposure, including:

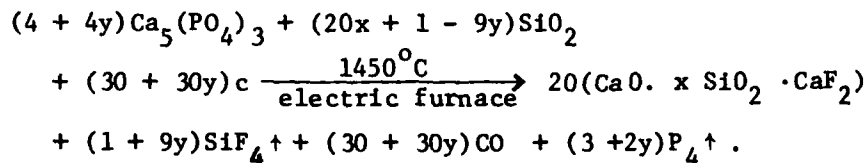
- chemical composition, physical form, and physical/chemical properties affecting environmental transport of raw materials used in formulations, fabricated products, combustion products, and transformation products.
- routes of transport in both the workplace and ambient environment.
- estimated concentrations of chemical species in affected areas of the workplace and ambient environment.
- duration of exposure of receptor organisms.

Finally, a number of production and field use scenarios are described, to serve as a basis for subsequent hazard assessment.

3.2 Environmentally Significant Properties of Raw Materials and Products

3.2.1 White Phosphorus

White phosphorus is one of the two raw materials in WP-F munitions. White phosphorus (P_4) is a colorless to yellow waxy solid at room temperature. P_4 is commercially produced by reducing phosphate rock. Van Wazar (1958) gives the following chemical equation of production:



When x is approximately equal to 1 and y less than or equal to 1/2, the vapor is condensed and collected under water to yield white phosphorus.

White phosphorus is very reactive and spontaneously combusts in atmospheric oxygen to yield phosphorus oxides. To prevent air oxidation it is stored under a blanket of water. White phosphorus also readily reacts with halides

to form the tri- and pentahalides of phosphorus. Alkaline earth and electropositive metals combine with white phosphorus to form the corresponding phosphides. White phosphorus reacts with alkali hydroxides to form phosphine and hypophosphites (Merck, 1976). White phosphorus is converted to red phosphorus by heating in a closed system (Van Wazar, 1958). The physical/chemical properties of white phosphorus are presented in Table 6. White phosphorus generally contains arsenic and other trace impurities. An analysis (Snelson et al., 1980) of elemental impurities in white phosphorus is presented in Table 7.

White phosphorus emitted to the air may undergo oxidation. Since P_4 is only very slightly soluble in water it probably reaches an aquatic or soil system via dry deposition. If the P_4 is covered with an oxide pacifying layer which is extremely hygroscopic, washout and rainout could be important air to surface transport mechanisms.

In aquatic systems white phosphorus is very slightly soluble, (3 mg/L). Dissolved oxygen will react with dissolved or suspended white phosphorus in water to form lower oxyacids of phosphorus. The half-life of white phosphorus in water is in the range of two minutes to 240 hours (Sullivan, 1979). White phosphorus can exist much longer in anaerobic sediments.

The transformations of white phosphorus in the soil are similar to the aquatic systems. Since white phosphorus is not very soluble in water, its mobility in soil systems is probably low. Oxidation to the lower oxyacids of phosphorus is the principal transformation path. The rate is highly dependent on the available oxygen in the soil.

In the time frame of weeks to months, white phosphorus is predominantly oxidized to phosphates. In aquatic systems the phosphate is partitioned between the sediments and aqueous phase, 90% and 10% respectively (Edzwald). Iron, aluminum, and calcium phosphates predominate in the control of the sediment, aqueous partitioning. Phosphate is an essential nutrient in algae growth and will be taken up in biological systems. The decay of biological material releases organic phosphates to the sediments.

Similarly phosphates in soil systems 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 runoff and leachate processes.

White phosphorus can exist for long periods in oxygen-deprived sediments or soils. If a large reservoir is present in a soil or aquatic system, its release poses a serious problem to the surrounding eco-system. Residence time of white phosphorus in air depends on its particle size and surface characteristics. As previously noted, pacified P_4 may have a hygroscopic surface oxide layer in which case it would be rained or washed out or possibly undergo atmospheric oxidation.

TABLE 6

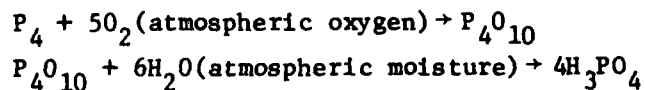
Physical/Chemical Properties of α -White Phosphorus

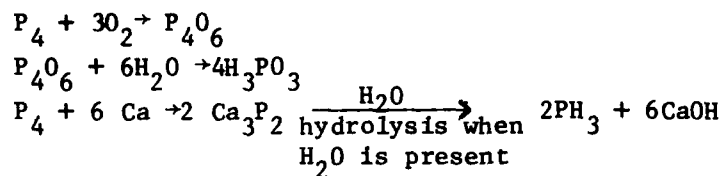
Formula: P_4
Appearance: colorless to yellow, waxy solid
Molecular Weight: 123.90
M.P.: 44.1°C
B.P.: 280.5°C
Crystal Structure: cubic
Density: 1.828 g/cm^3
Autoignition Temperature: 30°C in moist air
Critical Temperature: 695°C
Critical Pressure: 82.2 atm.
Heat of Fusion: $600 \pm 3 \text{ cal/mole } P_4$ at 317.26 K°
Heat Capacity: at 25°C 22.18 cal/mole/degree
 at 44.1°C 22.73 cal/mole/degree

Heat of Sublimation: 13.4 kcal/mole P_4
Heat of Combustion: $710.2 \pm 1.0 \text{ kcal/mole } P_4$
Sublimation Pressure (mm Hg): 0.025 at 20°C
 0.072 at 30°C
 0.122 at 40°C

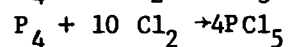
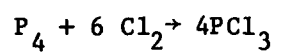
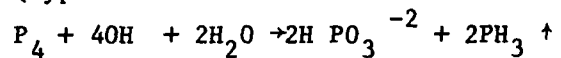
Vapor Pressure: 1 mm Hg at 76.6°C
Solubility: Water: 3 mg/L at 15°C
 slightly soluble
 Absolute alcohol: 2.5 g/L
 Ether: 10 g/L
 Chloroform: 25 g/L
 Benzene: 28.5 g/L
 Carbon Disulfide: 1250 g/L

Chemistry:





(Typical of alkaline earth and electropositive metals)



References

- Wasti, 1978
- Sullivan, 1979
- Van Wazar, 1958

TABLE 7

Analysis of Elemental Impurities in White Phosphorus

<u>Metal</u>	<u>Quantity (µg/g)</u>
Boron	715
Cadmium	0.88
Magnesium	3.6
Zinc	.88
Silicon	377
Copper	1.22
Nickel	0.96
Manganese	0.58
Calcium	18.3
Molybdenum	0.09
Cobalt	0.57
Aluminum	20.0
Vanadium	4.2
Chromium	0.49
Iron	94
Lead	1.28
Barium	0.45
Sodium	9.5
Arsenic	84

Reference

Snelson, et al., 1980

3.2.2 Felt Wedges

The felt wedges used in WP-F munitions contain no preservatives, bactericides, or fungicides, etc. An elemental analysis is presented in Table 8. Expected combustion products are predominantly carbon dioxide and water. Other probable products are carbon monoxide, nitrogen oxides, sulfur dioxide, and some organic constituents.

3.2.3 Phosphoric Acid

Phosphoric acid is a major by-product of the wet-fill production of white phosphorus smoke munitions. Oxidized phosphorus is vented to a scrubber where water is the liquid scrubbing agent. The fugitive emissions from the system are 255 pounds per hour of phosphoric acid aerosol when the scrubber is operating properly and as high as 5100 pounds per hour in the case of a scrubber breakdown and continued production. The bulk of phosphoric acid aerosol is washed out of the air. Some chemical reaction in the atmosphere with ammonia may take place but washout is the primary fate of the atmospheric aerosols.

The physical and chemical properties of phosphoric acid are presented in Table 9. Pure phosphoric acid (H_3PO_4) is a colorless solid at room temperature. As a pure material, the acid has no oxidizing properties below 350°C. Phosphoric acid is prepared by oxidation of white phosphorus in excess air and subsequent hydrolysis.

Phosphoric acid will react with bases in most environmental mediums to yield the phosphate salts. Metals are attacked by phosphoric acid to form the metal phosphates. Ammonia reacts with phosphoric acid to produce the ammonium salt which can be utilized by plants and other biota as a source of phosphorus.

The major reaction of phosphoric acid in aqueous environments is salt formation. In acidic environments or small systems the added acidity of phosphoric acid may be of consequence. The phosphate ion will become partitioned between the sediment and aqueous phase. Once it is in the sediment phase, the sediment may serve as a long-term phosphate source for the aquatic environment. Phosphates are also an essential plant nutrient and are incorporated into the organic phase by plant uptake.

Again in the soil phosphoric acid is generally converted to inorganic or organic phosphates.

3.2.4 Red Phosphorus

Red phosphorus is one of the two principal raw materials in RP-BR smoke munitions.

TABLE 8
Elemental Combustion of Felt Wedges

<u>Elemental Analysis</u>	<u>Weight Percentage</u>
Carbon	48.32%
Hydrogen	7.58%
Sulfur	2.75%
Nitrogen	14.09%
Ash	0.78%
Phosphorus	0.01%
Total Halogen (as Cl)	
Oxygen (by difference)	26.22%

Reference

Snelson et al., 1980

TABLE 9

PROPERTIES OF ORTHOPHOSPHORIC ACID - H₃PO₄

Orthophosphoric Acid - H₃PO₄

Material: colorless crystalline solid - Cotton and Wilkinson

M.P.: 42.35°C

B.P.: -261°C

Density: -1.8741 g/ml

Heat Capacity: 25.3 cal/deg mole at 25°C

Pure material - no oxidizing properties below 350°-400°C

pk₁: 2.15

pk₂: 7.1

pk₃: 12.4

Rxn: will form ammonium and metal phosphates, fluorine will replace oxygen to form fluorophosphate; phosphate ions will complex metals in solution.

References: Van Wazar , 1958

Red phosphorus is a red-brown amorphous solid at room temperature. Red phosphorus is made by heating white phosphorus at 400°C for a few hours in a closed system (Cotton and Wilkinson, 1972). Red phosphorus is the most stable form of elemental phosphorus. At room temperature red phosphorus is relatively unreactive but does undergo slow air oxidation and subsequent reaction with water vapor to yield phosphine (PH₃) and phosphorus oxyacids. The air oxidation is accelerated by metals such as nickel, copper, and iron, and can lead to spontaneous combustion at room temperature (Van Wazar, 1958).

The chemistry of red phosphorus is similar to that of white phosphorus, but more vigorous reaction conditions are necessary. The phosphorus halides can be formed combining the halogen and red phosphorus at elevated temperatures. Also the metal and alkaline earth phosphides can be formed at elevated temperatures. The auto-ignition temperature is 260°C and the combustion products are the same as those of white phosphorus. The physical/chemical properties are presented in Table 10.

The transformation products of red phosphorus are analogous to those of white phosphorus. The rate of the transformation is slower but the end products are virtually the same. The slow air oxidation probably produces more total phosphine than the spontaneous combustion of white phosphorus but at lower ambient concentrations over a long period of time. The slower rate of oxidation of red phosphorus is not a major problem as red phosphorus is relatively non-toxic if no white phosphorus impurities are present.

3.2.5 Butyl Rubber

Butyl rubber is poly(isobutylene); in RP-BR smoke munitions, the butyl rubber serves as a matrix to bind red phosphorus. The rubber is not reactive.

Butyl rubber is slowly degraded in the environment. Atmospheric ozone will oxidize the rubber. Microbial activity will also break down the rubber structure. The degradation process is slow and the products are lower molecular weight hydrocarbons and carbon dioxide.

Production plans specify the use of Exxon 365[®] which contains no styrene. The environmental impact of the material substitution will be negligible.

3.2.6 Methylene Chloride

Methylene chloride is mixed with butyl rubber in the formulation of RP-BR smoke munitions. Methylene chloride is a colorless, low boiling point liquid. It is produced by the reaction of chlorine with methane which

TABLE 10

Physical/Chemical Properties of Red Phosphorus

Formula: P_4

Molecular Weight: 123.90g

Appearance: red-brown powder

M.P.: sublimes at 416°C

Heat of Sublimation: 19.7 kcal/mole

Density: 2.34 g/cm^3

Auto-Ignition Temperature: 280°C in air

Critical Temperature: 589°C

Critical Pressure: 43.1 atm

Heat Capacity: 5.1 cal/deg mol (P)

Solubility: very slightly soluble in water

insoluble in most organic solvents

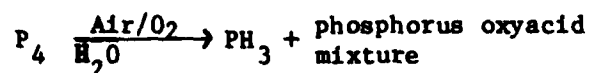
soluble in phosphorus tritronide

Chemistry:

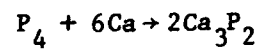
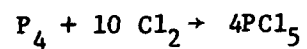
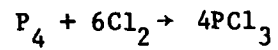
Red phosphorus most stable form of elemental phosphorus

- structure -  polymeric

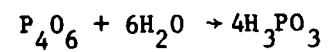
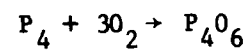
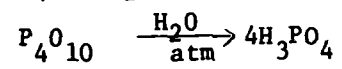
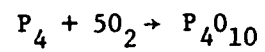
Room temperature - relatively unreactive



Higher temperature:



Combustion:



References

Kitchens, 1978
Van Wazar, 1958
JANAF, 1971
Sax, 1979

is promoted by ultraviolet light. Methylene chloride is a relatively stable compound. The vapor heated to 450°C in air over copper oxide will yield small amounts of phosgene (Kirk-Othmer). Methylene chloride will react with hydroxide radicals to form carbon monoxide, carbon dioxide, and phosgene. Iodine will react with methylene chloride at elevated temperature to yield methylene iodide and chlorine. The physical/chemical properties of methylene chloride are presented in Table 11.

In the atmosphere methylene chloride will react with hydroxyl radicals to form carbon monoxide or carbon dioxide and phosgene. The atmospheric half-life is .3 to .6 years. Methylene chloride is quite stable in water. Hydrolysis of methylene chloride is a very slow process with a predicted half-life of 700 years. However in aerated waters the half-life may be reduced to as low as 18 months. The transformations of methylene chloride in soils are not presently well defined.

Significant amounts of methylene chloride in the atmosphere probably reach the stratosphere where it reacts with ozone (Berkowitz, et al., 1978). The other major fate of atmospheric methylene chloride is attack by hydroxyl radicals to form carbon monoxide, carbon dioxide, phosgene, and hydrochloric acid. Methylene chloride in surface water is probably transferred to the atmosphere considering its high vapor pressure and low water solubility. In ground water methylene chloride will remain stable. In soil environments, again one would expect considerable escape of methylene chloride to the atmosphere with the remaining soil fraction being relatively stable.

3.2.7 Phosphorus Pentoxide

Phosphorus pentoxide (P_4O_{10}) is the major combustion product of phosphorus but is rapidly hydrolyzed to yield phosphoric acid (Van Wazar, 1958). Commercially phosphorus pentoxide is prepared by oxidized elemental phosphorus in dry air. Phosphorus pentoxide is very hygroscopic and used as a drying agent. It is such a powerful dehydrating agent it will react with pure nitric acid to yield N_2O_5 . Phosphorus pentoxide reacts with water to form oxy-acids of phosphorus and with alcohols to yield organic phosphates. The physical/chemical properties of phosphorus pentoxide are presented in Table 12.

3.2.8 Phosphorus Trioxide

Phosphorus trioxide (P_4O_6) is a colorless liquid at room temperature. It is formed by burning white phosphorus in an oxygen deficient environment.

TABLE 11

Physical/Chemical Properties of Methylene Chloride

Formula: CH_2Cl_2

Appearance: colorless liquid

Molecular Weight: 84.93

M.P.: -95°C

B.P.: 40°C

Density: 1.3266 g/cm^3

Critical Temperature: 237°C

Critical Pressure: 60 atm

Heat of Fusion: 1.10 kcal/mole

Heat of Vaporization: 6.68 kcal/mole

Heat Capacity: 24.5 cal/mole ($15-45^\circ\text{C}$)

Heat of Combustion: 144.5 kcal/mole

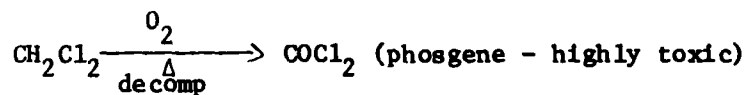
Vapor Pressure: 349 mm Hg at 20°C

Solubility: water - slightly soluble

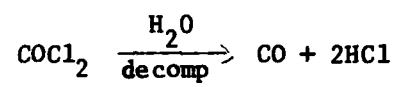
alcohol - soluble in all proportions

ether - soluble in all proportions

Toxic Effects: narcotic, eye irritant



However, in presence of moisture:



Atmosphere: will react with atmospheric radicals to be decomposed into phosgene, CO, etc.

References

Berkowitz et al., 1978

TABLE 12

PROPERTIES OF PHOSPHORUS PENTOXIDE

Phosphorus Pentoxide P_4O_{10} (H form)

Material: white crystalline material

Sublimation: $360^{\circ}C$ at 1 atm

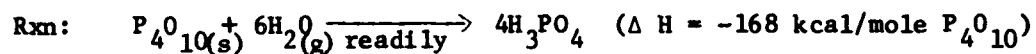
Melting Point: $420^{\circ}C$

Heat Vaporization: 16.2 kcal/mole

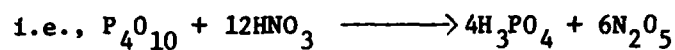
Heat of Fusion: 6.5 kcal/mole

Heat of Sublimation: 22.7 kcal/mole

Heat Capacity: 50.6 cal/deg mole at $25^{\circ}C$



:will dehydrate other oxy acids



References

Van Wazar, 1958
JANAF, 1971

Such oxygen deficient combustion would account for several compounds identified in the white phosphorus-felt wedge combustion products. Phosphorus trioxide is hydrolyzed in the presence of atmospheric moisture to yield phosphorous acid. Phosphorous acid when heated will form phosphoric acid and phosphine. When heated phosphorus trioxide breaks down into phosphorus dioxide and red phosphorus. Both phosphorus acid and phosphine have been identified as combustion products of WP-F formulations and a red solid suspected to be red phosphorus has been noted (Snelson et al., 1980).

The physical/chemical properties of phosphorus trioxide are presented in Table 13.

As in the case of phosphorus pentoxide the trioxide is rapidly hydrolyzed. The major hydrolysis product is phosphorous acid. Under conditions of high temperature some phosphorus trioxide will decompose. Phosphorus dioxide and red phosphorus are the major decomposition products.

3.2.9 Phosphine

Phosphine is a colorless gas at room temperature. It is extremely toxic. Phosphine is oxidized to form oxy-acids of phosphorus and water when an oxygen and phosphine mixture is ignited. The formation reaction of phosphine during combustion of elemental phosphorus is possibly: $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$. The physical/ chemical properties are presented in Table 14.

Phosphine may persist in the atmospheric environment for weeks to months. It is not very soluble in water and not expected to accumulate in aqueous or soil environments. Eventually it will be oxidized to oxy-phosphorus compounds.

3.2.10 Phosphorous Acid

Phosphorous acid has been identified as a combustion product of WP-F formulations. Pure phosphorous acid ($H_2[HPO_3]$) is a colorless solid. It is prepared by reacting phosphorus trichloride with water under vacuum. Phosphorous acid will form phosphoric acid and phosphine at high temperatures. It also reacts with water at high temperatures to form phosphoric acid and hydrogen. Phosphorous acid will form phosphite salts such as ammonium phosphite.

The physical/chemical properties of phosphorous acid are presented in Table 15.

Phosphorous acid undergoes several transformations in the environment which yield phosphoric acid and phosphite salts. The phosphite salts are gradually oxidized to phosphates. Land and water environments are the sinks for the phosphorous acid transformation products.

TABLE 13

PROPERTIES OF PHOSPHORUS TRIOXIDE - P₄O₆

Phosphorus Trioxide - P₄O₆

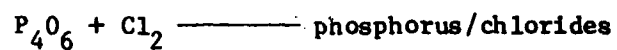
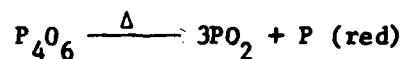
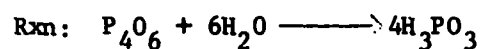
Material: colorless liquid at room temperature

Heat Capacity: 34.4 cal/deg mole at 25°C

Melting Point: 23.8°C

Boiling Point: 175°C

Formation: P₄ (white phosphorus) O₂ (deficit) 50% yield P₄O₆ + P₄O₁₀



References

Van Wazar, 1958

JANAF, 1971

TABLE 14

PROPERTIES OF PHOSPHINE - PH₃

Phosphine - PH₃

Material: colorless gas

M.P.: -133.8°C

B.P.: -87.8°C

Heat of Fusion: .27 kcal/mole

Heat of Formation: 2.29 kcal/mole

Critical Temp.: 51°C

Critical Pressure: 64 atm

Rxn: Thermodynamically PH₃ should be strongly dissociated at room temperature. However, the kinetics are infinitely slow at room temperature below 300°C.

Oxidized by oxygen to form oxyacids of phosphorus and water. No information on rate is given, but the oxidation is quite facile when the PH₃ mixture is ignited.

References

Van Wazar, 1958

Cotton and Wilkinson, 1972

TABLE 15

PROPERTIES OF PHOSPHOROUS ACID - H₂[H PO₃]

Phosphorous Acid - H₂[H PO₃]

Probably formed from combustion product P₄O₆ reacting with water.

Material: deliquescent colorless solid

M.P.: 70.1°C

pk: 1.8

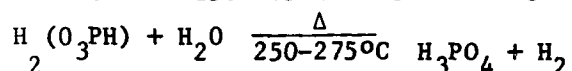
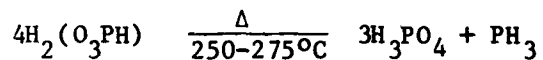
Heat of Fusion: 3.07 kcal/mole

Heat of Solution: -0.13 kcal/mole

Specific Gravity: 1.65 g/cm³ at 21°C

Preparation: PCl₃ + 3H₂O $\xrightarrow[\Delta]{\text{vacuum}}$ H₂ [H PO₃] + 3 HCl

Rxn:



Will form phosphite salts, i.e., (NH₄)H(O₃PH)

alkali metal and ammonium salts are soluble while the alkaline earth phosphite salts are not.

References

Van Wazar, 1958

3.2.11 Summary

The physical/chemical properties of the production raw materials, released species, and possible transformation products are summarized in Table 16.

3.3 Routes of Environmental Contamination and Estimated Concentrations

3.3.1 Production

3.3.1.1 Workplace Air

Industrial hygiene evaluations of white phosphorus munitions production operations were conducted by the U.S. Army Environmental Hygiene Agency in 1975 and 1977 and reports from these surveys have been reviewed (Survey Nos. 35-036-75/76 and 35-0112-78). The 1975 survey reported that white phosphorus measurements on a Wet Fill production line exceeded the OSHA time-weighted average exposure limit of 0.1 mg/m^3 for an 8-hour period. At one location measurements of 0.224 mg/m^3 and 0.450 mg/m^3 were taken. The authors of this report suggest that because of problems in quality assurance, the measured levels may have underestimated the true conditions.

During the 1977 survey air samples for phosphorus were taken at the Dry Fill line during the filling of about 200 munitions. All samples were found to be well below the OSHA standard ($1.2 - 0.7 \text{ } \mu\text{g/m}^3$). The report cautions that "samples were not collected during full operations, and the concentrations would be expected to increase when full production capacity is resolved." The report also notes that oxidation of WP to phosphorus pentoxide, which has the appearance of white smoke, was observed at the burster insertion station at the inlet of the filling cabinet, and on a vent serving the WP storage tank.

TABLE 16

PHYSICAL/CHEMICAL PROPERTIES OF RAW

MATERIAL (reference)	APPEARANCE	PROCESS INTRODUCTION POINT	MELTING POINT	BOILING POINT	DENSITY	AUTOIGNITION TEMPERATURE	CRITICAL TEMPERATURE	CRITICAL PRESSURE	HEAT CAPACITY (cal/mol deg)	HEAT OF FUSION (cal/mol)
White Phosphorus P_4 (3,5)	Colorless to yellow waxy solid	Raw material	44.1°C	280.5°C	1.828 g/cm ³	30°C (moist air)	695°C	82.2 atm	22.18 at 25°C 22.73 at 44.1°C	600 ± 3 per mole of P_4
Red Phosphorus (2)	Red-brown powder	Raw material	sublimes at 416°C		2.34 g/cm ³	260°C in air	589°C	43.1 atm	5.1 at 25°C /mole P	
Methylene Chloride CH_2Cl_2	Colorless liquid	Raw material	-95°C	40°C	1.3266 g/cm ³	624 -622°C	237°C	60 atm	24.5 at 15°- 45°C	1100
Phosphorus Pentoxide P_4O_{10} (1,4)	White crystal	Combustion product	420°C (sublimes at 360°C 1 atm)		2.3 g/cm ³				50.6 at 25°C	8200
Phosphorus Trioxide P_4O_6	Colorless liquid	Combustion product	23.8°C	175.4°C	2.135 g/cm ³				34.4 at 25°C 41.2 at 127°C	
Orthophos- phoric Acid H_3PO_4 (1,4)	Colorless crystalline solid	Combustion product	42.35°C	261°C	1.8741 g/cm ³				25.3 at 25°C	
Phosphorus Acid $H_2(HPO_3)$ (1,4)	Deliquescent colorless	Combustion product	70.1°C		1.65 g/cm ³					3070
Polyphos- phoric Acid 2-6 (1,4)		Combustion product								
Phosphine PH_3 (4)	Colorless liquid	Combustion product	-133.8°C	-87.8°C			51°C	64 atm	8.9 at 25°C	270

TABLE 16

CAL PROPERTIES OF RAW MATERIALS AND COMBUSTION PRODUCTS

NAME	HEAT CAPACITY (cal/mol deg)	HEAT OF FUSION (cal/mol)	HEAT OF COMBUSTION (kcal/mol)	VAPOR PRESSURE (mm Hg)	HEAT OF SUBLIMATION (kcal/mole)	SOLUBILITY	ENVIRONMENTAL TRANSFORMATIONS	ENVIRONMENTAL FATES
White Phosphorus	22.18 at 25°C 22.73 at 44.1°C	600 ± 3 per mole of P ₄	710.2 ± 1.0	1 at 76.6°C	13.4 per mole of P ₄	Slightly soluble in hot H ₂ O 2.5 g/l EtOH 10 g/l ether 25 g/l CHCl ₃ 125 g/l carbon disulfide	$4P + 5O_2 \xrightarrow{\text{Combustion}} P_4O_{10}$ $P_4O_{10} \xrightarrow{\text{Atmospheric Moisture}} 4H_3PO_4$ $4P + 3O_2 \xrightarrow{\text{Combustion}} P_4O_6$ $P_4O_6 \xrightarrow{\text{Atmospheric Moisture}} 4H_3PO_3$ PH ₃ (trace)	P ₄ - Hazardous waste landfill Aquatic and soil Fate is oxidation to phosphates via lower oxides
Red Phosphorus	5.1 at 25°C /mole P		703.2 ± 5			Very slightly soluble in H ₂ O Insoluble in most organic solvents	See white phosphorus transformations	
Black Phosphorus	24.5 at 15°C-45°C	1100	144.5	436 at 25°C		Slightly sol. in H ₂ O Sol. in EtOH Sol. in ether	Will react with atmospheric radicals to form phosgene, CO, etc.	Photochemical decomposition
Yellow Phosphorus	50.6 at 25°C	8200			22.7	Hydrolysis	Reacts with atmospheric moisture to form oxyacids of phosphorus	Aquatic and soil deposition of phosphates and lower oxides
White Phosphorus	34.4 at 25°C 41.2 at 127°C					Hydrolysis	$P_4O_6 \xrightarrow[\text{vapor}]{H_2O} 4H_3PO_3$	Forms H ₃ PO ₄ , PH ₃ , phosphites
White Phosphorus	25.3 at 25°C					All proportions	pk ₁ =2.15, pk ₂ =7.1 pk ₃ = 12.4 phosphates	Land and water deposition, calcium, iron and aluminum phosphate salt formation
White Phosphorus		3070				All proportions	pk ₁ = 1.8 $4H_2(HPO_3) \xrightarrow[250-275^\circ C]{\Delta} 3H_3PO_4 + PH_3$ phosphite & phosphate salt formation	Land and water deposition, oxidation (slow) to phosphates, possible production of phosphine
White Phosphorus							Will form phosphates	Land and water deposition, conversion to phosphate
White Phosphorus	8.9 at 25°C	270				Sparingly soluble	Oxidized to form oxyacids of phosphorus	Oxidized or dissociated

- References: (1) Cotton and Wilkinson 1972
 (2) Kitchens, 1978
 (3) Snelson, 1980
 (4) Van Wazar, 1958
 (5) Wasti, 1978

Unfortunately, no samples were taken for phosphorus pentoxide. The report observes that "appropriate personal protective equipment" was being employed and concludes that "the operation presents no serious occupational hazards to the operating personnel".

Members of the Arthur D. Little case team surveyed the WP production facilities at Pine Bluff Arsenal. However, working conditions and work practices could not be observed because the lines were not operating. We were able to view a film of the Dry Fill line in operation and noted a dramatic improvement in control of phosphorus emissions in comparison to the older Wet Fill process.

In general, the combination of environmental controls and enclosures, personal protective equipment, and emergency showers and drench tanks suggest that efforts are being made to minimize occupational safety and health hazards. When full-scale production begins, standard industrial hygiene practice will dictate frequent sampling to evaluate levels of exposure and thorough programs to install and maintain ventilation systems and other environmental controls. Pine Bluff officials recognize that the greatest degree of control would be achieved by replacing the Wet Lines with Dry Lines.

Requirements for protecting employees from exposure to red phosphorus will be similar to those developed for white phosphorus. Pine Bluff officials were more concerned about the use of methylene chloride as a solvent for processing butyl rubber. In order to control solvent fumes an enclosed processing system will be utilized and where engineering controls are not feasible, respiratory protection will be available. The current OSHA standard for methylene chloride is 500 ppm averaged over an eight-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for 5 minutes in any two-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm averaged over a 10-hour work shift, with a ceiling level of 500 ppm. NIOSH cautions that levels of methylene chloride may require additional control where carbon monoxide is present. Although RP-BR is not currently produced by the U.S. Army, production plans have been developed and suggest that solvent control will be particularly difficult during the transfer of RP-BR pellets to drying ovens. If this process is implemented, Pine Bluff officials recognize that industrial hygiene sampling should be undertaken to characterize the levels of exposure and respiratory protection should be provided until permanent engineering controls can be installed.

Although the duration of exposures during production may be reduced because of control measures, it should be noted that the potential duration of exposure includes the total work shift of 8 hours per day, 5 days per week.

3.3.1.2 Stack Emissions to Ambient Air

The air pollution control systems for white and red phosphorus smoke munitions are described in 2.2.3.1. During production of the WP-F munition the major phosphorus compound escaping the stacks is phosphoric acid. Assuming complete conversion to phosphoric acid aerosol, the emissions are 255 pounds per hour under normal conditions when the scrubber is operating properly. In the abnormal event of a scrubber breakdown without discontinuation of production, emissions can be as high as 5100 pounds per hour.

The Pine Bluff Arsenal has three points of emission of phosphoric acid aerosol. For assessment purposes, all phosphoric acid emission sources were aggregated and assumed to emanate from a single location. This will represent worst case scenario emission conditions. The assumed characteristics of this single source are as follows:

- emission rate, 4.7 g/sec. H_3PO_4
- stack height, 30.5m
- stack diameter, 1.1m
- stack temperature, 360K
- exit gas velocity, 6.1 m/sec.

Six different meteorological scenarios were chosen to represent common types of atmospheric conditions that may be encountered at the arsenal. The conditions are listed below:

* * * M E T E O R O L O G Y * * *					
CONDITION NO	THETA (DEG)	U (M/SEC)	KST	HL (M)	T (DEG K)
1	270.0	2.000	1	5000.0	293.0
2	270.0	3.000	2	5000.0	293.0
3	270.0	5.000	3	5000.0	293.0
4	270.0	8.000	4	5000.0	293.0
5	270.0	3.000	5	5000.0	293.0
6	270.0	2.000	6	5000.0	293.0

where theta is the wind direction, U is the wind speed, KST is the atmospheric stability class (explained below), HL is the mixing height and T is the ambient temperature. The dispersion of pollutants is a function of the atmospheric stability class. The atmosphere becomes more turbulent as stability class decreases. Thus, a low stability class corresponds to more

enhanced atmospheric dispersion. The wind speeds chosen are characteristic of their corresponding stability class. A high mixing height was chosen to allow for a thoroughly mixed layer for pollutant transport.

Fifteen receptor locations were chosen directly downwind from the aggregated source emission location. The receptors are listed below:

* * * R E C E P T O R S * * *			
NO	RREC (KM)	SREC (KM)	Z (H)
1	0.100	0.0	0.0
2	0.200	0.0	0.0
3	0.300	0.0	0.0
4	0.400	0.0	0.0
5	0.500	0.0	0.0
6	0.600	0.0	0.0
7	0.700	0.0	0.0
8	0.800	0.0	0.0
9	0.900	0.0	0.0
10	1.000	0.0	0.0
11	1.100	0.0	0.0
12	1.200	0.0	0.0
13	1.300	0.0	0.0
14	1.400	0.0	0.0
15	1.500	0.0	0.0

The nearest property line to the emission location is 4000 feet or approximately 1219m. This modeling was done to simulate worst case H_3PO_4 concentrations near the Pine Bluff Arsenal property line. For some atmospheric stability classes, the maximum concentration may not be reached within the bounds of the arsenal.

The results of the modeling are given in Table 17, which shows the ambient concentrations in micrograms/cubic meter at each of the 15 receptors for all of the meteorological scenarios.

As can be seen from Table 17, the maximum 1-hour average concentration of $106 \mu\text{g}/\text{m}^3$ occurs 300m directly downwind of the aggregated emission source for meteorological scenario one. A maximum 24-hour average concentration would be expected to be 40% of the predicted 1-hour maximum or $42 \mu\text{g}/\text{m}^3$. This is due to increased meander of the wind direction over the longer time period.

TABLE 17

Ambient Concentrations of H_3PO_4 Aerosol Around Pine Bluff Arsenal

* All Concentrations are in micrograms/cubic meter.

Meteorological Scenario	Receptor Number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	.6	76	106	82	55	34	22	15	11	8	6	5	4	3	2
2	1.0	40	88	89	75	61	49	39	32	27	23	19	17	14	13
3	--	12	55	75	75	68	59	51	44	38	33	29	26	23	20
4	--	--	6	21	36	44	48	48	44	44	41	38	35	37	31
5	0.0	--	--	--	--	--	2	4	7	11	14	18	21	24	26
6	0.0	0.0	0.0	--	--	--	--	--	--	--	--	.2	.7	1	2

Note: All dashes in places are concentrations less than $0.1 \mu\text{g}/\text{m}^3$ but greater than zero.

It was mentioned earlier that the higher the stability class, the less atmospheric dispersion. This is verified by examining meteorological scenarios five and six. Since the atmosphere is very stable in these cases, there is little turbulence to bring the pollutant down to ground level. Therefore it takes both a greater time and distance for the maximum ground level concentration to occur downwind from the source. In these cases, the maximum concentration is not reached within the bounds of the arsenal. For stability class 5 the maximum one-hour average concentration would be $34 \mu\text{g}/\text{m}^3$ occurring 2.5 kilometers from the source and would be $36 \mu\text{g}/\text{m}^3$ at 5 kilometers from the source under stability class 6.

Stability classes five and six most commonly occur at night when the winds are light. Conversely, stability classes one and two occur during daylight when the solar radiation is strong to moderate and the winds are light. The most prevalent stability classes in the area are three and four, with four being assumed for overcast conditions during day or night.

Meteorological scenarios three and four should be considered to occur the most frequently. For both scenarios the maximum H_3PO_4 concentration occurs well within the boundaries of the arsenal.

Data on the combustion products of white phosphorus (Snelson, personal communication) suggest that under some conditions as much as 1 part per thousand of spontaneously combusting white phosphorus may survive in the stack emission gases and be released into the ambient air. The formation of a pacifying surface oxide layer is a possible mechanism to explain the existence of the extremely oxygen-sensitive white phosphorus in air. The white phosphorus level will be further reduced by the scrubbing system. A level of 1g per kg of white phosphorus oxidized is a worst case upper limit on possible air emission of elemental phosphorus. This leads to a maximum one-hour average exposure level of $0.5 \text{ mg}/\text{m}^3$ of P_4 . Assuming a more likely level of 1mg per kg of white phosphorus emission results in an estimated maximum one-hour exposure of $0.5 \mu\text{g}/\text{m}^3$ of P_4 .

The production of the RP-BR smoke munitions emits five pounds per hour of methylene chloride under normal operating conditions. This emission rate results in a calculated ambient air concentration of $22 \mu\text{g}/\text{m}^3$ at the boundary of the Pine Bluff Arsenal which is 4000 feet from the proposed emission source.

In the event of a system breakdown the uncontrolled emissions of methylene chloride will be 0.23 kg/hr. This leads to a calculated concentration of $230 \mu\text{g}/\text{m}^3$ at the boundary of the Arsenal.

3.3.1.3 Land/Water Deposition of Air Emissions for Production

The majority of phosphorus compounds released and dispersed to the air will be rained out as phosphoric acid or phosphates. Some phosphorous acid and phosphite will also be formed and rained out. Methylene chloride from RP-BR production will undergo photodecomposition in the atmosphere to form products such as carbon monoxide.

The rained out phosphorus compounds will be deposited in the water and soil system in low concentrations which should pose minimal problems. Phosphates in aquatic systems will generally partition between the sediment and aqueous phase, 90% and 10% respectively. The aquatic bio-systems will uptake some phosphate and incorporate into an organic phase. The phosphorus compounds deposited by rain on the soil will be subject to leaching and run-off losses to water systems. Also biological uptake by plants and incorporation into an organic phase and soil adsorption are likely fates for some of the phosphates.

Calculations were made to determine the flux of phosphoric acid aerosol to the land surface near the Pine Bluff Arsenal. The flux to land is directly dependent on the deposition velocity and the ground-level ambient concentration of the phosphoric acid aerosol. The deposition velocity in turn is greatly dependent on the particle size of the aerosol and the surface roughness that the aerosol contacts. The particle size of the aerosol emitted from the scrubber is approximately ten micrometers leading to an estimated deposition velocity of 0.01 meters/second. The flux to the surface at the location of maximum ambient concentration would be $7 \mu\text{g}/\text{m}^2$ sec. This should be considered as a conservative upper limit.

White phosphorus emitted to the air may undergo oxidation. Since P_4 is only very slightly soluble in water it probably reaches an aquatic or soil system via dry deposition. A useful upper limit air to surface flux at the location of maximum ambient air concentration would be $7 \text{pg}/\text{m}^2$ sec. If the P_4 is covered with an oxide pacifying layer which is extremely hygroscopic washout and rainout could be important air to surface transport mechanisms. The P_4 will be oxidized to phosphates. The half-life could range from seconds to several months and is highly dependent on the soil and phosphorus surface conditions. A useful upper limit steady-state soil P_4 concentration is estimated to be $1 \text{mg}/\text{m}^2$.

Based on the operating policy of zero pollutant discharge at Pine Bluff it is assumed that the production line would be shut down if the scrubbing system was not functioning. If operations continued in such an event the environmental exposure would be two orders of magnitude greater than under normal operating conditions and contain more problem pollutants.

3.3.1.4 Water Discharges for Production

The water pollutant control system for the WP-F smoke munition production is described in section 2.2.3.2. When the system is operating properly the treated phosphy water is recycled and there is zero discharge of phosphy water to the environment. Levels of 14-37 mg/L P₄ or 450 mg/L total phosphorus have been reported (Sullivan et al., 1977) in the phosphy water at Pine Bluff. Ozone is an effective oxidizing agent but no data on the operating effectiveness of the ozonating system are available.

An accident scenario considered is the breakdown of the phosphy water treatment and recycling system and a return to the practice of discharging phosphy water to Yellow Lake. Assuming white phosphorus concentrations of up to 40 mg/L in discharged phosphy water and 100% transport to Yellow Lake, threshold toxicity concentration of 1 ppb of white phosphorus would be reached in the lake water in roughly an 8-hour production shift or 5000-gallon discharge of phosphy water. The lake water pH would not be significantly affected. The total phosphorus concentration for an 8-hour uncontrolled release would reach 11 to 12 ppb. The half-life of the white phosphorus is 40 minutes to 240 hours. The initial by-products of lower oxy-acids of phosphorus are transformed to phosphates in time frame of weeks to months. Continuous discharge would have serious impact on the water quality of Yellow Lake and possibly other eventual receiving streams.

The formulation of RP-BR munitions is a dry process and no aqueous releases during the production process are expected. Similarly no air or soil emissions are probable. Possibly trace amounts of red phosphorus are emitted to the air during the drying of the red phosphorus-butyl rubber formulation but one would not predict significant amounts from such an input.

Water used to clean the production area may contain phosphorus compounds and methylene chloride. It is not possible to assess the risk of environmental contamination since no information was available concerning concentrations in the clean-up water.

3.3.1.5 Solid Waste Discharges for Production

As described in section 2.2.3.3 the solid residual from WP-F munition production is either incinerated or deposited in a hazardous waste landfill. Solid wastes generated by RP-BR munitions have not been identified but are assumed to be minimal. Any phosphorus waste would probably be incinerated.

The solids deposited in the hazardous waste landfill will remain there, assuming the landfill is properly designed to contain them. Possible escape routes are groundwater leaching or run-off.

During containment in a hazardous waste landfill white phosphorus should be oxidized to some less toxic oxy-phosphorus form. In an escape event the mobility of white phosphorus is expected to be low due to its very limited solubility. In material soils, oxidation to the lower oxy-acids of phosphorus is the principal path. The rate of oxidation is highly dependent on the available oxygen in the soil. The oxy-acids will be transformed to both inorganic and organic phosphates.

3.3.2 Field Use

The use of the smoke screening munitions will release combustion products directly to the air and soil. Water systems will be the sink for the products. Figure 7 outlines the products and environmental fates. Previous tables summarized the physical/chemical properties of the products. More detailed information on physical/chemical and fate properties is contained in Section 3.2.

The major products emitted to the air will be oxy and oxy-acid compounds of phosphorus. The oxy-acids will be subject to salt formation. The phosphorus compounds will be rained out and deposited on land and aqueous systems. In aqueous systems the phosphates will partition between the sediments and the aqueous phase, approximately 90% and 10% respectively. Phosphates will be taken up by plant systems and incorporated into an organic phase. The compounds will slowly be oxidized to phosphate compounds. (Edzwald, 1977).

The deposition on the soil of the rained-out compounds will be subject to further release to aqueous systems by leaching and run-off processes. The soil system will also incorporate phosphates into an organic phase via plant uptake.

The P_4 and PH_3 detected in the combustion products will be rained out (aerosol group) or remain to react in the atmosphere. P_4 could and should undergo oxidation to form an oxy-phosphorus compound. P_4 deposits in aqueous or soil systems could have toxic impacts even at very low concentrations (1 ppb). PH_3 remaining in the atmosphere will eventually be oxidized. PH_3 introduced into aqueous or soil systems can exert toxic effects (see Section 4). It will probably be oxidized to form less toxic phosphorus compounds.

The spent munition casing, ash, organic phosphorus, and red phosphorus will be deposited at the point of use. The contaminants may subsequently reach aqueous systems by leaching or runoff paths. Metals may be dissolved in aqueous systems. The phosphorus compounds have already been discussed in relation to both aqueous and soil systems.

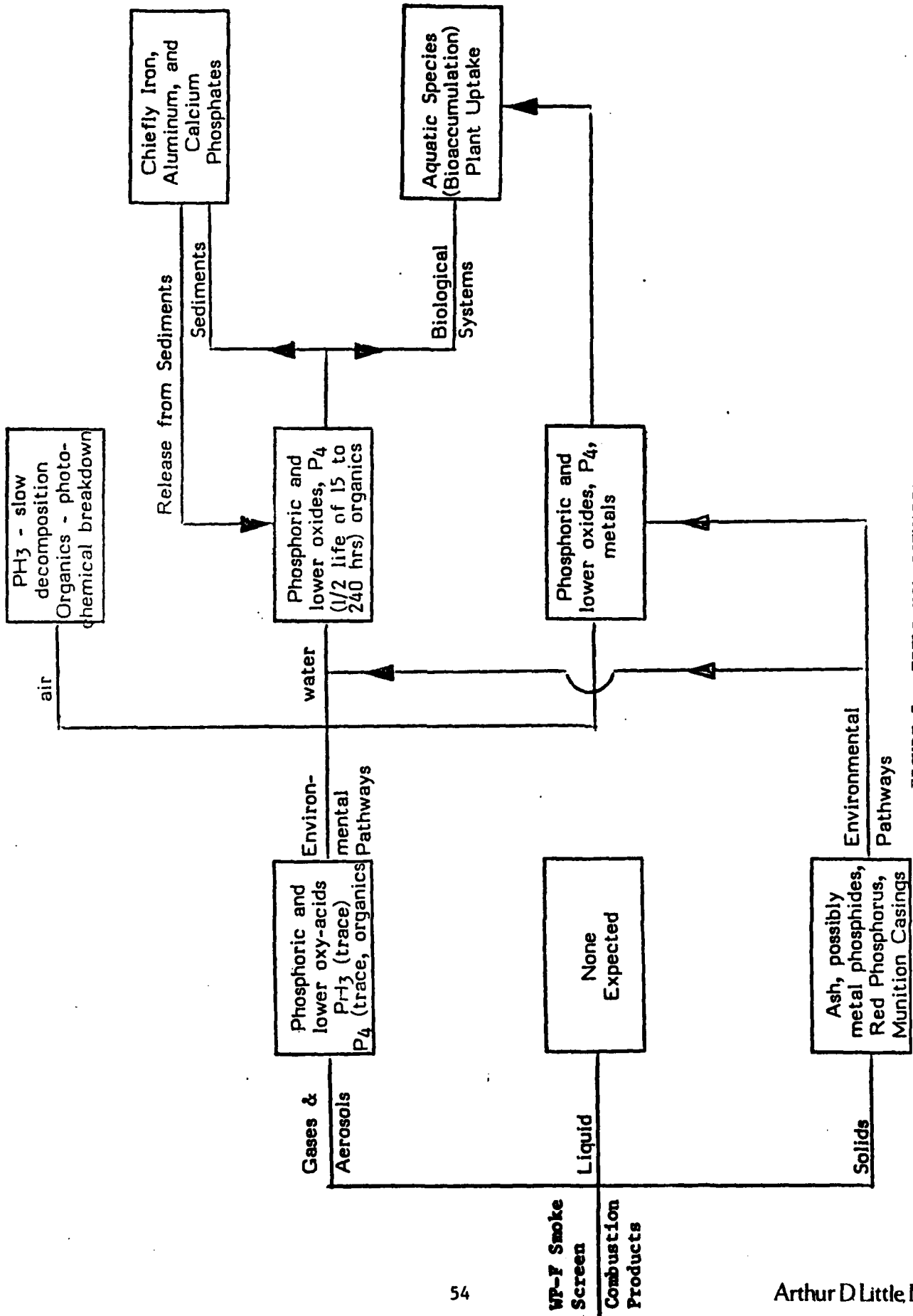


FIGURE 7. FIELD USE SCENARIO

3.3.2.1 Deployment of Red Phosphorus - Butyl Rubber Shells

At the present time there is only one type of red phosphorus butyl rubber (RP-BR) smoke screen produced. It is the L8A1 self protection grenade mounted on a tank. There are 12 of these grenades mounted on a tank, and they are used as a self protective device by the tanks. Those grenades are small and are not meant to produce battlefield size smoke screens.

The grenades are shot from the tank in a 110° to 120° arc. They explode in the air when they are about 75 meters from the tank and pieces of butyl rubber impregnated with red phosphorus fall to the ground and burn for about two minutes. Test burns of red phosphorus have been conducted (Tarnove, 1980). Results indicate P_4O_{10} is the only measurable oxide form and is rapidly hydrolysed. The immediate hydrolysed products are best theoretically represented as a 1:6 molar mixture of tetrametaphosphoric acid and pyrophosphoric acid respectively. After several hours all the hydrolysed oxides are in the orthophosphoric acid form. The former reaction scenario is important to understanding smoke screening effectiveness but for the purpose of the environmental and health impacts it is useful to express exposure in terms of orthophosphoric acid rather than the intermediates. The intermediates are weaker acids and the use of orthophosphoric acid will be a conservative approach to direct exposure in the smoke screen.

Organic compounds other than carbon dioxide, carbon monoxide, and low weight hydrocarbons are not expected to be major combustion products of the pyrolysis of butyl rubber.

As mentioned before, these grenades are small with a fill weight of 360 gms, 95% of which is red phosphorus. The concentrations produced by these shells were estimated assuming a small cloud generation scenario. In this case the burning red phosphorus is considered as a ground level quasi-instantaneous source.

The Smoke Effectiveness Manual Model (SEMM) was used because of its capabilities in simulating concentration scenarios for an instantaneous source (see Appendix A). Concentrations of P_2O_5 were computed directly downwind and also off axis from the explosion for the times $t = 30, 60, 90,$ and 120 seconds.

The assumed wind speed, U , was 3.0 m/s representing an ideal condition for smoke deployment. The atmospheric stability was neutral, also an ideal condition for smoke deployment.

All the concentrations are milligrams/cubic meter of P_2O_5 . P_2O_5 will react with water vapor in the atmosphere to form phosphoric acid. The phosphoric acid formed is directly proportional to the water vapor content of the air.

Tables 18 through 22 show computed concentrations of P_2O_5 both downwind and crosswind from the explosion site. The crosswind distance varied from case to case because of the dispersion characteristics of the puff. For distances further downwind the puff has a greater crosswind diameter; thus larger crosswind distances had to be adjusted from case to case. As can be seen from these tables, the P_2O_5 concentration falls off quickly along the edges of the puff.

The maximum ambient concentration of 5.8 g/m^3 of P_2O_5 would occur at a given receptor for only a few seconds as the puff is transported by the wind. The corresponding concentration of unreacted P_4 and PH_3 at the same receptor would be 5.8 mg/m^3 respectively.

3.3.2.2 Deployment of White Phosphorus-Felt and Munitions

Experiments are presently being conducted to determine the combustion products of WP-F munition. Products of test burns have been identified but not quantified (Snelson, 1980). The products reported are:

Aerosol

PH_3 (trace amounts)

P_4 (white phosphorus)

Phosphorous acid

Ortho-phosphoric acid
(polymers 2-6)

Several light nitrogen
or phosphorus-con-
taining compounds

A large number of polar
organic compounds

Gaseous

PH_3 (trace amounts)

P_4 (white phosphorus)

Several light nitrogen or phosphorus-
containing compounds

The test burns were conducted in 50% relative humidity. Preliminary results are that the yield of white phosphorus in the combustion products ranges from one part per million to one part per thousand by weight of the original white phosphorus subject to combustion (Snelson, personal communication).

TABLE 18

SMOKE DISPERSAL AFTER L8A1 GRENADE DEPLOYMENT (95% RP)*

<u>t = 30 sec. post-deployment</u>		<u>t = 60 sec. post-deployment</u>	
<u>x(m)</u> [§]	<u>mg/m</u> ³ †	<u>x(m)</u>	<u>mg/m</u> ³
0	4.9 x 10 ⁻¹⁴	0	-
10	2.6 x 10 ⁻¹⁰	50	3.7 x 10 ⁻⁸
20	4.8 x 10 ⁻⁷	75	1.3 x 10 ⁻⁴
30	3.4 x 10 ⁻⁴	100	7.7 x 10 ⁻²
40	8.5 x 10 ⁻²	110	6.1 x 10 ⁻¹
50	7.8	120	3.7
60	264.5	130	17.1
70	3.3 x 10 ³	140	59.8
80	1.5 x 10 ⁴	150	157.6
90	2.46x 10 ⁴	160	315.1
100	1.5 x 10 ⁴	170	478.4
		180	549.7
		190	478.4
<u>t = 90 sec. post-deployment</u>		<u>t = 120 sec. post-deployment</u>	
<u>x(m)</u>	<u>mg/m</u> ³	<u>x(m)</u>	<u>mg/m</u> ³
0	-	0	-
100	1.2 x 10 ⁻⁶	100	5.0 x 10 ⁻¹⁰
150	1.5 x 10 ⁻²	200	4.8 x 10 ⁻³
200	7.5	250	8.3 x 10 ⁻¹
215	25.5	300	21.5
230	64.9	310	32.7
240	102.6	320	46.2
250	141.9	330	60.3
260	172.7	340	72.9
270	184.5	350	81.9
280	172.7	360	85.1
		370	81.9

* Deployment conditions: Z = 0 m; U = 3m/sec; neutral stability.

§ Centerline distance downwind

† Concentration of P₂O₅

TABLE 19
SMOKE DISPERSAL AFTER L8A1 GRENADE DEPLOYMENT (95% RP)

L8A1 RP-BR Grenade	Neutral Stability; Z=0.0m	Wind Speed (U) = 3.0m/sec. blowing in x direction		
t = 30 sec.	All concentrations are P ₂ O ₅			
x (m)/y (m)	x (mg/m ³)			
2	4	6	8	
40	21 x 10 ⁻³	2.8 x 10 ⁻⁴	2.1 x 10 ⁻⁷	8.9 x 10 ⁻¹²
50	1.9	2.5 x 10 ⁻²	1.9 x 10 ⁻⁵	8.3 x 10 ⁻¹⁰
60	62	8.5 x 10 ⁻¹	6.4 x 10 ⁻⁴	2.8 x 10 ⁻⁸
70	780	11	8 x 10 ⁻³	3.5 x 10 ⁻⁷
80	3.5 x 10 ³	48	3.7 x 10 ⁻²	1.5 x 10 ⁻⁶
90	5.8 x 10 ³	78	6 x 10 ⁻²	2.5 x 10 ⁻⁶
100	3.5 x 10 ³	48	3.6 x 10 ⁻²	1.5 x 10 ⁻⁶

TABLE 20

SMOKE DISPERSAL AFTER L8A1 GRENADE DEPLOYMENT (95% RP)

Wind Speed (U) = 3.0m/sec
blowing in x direction

Neutral Stability; Z = 0.0m

L8A1 RP-BR Grenade

t = 60 sec.

All Concentrations are P₂O₅

		x (mg/m ³)		
x (m)/y (m)	5	10	20	30
110	4 x 10 ⁻¹	.1	1.2 x 10 ⁻³	6.4 x 10 ⁻⁷
120	2.5	.8	8.3 x 10 ⁻³	3.9 x 10 ⁻⁷
130	11.7	3.7	3.9 x 10 ⁻²	1.8 x 10 ⁻⁵
140	41.4	13	13.3 x 10 ⁻¹	6.4 x 10 ⁻⁵
150	108	35	0.3	1.7 x 10 ⁻⁴
160	216	69	0.7	3.5 x 10 ⁻⁴
170	327	104	1.1	5.1 x 10 ⁻⁴
180	375	117	1.4	5.8 x 10 ⁻⁴
190	327	104	1.2	5.1 x 10 ⁻⁴

TABLE 21
SMOKE DISPERSAL AFTER L8A1 GRENADE DEPLOYMENT (95% RP)

Neutral Stability; Z = 0.0m
Wind Speed (U) = 3.0m/sec
Blowing in x direction

L8A1 RP-BR Grenade

t = 90 sec.

All Concentrations are P₂O₅

x(m)/y(m)	10	20	30	40
200	3.7	0.4	9 x 10 ⁻⁴	4.6 x 10 ⁻⁵
215	12.2	1.3	3 x 10 ⁻²	1.6 x 10 ⁻⁴
230	31	3.2	8 x 10 ⁻²	4.1 x 10 ⁻⁴
240	48	5.1	0.1	6.4 x 10 ⁻⁴
250	67	7.1	0.2	9 x 10 ⁻⁴
260	83	8.7	0.2	1 x 10 ⁻³
270	87	9.2	0.2	1.2 x 10 ⁻³
280	83	9.0	0.2	1 x 10 ⁻³

x (mg/m³)

TABLE 22
SMOKE DISPERSAL AFTER L8A1 GRENADE DEPLOYMENT (95% RP)

Neutral Stability; Z = 0.0m Wind Speed (U) = 3.0m/sec
 blowing in x direction

t = 120 sec.

All concentrations are P₂O₅
 x (mg/m³)

L8A1 RP-BR Grenade	10	20	30	40
x(m)/y(m)				
300	14	3.5	0.4	2 ± 10 ⁻²
310	21	5.3	0.6	0.2
320	30	7.6	0.8	0.3
330	39	10	1.1	0.4
340	46	12	1.3	0.5
350	53	14	1.4	0.6
360	55	15	1.5	0.6
370	53	14	1.4	0.6

The major combustion product of WP-F formulations is expected to be phosphoric acid. Worst case assumption of 100% yield of phosphoric acid from WP-F combustion is used to project releases in this section.

When the WP-F shell is deployed, the felt impregnated with WP is scattered by the explosion in a radius of about 100m and burns for about 7 minutes. Depending on the source receptor relationship, this explosion could be considered as a quasi-continuous source. If the time it takes a parcel of air to travel from the explosion site to the receptor site is less than 7 minutes, the source can be considered continuous. In a 3m/sec wind (6.7 mph) a parcel of air will travel 1260m in 7 minutes. For a wind speed of 3m/sec the source can be considered continuous in the region of concern.

Modeling of a continuous source is carried out using Turner's equation (1970) which is as follows:

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z U} \exp \left\{ - 1/2 \left[\left(\frac{y}{\sigma_y} \right)^2 + \left(\frac{H}{\sigma_z} \right)^2 \right] \right\}$$

where: χ is concentration of pollutant at point x,y,z (g/m^3)

Q is emission rate (g/s);

σ_y and σ_x are the standard deviations of the concentration in the plume;

U is the wind speed (m/s);

y is the crosswind distance from the release point (m); and

H is the effective height of release(m).

(See Appendix A for additional details.)

Since the effective height of release is at ground level (H=0) the term containing H drops out. If the concentration is only to be examined directly downwind of the exploded shell, the crosswind distance will be zero (y=0) and the term containing y drops out. To calculate the concentration at a receptor directly downwind of a ground level source the equation reduces to the following:

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u}$$

This equation will be used in computing concentrations for the various scenarios to be discussed later.

Two types of smoke disposal scenarios were investigated. The first scenario is a small cloud generation, and concentrations were computed as a function of both downwind and crosswind distances. The second scenario is a smoke screen maintained in a steady-state. A concentration of P_2O_5 was chosen so that when released in air it could maintain a smoke screen that inhibits both visible light and infrared radiation. Calculations were done to investigate how many shells of WP-F it would take to maintain a concentration of P_2O_5 in a battlefield 100m square. An analytical expression was developed to relate the duration of the smoke screen to the number of shells required to maintain a steady state concentration over the duration. The 155 mm WP-F shell was assumed in both scenarios since it is the only shell that contains felt filler material.

3.3.2.2.1 Small Cloud Generation

The explosion of a single 155 mm WP-F shell was considered to be quasi-continuous. When the shell explodes in the air, felt pieces are scattered around the shell with a radius of about 100 m. This area corresponds to an area source of 177 m on each side. The shell contains felt impregnated with 5980 grams of white phosphorus. Since a burn time of 7 minutes (420 seconds) was chosen to be representative of a typical shell burn, the emission rate Q in grams per second would be:

$$\frac{5980 \text{ gms}}{420 \text{ sec.}} = 14.2 \text{ g/s}$$

This emission rate was assumed over the entire 177 m square area.

The model used in this analysis was Turner's equation (1970) which was mentioned earlier in the text. In this case H , the effective height of release was considered to be zero because it is a ground level source.

The center of the area source was considered to be ground zero. Both downwind and crosswind distances are measured from this point. Because of the limitations of Turner's model, the closest downwind distance away from the area that could be modeled with confidence was 100 m. Since the area source is 177 m square, a distance of 100 m from the center will be 11.5 m off the leading edge of the area source.

The meteorological parameters remained constant throughout this analysis. Again, ideal smoke deployment conditions were used; wind speed $u = 3.0$ m/s; and a neutral atmospheric stability.

Concentrations in micrograms/cubic meter of P_2O_5 in the atmosphere as a result of the phosphorus emission rate were computed for various downwind distances. Again the receptor height z equaled zero throughout the analysis.

Table 23 shows the expected ambient concentrations of P_2O_5 for a number of downwind distances. The maximum concentration is 16.3 mg/m^3 . The time period of exposure under this scenario would be no greater than 7 minutes. Table 24 contains both downwind and crosswind concentrations of P_2O_5 . As can be seen from Table 24 the plume from the area source spreads out slowly as it moves downwind.

These concentrations are expressed as P_2O_5 , and actual phosphoric acid concentrations will be greater because they are a function of the ambient relative humidity. For a relative humidity of 50% it was observed that the yield factor of phosphoric acid aerosol to P_2O_5 initial smoke was five to one. (See Appendix B.)

If approximately one part per thousand of the original P_4 does not oxidize in the atmosphere, the maximum concentration of P_4 aerosol would be $7 \mu\text{g/m}^3$. If one ppm of the total P_4 reacts to form phosphine (PH_3) the expected ambient concentration of phosphine would be 7 nanograms/ m^3 . At the location of maximum ground level concentration the flux to the land surface of P_2O_5 and P_4 aerosol would be $0.16 \text{ mg/m}^2 \text{ sec}$ and $0.07 \mu\text{g/m}^2 \text{ sec}$ respectively.

3.3.2.2 Steady-State Smoke Screen

As mentioned before, this scenario will be a simulated steady-state to develop an analytical expression relating duration of smoke screen with number of shell explosions needed to maintain the screen. The steady-state concentration chosen for this analysis was 0.288 g/m^3 of P_2O_5 . This concentration of P_2O_5 will be sufficiently high to inhibit both visible and infrared radiation at relative humidities higher than 50%.

A 100m square area was chosen for the investigation. A concentration of 0.288 g/m^3 of P_2O_5 would be maintained over different periods of time.

According to Turner (1970), the expression to calculate concentration at a receptor directly downwind of a ground level source is:

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \quad (1)$$

(See Appendix A)

In this analysis, the above expression will be used to solve for the emission rate Q . The number of bombs required to maintain the smoke screen over different time periods will be calculated based on the emission rate. The expression for Q is:

$$Q = \pi \sigma_y \sigma_z u \chi \quad (2)$$

TABLE 23

EXTENDED SMOKE DEPLOYMENT

155 mm WP-F Shell: Neutral Stability; Receptor Height (Z) = 0

Wind Speed (U) = 3.0 m/s: Area Source 177m on a side corresponds to a radius of 100m for felt dispersion.

x(m) is distance directly downwind measured from the center of the area source.

All concentrations are mg/m^3 of P_2O_5

x(m)	X	x(m)	X
100	16.3	850	1.3
150	10.7	900	1.2
200	7.9	950	1.1
250	6.3	1000	1.1
300	4.9	1050	1.0
350	4.0	1100	0.9
400	3.4	1150	0.9
450	3.0	1200	0.8
500	2.5	1250	0.8
550	2.3	1300	0.7
600	2.1	1350	0.7
650	2.0	1400	0.7
700	1.7	1450	0.6
750	1.6	1500	0.6
800	1.4		

TABLE 24
EXTENDED SMOKE DEPLOYMENT

155 WP-F Shell x (m)/y(m)	Neutral Stability All Concentrations are P ₂ O ₅ x(mg/m ³)			Wind speed (U)=3.0 m/sec blowing in x direction x and y measured from the center of the area source	
	50	100	150	200	750
100	9	1.5		-	-
200	5	1.2	0.1	-	-
300	3.4	1.2	0.1	-	-
400	2.6	1.1	0.2	-	-
500	2.0	1.0	0.2	-	-
600	1.7	0.9	0.3	0.1	-
700	1.4	0.9	0.4	0.1	-
800	1.2	0.8	0.4	0.1	-
900	1.1	0.7	0.4	0.1	-
1000	0.9	0.7	0.4	0.2	-
1100	0.8	0.6	0.4	0.2	-
1200	0.8	0.6	0.4	0.2	0.1
1300	0.7	0.5	0.3	0.2	0.1
1400	0.6	0.5	0.3	0.2	0.1

The parameters σ_y and σ_z are based on the fact that a 100m square area source is being used and that the atmospheric stability is neutral. For this analysis, the parameters have the following values:

$$\begin{aligned}\sigma_y &= 23.3\text{m}; \\ \sigma_z &= 4.6\text{m}; \text{ and} \\ U &= 3\text{m/sec.}\end{aligned}$$

Substituting these parameters back into equation (2) yields the following expression for Q.

$$Q = 1010.1 \text{ m}^3/\text{sec.} \cdot \chi$$

Since χ equals 0.288 g/m^3 of P_2O_5 , the emission rate Q of P_4 needed to maintain this concentration will be 127 g/sec. This was calculated by substituting χ equals 0.288 g/sec. into equation (3).

The fill weight of a 155 mm white phosphorus-fill shell is 5980 gm. On this basis, an expression was developed to quantify the number of shells needed to maintain the smoke screen over a period of time. The expression is as follows:

$$\left(\frac{127. \text{ gm/sec}}{5980. \text{ gm}} \right) \times \left(\begin{array}{c} \text{Period of time} \\ \text{in seconds} \end{array} \right) = \begin{array}{c} \text{Number of} \\ \text{shells} \end{array} \quad (4)$$

Equation (4) simplifies to:

$$(0.02 \text{ sec}^{-1}) \times (\text{period of time in seconds}) = \text{number of shells} \quad (5)$$

For an example, if one wanted to maintain a concentration of 0.288 gm/m^3 of P_2O_5 over a 100m square area for 1 hour (3600 sec), 72 shells would be needed.

Any period of time can be input into equation (5) to find out the number of shells needed to maintain the smoke screen.

The maximum ambient concentrations of unreacted P_4 and of PH_3 was determined as follows. For P_4 , assuming an unreacted ratio of one part³ per thousand, the maximum concentration would be 0.12 mg/m^3 . The estimated PH_3 concentration would be $0.12 \text{ } \mu\text{g/m}^3$. The flux to the land surface at the maximum receptor location for P_2O_5 and P_4 , due to deposition would be $2.9 \text{ mg/m}^2 \cdot \text{sec}$ and $1.2 \text{ } \mu\text{g/m}^2 \cdot \text{sec}$ respectively.

3.4 Exposure Scenarios

In this section the WP-F and RP-BR life cycles are considered to consist of two distinct phases: (1) production of smoke screen munitions and related demilitarization and disposal activities, and (2) use of smoke screens under training and battlefield conditions. For both phases, scenarios are developed for human and flora/fauna exposure to smoke screen raw materials and products. Scenarios are based upon available data and judgment as to realistic sequences of events. It should be noted that reference to specific scenarios does not exclude the possibility that other scenarios could occur.

3.4.1 Production and Disposal

Production and disposal activities are assumed to be restricted to the existing facilities at the Pine Bluff Arsenal (PBA) which have been described in Chapter 2.

3.4.1.1 White Phosphorus-Felt

3.4.1.1.1 Production Facility (Wet and Dry)

Human Exposure

The facilities at Pine Bluff Arsenal for producing white phosphorus-felt screening smokes have been described in Chapter 2. At present, it is assumed that production will require the use of both wet and dry lines, although plans have been made to phase out the wet lines when funds become available. The most likely exposure scenario for both wet and dry line production is skin contact from spills or splashes of liquid white phosphorus. Such an event is less likely with the dry line because of the enclosed nature of the system. Even on the wet line, events leading to skin contact are likely to be limited to a single employee. Furthermore, spills and splashes will not usually result in skin contact because employees wear protective clothing. If skin contact does occur, baths are available for emergency use.

For example, consider the Fill, Close, and Packout (Dry Fill) operation phase which includes operation No. 12: "Load Burster Casing into Filled Canisters." In this scenario the station workforce includes 1 operator and 3 other transient workers who at times are in the work area. The operation is located at the Burster Casing Drop Station (Figure 2) where the operator manually inserts burster casings. The operator is required to wear rubber gloves to prevent burns, but it is possible that during the insertion operation WP could spill or splash and get inside the gloves thus causing a burn. Such an event would require immediate first-aid to reduce the extent of injury.

There is no evidence that employees are chronically exposed to airborne phosphorus. The utilization of ventilation and process enclosures helps to control airborne concentrations. Surveillance of dental health is an additional control procedure which helps to exclude more susceptible employees from the workplace.

On the other hand, improper maintenance of controls or noncompliance with safety rules can lead to hazardous exposures.

Flora/Fauna Exposure

Resumption of wet and/or dry production WP-F at PBA would be expected to create an ecological exposure scenario far more controlled than that which prevailed during previous production cycles before the advent of the present waste treatment infrastructure at PBA. Air emissions would be reduced significantly over past predominantly wet-fill operations. While data are lacking on potentially applicable vegetative damage thresholds, the apparent persistence of a representative mix of mature vegetation in the areas north and east of the WP plant suggest that resumed production is not likely to lead to unacceptable exposure conditions.

Past PBA "phossey water" disposal practice, via surface ditch and creek drainage to Yellow Lake, resulted in documented correlation with depauperate aquatic ecology in the subject creek and periodic fish kills in Yellow Lake (Sullivan, et al, 1979). The present closed-loop system would maximize future re-use of phossey water and provide limited input to the new central waste water treatment plant, eliminating incremental production or disposal contributions to the previous waterborne-exposure pathway. The biomonitoring component of the waste water treatment system would be well suited to early detection and prevention of any phosphorus-related toxicity to aquatic organisms.

3.4.1.1.2 Pollution Control/Waste Facility

Human Exposure

Pollution control for WP-F emissions is expected to be an enclosed zero-discharge system and so exposures to toxic or hazardous substances are not likely under normal operations. However, employees may be exposed during maintenance operations, particularly during transfer of incinerator ash or settling pond sludge to landfills. Skin contact with residual phosphorus in sludge could result in burns. Skin contact with ash is not likely to be a problem.

Flora/Fauna Exposure

Exposure of flora and fauna to waste treatment and disposal-related aspects of WP-F production would occur at and near two locations on PBA. The first location is the recently completed central waste water treatment facility near the eastern boundary of the Arsenal, and the second is an anticipated hazardous waste disposal landfill in the northern portion of PBA.

Because these locations and facilities would likely involve co-disposal of WP-F and RP/BR-related wastes with chemical wastes from various other PBA activities, and because the details of RP/BR production have not been finalized, it is impractical to attempt an a priori, definitive prediction of the resultant exposure scenarios. However, there is good evidence to support the belief that, at least for the water treatment system, means already exist to ensure the absence of unacceptable exposure conditions. The water treatment system incorporates an effluent biological monitoring component prior to final discharge. This component, which is reportedly to consist of a live bluegill sunfish in a test tank, would be expected to serve as an excellent "bottom line" advanced indicator of any potential phosphorus-related toxic exposure conditions. This chosen bioassay organism is the one reported to have exhibited the greatest relative sensitivity to P_4 toxicity (Sullivan, et al, 1979), and may exhibit measurable responses at lower concentrations than would be detectable by typical water quality analytical procedures.

The anticipated hazardous waste landfill would be expected to receive still bottoms from WP-Felt production and potentially, other solids from P_4 recovery processes. (The nature of solids that might be received from red phosphorus production is not known at this time.) The design, preparation, and management of the landfill site is expected to determine the extent to which, if any, the resulting exposure conditions could be hazardous to area biota. The expected phosphorus degradation products (especially phosphoric acids) would be expected to exist in leachate from phosphorus-rich wastes. While not representing biological exposure hazard by themselves, co-generation in the presence of high concentrations of metals in a landfill leachate (or runoff) could create the potential for isolation and enhancement of metal toxicity (Burrows, et al, 1973). There is no empirical basis for predicting whether or not such conditions might exist should phosphorus smoke munitions production resume at PBA. Leachate monitoring and collection are technically feasible mitigative possibilities should the need arise. Other containment measures (e.g., capping) are also available for consideration, if necessary, should the landfill operation present opportunities for undegraded P_4 -laden sediments to reach surrounding biota.

3.4.1.2 Red Phosphorus - Butyl Rubber

3.4.1.2.1 Production Facilities

Human Exposure

The development of production facilities at PBA for red phosphorus - butyl rubber screening smokes is in the planning stages and so there is no prior experience (except from England) upon which to base a discussion of exposures. The proposed system has been described and current information suggests that concern should focus on exposure to emissions of the methylene chloride solvent. The literature suggests that hazardous exposures to methylene chloride may occur during industrial operations. For example, a chemist was exposed repeatedly to concentrations ranging from 500 to 3600 ppm and developed signs of toxic encephalopathy. (ACGIH, 1976).

In another case, four workers exposed to unmeasured high concentrations for one to three hours developed eye and respiratory irritation. Subsequently, all became comatose and one worker died. (Moskowitz and Shapiro, 1952.) During the production of RP-BR, workers may be exposed to high levels of methylene chloride when the solvent is added to the kneader-extruder and when the extruded granules are transferred to the outdoor drying ovens. The actual level of exposure will depend upon the effectiveness of ventilation systems. Even if ventilation is not effective, it is expected that respiratory protection will be utilized to limit inhalation exposure. Methylene chloride can also be absorbed through the skin and so exposure may occur from spills or from handling plasticized such as currently used to prevent phosphorus exposure will reduce the hazard of skin absorption. In general, the implementation of standard industrial hygiene practices will limit the risk of hazardous exposure to RP-BR and its raw materials.

Flora/Fauna Exposure

The area and setup designated for possible use for production of Red Phosphorus/ Butyl Rubber (RP/BR) at Pine Bluff Arsenal (PBA) affords little (if any) potential for flora/fauna exposure to significant ambient concentrations of any production-related emissions. The facility would be located in an existing, though presently inactive, building in an open, developed portion of the post, where floral and faunal diversity is minimal. The envisioned

production concept involves removal of waste water and solid wastes to centralized treatment and/or disposal locations elsewhere at PBA. Thus, any production-derived waterborne exposure potential would likely be realized at those disposal sites (see above).

The quantified, production-related air emissions from the facility include escape of 10% of the methylene chloride to be used in the production process. No projections of the resultant ambient air concentrations of methylene chloride are available, but the available data for overall volatile hydrocarbon emissions strongly suggest that there is no reason to expect mammalian inhalation damage thresholds (in the 1,000 ppm and greater range) to be approached. Specifically, it has been calculated that emissions would need to increase by slightly more than a factor of seven to result in ambient air concentrations equal to the .25 ppm volatile hydrocarbon standard about 4,000 feet from the facility.

3.4.1.2.2 Pollution Control/Waste Facility

Human Exposure

Excess methylene chloride will be vented to the atmosphere from the drying ovens and so exposure at the pollution control/waste facility should be limited.

Flora/Fauna Exposure

The ecological exposure potential from waste treatment and disposal for RP-BR production would be essentially the same as described in Section 3.4.1.1.2 for WP-F. Variance may exist due to the possible differences in details of intermediate treatment processes, but these would generally be expected to be undetectable in the context of ultimate disposal-related ambient ecological exposure potential at the central water and land disposal facilities. Until such time as the RP/BR system may be better defined, further comparisons are considered impractical.

3.4.2 Training and Field Use

The use of WP-F and RP-BR under training and battlefield conditions is described using three different scenarios. The first scenario concerns RB-BR in the L8A1 vehicle-mounted grenade and the generation of small localized clouds. The other two scenarios concern WP-F deployment either for one-time coverage over a large area using 60-81 mm mortars or longer range rockets and 105 mm or 155 mm projectiles for sustained coverage over a large area. The training and field use scenarios described

below are based primarily on information provided in the following two references:

- Small Unit Smoke Operations
Report No. TC 3-50-2
December 1978
- Concept: Smoke A Combat Multiplier
U.S. Army Combined Arms Combat
Development Activity
August 1978

The second document, in particular, notes that smoke applications are highly variable and that no single scenario can be regarded as "typical," or representative of the "official" smoke concept for the U.S. Army. Scenarios are useful, however, to illustrate the circumstances under which smoke screens could be deployed.

3.4.2.1 RP-BR: Small Cloud Generation

Human Exposure

An anticipated application for RP-BR smoke is the L8A1 vehicle-mounted grenade which is designed for rapid smoke generation to conceal or screen individual vehicles. When a vehicle is fired upon, the vehicle commander can launch grenades and take evasive action behind the smoke cloud. The manual, Small Unit Smoke Operations, presents an example of such an operation:

- "● While moving across an open area, a squad leader sees a bright flash of light and a cloud of dust on his right flank about 1,500 meters from his position. He then sees a trail of black smoke heading directly for his vehicle.
- According to company SOP, the squad leader shouts, "Smoke, Sagger right!" Crew reaction is immediate. Squad members riding in the cargo hatch of the armored personnel carrier (APC) throw three HC smoke grenades over the right side of the vehicle. The driver then makes a 90° turn to the left so that the smoke cloud is between the vehicle and the Sagger.
- Once the vehicle is behind the smoke screen, a squad member riding in the rear of the vehicle throws a hand grenade into the cloud to make the enemy gunner think he has scored a hit. The Sagger, however, flies through the smoke and misses the APC.

- The squad leader then calls for mortar fire on the suspected enemy position. He also calls for smoke to be placed between his location and the probable enemy position."

While the example describes the use of HC smoke, it is assumed that RP-BR grenades could be deployed under similar circumstances. Since deployment for vehicle screening is an emergency maneuver, consideration of meteorological conditions and exposure of personnel will have lower priority than the immediate need to evade enemy fire. Given these circumstances, it is expected that troops will occasionally be exposed to the RP-BR cloud and, although doctrine requires the use of protective masks, it is unlikely that they will be utilized at the outset of the maneuver.

Dispersion modeling shows that high concentrations of P_{2O_5} can be expected as a result of L8A1 grenade deployment. Calculations based on the centerline of dispersion show how the maximum concentration disperses over time. For example, 30 seconds after deployment (under ideal conditions and windspeed of 3 m/sec.) the point of maximum concentration will be 90 meters downwind from the deployment site. The concentration at ground level will be 2.5×10^4 mg/m³. If the prevailing wind speed is greater, the point of maximum concentration will travel farther over the 30-second period but the concentration will be reduced because of increased dispersion.

The relationship between smoke dispersal and troop exposure can be described graphically. Figure 8 shows a simplified battlefield situation in which a vehicle deploys grenades and changes direction to move out of enemy range. In this example the vehicle travels at a constant 20 mph and after 30 seconds is 270 m from the site of deployment and 180 m from the point of maximum smoke concentration. At that point in time the vehicle and its passengers are exposed to less than 1.17×10^{-19} mg/m³.

It is possible to develop an example which shows the vehicle traversing the point of maximum concentration, however, this is unlikely because the rationale behind RP-BR grenade deployment is to create a smoke screen between the vehicle and enemy positions in order to permit escape.

- Flora/Fauna Exposure

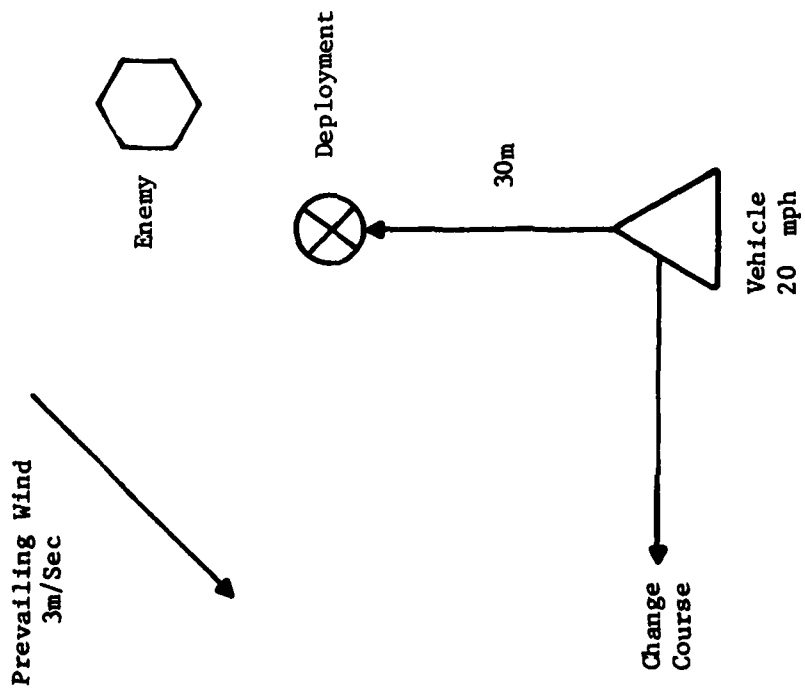
Two potentially significant ecological exposure pathways for field use of RP-BR grenades are: (1) deposition/washout of aquatic systems; and (2) exposure of terrestrial organisms to airborne smoke.

Because of the extremely toxic nature of P_4 residues in aquatic systems (see Section 4), deposition/washout of any undegraded P_4 , especially

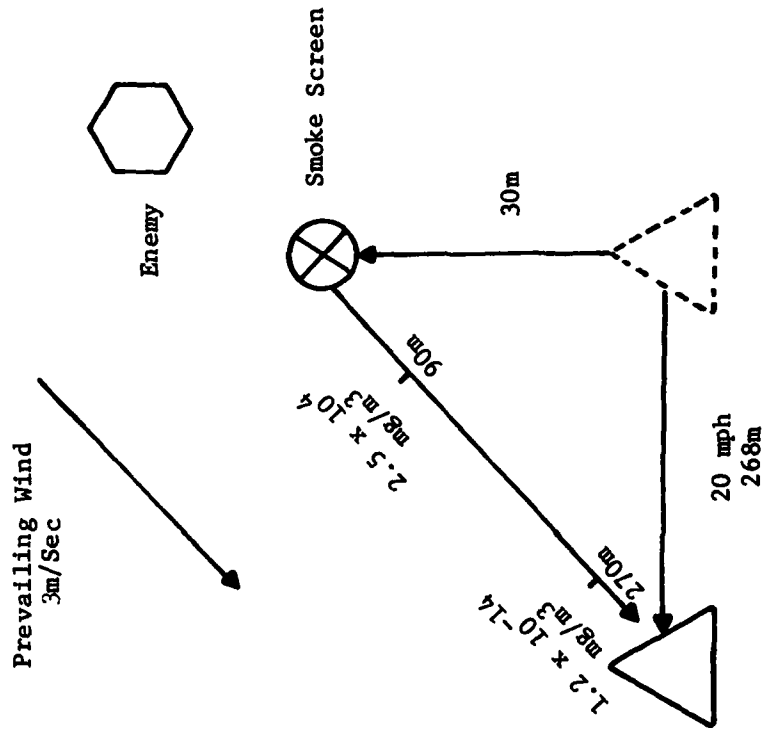
FIGURE 8

RP-BR DEPLOYMENT SCENARIO

DEPLOYMENT



DEPLOYMENT + 30 SECONDS



to small water bodies, may create exposure risks to resident finfish, invertebrates, and/or waterfowl, even if resultant P_4 concentrations are in the low ppb range. Unfortunately, there is no information available on the range and frequency of occurrence of P_4 deposition to aquatic systems from RP-BR or WP-F smokes in training or other field use. An area receiving repeated deposition (i.e., in training) would be expected to be most vulnerable.

It is known that most of the phosphorus in smoke oxidizes to forms that are relatively insignificant in any form of short-term aquatic exposure (i.e., phosphites and phosphoric acids). It is conceivable, but speculative, to hypothesize that repeated use of a specific training area for smoke deployment might result in sufficient deposition of P_4 degradation products to be a beneficial (or adverse) stimulant of aquatic plant production, or of isolation and enhancement of the availability of trace metals in the system to aquatic organisms.

Reference points for consideration of potential terrestrial organism exposure can be largely confined to comparison of smoke concentration to experimentally established thresholds for mammalian toxicity. Comparisons for vegetation or other animals would be speculative in the absence of experimental data and with the knowledge that even among mammals there is evidence of widely variable sensitivity (see Section 4).

Available data from tests with RP smoke indicate peak concentrations of about 200 mg/min/m³ (form of phosphorus unspecified). If such levels characterized training and field exposure scenarios, the potential for acute, lethal mammalian exposure would likely be minimal, as this is about an order of magnitude below the (phosphorus acid equivalent) inhalation LC₅₀'s of RP-BR smoke for the most sensitive species tested (see Section 4). Sublethal effects on mammals, such as irritation of the eyes, would be a reasonable expectation.

Calculated hypothetical exposure scenarios for RP-BR smokes suggest the possible occurrence of peak concentrations of about 10,000 mg/m³ at a given distance after 30 seconds (i.e., 5,000 mg/min/m³), which would fall within the range of the aforementioned LC₅₀'s. However, the calculations further suggest a decline of the peak by about two orders of magnitude after one minute has elapsed. This suggests that field exposure conditions lethal to mammals are unlikely to exist or persist under most circumstances. (Note here that the above calculations are based on predicted concentrations of P₂O₅, not phosphoric acid, which was the basis for the toxicity values.)

3.4.2.2 WP-F: Large Area, One-Time Coverage

Human Exposure

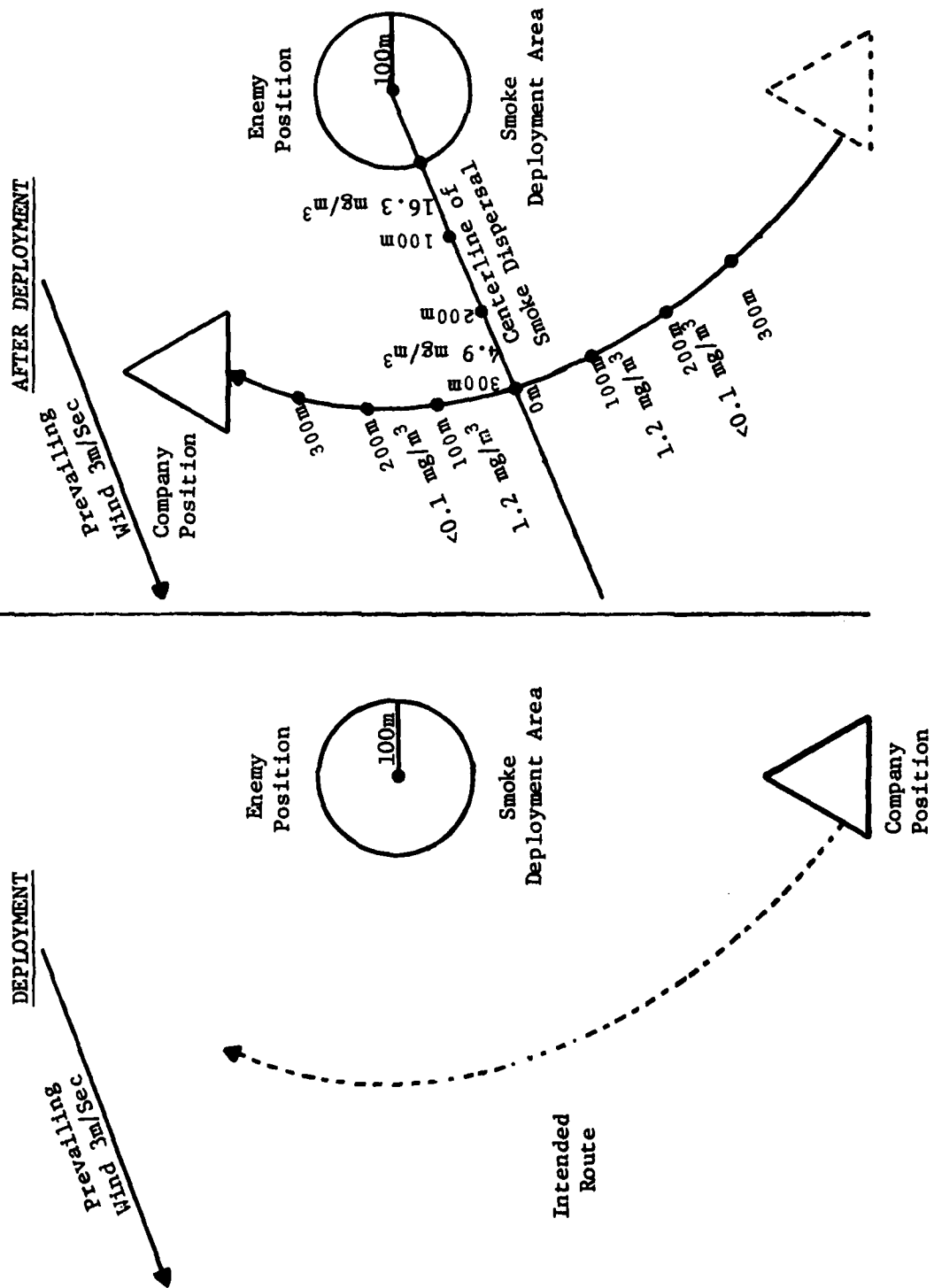
WP-F smoke can be deployed using 60-81 mm mortars or rockets to blind enemy observation of troop or vehicle movements (N.B. over longer ranges field artillery could be utilized). For example, a barrage of WP-F mortars could be placed directly on an enemy observation post prior to conducting a maneuver. In this case, it is assumed that effective screening requires one-time coverage of a large area. The manual, Small Unit Smoke Operations, presents an example of such an operation:

- "• A company team is conducting a movement to contact. After moving through a thick wooded area, the team reaches an open valley flanked on one side by five small hills.
- The team commander studies the valley visually and by map and decides that the first hill to his right is a likely spot for an enemy observation post.
- He calls for mortar fire to deliver smoke on the hill. When a large smoke cloud develops, he begins the advance up the valley.
- As the team passes the second hill, however, it starts to receive indirect weapons fire. The team commander suspects that an enemy observation post is located on one of the other hills to his right, but he is not sure of its exact location. For this reason, he decides to produce a smoke screen between his position and the remaining hills on the valley. He does this with mortar and field artillery fire.
- Within a few minutes, the smoke screen is thick enough to reduce observation and the team continues its advance."

Figure 9 is a graphic description of this scenario. Calculations of smoke dispersal assumed the deployment of a single 155 mm WP-F shell containing 5980 grams of WP-F which burns for 7 minutes. The scenario uses these data and assumes that the same amount of smoke is delivered by deploying several smaller mortars or rockets. In this case smoke deployment is intended to obscure enemy observation of troop movements which will pass by the enemy position. Under the scenario conditions the troop will cross the centerline of cloud dispersal at a distance of 300 m from the edge of the smoke deployment area. As the troops approach the centerline they will encounter the following smoke concentrations:

FIGURE 9

WP-F MORTAR DEPLOYMENT SCENARIO



<u>Distance from Centerline (m)</u>	<u>Concentration mg/m³</u>
200	less than .1
150	.1
100	1.2
50	3.4
Centerline	4.9

Maximum exposure occurs as the troops cross the centerline of smoke dispersal (4.9 mg/m³). If the traverse occurs closer to the deployment area, exposure will be higher (i.e., at 200 m: 7.9 mg/m³; at 100 m: 16.3 mg/m³).

Flora/Fauna Exposure

The same factors basically apply to considerations of ecological exposure due to large area, one-time coverage with WP-F smokes as were discussed above for RP-BR smokes (section 3.4.2.1). The same important areas of uncertainty exist concerning aquatic and terrestrial organism exposure conditions, and the same generic likelihood that a training area used repeatedly would experience the greatest potential for cumulative impacts from P₄ residues and/or degradation products. Calculated values for atmospheric concentrations in this type of a field scenario suggest that maxima of no more than about 35 mg/m³ (phosphoric acid at 50% humidity) would exist. Such a level would be orders of magnitude below reported mammalian effects levels (see Section 4), but exposure effects for other organisms remain uncertain.

3.4.2.3 WP-F: Large Area, Sustained Coverage

Human Exposure

For deployment over a greater range and for maintaining sustained coverage, 105 mm or 155 mm WP-F projectiles can be utilized by field artillery. For example, a commander attacking a defensive enemy position could request a sustained smoke screen on likely avenues of approach (map of the earth, contour, or low level) for enemy helicopters. Such a smoke screen may force enemy helicopters to abort their attack or to operate at higher and more vulnerable altitudes.

In order to maintain an effectively obscuring concentration of smoke (0.288 gm/m³) over a 100 m square area for 1 hour, deployment of 72 WP-F 155 mm shells would be required. Smoke dispersal calculations have not been made for this scenario; however, they are expected to be similar to those presented in previous sections, except that the duration of smoke generation and dispersal will be longer.

Flora/Fauna Exposure

This scenario would entail almost the same ecological considerations as the two preceding scenarios, with the exception that the cumulative exposure potentials due to deposition/washout would obviously be greater. The assumed maintenance of an atmospheric concentration of about 300 g/m³ of P₂O₅ (i.e., about 1,500 mg/m³ of phosphoric acid at 50% humidity) brings about the likelihood of at least irritation-level exposure for mammalian receptors, and the possibility of approach of lethal thresholds for the most sensitive species (see Section 4).

Section 3

Appendix A

Background Theory/Discussion of Dispersion Models

To determine concentrations of white phosphorus felt or red phosphorus butyl rubber caused by shell explosion in the field, various models that consider instantaneous sources were investigated. An instantaneous source has very short-term pollutant release time, on the order of seconds. An explosion of a smoke producing shell would therefore be considered an instantaneous source. To determine concentrations at any position downwind, one must consider the time interval after the time of release and diffusion in the downwind direction as well as lateral and vertical diffusion.

The determination of the path or trajectory of the "puff" is both very important and difficult if concentrations are to be determined at specific points. Determining the trajectory is of less importance if knowledge of the magnitude of the concentrations for particular downwind distances or travel times is required without the need to know exactly at what points these concentrations occur.

In the following pages, three different instantaneous source models will be discussed. Adaptations of the algorithms used in these models, applicable to smoke bomb explosions will be used to calculate concentrations produced on the battlefield.

Turner's (1970) equation presents an equation for calculating concentrations from an instantaneous source. This equation was rewritten from Sutton's (1932) equation. The equation is as follows:

$$\begin{aligned} X(x, y, z; H) = & \frac{2 QT}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp \left[-1/2 \right. \\ & \left. \left(\frac{x - Ut}{\sigma_x} \right)^2 \right] \exp \left[-1/2 \left(\frac{H}{\sigma_z} \right)^2 \right] \\ & \exp \left[-1/2 \left(\frac{y}{\sigma_y} \right)^2 \right] \end{aligned} \quad (5.21)$$

where: QT is total mass release (gm);
U is the wind speed (m/sec);
z is time after release (sec);
H is height of release (m);
x is downwind distance from release point (m);
y is crosswind distance from release point (m); and
 σ_x , σ_y , and σ_z are the standard deviations of the concentration distribution in the puff (m).

It should be noted that the x axis is always oriented in the downwind direction. Consequently, σ_x is the standard deviation of the concentration distribution of the puff in the downwind direction.

Wind speed primarily influences the downwind position of the center of the puff as is shown by examination of the exponential term involving σ_x and U. Wind speed can also influence the dispersion indirectly, because the dispersion parameters σ_x , σ_y and σ_z may be functions of wind speed.

Since much less is known of dispersion in the downwind direction than is known of lateral and vertical dispersion, it is difficult to make reasonable estimates of σ_x . Turner (1970) indicates that in general one should expect the value of σ_x to be about the same as σ_y . Initial puff dimensions from an explosion can be approximated by finding a virtual distance to give the appropriate initial standard deviation for each direction. Then σ_y will be determined as a function of $\chi + \chi_y$, σ_z as a function of $\chi + \chi_z$ and σ_x as a function of $\chi + \chi_x$.

Slade (1965) has suggested values for σ_y and σ_z for quasi-instantaneous sources. These are found in Table 1.

TABLE 1
Estimation of Dispersion Parameters for
Quasi-Instantaneous Sources

	x = 100m		x = 4km	
	σ_y	σ_z	σ_y	σ_z
Unstable	10	15	300	220
Neutral	4	3.8	120	50
Very stable	1.3	0.75	35	7

Sutton (1953) presents an equation for calculating concentrations from an instantaneous point source.

$$X(x, y, z, t) = \frac{Q}{\pi^{3/2} C_x C_y C_z (U t)^{3/2} (2-n)} \exp \left[-(\bar{U} t)^{n-2} \left(\frac{x^2}{C_x^2} + \frac{y^2}{C_y^2} + \frac{z^2}{C_z^2} \right) \right]$$

Where: Q is total mass of smoke generated (g);
 \bar{U} is constant wind speed (m/sec);
 t is time after release (sec);
 x, y and z (m), are measured from an origin moving with
 the cloud at constant speed, U:
 Cx, Cy and Cz (m), are functions of the kinematic viscosity
 and the constant wind speed.

When n=0 the equation will assume that for all degrees of turbulence, the radius of the cluster will not increase more rapidly than the distance traveled. N=1/4 gives a reasonably accurate description of diffusion in the atmosphere for distances varying from meters to tens or hundreds of kilometers.

Drivas and Shair (1974) carried out a tracer study to test the validity of several theoretical models which can be used in predicting the dispersion from an instantaneous cross-wind line source. The tracer gas, sulfur hexafluoride, was released by an automobile to simulate a quasi-instantaneous line source. The automobile was moving along an urban highway in Los Angeles. Concentrations at various locations from 0.4 to 3.2 km downwind of the highway were recorded at ground level as a function of time.

In general, a plot of the measured concentrations vs. time, yielded curves that, except for the shortest downwind distance at 0.4 km, were decidedly nonGaussian. The curves exhibit a skewness to the right which increases with increasing downwind distance.

The Gaussian equation for determining the ambient concentrations from an instantaneous crosswind line source was tested in order to compare theoretical results with the actual experimental data. The equation used values of the variables taken from Slade (1968). The equation is as follows:

$$x = \frac{QL}{\pi \sigma_{XI} \sigma_{ZI}} \exp \left[-\frac{(x - \bar{U}t)^2}{2\sigma_{XI}^2} \right]$$

Where: QL is total mass of release (g);
 \bar{U} is constant windspeed (m/sec);
 t is time after release (sec);
 x is downwind distance from release point(m); and
 σ_{XI} and σ_{ZI} (m), are the standard deviations of the concentration distribution in the puff.

The mathematical description of σ_{XI} and σ_{ZI} is:

$$\sigma_{XI} = 0.06 (Ut)^{0.92} \quad \text{and};$$

$$\sigma_{ZI} = 0.15 (Ut)^{0.70}$$

The results of testing the models yielded two major discrepancies: (1) the peak concentrations for the case tested were over-estimated by a factor of 20; and (2) the time associated with the movement of the concentration peak downwind was grossly in error. The second result is because the model predicts a constant average velocity for the movement of the peak concentration. The experimental data show an apparent velocity which increases with time.

The field investigations of Drivas and Shair (1974) have shown that the use of simplified Gaussian source models may lead to large over-predictions, and that the calculated ambient concentrations are heavily dependent on the trivariate σ 's used in the puff equation.

Three major instantaneous source models have been presented for background. The next section will detail the model which will be used to calculate concentrations of WP-F and RP-BR in battlefield use.

A modified version of Sutton's model intended to improve the σ determinations was developed by the Army Materiel System Analysis Activity (AMSAA). This model referred to as the Smoke Effectiveness Manual Model (SEMM), was derived from the JTCG Smoke Observation Model No. 1 (SOM-1), developed by M.C. Johnson. To make the model more manageable, Mr. G. Hanna of AMSAA and the Oklahoma State University engineering Field Office at Eglin Field, Florida, revised the SOM-1 by removing transmission and brightness calculations that were in question. Instead they left this information to be supplied by calibrated test results. Additional features were also included such as the effects of weapon delivery errors and a comprehensive analysis of the density distribution of the smoke cloud. The model has the following distinctive features:

- The smoke model is a transport and diffusion model and requires transmission data;
- The model assumes an uncorrelated Gaussian trivariate distribution for each obscuring burst;
- The model produces "holes" or discontinuities in the smoke screen due to the aiming and precision errors of induct firing weapons; and
- The model is used for detection but with proper data can be used for recognition and identification.

The Gaussian trivariate distribution of aerosols chosen for this model evolved from the works of Sutton, Calder, and Milly. In order to establish values for the model's constants, Milly (1958) compared the model against numerous test data on various types of munitions.

The AMSAS model can be used for both WP-F and RP-BR munitions.

When exploded, the phosphorus munition develops an initial size and proceeds to diffuse and advect according to meteorological conditions. The bursts are assumed to have a trivariate Gaussian distribution with standard deviations σ_x , σ_y , and σ_z at any time and given by Johnson (1972) as:

$$\begin{aligned}\sigma_x &= 0.1522 \left(\frac{Ut + A}{1.0}\right)^{.9294} \\ \sigma_y &= 3.41 \left(\frac{Ut + B}{100}\right)^a \\ \sigma_z &= 1.35 \left(\frac{Ut + C}{20}\right)^b\end{aligned}\quad (2.1)$$

The term U is the mean wind velocity near the ground and t measures the age of each burst. Exponents a and b are functions of the temperature difference between .5m and 4m above the ground. The terms A, B, and C account for the initial burst size of the munition. They are represented mathematically by the following:

$$\begin{aligned}A &= 1.0 \left(\frac{\sigma_{xs}}{.1522}\right)^{1/.9294} \\ B &= 100 \left(\frac{\sigma_{ys}}{3.41}\right)^{1/a} \\ C &= 20 \left(\frac{\sigma_{zs}}{1.35}\right)^{1/b}\end{aligned}\quad (2.2)$$

The terms σ_{xs} , σ_{ys} , and σ_{zs} are the source values of the standard deviation and depend on the fill weight of the munition. The constants in the equations describing A, B, and C were established by Milly (1958), in accordance with test data. The equations have been modified somewhat by past users. The diffusion characteristics of the burst and consequently that of the smoke screen, are a function of the growth of σ_x , σ_y , and σ_z with time.

During deployment of the smoke screen from the individual bursts, the density of the screen at any point is the sum of the densities of the individual bursts taken at that point. With a mean ground wind velocity \bar{U} in a direction X, the cloud density at any point, x, y, z in the wind axis system is described by the following equation:

$$DEN = \frac{2}{(2) 3/2} \sum_1^N \frac{Q\lambda\Omega}{\sigma_x \sigma_y \sigma_z} \exp \left\{ -1/2 \left[\frac{(x-Ut)^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{(z-z(t))^2}{\sigma_z^2} \right] \right\} \quad (2.3)$$

- Where: Ω is the munition efficiency with which the smoke producing material is used.
- Q is the weight of the smoke producing material prior to explosion, excluding weight lost in the plume.
- Ω is the yield factor associated with the physico-chemical reaction process which converts smoke producing material into smoke. For hygroscopic agents this quantity is mainly a function of relative humidity.
- $z(t)$ is the function which describes the vertical motion of the smoke due to updrafts from heat released during production.
- N is the number of bursts of WP forming the smoke screen.
- x is downwind distance
- y is crosswind distance.

Integration of the density equation is carried out along various lines of sight L_i originating at the observer's position and passing through the screen. Mass per unit area of the obscurant along line L is described by the following equation:

$$\text{MASS (L)} = \sum_{i=1}^N \int_0^L (\text{DEN}) dL \quad (2.4)$$

The AMSAA model SEMM is widely accepted throughout the smoke obscuration community. The white phosphorus portion of the smoke model was run using test data obtained from the Smoke Inventory Tests. To investigate the model's predictive ability, tests employing one and three rounds of 105 mm WO M60A2 munitions and three and six rounds of 155 mm WP M1DE2 munitions were carried out for comparative analysis. Each group of rounds was statistically fired simultaneously in a linear array parallel to the observer's line of sight (LOS). A time history of smoke concentration was recorded as the cloud passed the observers LOS and a comparison of concentration was made with the corresponding predicted value obtained from the smoke model.

The concentration length (CL) represents the mass of smoke occupying a volume one square meter in cross section extending along the observer's LOS. The comparisons made to date between model and test results, reveal that the model predicts the thresholds quite favorably. A characteristic of most test

and model comparisons is the tail-off of smoke that persists after the main body of smoke has passed downwind. Apparently, this effect is caused by filler material containing solid chunks which do not form the initial flash but continue to burn on contact with the ground. Degradation of the model's prediction capabilities is not effected by this phenomenon until volleys of the larger 155 mm munitions are involved. Difficulties arise where the WP model results predict higher peak values of CL's and shorter duration times at lower CL's. Both effects are again apparently due to some of the filler material not being consumed during the initial burst and burning on the ground afterwards. On the whole the comparisons made between the test data and model results were quite favorable.

INPUTS TO SEMM

The model requires two types of inputs to produce results, selected inputs and fixed inputs. The selected inputs are important because they determine the history of the smoke cloud. The fixed inputs have a lesser influence on the dispersion of the smoke cloud and are not easily discernible or calculable on the battlefield.

Meteorological conditions have been selected and grouped into five combinations of atmospheric stability and wind velocities in accordance with the Pasquill grouping of parameters. These are contained in Table 2 below.

TABLE 2. METEOROLOGICAL CONDITIONS

<u>Stability</u>	<u>Wind Speed, knots</u>	<u>Approx. Pasquill Category</u>
(Stable)	5	E to F
(Neutral)	5	D to C
(Neutral)	10	D to C
(Neutral)	15	D to C
(Unstable)	5	A to B

Wind directions are chosen with reference to the observer-to-target LOS. These are head or tail wind, crosswind and quatering wind.

The model handles various munition types and volley sizes. The actual usage of these inputs will be described in the field usage portion of this document.

Military screening smokes most commonly consist mainly of hygroscopic products of chemical reactions which form dilute solutions in the presence of atmospheric water vapor. This results in a smoke cloud actually consisting of suspensions of small liquid droplets. Both types of phosphorus munitions fall into this class. The mass of smoke they produce is greater than the mass of the original dry agent. The amount of smoke produced by these munitions is directly proportional to the water vapor content of the air, i.e., relative humidity. The greater the relative humidity the greater the amount of smoke produced. This relationship is expressed in the form of a yield factor which is the ratio of the wet smoke mass produced to the mass of dry agent consumed. Yield factors versus relative humidity were plotted for various smoke agents. This plot is found in Figure 1.

Research done by Milly (1958) concludes that the diffusion of smoke bursts is controlled by the meteorological dependent quantities α and β . These quantities are determined by the local average temperature difference between a height of 4 meters and 0.5 meters. The quantities α and β are important, because they are used in calculating the standard deviations of the trivariate smoke density distributions in directions perpendicular to the wind direction. Figure 2 shows a plot of $\alpha=\beta$ versus temperature difference.

SEMM uses the munition fill weight modified by an efficiency factor to account for two effects: (1) the amount of fill actually converted to dry smoke and (2) the amount of smoke which is lost in the rising plume. The first depends on test results while the second is dependent on atmospheric stability and is used instead of a smoke rise function. The product of fill weight and efficiency is called the effective fill weight. In a conversation with Mr. Robert Marchetti of U.S. Army Material Systems Analysis Activity at Aberdeen Proving Ground, MD, he stated that for all phosphorus munitions and stabilities classes, an efficiency of 10% should be assumed. The effective fill weight will be outlined when smoke dispersion scenarios are discussed.

When a phosphorus munition explodes, the smoke originates as the result of a bursting charge which ignites and separates the filler material. The distribution of this material is assumed to have the same Gaussian characteristics of the subsequently diffused cloud. This initial burst is characterized

by the source sigmas, σ_{xs} , σ_{ys} , σ_{zs} which are strongly dependent on the effective fill weight. The diffusion process of the smoke screen is defined by the sigma growth with time. Figure 3 shows a plot of the source sigmas (m) versus white phosphorus effective fill weight.

There are more model inputs that refine model results for specific cases.

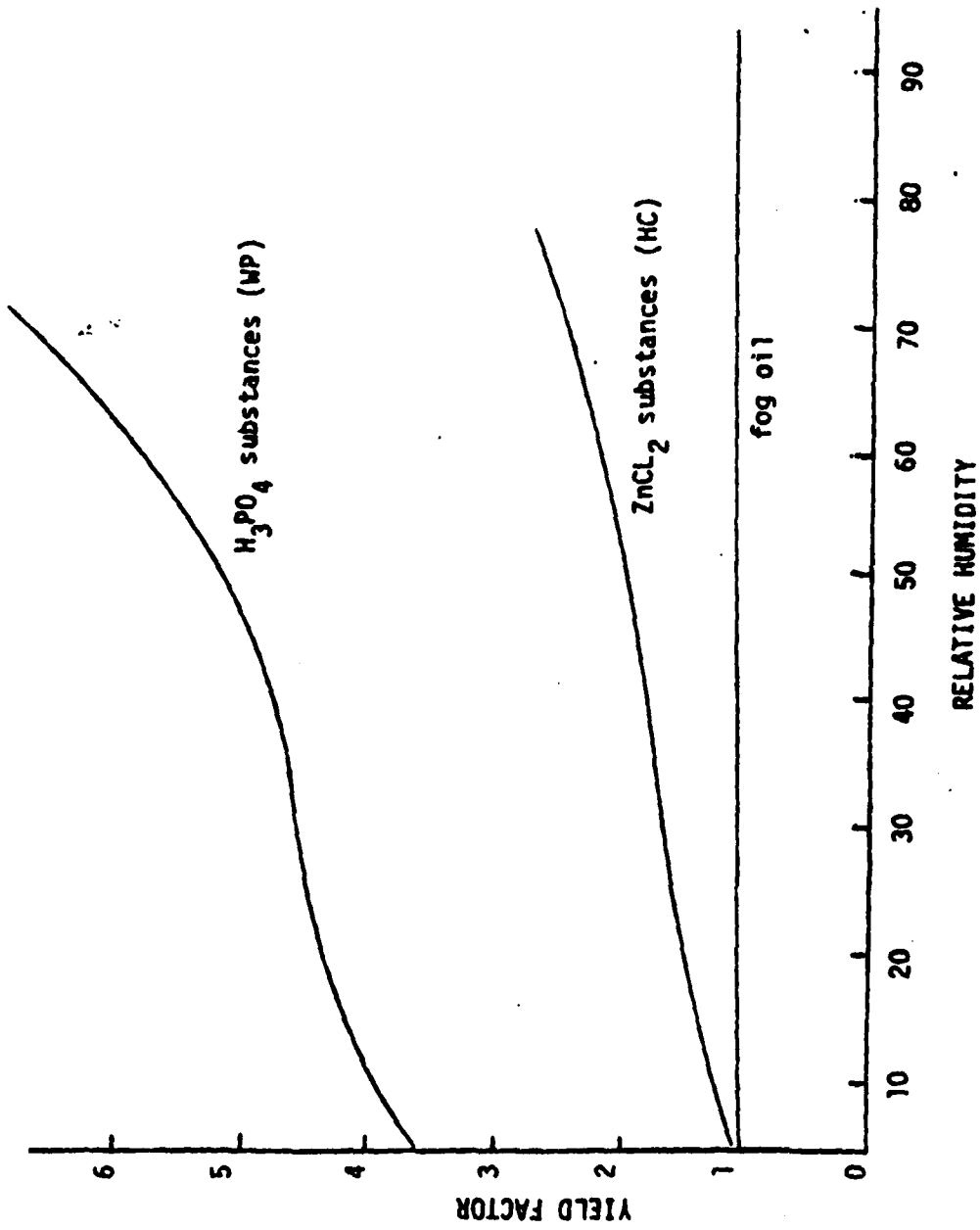


FIGURE 1
YIELD FACTOR AS A FUNCTION OF RELATIVE HUMIDITY
FOR VARIOUS SMOKE PRODUCING SUBSTANCES

Reference: Marchetti, 1979

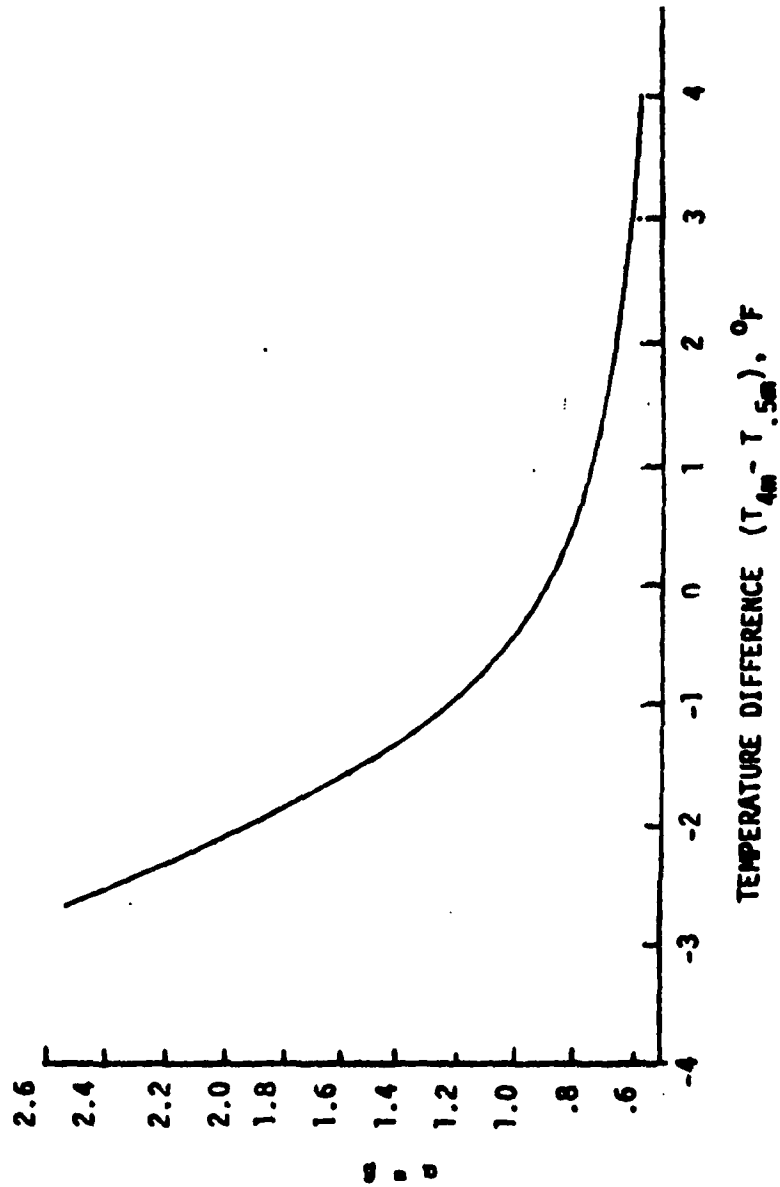
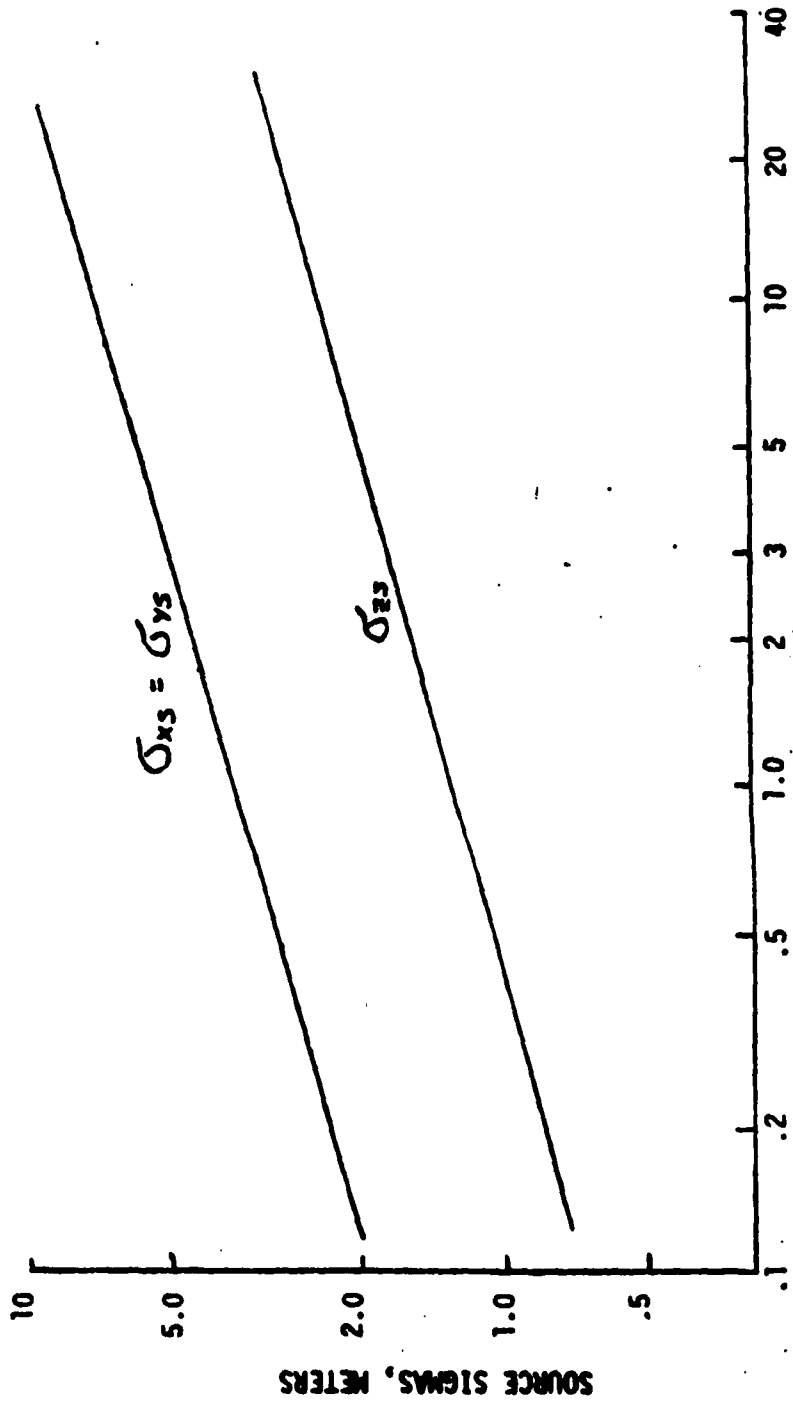


FIGURE 2

($\alpha = \beta$) vs. TEMPERATURE DIFFERENCE

Reference: Marchetti, 1979



WP EFFECTIVE FILL WEIGHT, LBS

FIGURE 3

SOURCE SIGMAS VS. FILL WEIGHT

Reference: Marchetti, 1979

Section 3

Appendix B

Particle Size of Smoke Aerosols

Effects of Humidity

Water vapor concentration in the air affects the amount of smoke that is generated from the combustion products of the phosphorus preparations. The combustion products react with atmospheric moisture to form hydrated H_3PO_4 . Figure 1 indicates the yield of smoke as a function of humidity. The chart can be used to estimate smoke yield when the amount of phosphorus burned is known. The figure shows that the dependence on humidity is significant, with 50-90% more smoke formed at 70% relative humidity than at 10% relative humidity.

Particle Size Distribution

Smoke particle size is the most important aspect in determining usefulness as an obscurant. It is also an important factor in the environmental fate of smoke and in the analysis of exposure. Particles smaller than a few microns have relatively high opacity to light transmission in the visible and infrared ranges. Particles of this size are respirable and may be respired but not remain airborne possibly as long as a month. Widespread dispersal in the atmosphere is therefore possible. Larger particles tend to settle out of the air in the immediate vicinity of their introduction.

Field tests and tests in wind tunnels have been done to determine particle size distribution from various phosphorus submunitions. Results are shown in Table 1. A white phosphorus grenade was tested and results of the particle size analysis are shown in Figure 2. Figures 3 - 6 show particle size distribution of other munitions shown in Table 1. Most particles are less than $3 \mu m$ in diameter which puts them in the respirable range. Particles of this size are also apt to remain airborne for a long time, depending on weather conditions.

Red phosphorus grenades were also tested. Table 2 shows the results of eight tests, while Figure 7 shows graphically the particle size distribution from these tests.

While the figures discussed so far seem to indicate a stable particle size distribution, tests in which smoke clouds were analyzed at different times and at different spatial locations within the cloud as it evolved show that smoke particle size distribution varies considerably. Figure 8 illustrates that behavior from a test of a red phosphorus grenade.

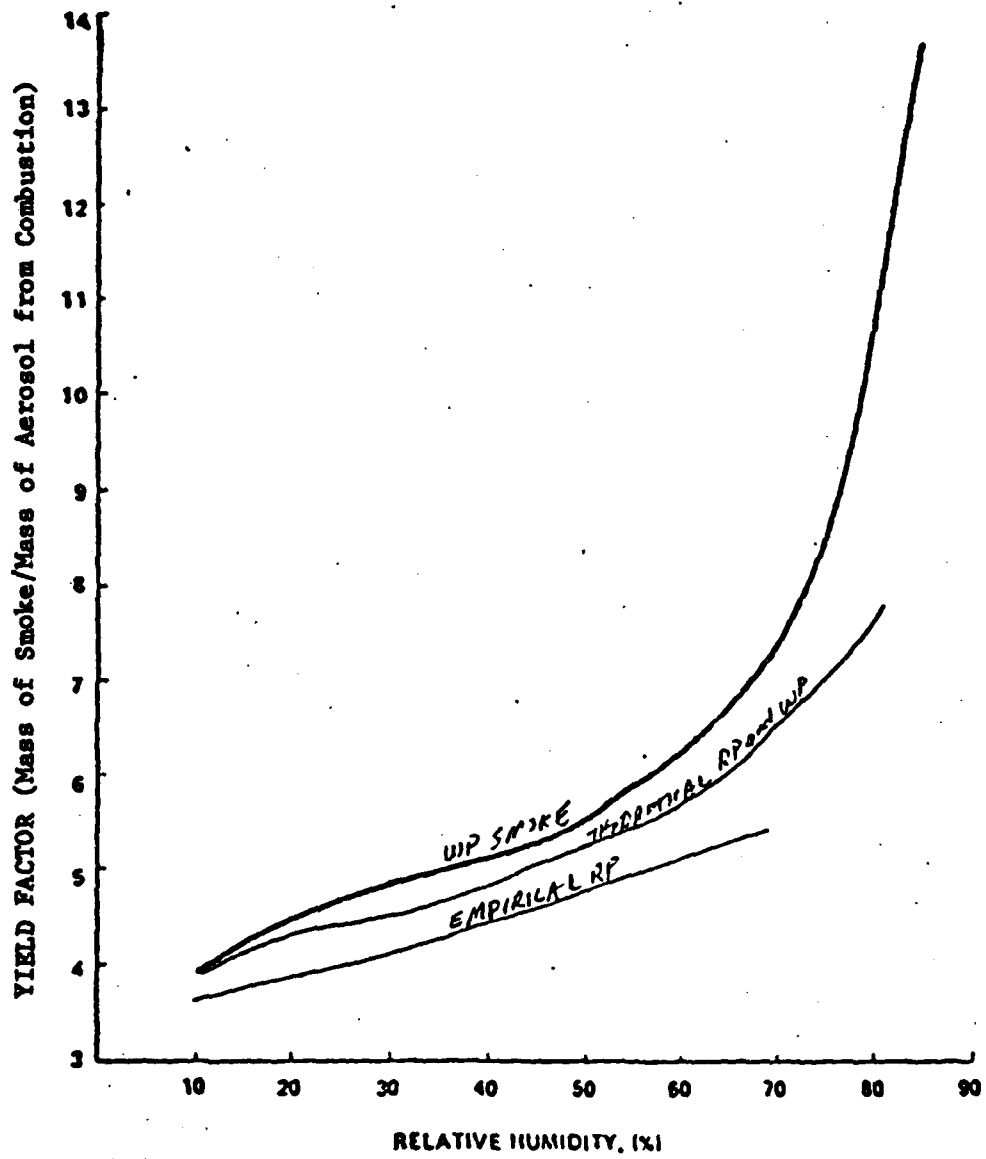


FIGURE 1

YIELD FACTORS OF A PHOSPHORUS SMOKE AS A
FUNCTION OF RELATIVE HUMIDITY

Source: Anon., 1978

Type of Submission	Initial Mass, M ₀ , g	Mass of Aerosol, M _a , g	Munition Yield Factor, MVF = M _a /M ₀	Relative Humidity	Smoke Concentration \bar{c} (lm) g/m ³ (\bar{u} = 1 m/sec)	Fraction of Particulate in Particle Size Range Diameter						Number Median Density μ m
						.3-.4 μ m	.4-.6 μ m	.6-.8 μ m	.8-1.0 μ m	1.0-1.5 μ m	1.5-3.0 μ m	
6-in. WP Wick	106	71	0.67	43-72	.91	0.23	0.20	0.14	0.25	0.19	0.00	0.64
3-in. WP Wick	63	45	0.71	71-88	.24	0.32	0.18	0.10	0.15	0.10	0.14	0.64
2.75-in. Rocket WP Wedge	210	140	0.66	62-80	2.7	0.31	0.17	0.11	0.19	0.19	0.03	0.61
81 mm Navy RP Wedge	58	31	0.53	59-60	.57	0.35	0.20	0.12	0.18	0.12	0.04	0.54
155 mm Navy WP Wedge	39	25	0.64	66-72	.58	0.25	0.15	0.10	0.15	0.11	0.23	0.79
					Average	0.29	0.18	0.11	0.18	0.16	0.09	

TABLE 1
RESULTS OF PHOSPHORUS SUBMISSIONS TESTS

Source: Rubel, G.O. (1978)

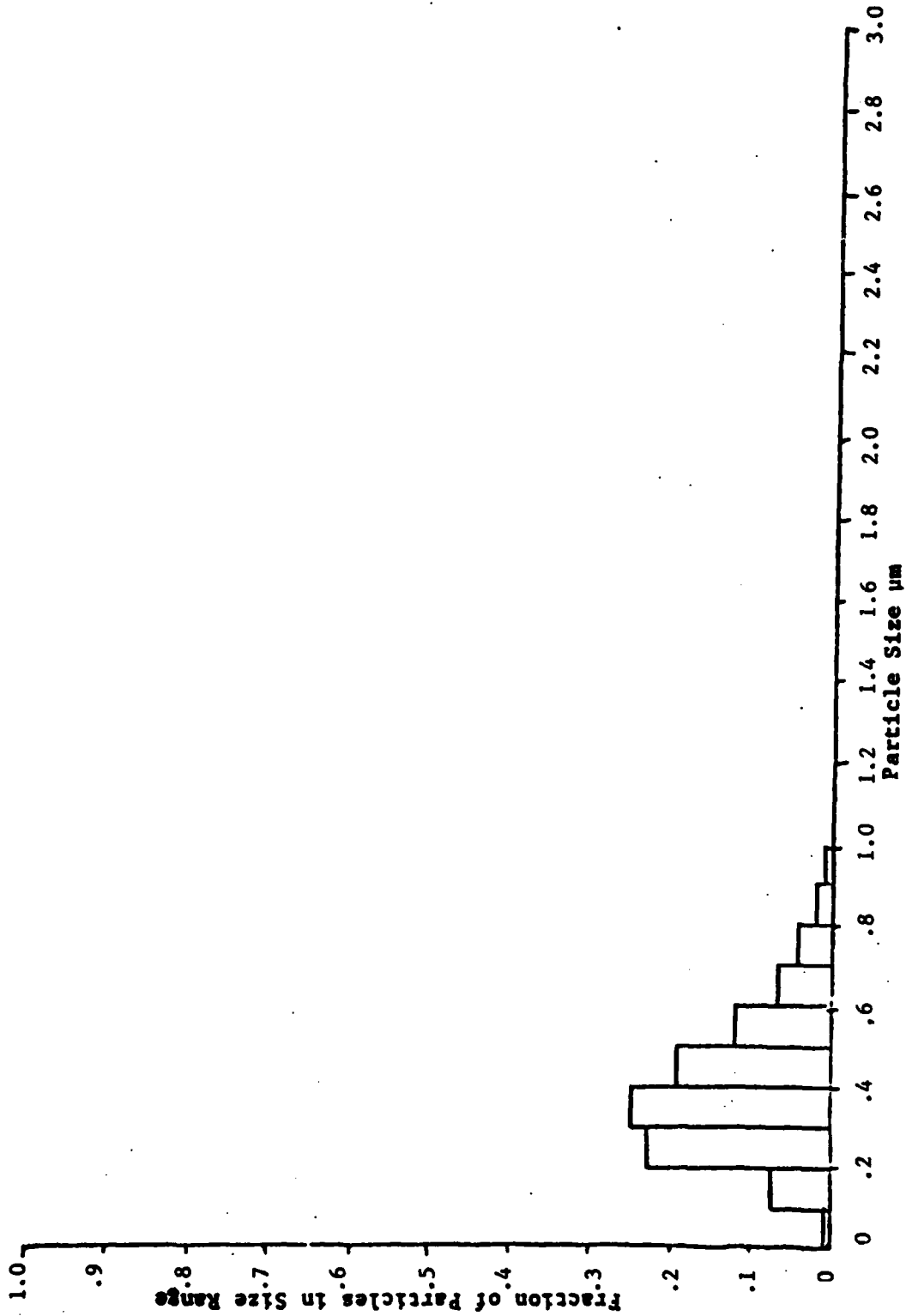


FIGURE 2
RADIUS DISTRIBUTION FOR PHOSPHORIC ACID (WP) SMOKE

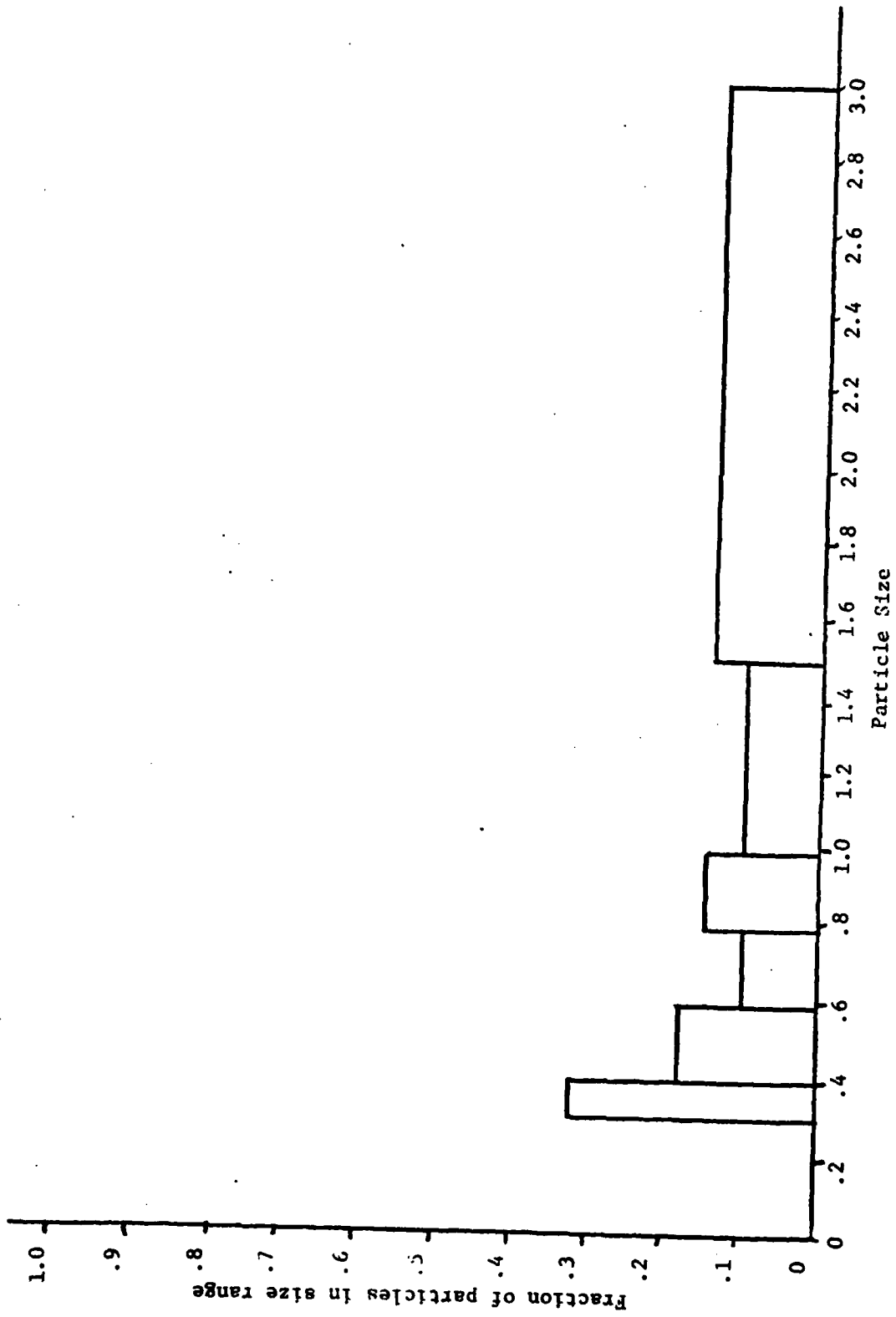


FIGURE 3
SMOKE PARTICLE SIZE DISTRIBUTION FROM THREE-INCH WP WICK

Source: Rubel, G.O. (1978)

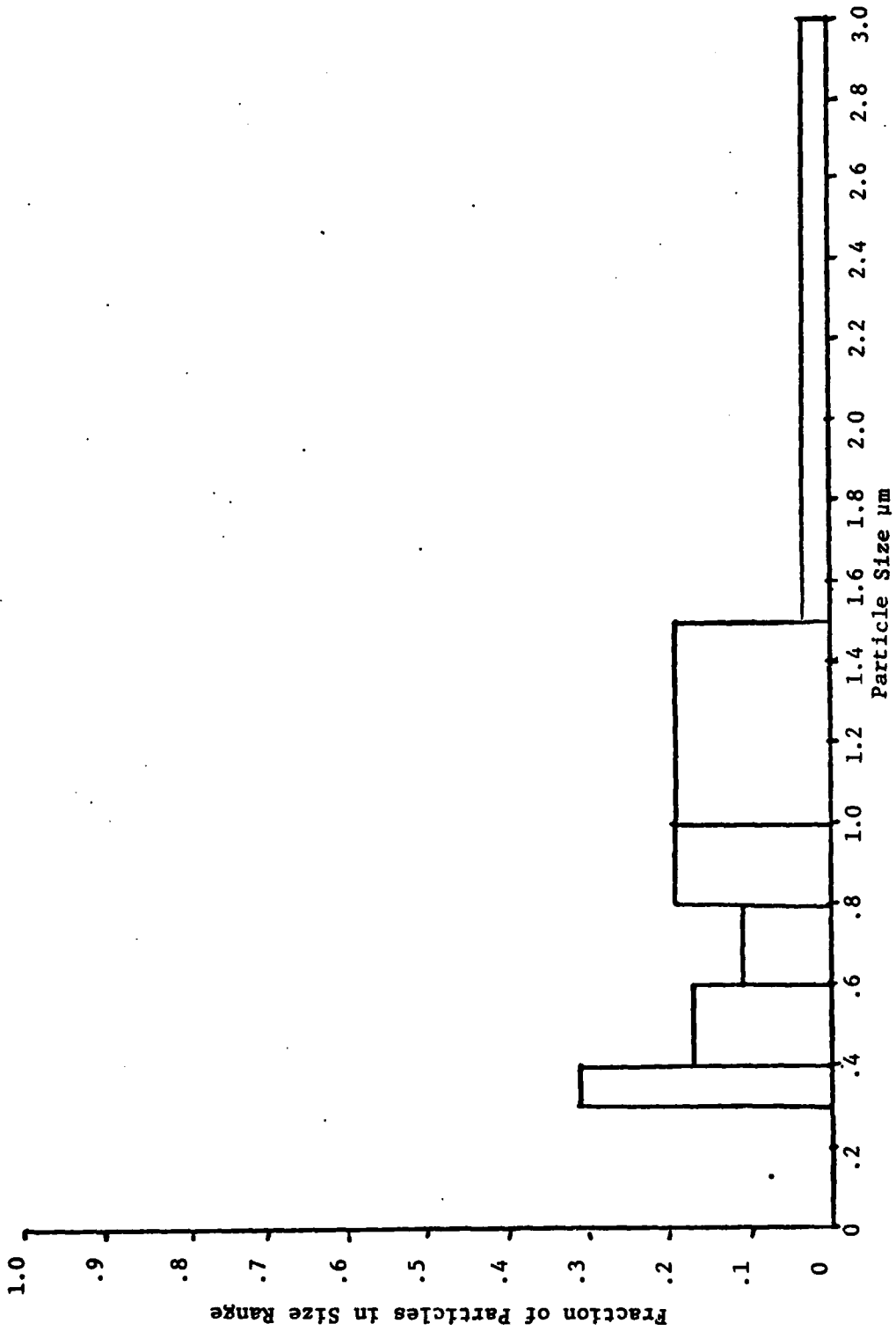


FIGURE 4

SMOKE PARTICLE SIZE DISTRIBUTION FROM 2.75-INCH ROCKET WP WEDGE

Source: Rubel, G.O., (1978)

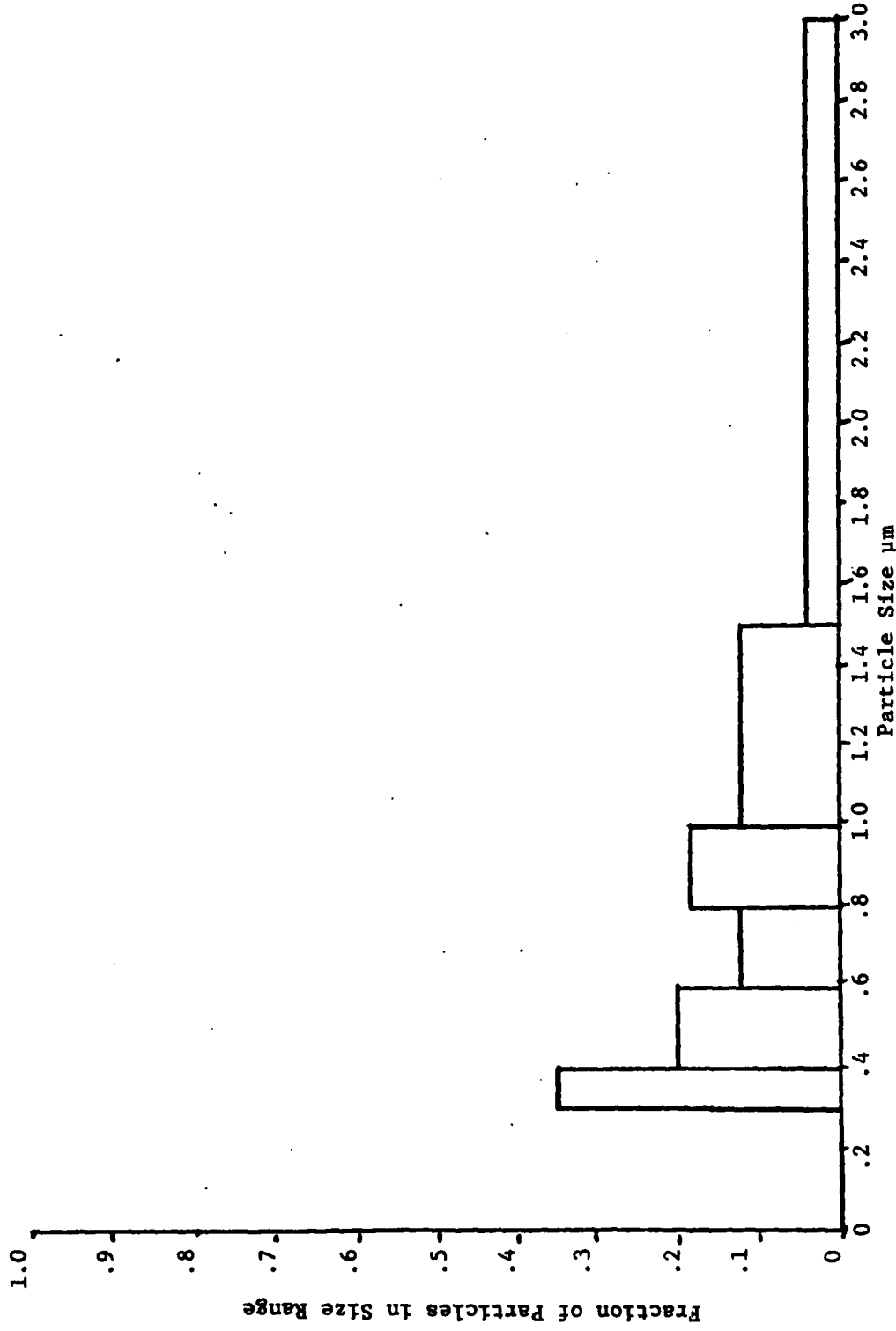


FIGURE 5
SMOKE PARTICLE SIZE DISTRIBUTION FROM 81mm NAVY RP WEDGE

Source: Rubel, G.O., (1978)

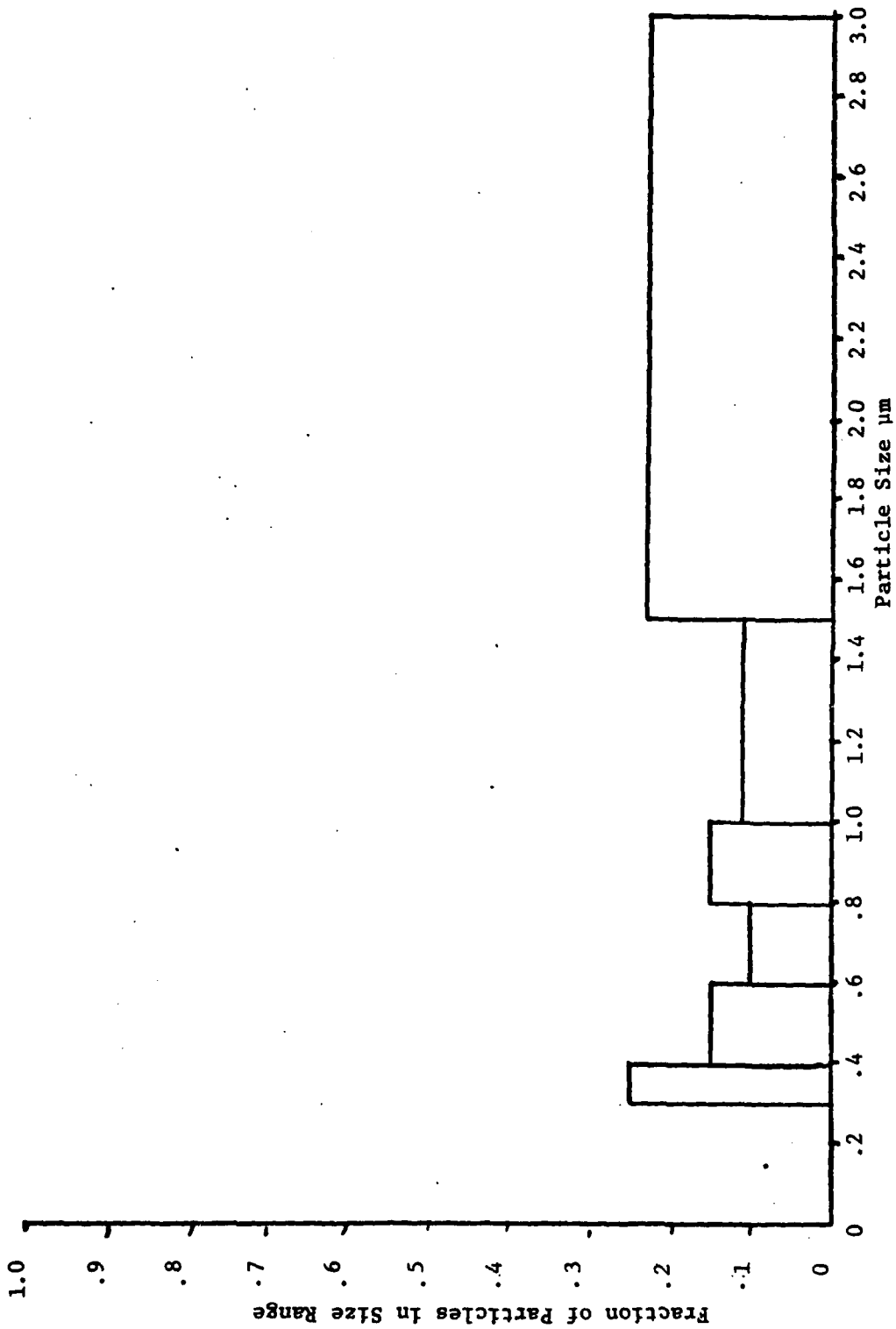


FIGURE 6
SMALL PARTICLE SIZE DISTRIBUTION FROM 155mm NAVY RP WEDGE

Source: Rubel, G.O., (1978)

TABLE 2
L8A1 RP GRENADE SMOKE PARTICLE SIZE DISTRIBUTION
(95% RP, 5% BR)

Fraction of Particles in Size Range

Size Range μm	Trial								\bar{x}	σ
	1	2	3	4	5	6	7	8		
0.3-0.4	.17	.23	.56	.15	.18	.26	.20	.04	.22	.15
0.4-0.6	.19	.23	.32	.16	.20	.29	.22	.33	.24	.06
0.6-0.8	.19	.20	.08	.20	.22	.20	.21	.26	.20	.05
0.8-1.0	.17	.14	.02	.18	.17	.13	.16	.18	.14	.05
1.0-1.5	.19	.14	.01	.20	.17	.10	.17	.15	.14	.06
1.5-3.0	.12	.05	.01	.12	.05	.02	.07	.03	.06	.04

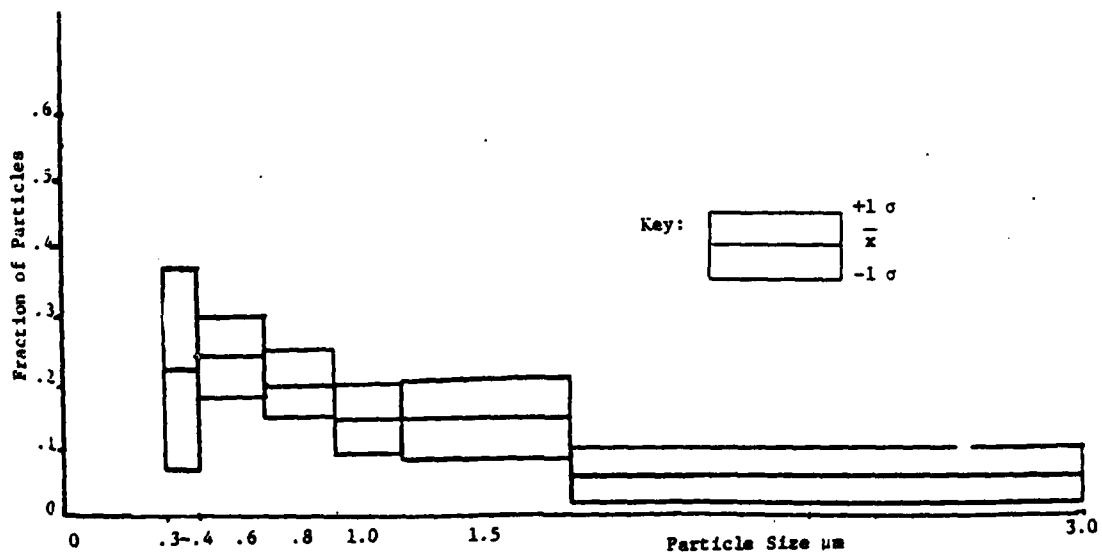
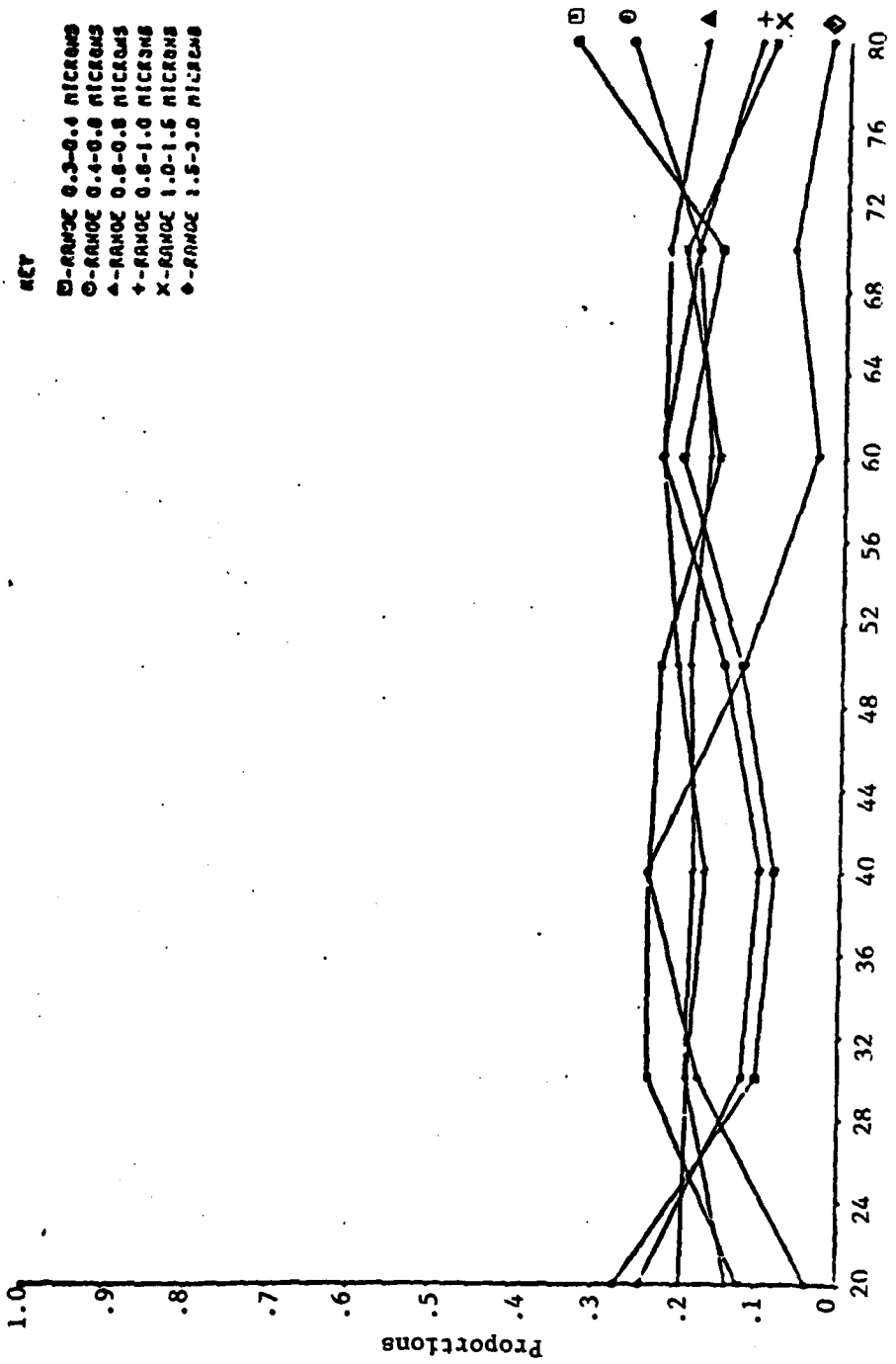


FIGURE 7
L8A1 RP GRENADE SMOKE PARTICLE SIZE DISTRIBUTION
MEAN AND 2σ LIMITS OF DATA FROM EIGHT TESTS

Source: Rubel, G.O., (1978)



Time from Function (Seconds)
FIGURE 8

PROPORTION OF PARTICLES IN VARIOUS RANGES (see Key) AS A FUNCTION OF TIME BASED ON NUMBER

4.0 TOXICOLOGY OF WP-F AND RP-BR SMOKES

4.1 Human Health Effects

This section discusses the human health effects of exposure to toxic materials used by the Army in the manufacture and deployment of white phosphorus/felt and red phosphorus/butyl rubber smoke munitions. Table 25 lists the specific materials discussed, and indicates exposure potential during production and/or smoke deployment and important exposure routes.

Table 25

Toxic Substances Encountered During Production and Deployment

WP/F and RP/BR

<u>Toxic Substance</u>	<u>Exposure During:</u>		
	<u>Production</u>	<u>Smoke Deployment</u>	<u>Via Primary Routes of Risk</u>
Phosphorus (Red)	X	?	Inhalation
Phosphorus (White)	X	X (?)	Inhalation, ingestion, skin
Phosphoric Acid	X	X	Inhalation, skin
Phosphorus Acid	X	X	Inhalation, skin
Phosphine	?	?	Inhalation
Methylene Chloride	X	NO	Inhalation, skin

Both human-exposure/effects data and animal-experimental data have been utilized in the evaluation of health effects. Where possible and appropriate, interspecies differences in sensitivity and physiological response to the toxic chemicals have been considered. In many instances, however, interspecies differences with respect to particular dose/response relationships have not been reported, and therefore, the reliability of extrapolations between species is questionable.

As will be made clear, there are major data gaps. Most conspicuous are those concerning the composition of phosphorus smoke and the health effects due to intermediate and long-term exposure to the smoke. Much of the animal exposure data concerns the acute lethal response to smoke, while human exposure data concern very brief non-lethal exposures and are insufficiently quantitative.

A number of reviews have been written on the toxicity of phosphorus. These reviews are cited and summarized in the following section. Proportionally greater effort has been expended to augment these reviews and clarify, where possible, those subject areas for which new data have become available.

4.1.1 Pharmacokinetics of Red and White Phosphorus

4.1.1.1 Absorption of White Phosphorus

White phosphorus is readily absorbed upon ingestion. Experimental studies in rats indicate that absorption is rapid and at least 60% of the dose is absorbed from the gastrointestinal tract. The percentage is probably much higher because the role of biliary excretion of absorbed phosphorus has not been determined (Lee, et al., 1975; Ghoshal, et al., 1971). Gastrointestinal absorption in humans is similarly rapid and complete. The influence of vehicle on mortality was examined by Diaz-Rivera, et al., (1950), but their analysis does not concomitantly take into account the amount ingested or the influence of vomiting or of gastric lavage on mortality. It may be that the vehicle has some effect on rate of absorption, but it seems the differences may be of marginal importance.

Absorption of white phosphorus via inhalation in the form of vapors, oxides and/or dust particles must certainly occur, but studies in man or animals of the retention in lungs, the profile of deposition along the respiratory tract, and the chemical species involved have not been reported. The chemical reactivity of white phosphorus and its relatively low vapor pressure strongly suggest that most of the inhaled species would be the oxides; however, the extreme toxicity of white phosphorus (P_4) and of phosphine (PH_3) could be more important than the oxides even if P_4 and PH_3 are at very low concentrations.

4.1.1.2 Absorption of Red Phosphorus

Red phosphorus does not appear to be readily absorbed from the gastrointestinal tract, and this probably accounts for its very low oral toxicity. We have seen no data to indicate the actual extent of absorption.

Inhalation of red phosphorus aerosol was studied in mice by Dalhamn and Hohma (1959). They reported that in factories where red phosphorus is produced by sublimation of white phosphorus, concentrations of red phosphorus in air were up to 40 mg/m^3 . They had observed 4 cases of acute, atypical pneumonia of sudden onset at one of these factories. In their animal studies they exposed 15 mice to an aerosol of ^{32}P -labeled red phosphorus at a concentration of 5 mg/m^3 for one hour and reported early deposition in the lung, nose, and digestive system. The amount absorbed and the percent retention was not and cannot be determined from their published autoradiographs. It appears that deposition in lungs and nose is followed by partial clearance of the particles from the lungs by mucociliary transport into the digestive system. By 48 hours, no radioactivity was detected in the digestive tract because of either absorption or elimination, but radioactivity was still quite apparent in the lungs. After 10 days, radioactivity was still apparent in the lungs, although the concentration cannot be determined.

Absorption of phosphorus as a consequence of burns is discussed under a separate heading below.

4.1.1.3 Metabolism and Excretion

The metabolism of elemental phosphorus is not completely understood. When white phosphorus is ingested, it is not known what chemical species are actually absorbed or how they are metabolized. Disposition of the radioactivity of orally administered ^{32}P -labeled white phosphorus has been examined in rats by two groups at different toxic levels. Lee, et al. (1975) dosed female rats with 0.3 mg/kg ($\sim 1/10 \text{ LD}_{50}$) ^{30}P -labeled white phosphorus mixed in peanut oil. Table 26 gives the disposition of the radioactivity at 4 hours and at 1 and 5 days. These data indicate that a relatively high proportion of the absorbed dose is retained in the liver. Table 27 indicates that the highest concentrations at day 5 were in liver, bone, and kidney. About 80% of the activity was excreted by day 5 - 47% in the urine and 33% in the feces. TLC analysis of urine at 4 and 24 hours showed that about 40% of the urinary excretion was inorganic phosphate such as pyrophosphate ($^-\text{H P}_2\text{O}_7$) and orthophosphate ($^-\text{H PO}_4$ and $^-\text{H}_2\text{PO}_4$), which are biologically normal forms of phosphorus. Another 40% was unidentified. TLC analyses of liver extracts ($\text{CH Cl}_3:\text{MeOH}92:1$) indicated 32% and 58% as inorganic phosphates at 4 and 24 hours, respectively; 66% and 42% of the extract at 4 and 24 hours, respectively, were not identified. Since organic phosphate compounds constitute a large proportion of total phosphorus compounds in normal body fluids, we interpret these data to suggest that most of the phosphorus is rapidly oxidized and directed into the general phosphate pool.

Ghoshal, et al. (1971) intubated rats with ^{32}P -white phosphorus at 7.5 mg/kg, well above the lethal level, and recovered up to 70% of the radioactivity in the liver by 2 - 3 hours. Table 28 gives the percentage of radioactivity associated with various fractions of liver homogenate. The authors considered the 5% associated with the TCA precipitated microsomal fraction of some interest since this fraction contains membranes and polysomes from the endoplasmic reticulum, a site of intracellular toxicity. The differences reported by Lee, et al. (1975) and Ghoshal, et al., (1971) in levels of ^{32}P increased in the liver can be attributed partly to the large difference in dose. At very high levels the liver could have been relatively more unable to metabolize and eliminate the toxic compounds.

4.1.2 Acute Toxicity

White phosphorus is a highly toxic substance while red phosphorus is considered non-toxic by the oral route because of poor absorption (Sittig, 1979; Sax, 1979; Gosselin, et al., 1976; Patty, 1963). Table 29 presents some estimates of lethal doses in humans and other mammals. The lethal dosages are roughly comparable between mammalian species. The apparent LD_{50} is somewhat higher in man than in other mammals; however, this figure, estimated from the 56 case studies of phosphorus poisoning reported by Diaz-Rivera, et al. (1950), does not take into account that both vomiting and gastric lavage significantly reduced the actual amount of phosphorus absorbed. Rats and mice cannot vomit.

TABLE 26
DISTRIBUTION AND EXCRETION OF RADIOACTIVITY IN
RATS RECEIVING ³²P WHITE PHOSPHORUS

	<u>% of Administered Dose</u>		
	<u>4 Hours</u>	<u>1 Day</u>	<u>5 Days</u>
Gastrointestinal Tract Plus Contents	57.0 ± 3.4 ^{c/}	15.3 ± 4.0	1.7 ± 0.2
Feces	2.0 ± 1.0	16.6 ± 3.8	33.0 ^{d/}
Whole Blood ^{a/}	6.1 ± 1.1	4.1 ± 0.5	1.7 ± 0.0
Urine	17.1 ± 2.2	34.5 ± 6.1	46.7 ^{d/}
Liver	16.1 ± 4.6	16.9 ± 0.7	6.3 ± 0.3
Kidneys	0.7 ± 0.2	0.8 ± 0.1	0.4 ± 0.0
Spleen	0.1 ± 0.0	0.1 ± 0.0	0.1
Brain	0.1 ± 0.0	0.1	0.1
Lungs	0.4 ± 0.0	0.3 ± 0.1	0.2 ± 0.0
<u>Skeletal Muscle^{b/}</u>	<u>4.0 ± 0.0</u>	<u>5.5 ± 0.2</u>	<u>6.0 ± 0.6</u>
Recovery	98.6 ± 5.0	94.0 ± 3.3	96.0

a/ Based on 7.0% of the body weight.

b/ Based on 40% of the body weight.

c/ Mean ± S.E. of three rats.

d/ Pooled samples from three rats.

Source: Lee et al., 1975

TABLE 27.

TISSUE/PLASMA RATIOS OF RADIOACTIVITY IN RATS
RECEIVING A SINGLE DOSE OF ³²P WHITE PHOSPHORUS

	<u>Tissue/Plasma Radioactivity Ratio^{a/}</u>		
	<u>4 Hours</u>	<u>1 Day</u>	<u>5 Days</u>
Liver	17.7 ± 2.5 ^{b/}	51.4 ± 3.9	103.2 ± 10.0
Kidneys	4.2 ± 1.0	14.4 ± 1.2	33.5 ± 4.1
Spleen	1.8 ± 0.4	6.4 ± 2.6	18.6 ± 2.6
Brain	0.3 ± 0.0	0.7 ± 0.0	3.6 ± 0.4
Lungs	2.6 ± 0.1	5.8 ± 0.5	16.5 ± 1.0
Skeletal Muscle	0.4 ± 0.0	1.8 ± 0.1	8.7 ± 0.5
Bone	1.7 ± 0.1	12.7 ± 0.1	66.9 ± 17.2

a/ Radioactivity in 1 ml or gm of wet tissue per radioactivity
in 1 ml of plasma

b/ Mean ± S.E. of three rats.

Source: Lee et al., 1975

TABLE 28
METABOLISM OF PHOSPHORUS

% of Total ³²P in Liver at 2 Hours

<u>Fraction</u>	<u>non-TCA Precipitated</u>	<u>TCA Precipitated*</u>
Supernatant	52	2
Microsomal	13	5
Mitochondria	10	0.5
Nuclear Fractions	15	1

* Trichloroacetic acid precipitates proteinaceous material.

Source: Ghoshal et al., 1971

TABLE 29

ACUTE TOXICITY OF WHITE PHOSPHORUS

<u>Animal Species</u>	<u>Route</u>	<u>Dose</u> (mg/kg)	<u>Effect</u>	<u>Reference</u>
Rat - Male	Oral	3.76	LD ₅₀	Lee et al., 1975
Female		3.03		
Mouse - Male		4.85		
Female		4.82		
Dog - Female	S.C.	0.4	LD	Buchanan et al., 1954
Rabbit	S.C.	4.1-10	LD	Neubauer, 1911 (cited in Wasti et al., 1978)

			<u>% Mortality (Cases)</u>	
Human	Oral	90.00*	100	(1) Diaz-Rivera et al., 1950
		66.00	100	(1)
		22.00	90	(21)
		1.1	17	(18)
		0.6	14	(14)
		0.3	100	(1)

* Assumes an average 70 kg body weight.

The classical picture of acute phosphorus poisoning in humans has been described as occurring in three stages. In stage I, violent gastrointestinal symptoms occur very shortly after ingestion due to local gastric irritation. There is almost always vomiting. The vomitus usually has the garlic smell of phosphorus, and often contains blood and pieces of gastric mucosa. Death may occur within 12 hours or up to 48 hours from hypotensive shock. Stage II has been described as a relatively symptom-free period lasting from 8 hours to several days. Diaz-Rivera, et al. (1950) point out, however, that patients are rarely symptom free; on the contrary, they are usually in extreme discomfort. Hepatomegaly may become apparent during this period; according to Diaz-Rivera, et al. (1950), the earlier it appears, the poorer the prognosis. Hepatic damage has been noted as early as 6 hours after ingestion at post mortum examination (Diaz-Rivera, et al. 1950). Animal studies indicate that triglyceride accumulation is detectable by 4 hours. In stage III, severe gastrointestinal symptoms return with hematemesis, partly due to depression of serum clotting factors secondary to hepatic damage. Death in the third stage usually results from liver failure, but also may be due to cardiovascular collapse or, rarely, kidney failure. Regardless of the cause of death, kidney and liver damage are usually present.

Detailed cardiovascular toxicity has been documented in one poisoning episode of a 16-year old girl who ingested 1100 mg of white phosphorus. Vascular damage was evidenced by extremely low systemic resistance despite low blood pressure and the failure of alpha-adrenergic agents to increase the resistance substantially. The myocardial effect was evidenced by elevated ventricular end-diastolic pressure, extremely poor contractions noted on angiography, and a very slow left ventricular pressure rise in the presence of high preload (Talley, et al., 1972).

4.1.2.1 Mechanism of Action in Liver Toxicity

Phosphorus poisoning virtually always causes a fatty infiltration of the liver which is due to the inability of the poisoned tissue to metabolize incoming triglycerides to β lipoproteins (Truhaut, et al., 1974). There are a number of structural and biochemical changes that could lead to this triglyceride accumulation. Phosphorus causes a disruption of the endoplasmic reticulum (Pani, et al., 1972; Barber, et al., 1963) which would prevent the orderly synthesis and secretion of lipoproteins. Mitochondria, the intercellular site of fatty oxidation, are swollen and the mitochondrial cristae are disorganized in phosphorus-poisoned rats (Ghoshal et al., 1969). Phosphorus produced a disintegration of liver polysomes, the sites of mRNA transcription to protein, as early as 3 hours after dosing, just prior to a significant increase in fatty infiltration (Dianzani, 1972). The precise biomolecular mechanism(s) of phosphorus induced hepatotoxicity is not known; also the active molecule(s), whether phosphorus itself or/and some intermediate, has not been identified.

It seems likely that PO_4 imbalance is not the cause, since rarely have serum PO_4 and Ca^{++} irregularities been found in humans or animals following phosphorus poisoning except very near death. Normal phosphorus ingestion and excretion, much of it as organic and inorganic phosphates, are on the order of 0.5-2 gms/day in young adults (Ciba-Geigy, 1971). This quantity is much greater than the 0.1g dose, the approximate level dose of white phosphorus in an adult human.

4.1.2.2 Phosphorus Burns

Phosphorus burns, as encountered in industrial accidents or on the battlefield, cause serious injury locally and sometimes systemically. The local injury is caused both by the heat of the burning phosphorus and by the production of corrosive meta- and ortho-phosphoric acids (HPO_3 and H_3PO_4 , respectively).

The cause(s) of systemic toxicity sometimes seen with serious phosphorus burns remains somewhat unclear. One or more of the following hypotheses seem possible:

1. Systemic toxicity is typical of severe burn trauma which normally causes fluid/electrolyte imbalances and often is complicated by infection.
2. Systemic toxicity results from absorption of elemental or toxic forms of phosphorus in phosphorus burns.
3. Systemic toxicity may be treatment related; e.g., copper ion toxicity.

Walker, et al. (1945) evaluated 27 cases of phosphorus burn casualties that occurred during white phosphorus loading operations at Edgewood Arsenal. There was a clear-cut relationship between the size of the area burned and mortality. All burned areas were treated with compresses soaked in 5% copper sulfate while awaiting debridement and application of dressing. Somewhat decreased plasma Na^+ and Cl^- concentrations were common. Phosphate excretion in the urine tended to be decreased rather than increased; an increase could be expected as a consequence of absorption of phosphorus through the burned tissue. A fall in phosphate excretion is common in kidney impairment which itself can have a variety of causes. There were 5 cases of probably local or systemic infection indicated by fever and confirmed in 3 cases by a culture from a burn wound. Two cases of massive hemolysis were associated with elevated plasma CO_2 , elevated non-protein nitrogen and most significantly, a positive test for sickle-cell trait. (Persons with sickle-cell trait are predisposed to fragmentation and early destruction of erythrocytes. Infection, lowered blood oxygen, or anemia from other causes may precipitate a hemolytic episode (Beeson and McDermott, 1975).

Walker et al. (1945) concluded that there was no evidence of systemic injury due to absorption of phosphorus. Most of the complications seem typical of those encountered in serious burn injuries such as those caused by fluid and electrolyte imbalances and infection.

Summerlin et al. (1967) reported on 3 cases of massive hemolysis following white phosphorus burns. Since the patients were treated with CuSO_4 , these authors considered Cu^{++} as a possible toxic entity. Urinary excretion of copper was very significantly elevated, but serum levels were lower than normal; serum Ca^{++} and PO_4^{---} were normal or close to normal. Two of the patients also had malarial forms in the blood. (In malaria, hemolysis can be caused by destruction of red blood cells by the parasite.) These authors were unable to conclude that phosphorus absorption was the cause of massive hemolysis. They discussed the close similarities between phosphorus poisoning and copper poisoning.

Animal experimental models have not greatly aided the understanding of phosphorus absorption during and following burns because of inadequate experimental design. Frequently, inappropriate conclusions have been drawn from the experimental results. Bowen et al. (1971) reported on a study in which a standard white phosphorus burn was applied to rabbits. For comparison a hot iron was used₂ to burn an area of the skin the size of the phosphorus burn - two 47 cm² circular areas on the back, equivalent to approximately 10-20% of the body surface. Most importantly, there was mortality of 65-85% in phosphorus-burned rabbits and none in the hot-iron-burned rabbits. The phosphorus-burned rabbits showed elevated plasma PO_4^{---} and decreased Ca^{++} , especially prior to death. Electrocardiographic abnormalities were also seen in a group of phosphorus-burned rabbits, but not in the hot-iron-burned rabbits. One must question whether the plasma electrolyte changes were cause or effect, and whether the burns were really comparable in terms of thermal injury and consequent fluid/electrolyte imbalance. While the type of phosphorus burn may be comparable to those encountered in human accidents, the data do not rule out an alternative possibility, that the cause of the PO_4^{---} , Ca^{++} and electrocardiographic changes were secondary to systemic injury caused by a severe burn trauma from the phosphorus, and that the changes were unrelated to phosphorus absorption.

In a similar type of experiment, Walker et al. (1969) ignited 25 mg of WP on young pigs (weight of pigs not given) and allowed the WP to completely burn. These authors analyzed the smoke particles, the cold-water rinse residue from the burned skin, and the skin itself for phosphorus compounds. The percentage of white phosphorus remaining in the residue was small. Most of the phosphorus was recovered in the smoke (67%). Of the 11 per cent analyzed in skin as H_3PO_4 , only about half was determined to be from the burned WP and most of this was contained in the first 1/2 mm thickness of the burned skin. The other half was determined to be part of normal skin. These data do not support the hypothesis of phosphorus absorption in phosphorus burns.

Ben-Hur et al. (1972) subjected rats to a somewhat unusual type of phosphorus-burn injury. Ten or 50 mg of WP was placed into a 1.5 cm incision in the inguinal region, then ignited with hot metal and allowed to burn for about 4 min. by alternately opening and closing the wound. Following the burn, the wound was sutured without rinsing the wound. Upon opening the wound, up to 2 days later, there was a garlicky smell, and fluorescence, both signs indicative of the presence of unburned white phosphorus. Fifty percent of the rats died by 3-4 days, but whether at the 10 or 50 mg dose was not indicated. Blood and urine biochemistry, 24 hours after the procedure, showed that serum PO_4^{---} was elevated to 10 mg% from a control of 4-5 mg%. However, there were other indications of severe fluid and electrolyte imbalance: elevated serum levels of the following, urea, GPT (non-specific indicator of tissue damage), K^+ and osmolality; and decreased serum Na^+ and creatinin clearance. Clearly, both phosphorus absorption and burn/wound trauma probably combined to induce these changes. Data were not reported on rats burned with a hot brass plate or rats which were given the same treatment as the phosphorus burned rats except that the phosphorus was not ignited.

In a later study (Ben-Hur et al., 1973), the effect of therapy on phosphorus burned rats was studied. In this series of experiments, it seems that a different burn model was used although it was not described in detail, but simply referred to as a 15% wound surface onto which 25 mg of white phosphorus was or was not burned.

Logically, it would make more sense if Group 1 was subjected to phosphorus burn and, indeed, the discussion seems to indicate it was, but the description of the groups contradicts this inference: "A 15% wound surface was immersed for half an hour in a 3% copper sulfate solution (Group 1). Twenty-five mg of white phosphorus was ignited on a 15% wound surface (Group 2). A burn similar to that induced in Group 2 was treated by a solution of 5% sodium bicarbonate plus 3% copper sulfate in a 1% hydroxyethyl cellulose suspension. Lauryl sulfate (1%) was added to this suspension (Group 3). Group 4 was a control group, as described above." The "Above" control groups were given the incision wound which does not seem appropriate in this experiment.

From the authors' discussion it appears that Group 3 treatment prevented abnormal fluid and electrolyte imbalance and helped wounds to heal. These authors concluded that the fluid and electrolyte abnormalities and increased mortality of Groups 1 and 2 were due to absorbed elemental phosphorus; however, this conclusion cannot be reached logically based on their published data since the contribution of copper toxicity and/or trauma is not clarified between Groups 1 and 2. Assuming Group 1 did receive phosphorus, one must ask what the effect is of lauryl sulfate or sodium bicarbonate alone, and how the suspending agent, hydroxyethyl cellulose, effects the treatment. If the purpose of the bicarbonate was to prevent copper absorption as they point out, why didn't they conclude that copper toxicity was a contributing cause of death in Group 1?

Assuming Group 1 did not receive a phosphorus burn as the description of the experimental groups indicates, the study indicates some treatment is better than none. The authors suggest that absorbed phosphorus causes renal impairment and that $\uparrow\text{PO}_4$ is secondary to renal damage. While it is debatable whether absorbed phosphorus causes the renal damage, the mechanism of elevated serum PO_4 when it occurs in other diseases is often caused by renal insufficiency. Recall that Walker et al. (1945) reported decreased urinary PO_4 excretion in some phosphorus burn patients.

It cannot be concluded from the reports of white phosphorus burn casualties and animal experimentation that significant phosphorus absorption in phosphorus burns occurs. This conclusion may be at odds with that implied in some recent reviews (Burrows et al., 1973; Wasti et al., 1978). Resolution of this issue may help determine the optimum therapeutic treatment of phosphorus burns.

4.1.3 Inhalation Toxicity

Some information concerning composition of smoke generated from white phosphorus/felt munitions is available. Known components are PH_3 , P_4 , phosphorous acid, phosphoric acid, polymers 2-6 of polyphosphoric acid (Snelson et al., 1980). The percent composition was not identified.

The report by Snelson, et al. (1980) indicates many unidentified materials which are described as "polar organic," "light nitrogen containing" and "light phosphorus containing" compounds. In addition, the various components of the smoke will change with heat of combustion and the humidity of the atmosphere during use. The smoke from red phosphorus and white phosphorus is generally similar in composition but rigorous analysis does not appear to have been performed.

Although it is sometimes possible to evaluate toxicity of a complex mixture by a study of the chemical composition, the basic toxicity of the individual materials obtained from a handbook such as Registry of Toxic Effects of Chemical Substances (1978) does not provide sufficient information concerning inhalation hazards.

For example:

PHOSPHINE - TLV 0.3ppm; a severe pulmonary irritant.
Lowest lethal dose by inhalation - human
 1000 mg/m^3 , rat 4 hours LC_{50} 11 ppm,
mammal 1000 ppm/5 minutes.

PHOSPHORIC ACID - TLV 1 mg/m^3 ; mild eye, upper respiratory tract irritant. Lowest toxic concentration, human, 100 mg/m^3 .

PHOSPHORUS - TLV 0.1 mg/m^3 ; severe irritant, anemia, bone necrosis, blepharospasm, photophobia. Inhalation data not available.

Although we do not know the actual composition of smoke with regard to quantitation of individual species, each of these agents is identified as an irritant. The mixture can easily be predicted to have an irritant effect. An irritant is defined as material which will cause an inflammatory reaction at the point of contact. The duration, concentration and potency will all affect the degree of the response. Mild irritation may be limited to redness and swelling. Severe irritation is not unlike a thermal burn with frank tissue destruction, erosion of surfaces, increased blood vessel permeability, severe swelling and pain. The consequences of irritant contact depend of course on the nature of the membrane involved. Moderately severe skin irritation is unlikely to have serious consequences. Moderately severe irritation in the lung is frequently fatal due to the critical fluid membrane requirements for effective gas exchange. There may, of course, be systemic toxic effects in addition to the general irritant effect.

4.1.3.1 Particle Size

Particle size of white phosphorus smoke was studied by Milham, et al. (1977) and found to be remarkably consistent in range and distribution. Mass median diameter ranged between 0.8 and 1.2 μM with a log normal distribution. The shape of the curve changed slightly with changes of humidity or modification of the formulation. Particle size can be expected to change with changes in relative humidity, thus after being inspired into the saturated atmosphere of the upper respiratory tract, these measured values may change by 25%. Studies of particle deposition have demonstrated pulmonary deposition site to be dependent on particle size. (Task Group on Lung Dynamics, 1966; Chan, et al., 1980; Wolff, et al., 1979). These studies are important in the description of the fate of aerosols of water soluble materials. However, results relating lethal effect to particle size have been inconsistent and predictions for an uninvestigated aerosol mixture are not in order. Considerable phosphoric and phosphorous acid probably dissolve in the fluid layer covering mucus membrane of the nose, mouth or trachea and upper respiratory tract. As a result, lung exposure may be less than might be predicted from models that do not take into account the effects of solubility.

4.1.3.2 Experimental Studies

Since there are not sufficient data to draw conclusions on the basis of chemical analysis of the smokes, the effect of the mixture as a whole can be evaluated by exposing animals to the mixture and observing the effects. A variety of animals has been used for such study. The human is, of course, of greatest interest since we wish ultimately to make predictions concerning human consequences of such exposures.

4.1.3.3 Human Exposures to Phosphorus Smoke

A medical report concerning an accidental 15 minute exposure of humans to white phosphorous smoke indicated severe respiratory symptoms, including necrosis of bronchial epithelium, edema of larynx and vocal cords, rales, cough and sputum production. These are symptoms of upper and lower respiratory tract irritation. A number of exposed individuals were hospitalized. Eight months following the exposure, one of the victims was still almost unable to speak. This exposure was not quantitated nor was the composition of the burning material carefully identified (Walker, et al., 1945).

In other studies (Cooper and Owens, undated; White and Armstrong 1935; Cullumbine, 1944) exposures to phosphorus smoke of as little as 5 minutes to concentrations of 188 mg/m^3 caused mild symptoms lasting up to 3 days. Sixteen minutes was the longest exposure time in these studies. Symptoms included sore throat, headache, coughing and nasal congestion. Shorter exposures to higher concentrations caused similar symptoms. The effects of exposures longer than 15 minutes to these concentrations is unknown. A concentration of 1000 mg/m^3 is considered intolerable and 700 mg/m^3 is described as minimum harassing concentration. "Minimum harassing" is defined as a concentration at which masks are mandatory (Cullumbine, 1944).

No data from human subchronic exposures to WP smoke are available nor are there histopathological data from acute or chronic exposures of humans to smoke.

4.1.3.4 Laboratory Animal Exposure

Data obtained from exposures of animals to white or red phosphorus, vapor or smoke, is presented in Table 30. In most cases, there is not sufficient data in the published reports to calculate an LC₅₀ or to evaluate the conditions of the exposure. In particular, no oxygen or carbon dioxide measurements were made to demonstrate levels in the exposure chamber during the exposures. In a closed chamber this is particularly important since low O₂ or high CO₂ would easily cause death of the animals under study. In addition, the composition of smoke depends on relative humidity which was generally not reported.

Inhalation studies have been reviewed by Wasti et al. (1978). From these studies and others (Brown, et al., 1980a; Weimer, et al., 1977) the approximate midpoint of the mortality curve (LC₅₀) has been very roughly estimated based on the data listed in Table 30 for several animal species. Sensitive species include guinea pig and mouse (estimated LC₅₀, 400-500 mg/m³). Rat and dog show intermediate sensitivity (estimated LC₅₀, 1300-1900 mg/m³) and goat is quite resistant (estimated LC₅₀, 6000 mg/m³). In mice, deaths (4/20) at concentrations as low as 100 mg/m³ have been reported (White and Armstrong, 1935). One hour exposure of rats to the concentrations indicated resulted in the mortality shown below (Brown, et al., 1980b).

<u>Concentration</u>	<u>No. Deaths/No. Exposed</u>
1196 mg/m ³	2/10
1295 mg/m ³	5/10
1394 mg/m ³	6/10

Studies in rats exposed to smoke from red phosphorus demonstrated significant lethal effects at a concentration similar to that seen with white phosphorus smoke. The duration of exposure, however, was much longer. Thus, a one-hour exposure to 1537 mg/m³ resulted in mortality of 1/10, a two-hour exposure to 1676 mg/m³ resulted in mortality of 4/10, and three-hour exposure to 1572 mg/m³, 8/10 (Weimer, et al., 1977). In studies by the same workers guinea pigs were shown to be susceptible under much less severe exposure conditions. Ten-minute exposure to 352 mg/m³ red phosphorus smoke resulted in death of 4 of 10, at an exposure concentration of 800 mg/m³, 9 of 10 died. An important difference is the exposure time.

TABLE 30

SUMMARY OF INHALATION EXPOSURE/LETHAL EFFECTS DATA IN ANIMAL STUDIES

Species	Acute Exposure Red phosphorus-Butyl Rubber Smoke		Acute Exposure White phosphorous Vapor		Acute Exposure White phosphorous Smoke		Acute Exposure White phosphorous/felt Smoke		Subchronic Exposure White phosphorous/felt Smoke		Acute Exposure Phosphine	
	Concentration mg/m ³	Duration	Concentration mg/m ³	Duration	Concentration mg/m ³	Duration	Concentration mg/m ³	Duration	Concentration mg/m ³	Duration	Concentration mg/m ³	Duration
Rat	1625	2 1/2 hours (6)	<4460	1 hour (4)	1200	LC ₅₀ 60 min.	1161	15 min. (2)	63	529	4	hours (5)
Guinea Pig	485	15 min. (6)										
	352	10 min. (6)										
Rabbit	>1882	4 hours (6)										
Dog												
Mouse												
Human												
Goat												

References:

1. Wasti, 1978
2. Brown et al., 1980
3. Brown et al., 1980
4. White and Armstrong, 1935
5. RTECS, 1979
6. Weimer, 1977

4.1.3.5 Histopathology

In several studies histopathological evaluation was conducted on tissues taken immediately following a single exposure or two weeks after exposure. Since toxic insult to cells usually requires at least twenty-four hours to become manifest in histopathological changes, and since moderate damage is often repaired within two weeks, it is not surprising that those investigators found little to report. Those lesions which have been identified include inflammation of trachea and larynx. Perivascular lesions of lung and some lung hemorrhage were found in high dose rats. Minor liver and kidney changes (cloudy swelling) have been identified in mice several days post exposure (White and Armstrong, 1935).

4.1.3.6 Acute Physiological Non-Lethal Changes

The acute non-lethal effects of phosphorus smoke inhalation have included a variety of pulmonary signs: respiratory distress, pulmonary edema, pneumonia, atelectasis, and mucus production. The blood picture of rats and guinea pigs two weeks after a single exposure failed to show consistent changes. Rabbits showed a depression of hemoglobin and RBC following exposure to 150 mg/m³ white phosphorus (Maruo, 1955).

Some additional acute non-lethal effects have been studied but reports are such that evaluation of data is not possible. For example, pulmonary resistance following smoke exposure was not different from that of control animals. The time at which the measurement was taken (e.g., during exposure, following exposure, following recovery period of 2 hours, following full recovery) is an important consideration in the evaluation of the findings but was not included in the report (Brown, et al., 1980a).

4.1.3.7 Subchronic Inhalation Studies

Subchronic exposure (15 minutes/day x 5/wk x 13 weeks) of rats to smoke demonstrated an LC₄₀ (estimated) of 1160 mg/m³. The lower dose of 600 mg/m³ did not cause any deaths. Respiratory signs following high dose exposure included dyspnea and wheezing, which cleared within several hours of each exposure. Body weight, hematology, and blood chemistry were not consistently affected by the subchronic exposure. Histopathological findings at six weeks and 13 weeks demonstrated inflammation of the trachea, larynx and lung (Brown, et al., 1980b).

4.1.3.8 Reproductive Studies

A series of teratology and reproductive studies in rats has been completed which indicates the absence of effect of white phosphorous/felt smoke on organogenesis (day 6-15) and on male germ cells (dominant lethal

mutations). The high dose was 1000 mg/m³. However, details of the exposures - timing and duration - are not reported. In addition, there is no evidence that fetuses were subjected to internal and skeletal examinations. In a single generation reproductive study, significant pup loss was recorded following live birth. Surviving pups weighed consistently less in the high dose group than in the control or the low dose group. Again, details of the exposure are not presented (Brown, et al., 1980b).

4.1.3.9 Discussion

With the realization that human sensitivity to toxic materials is highly variable, one should expect an order of magnitude difference between most and least sensitive representatives of the species. One would therefore anticipate a concentration range for any toxic effect rather than a sharp cut-off point between effect and no effect.

Using animal data we see that isolated deaths due to inhalation exposure of white phosphorous smoke are recorded at concentrations as low as 100 mg/m (White and Armstrong, 1935). It appears that for most species tested, the critical concentration for LC₅₀ is close to 2000 mg/m. There is cause for concern in the abrupt rise of the dose/response relationship for lethal effects in rats. There is no information to suggest that the human experience will be significantly different from that of other animals. Unfortunately, most human exposure has been unquantitated. The few measured exposures suggest that the human will not be among the intensely sensitive species. However, the exposures which have been studied in humans at concentrations between 100 and 700 mg/m³ and which resulted in reversible pulmonary symptoms and mucus membrane irritation were of less than 15 minute duration. These concentrations might well cause very serious effects with longer exposure. Sparse animal data suggest that the single non-lethal exposure does not carry likelihood of chronic sequelae. In humans, scarring of the vocal cords has been noted.

One would guess that exposures longer than 15 minutes to concentrations approaching 2000 mg/m would result in increasing numbers of deaths among exposed humans. The longer the duration of the exposure at each concentration, the greater the number of fatalities expected. Actual human data at concentrations in this range have been for exposure times of 15 minutes or less and have resulted in no reported fatal incidents. There is no model by which extrapolation can be used to predict safe and unsafe exposure times. Moderate human exposure would be expected to cause symptoms of upper and lower respiratory tract irritation with more emphasis on nose and trachea than lung. If HCN or CO were to be generated in high enough concentrations, compromise of the oxygen delivery system would also be noted. Clearly, the actual composition of the smoke will determine the effect of the mixture. If the actual composition of the smoke is dependent on weather conditions (% humidity) or temperature of combustion (as is generally the case), the cumulative toxicity will also change.

Subchronic animal experiments demonstrated tracheal and laryngeal inflammation as would be expected from exposure to irritant materials. The possibility of osteomyelitis and bone necrosis resulting from chronic phosphorus smoke exposure has not been adequately investigated, although it is doubtful if this particular effect can be studied in animal models. More accurate analyses of smoke composition and concentration of constituents and the identification of the toxic entity causing "phossy jaw" would be appropriate preliminary steps before designing and performing chronic inhalation toxicity studies in animals.

4.1.4 Chronic Toxicity

The literature on the chronic toxicity of white phosphorus in humans has been extensively reviewed elsewhere (Hughes et al., 1962; Miles, 1972, Heimann, 1946; Kennon and Hallam, 1944). The principal toxic manifestation of occupational exposure to white phosphorus is necrosis of the jaw, also referred to as "phossy" jaw. The association between this malady and occupational exposure in the match-making industry was reported in Vienna in 1839, in England in 1862, and in France in 1858 (Hughes et al., 1962). The use of white phosphorous for making matches ceased long ago as the result of legislation and the introduction of much safer substitutes. Where white phosphorus still must be used, better ventilation of work areas, the use of protective clothing and respiratory equipment and the improvement in general health and dental hygiene of workers have markedly reduced incidence and severity of the disease in spite of an actual increase in the number of exposed workers. Nevertheless, "phossy" jaw remains a definite hazard.

In spite of the long history of the prevalence of this disease and numerous investigations into its etiology, several key questions remain unanswered:

- (1) What levels of exposure are toxic; put another way, what levels can be considered safe?
- (2) What is the toxic entity?
- (3) Why are the lower jaw, and less frequently, the upper jaw virtually the only sites in the osseous system noticeably affected?

1. There appears to be no data relating exposure levels of phosphorus vapors or phosphorus compounds with disease incidence in humans. It has been noted by most reviewers that the length of time that a worker was exposed before the disease was diagnosed was highly variable. Hunter (1957, cited by Hughes et al., 1962) says that cases have occurred up to two years after leaving exposure. In a report on 10 cases of jaw necrosis diagnosed between 1948-1958, the interval between first exposure and diagnosis ranged from 10 months to 18 years (Hughes et al., 1962). In all of these cases the dental health before exposure had been considered good and had been monitored periodically during and after industrial exposure to

phosphorus. There was no mention of how many other workers were similarly exposed and were studied for this report. No data on exposure levels were reported.

2. Vapors of elemental phosphorus and the intermediate oxide, P_2O_3 or its corresponding acid are the suspected toxic entities in chronic exposure (Miles, 1972; Hughes et al., 1962). (The intermediate oxide P_2O_3 exists as P_4O_6 in vapor phase and reacts rapidly with water to form H_3PO_3 , phosphorus acid.) Excepting high concentrations that would be extremely irritating, P_2O_5 or its acid H_3PO_4 would appear to be ruled out as the toxic entity because a normal human consumes and excretes (principally in the urine) between 1/2 - 2 gms of PO_4 per day.

Arsenic has also been considered as the causative entity or possibly as a co-factor because this element is normally part of the phosphate rock, from which phosphorus is prepared.

3. That the maxillary bones are preferentially affected in this disease suggested that the toxic entity had a local action. Caries and gingival inflammation could provide a route of entry to the bone.

However, the present consensus seems to favor the hypothesis that phosphorus or the toxic entity has a systemic effect and that the jaw bones, because of their unique vulnerability to infection via the teeth and gingiva, are the sites affected. Anecdotal reports of spontaneous fractures and chronic osteomyelitis being associated with occupational exposure to phosphorus have been cited as supporting this view (Miles, 1972 and Heimann, 1946, each cited several authors on this point).

Heimann (1946) summarized the hypothetical development of phossy jaw as follows: there is a reduction in diameter of the Haversian canal due to the laying down of new bone; consequently, there is restricted blood supply to the bone so that the bone becomes poorly nourished and vulnerable to infection via decaying teeth or the gingival margin. Concrete support for this hypothetical development seems to be lacking.

Experimental studies in animals have not demonstrated a jaw necrosis, but abnormal development of bone has been reported. Usually there is widening of the epiphyseal and subepiphyseal areas. These are the sites where most bone growth and remodeling occurs. Two studies are fairly typical of findings in experimental animals. Fleming et al. (1942) administered yellow phosphorus orally in the diet or by subcutaneous injection in oil. Rats receiving 0.8-0.05 mg/kg/day by subcutaneous injection lived an average of 6 months at the high dose and almost 2 years at the low dose. The histopathological changes in bone were described as "... a thickening of the epiphyseal line by new bone tissue with the extension of thin, more or less closely packed trabeculae into the shaft... noted in practically all of the animals receiving phosphorus." There was a dose/response relationship, and controls, receiving no phosphorus, did not display these changes. There were no remarkable differences between test and control animals in any of the other tissues examined including the

liver and kidney. Comparing subcutaneous and oral routes, these authors did not see growth depression when phosphorus was given subcutaneously, and observed that growth depression seen in rats receiving phosphorus orally in the diet (also see Sollman, 1925) was probably due to inanition. Alternatively or in addition, the food with phosphorus added may have been unpalatable.

In a more recent study, Whalan *et al.* (1973) incorporated white phosphorus in the diet of young rats. At 0.065 mg/rat/day the dose corresponds to ≈ 1.3 mg/kg/day in the 23 day old rats used in this study. After only 16 days, the changes seen were thickening and increased radiographic density of the metaphysis. Histologically, the trabeculae were found to be abnormally thickened, accounting for the increased density. Lying against the bone were abnormally small, elongated, and presumably inactive osteocytes -- specialized bone cells thought to be responsible for resorption of bone during growth and remodeling of the trabeculae.

In the older literature, a number of other chronic effects in man were reported including blood electrolyte changes, abnormal differential leukocyte counts, anemia, indefinite digestive complaints, loss of appetite, bleeding of the mucous membranes and albumin in urine, and in severe cases a general cachexia (see review and citations of Heimann, 1946). However, it is unclear which of these changes were specific toxic manifestations and which were secondary to either severe necrosis of the jaw with possibly consequent deterioration in nutrition, or liver toxicity with its sequelae. In the most recent case report series, Hughes *et al.* (1962) found no predictors or symptoms other than the dental problems. In a study of 48 healthy men working in a phosphorus plant and 28 controls, there were no detectable significant differences between the exposed group and the controls in the following:

Hematology and blood chemistry

- hemoglobin
- total white count
- differential count
- inorganic phosphorus
- alkaline phosphatase
- calcium
- magnesium

Other parameters examined

- urine creatinine
- radiographs of hands.

In one case discovered during this investigation, no abnormalities in hematology, serum chemistry, liver function tests, urine chemistry, and calcium metabolism were found. These authors concluded that the only clear indication of low-level chronic toxicity is the sudden appearance of an infected or painful tooth or area of the jaw that upon appropriate intervention fails to heal properly. Thus, a periodic dental examination program (2-4 month intervals), the insistence on maintenance of sound dental health, and the immediate removal from phosphorus exposure of persons needing dental work other than for minor procedures (small fillings and scaling) was concluded to be the only reasonable course of action.

4.1.5 Other Toxic Chemicals Used in Production of WP/F or RP/BR Smoke Munitions

Methylene Chloride

A large amount of work has been done and reported on the physiological behavior and toxicity of methylene chloride. Several good compilations of the key research have been made (Mitre Corp., 1976; NAS, 1977; U.S. EPA, 1977) including a current published survey by NIOSH (1976). A brief synopsis of the metabolism and major toxicological manifestations of methylene chloride exposure are presented below. Most of this work has previously been reviewed for the Army (ADL, 1978).

4.1.5.1 Absorption, Metabolism, Excretion

Methylene chloride is absorbed principally through the lungs and is partially eliminated unchanged in expired air. DiVincenzo (1972) found that the amount of methylene chloride present in blood and expired air was directly proportional to the exposure dose. Working with eleven male subjects, DiVincenzo found that between 50 and 66% of inhaled methylene chloride was absorbed during a 2 hour exposure to either 100 or 200 ppm methylene chloride. Excretion occurred mainly through the lungs with a small amount excreted in urine (22.6 and 81.6 $\mu\text{g}/24\text{-hr.}$ sample for the 100 and 200 ppm exposures, respectively). Some 40% of the dose, however, was unaccounted for. Stewart, et al. (1972 a & b) noted that humans acutely exposed to methylene chloride vapors exhibited sustained elevations of carboxyhemoglobin levels (COHb) and speculated that some methylene chloride was metabolized to carbon monoxide (CO) in vivo. This hypothesis was subsequently confirmed in both animal and human experiments.

For example, a study conducted with non-smoking human volunteers revealed a mean COHb level of 12% (in one case, it rose as high as 24% COHb) following an 8 hour inhalation exposure to 500 ppm methylene chloride. At a concentration of 100 ppm, blood COHb levels reached 5% after 8 hours exposure (Fodor, 1976). Another study conducted with non-smoking workers chronically exposed to 180-200 ppm methylene chloride found that COHb levels increased from a 4.5% COHb baseline to 9% after an 8 hour workday, but returned to baseline by the start of the next work day (Ratney, 1974). Increased COHb formation has also been demonstrated in rats (Miller, et al., 1973; DiVincenzo and Hamilton, 1975; Rodkey and Collison, 1977), rabbits (Roth, et al., 1975) and guinea pigs (Balmer, et al., 1976).

The proportion of methylene chloride excreted as CO, CO₂ or unchanged methylene chloride varies with dose -- the higher the dose, the higher the proportion excreted as unchanged methylene chloride.

Yesair, et al. (1977) demonstrated this in B6C3F1 mice given ¹⁴C-methylene chloride by the oral route. A dose of 1 mg/kg methylene chloride in corn oil was metabolized to ¹⁴CO(45%) and ¹⁴CO₂(50%); less than 3% of the radioactivity was eliminated as methylene chloride. When the dose was increased to 100 mg/kg, however, both metabolic pathways decreased (i.e., 20%¹⁴CO

and 25%¹⁴CO₂) and the level of unchanged methylene chloride eliminated in expired air increased to 40% of the administered radioactivity. Similarly, DiVincenzo and Hamilton (1975) found that with higher doses (412-930 mg/kg by IP injection), rats eliminated 91.5% of the radioactivity within 24 hours as unchanged methylene chloride in expired air (75% of this amount was eliminated within 2 hours of dosing). Minimal amounts were metabolized to CO (3%) and CO₂ (2%) with less than 1% excreted in the urine.

4.1.5.2 Human Effects

The predominant effect of human exposure to methylene chloride is depression of the central nervous system which is characterized by giddiness, irritability, drowsiness, loss of memory, diplopia, nausea, vomiting, numbness and the severe exposure, convulsions, cyanosis and unconsciousness (Mitre Corp., 1976; NIOSH, 1976; NAS, 1977; U.S. EPA, 1977). The lowest published toxic concentration of methylene chloride by inhalation in humans is 500 ppm for an 8 hour period (RTECS, 1975). Several fatalities have been linked to methylene chloride exposure particularly in the form of paint remover formulations (Moskowitz and Shapiro, 1952; Stewart and Hake, 1976). Methylene chloride vapors are local irritants to eyes, respiratory tract and skin (NIOSH, 1976). In a study conducted with human volunteers (Stewart, et al., 1972 a & b) no overt symptoms of illness were noted in subjects exposed to methylene chloride concentrations up to 515 ppm for 1 hour. After two hours exposure to 896 ppm methylene chloride, two of three subjects developed lightheadedness which disappeared within 5 minutes after exposure ceased. Another study found that CNS function as measured by performance in psychomotor tasks was impaired following exposure to methylene chloride exposures greater than 300 ppm for 3-4 hours (Winneke, 1974).

Examination of 103 workers chronically exposed to 50-100 ppm methylene chloride revealed no increased incidence of cardiovascular, gastrointestinal, genitourinary or CNS diseases when compared to non-exposed workers (Ballantyne, et al., 1976).

4.1.5.3 Animal Studies

In rats, an acute oral LD₅₀ value of 2136 mg/kg was reported while an oral dose of 1900 mg/kg was an LD₁₀₀ in rabbits (RTECS, 1975). Given intraperitoneally, doses of 1500 mg/kg in mice and 950 mg/kg in dogs methylene chloride produced mortality in 50% and 100% of these animals, respectively (RTECS, 1975). Balmer (1976) reported a 6 hour LC₅₀ value of 11,600 ppm for male guinea pigs.

Instillation of 0.1 ml methylene chloride into the eyes of New Zealand rabbits produced moderate inflammation of the conjunctiva and eyelids, excess lachrymation and chemosis. Corneal injury, as measured by corneal thickness, peaked at 6 hours (59% increase in corneal thickness), and did not return to normal for 8-9 days. A similar pattern was seen with 0.01 ml of methylene chloride, but the effects were less persistent (Ballantyne, et al., 1976).

The level of liver triglycerides increased 2.5 fold in male guinea pigs exposed by inhalation to 11,100 ppm methylene chloride for 24 hours. Simultaneous inhalation of 24,100 ppm ethanol antagonized this effect. However, when guinea pigs were exposed to 500 ppm methylene chloride for 5 days, simultaneous inhalation of ethanol appeared to potentiate the effects of methylene chloride (Balmer, et al., 1976).

Continuous exposure to 5,000 ppm methylene chloride for up to 7 days produced lethargy and dehydration in female ICR mice. Body weight steadily decreased and liver weights were significantly heavier through day 4. Liver triglycerides increased 12 fold for the first 3 days, then decreased until day 6 where they plateaued at concentrations 2-3 times above normal. Lesions were seen in the hepatocytes after only 12 hours of exposure (Weinstein, et al., 1972).

Continuous exposure of several species of animals to 5,000 or 1,000 ppm methylene chloride for periods up to 14 weeks was reported by Haun (1971) and MacEwen (1972). Results of these studies indicated severe weight loss in all species and signs of CNS depression in dogs, monkeys, rats and mice at 5,000 ppm, and in dogs and monkeys at the 1,000 ppm level. A significant number of dogs at 1,000 ppm and mice at 5,000 ppm died. Histopathological lesions of liver associated with hepatic failure were noted in dogs, rats, and mice. Haun also reported liver injury in monkeys at 1,000 ppm.

Heppel, et al. (1944) examined the effects of daily inhalation of 10,000 ppm methylene chloride 4 hours per day, 5 days per week for 8 weeks in several species. At necropsy, two of four dogs exhibited moderate centrilobular congestion in the liver with narrowing of liver cell cords and slight to moderate fatty degeneration (only the liver was examined). Slight to moderate fatty degeneration of the liver was also observed in 4 of 6 guinea pigs, but no microscopic lesions attributable to exposure were found in monkeys, rats or rabbits.

Bornmann and Loeser (1967) reported no adverse effects in rats maintained on drinking water containing 125 mg/l methylene chloride for 91 days and Yant (1930) found that mean consumption of 5,950 mg/l methylene chloride in their drinking water (time unspecified) produced no apparent signs of toxicity in dogs.

4.1.5.4 Teratogenesis

Schwetz, et al. (1975) exposed pregnant rats and mice to 1,250 ppm methylene chloride 7 hours per day on days 6-15 of gestation. Extra sternebra were found in 6 (50%) of the mouse litters compared to 3 (14%) of the control litters; cleft palates and rotated kidneys were present in 2 (17%) of the litters from exposed mice. An increased incidence of dilated renal pelvis and delayed ossification of the sternebra were noted in fetal rats indicating some evidence of fetal toxicity from methylene chloride for both species.

4.1.5.5 Mutagenesis

Filippova (1967) found methylene chloride was not mutagenic against Drosophila, and Simmon, et al. (1977) reported that methylene chloride did not increase the mitotic recombination in Saccharomyces cerevisiae D3. However, both Simmon et al. and Jongen, et al. (1978) found exposure to vapors of methylene chloride were highly mutagenic in the Ames Salmonella microsome test. Jongen, et al., noted a dose-related increase in mutation frequency in Salmonella typhimurium strains TA98 and TA100 exposed to 5,700-17,100 ppm methylene chloride in gas-tight boxes for 48 hours. Addition of induced liver microsomal fraction caused a slight enhancement of mutations over the values observed without activation. Similar results were reported by Simmon, et al.

Methylene chloride has also been found to induce transformations in an in vitro Fischer rat embryo cell system (F1706) (Price, et al. 1978)

4.1.5.6 Carcinogenesis

No long-term carcinogenicity data are currently available. Preliminary findings from a 2-year inhalation study suggest no evidence of cancer in rats or hamsters after 12 months, but the study has not been completed (Mod. Paint Coat, 1977).

Theiss, et al. (1977) examined the frequency of lung adenomas in strain A/st male mice injected intraperitoneally with 160, 400 or 800 mg/kg methylene chloride 3 times a week for 16-17 injections. The mice were killed 24 weeks after the first injection. The frequency of pulmonary adenoma was somewhat elevated at all 3 doses, but was not significantly different from controls at a p value of 0.05.

4.2 Effects on Flora and Fauna

In the last ten years, research sponsored by the U.S. Army has generated a significant amount of information on certain potential acute toxicity effects of white phosphorus (WP) and, to a lesser degree, red phosphorus/butyl rubber (RP/BR). The acute toxicity of white phosphorus and "phosphy water" to finfish and other aquatic organisms has been investigated, but parallel information is unavailable for RB/BR. The acute inhalation and oral toxicity of both compounds has been studied with laboratory mammals, but phytotoxicity information and toxicity data for other animals are generally lacking. Also generally lacking is information on the potential chronic toxicity thresholds for terrestrial organisms for the various exposure routes. There are some effects data based on field observations involving discharges of WP or phosphy water from smoke production to the environment, but these data are somewhat qualitative and lacking in some of the aspects required for thorough cause and effects characterization.

A recent compilation of information on WP effects on aquatic organisms was completed by Sullivan, et al. (1979). This compilation indicates that those portions of WP or phosphy water that remain as P_4 in the aquatic environment are acutely toxic to aquatic organisms at very low concentrations. In particular, LC_{50} 's for 96-hour exposure of finfish generally range from 2 to 154 $\mu\text{g}/\text{l}$. The most sensitive species, like the bluegill and fathead minnow, exhibit LC_{50} 's of 1-4 (95% confidence) and .4 $\mu\text{g}/\text{l}$ respectively in lab tests (Sullivan, et al. 1979). The reported range of levels acutely toxic to algae and aquatic invertebrates is generally on the order of 20-30 $\mu\text{g}/\text{l}$, indicating that finfish are likely the most sensitive receptors in a given aquatic system. The reported data also indicate rapid P_4 uptake and poisoning of finfish, but rapid depuration of sublethal levels in clean water.

Studies of field situations associated with WP smoke production have included reports of "extensive fish kills" after heavy rains in Yellow Lake, Pine Bluff Arsenal, AR (Sullivan, et al. 1979). Yellow Lake formerly received phosphy water discharges from the wet line of WP smoke production at Pine Bluff Arsenal, via a presently dry creekbed. While WP production was active at Pine Bluff, the Lake reportedly supported active finfish and waterfowl populations while exhibiting mean phosphorus concentrations in the .20-.25 mg/l range. The tributary creek that received the production plant's phosphy water discharge reportedly exhibited P_4 concentrations of about 1-3 mg/l , and was devoid of the major forms of invertebrate and vertebrate aquatic life (Sullivan, et al. 1979). During and following heavy rains, P_4 concentrations in fish livers reportedly rose by factors of 50-100 (or more), and large fish kills were reported. The authors suggested the potential introduction of larger amounts of P_4 -laden sediments in the Lake as possible explanations for the fish kills. Data of P_4 levels in the Lake at the time of the kills were unavailable. In any case, there is evidence to suggest that ambient P_4 levels in the ppm range could preclude fish survival.

Observed waterfowl mortality in the field has also been attributed to ingestion of phosphorus-laden materials by Coburn (1950) in Burrows, et al. (1973). Experimental data from laboratory studies indicated that levels of 3 mg/kg body weight were lethal to ducks within 6-33 hours (Burrows, et al. 1973).

Acute toxicity data for WP, WP/felt, and RP/BR for terrestrial organisms has been summarized by the Army's Chemical Systems Lab (Brown, Personal Communication, 1980). Table 3I displays that data. Mammals are the only terrestrial organisms for which such data are available and, even as a class, appear to exhibit differential sensitivities to P_4 exposure. Guinea pigs reportedly exhibited the greatest sensitivity to inhalation of simulated WP/felt and RB/BR smokes, suffering laryngeal damage and resultant mortality at concentrations in the 4,000-5,000 mg/minute/m³ concentration range (measured as phosphoric acid in the RB/BR experiments). Other mammals, including rats and dogs, experienced mortality only at time-dependent concentrations at least two orders of magnitude greater than those fatal to the guinea pigs (Weimer, et al., 1977). Oral dosage studies with rats produced LC₅₀'s in the .85-1.48 ml/kg range respectively for RP/BR and WP/felt, and there is reported evidence of sublethal (irritation) effects at atmospheric concentrations of RB/BR smoke equivalent to 178 mg/minute/m³ (as phosphoric acid) (CSL summary, undated, from Brown, 1980).

The potential effects of the degradation products of phosphorus smokes were discussed by Burrows, et al. (1973). Phosphite, hypophosphite, phosphine, and poly- and ortho-phosphoric acids all reportedly exhibit far less toxicity potential than residual P_4 in the environment. Phosphine may exert adverse effects on some finfish in concentrations of 3-6 ppm, while the other substances may be generally biostimulatory, or exhibit minor inhibitory effects on microphytes at concentrations greater than 100 ppm (Burrows, 1973).

TABLE 31

TOXICITY STUDIES IN PHOSPHORUS SMOKES

<u>Toxicology Studies</u>	<u>U.K. Red Phosphorus Butyl Rubber</u>	<u>L.C.W.S.L. Red Phosphorus Magnesium</u>	<u>CSL White Phosphorus FELT</u>
<u>Oral Lethality</u> LC ₅₀ - Rat	0.85 ml/kg		1.48 ml/kg
<u>Eye Irritation</u> (0.1 ml - Rabbit)	Severe	Moderate	Severe
<u>Skin Irritation</u> (0.5 ml - Rabbit)	Severe	Moderate	Severe
<u>Mutagenicity</u>			
a. Ames Bacteria	Not Tested		Negative
b. Drosophila	Negative		Negative
<u>Skin Sensitization</u> (Guinea Pig)	Negative		Negative
<u>Acute Inhalation</u>			
a. LC ₅₀ - Rat	227,715 mg min/m ³	186,060 mg min/m ³	94,125 mg min/m ³
b. LC ₅₀ - Guinea Pig	4,040 mg min/m ³		5,321 mg min/m ³
c. Blood Chemistry	Negative		Negative
d. Pathology	Negative		Negative

Table 31 (continued)

Toxicology Studies	U.K. Red Phosphorus Butyl Rubber		L.C.W.S.L. Red Phosphorus-Magnesium		CSL White Phosphorus FELT	
	(1)	(2)	(1)	(2)	(1)	(2)
<u>Subchronic Inhalation</u>						
a. Daily Exposure Dose (Ct)	178	1,319	3,750	7,500	2,887	8,833
b. Blood Chemistry	Negative				(3)	17,415
c. Pathology	Negative					
d. Pulmonary Function	Negative					
e. Reproduction:						
(1) Dominant Lethal Mutation	Negative					
(2) Teratology	Negative					
(3) Single Generation	Negative					
f. Physiology - Rat						
(1) Cardiovascular	Not Tested		Negative			
(2) Respiratory	Not Tested		Negative			
(3) Exercise	Not Tested		Negative			
g. Behavior						
(1) Spontaneous ACTIVITY	Not Tested					
(2) Passive Avoidance	Not Tested					

Source: CSL Toxicological Evaluation of Chemical Smoke Systems

5.0 HAZARD ASSESSMENTS

5.1 Methodologies for Hazard Assessment

5.1.1 Introduction

Hazard assessment, also known as risk assessment or risk analysis, consists of rational and systematic techniques for identifying hazards and quantifying risks. The basic elements of the hazard assessment process include:

- Hazard Identification: Types of hazards, sources, and properties.
- Hazard Quantification: Estimates of frequency, severity, and populations at risk.
- Hazard Assessment: Acceptability of risk and mitigating factors.

The major limitation of the hazard assessment process is incomplete data. This problem is particularly acute for assessing the hazards of future manufacture and use of the WP-F and RP-BR smokes. The basic approach that has been followed is to extrapolate from experience with other types of screening smokes and other types of industrial and environmental hazards. The situation is complicated further, however, because much of the data assembled for extrapolation will become obsolete as changes are made in the manufacturing process, training procedures, and field applications.

On the other hand, the existing data are useful and can function as a foundation for the development of scenarios and, given an array of assumptions, the assessment of future hazards.

5.1.2 Hazard Identification

The initial step in the hazard assessment process is the collection of data and their organization into a rational framework. In general, distinctions are made between: (1) hazards occurring during production or during use, and (2) the impacts of hazards on humans or the environment.

Hazard assessment begins with the identification of hazardous agents and their expected concentrations and physical states. For any given agent, a variety of concentrations and physical states may be expected. Human hazard assessment must consider potential routes of exposure such

as inhalation or skin contact, duration of exposure, population at risk for the set of previous agent-exposure conditions, and controls or personal protection which may ameliorate the effects of the exposure. Environmental hazard assessment must consider emission pathways, persistence in the environment, flora or fauna at risk, and pollution controls.

5.1.3 Hazard Assessment

The procedure for conducting the hazard assessment of WP-F and RP-BR production and use followed several steps:

- (1) Collection and organization of data on potential hazards.
- (2) Review of the life cycle phases of production and use and identification of possible failure modes and effects.
- (3) Estimation of the probability of hazards which have the potential for extensive environmental damage or severe personal injury by developing fault-trees.
- (5) Summarization and discussion of data limitations or assumptions of the results of the previous steps.

The hazard assessment process starts with an unstructured, qualitative, and agent-specific listing or identification of hazards. For purposes of assessment, a Failure Mode and Effects Analysis is developed. This analysis considers selected life cycle phases in the production and use of WP-F and RP-BR. For each phase, one or more potential initiating incidents were identified. For each incident there may be one or more failure modes and related effects. If the effect occurs, it is rated on a scale from 1 (minor injury), 2 (multiple minor injury), 3 (major injury), 4 (multiple major injury or single fatality), to 5 (multiple fatality). Finally, activities which can prevent the effects from occurring or lessen their severity are identified.

Fault-tree analysis was used to estimate the probability of occurrence of specific events. A fault-tree describes the chain of events which leads to a hazardous event such as "Environmental Damage in the Field" from use of WP-F or RP-BR. In fault-tree design the symbol \triangle is an "OR" gate; the probabilities of events entering an "OR" gate are added; the symbol \square is an "AND" gate; the probabilities of events entering an "AND" gate are multiplied. For example, consider the event "Damage to Flora/Fauna" which has a probability of occurrence conditional upon the probability of susceptible populations being present and the concentration of a pollutant being above some threshold of toxicity. Since both events are necessary, their probabilities are multiplied. In such a case, if it can be shown that the probability of having toxic concentrations is very low, then the probability of the resulting event "Damage" will also be very low even if the probability of having susceptible populations is high.

5.2 Hazard Assessment for Production Operations

5.2.1 Hazard Identification

Previous sections have described the raw and waste materials for RP-BR and WP-F production, and the products or by-products of smoke deployment. These materials are summarized in Table 32 and their potentially hazardous properties are described.

5.2.2 Hazard Quantification

The process of hazard assessment for the production of RP-BR and WP-F screening smokes includes the development of a generalized Failure Mode and Effects Analysis (FMEA). This methodology considers phases in the life cycle of production and provides a framework for reviewing various possible failures and their effects. This approach was originally developed for systems safety analyses of the mechanical components of U.S. Air Force and NASA projects. In this case, however, FMEA is not used for the analysis of potential component failures but, rather, for a general review of the production process.

The FMEA for production, shown in Table 33, addresses the following life cycle phases:

- WP-F Shell Filling
- WP-F Burster Insertion
- WP-F Leak Testing
- WP-F Pollution Control
- RP-BR Mixing
- RP-BR Extrusion
- RP-BR Pollution Control

The purpose of this analysis is to describe the relationship between potential failures and their effects. Furthermore, the adverse effects of failures identified in the FMEA can be minimized by the introduction of preventive measures such as:

- Use of enclosed systems to prevent spills and splashes.
- Strict enforcement of protective equipment rules.
- Exhaust ventilation to control emissions.

While methods such as FMEA are considered an integral part of the hazard measurement process, measurements of the quantitative levels of risks are necessary to prioritize the implementation of preventive measures and to make judgments about the acceptability of risks. Unfortunately, quantification is difficult, particularly when there is little information on past operating experience. In order to resolve this problem quantitative estimates of risk have been developed using a range of

TABLE 32

HAZARD IDENTIFICATION

Agents	Populations at Risk	Route & Duration Exposure	Potential Hazard	Controls
<p><u>Raw Materials:</u> White phosphorus, red phosphorus, felt, butyl rubber, methylene chloride.</p>	<p>Production Workers.</p>	<p>Inhalation and skin contact over 8-hr working shifts.</p>	<p>Skin burns and respiratory irritation; chronic degenerative disease.</p>	<p>Industrial hygiene, respirators, protective clothing, medical surveillance</p>
	<p>Pollution Control Workers.</p>	<p>Skin contact during periodic maintenance.</p>	<p>Skin burns.</p>	<p>Protective clothing.</p>
	<p>Local Community.</p>	<p>Inhalation due to air pollution from occasional releases or spills.</p>	<p>Respiratory irritation in susceptible populations.</p>	<p>Pollution controls.</p>
	<p>Local Flora/Fauna.</p>	<p>Ingestion following water or air pollution from occasional releases or spills.</p>	<p>Local impacts on aquatic life.</p>	<p>Pollution controls.</p>
<p><u>Combustion Products:</u> Phosphorus pentoxide, phosphorus trioxide, orthophosphoric acid, phosphorus acid, phosphine, various products of felt and butyl rubber combustion.</p>	<p>Troops</p>	<p>Inhalation and skin contact for short durations.</p>	<p>Respiratory irritation.</p>	<p>Respiratory protection.</p>
	<p>Local Community.</p>	<p>Inhalation during cloud dispersal.</p>	<p>Respiratory irritation in susceptible populations.</p>	<p>Natural dilution.</p>
	<p>Local Flora/Fauna.</p>	<p>Ingestion following cloud or residual deposition.</p>	<p>Local impacts on aquatic life.</p>	<p>Natural dilution or decomposition.</p>

TABLE 33
FAILURE MODE AND EFFECTS ANALYSIS-PRODUCTION

Life Cycle Phase	Initiating Incident	Failure Mode	Possible Effect Of Failure	Assessment of Hazard Level* (If Effect Occurs)	Remarks
Shell Filling	Automatic fill malfunction leads to phosphorus spill.	Phosphorus spill oxidizes to form concentrated cloud.	Several workers are exposed to airborne phosphorus; respiratory irritation.	1-2	Continual effort to promote safety and use of protective equipment. Rigorous maintenance programs help to reduce frequency of malfunctions.
Burster Insertion	Air bubble trapped inside filled shell; burster insertion causes phosphorus splash.	Employee not wearing protective equipment.	Skin contact with elemental phosphorus skin burns.	2-3	" "
Leak Testing	Leaking shell coated with phosphorus.	Operator not wearing protective equipment.	Operator splashed with phosphorus; skin burns.	1-3	" Also operator should be trained to insert burster gently to avoid splashing.
RP-F Pollution Control	System leakage.	Gloves not worn or tear in gloves.	Operator contacts phosphorus with hands.	1-3	Frequent inspection of gloves and compliance with protective equipment rules should reduce the frequency of this event.
RP-BR Mixing	Excess methylene chloride-butyl Rubber syrup is added.	Flow of phosphorus waste into nearby streams and depositions on land.	Local fishkills.	4-5	Effects should be localized.
RP-BR Extrusion	Inadequate ventilation or system failure.	Spill or splash of methylene chloride.	Operator has skin contact and inhalation exposure to methylene chloride.	1-2	Dermatitis and systemic effects result from chronic skin exposure. Inhalation of high levels may also be toxic. Protective clothing and ventilation are required.
RP-BR Pollution Control	Emissions of methylene chloride.	High airborne levels of methylene chloride.	Operator and others in work area have chronic exposure to methylene chloride.	4-5	Engineering controls are necessary to control airborne methylene chloride.
		High ambient levels of methylene chloride.	Minor effects.	1	Concentrations of methylene chloride in the ambient environment are not expected to be high.

* Hazard levels:

- 1 = Minor injury
- 2 = Multiple minor injury
- 3 = Major injury
- 4 = Multiple major injury or single fatality
- 5 = Multiple fatality.

estimates and by analogy to similar systems where quantitative data are available. Tables 34, 35, and 36 show several types of data which can be used in the development of a fault-tree analysis which results in an estimate of the probability that a hazardous event will occur.

Figure 9 is a fault-tree which was developed for leak testing of WP-F shells. Table 37 shows how known risk data were adopted for use in the fault-tree. This analysis is based upon filling and leak testing of one shell. If 1,000,000 shells are filled annually, then the model predicts approximately one WP burn per year from the leak testing operation. Historically, there have been about 4 WP burns per year at Pine Bluff Arsenal. No better agreement should be expected between the model and the work place experience, due to the necessary subjectivity of the assignment of probabilities to human actions and the dissimilarity of shell-filling operations to the industrial activities from which the failure rate data were derived. The fault tree analysis shows that engineering controls, to minimize the incidence of phosphorus-contaminated shells, and a safety program including the provision of individual protective equipment and training in its use, are equally important in minimizing the risk of injury at the leak testing station. If, for example, the incidence of overflow in the new dry-fill system is one in 100,000 shells, the model would predict only one WP burn every 10 years, providing that there is not a relaxation of safety procedures due to the perceived safety of the operation.

Under normal conditions, production operations are not expected to have adverse impacts on the environment. On the other hand, failure of the pollution control system could result in severe localized damage. Previous discussions estimated that phosphy water could be discharged at concentrations approaching 40 mg/L which is well above the toxicity threshold of 1 ppb. Failure of air pollution controls would result in high concentrations at the point of emission but, because of dilution, exposures downwind would not be severe. Calculations for methylene chloride emissions have shown that ambient concentrations at the Arsenal boundary would be well below current EPA standards for volatile hydrocarbons. Worst case calculations for ambient phosphoric acid indicate that a maximum concentration of 728 $\mu\text{g}/\text{m}^3$ would be found at 300m downwind from an aggregated emission source.

TABLE 34

FAILURE RATE DATA FOR TYPICAL EQUIPMENT

<u>Failure Mode</u>	<u>Mean Failure Rate or Failure at Demand Probability</u>
Valve ruptures	1.0×10^{-8} /hour
Tank ruptures	1.0×10^{-6} /year
Connection flange ruptures	1.0×10^{-8} /hour
Swivel ruptures	1.0×10^{-8} /hour
Expansion joint ruptures	1.0×10^{-8} /hour
Compressor ruptures	1.0×10^{-8} /hour
Pump ruptures	1.0×10^{-8} /hour
Relief valve fails to open on demand	1.0×10^{-5} /demand
Relief valve opens early	1.0×10^{-5} /hour
Automated valve fails to open on demand	1.0×10^{-3} /demand
Electronic system fails	1.0×10^{-6} /hour
Automatic shutdown device fails	1.0×10^{-4} /demand
Electric motor fails	1.0×10^{-3} /demand
Shutdown device fails on demand	1.0×10^{-4} /demand
Operator fails to observe	1.0×10^{-3} /demand
Operator fails to take action	3.0×10^{-4} /demand
Operator fails to observe audible alarm	3.0×10^{-4} /demand
Audible alarm fails on demand	1.0×10^{-5} /demand
>6-in. pipe rupture	1.8×10^{-9} /ft-yr

Source: Science Applications, Inc. (1975)
 Rasmussen, et al (1974).

TABLE 35

TYPICAL PROBABILITY OF HUMAN ERROR IN INDUSTRY

<u>Activity</u>	<u>Probability of Error/Task</u>
Critical routine task (e.g., tank isolation)	10^{-3}
Non-critical routine task (e.g., misreading temperature data)	3×10^{-3}
General error rate at high-stress activities that are occurring rapidly	2.5×10^{-1}
Non-routine operations (e.g., startup, maintenance)	10^{-2}
Checklist inspection	10^{-1}
Walk-around inspection	5×10^{-1}
<u>High-stress Operations:</u>	
Responding after major accident	
-first minute	1
-after 5 minutes	9×10^{-1}
-after 30 minutes	10^{-1}
-after several hours	10^{-2}
General human error of observance	5×10^{-2}
Operator actuation of switch	10^{-3}
Operator actuation of key-operated switch	10^{-4}
General human error of omission	10^{-2}

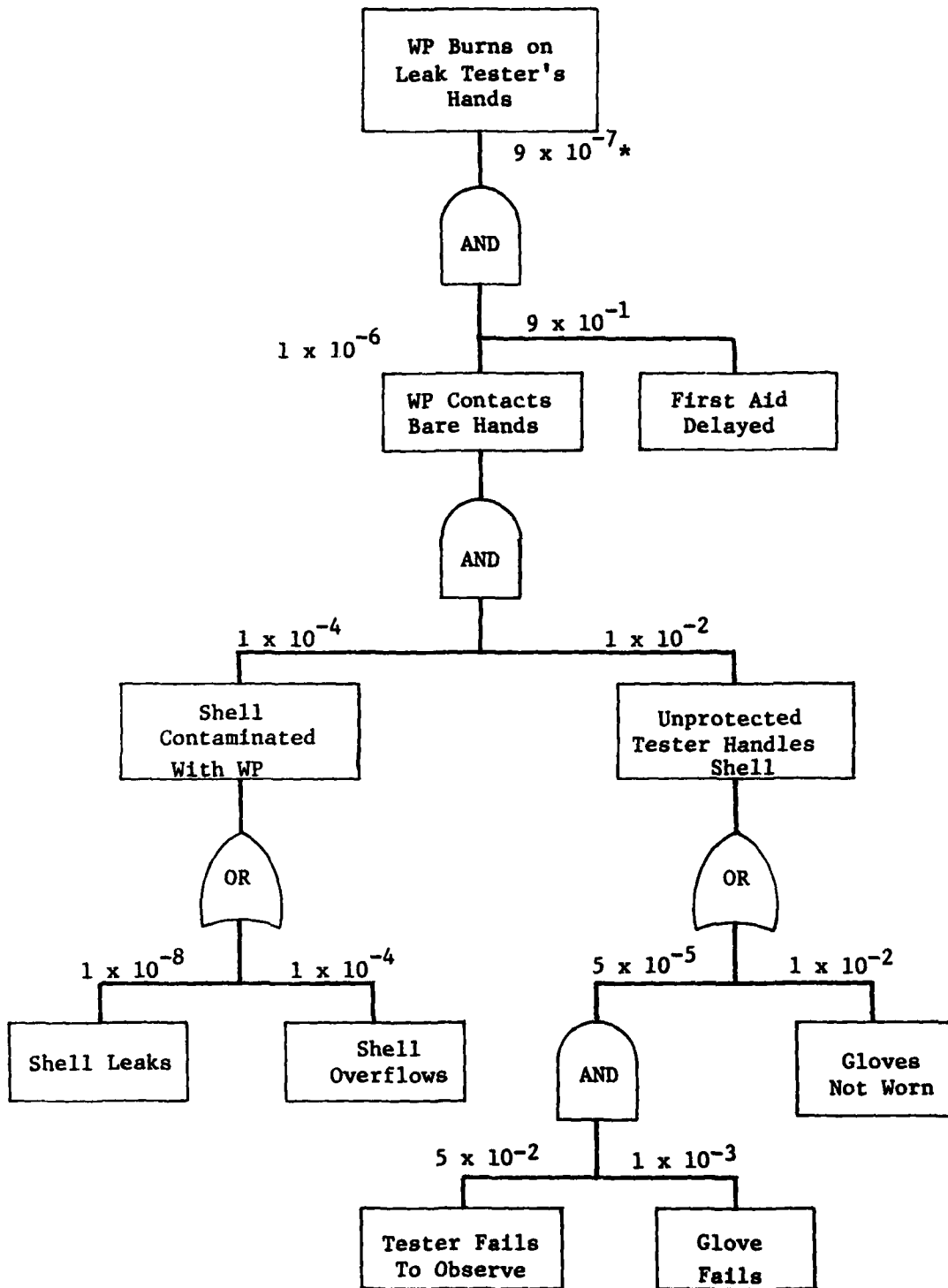
Source: Rasmussen, N., et al. (1974), and Walker, J.R. et al.

TABLE 36

FREQUENCY OF TYPICAL INDUSTRIAL HAZARDS

<u>Industrial Hazard</u>	<u>Frequency per Year</u>
Fire in liquid petroleum product tank (crude, naphtha, gasoline, etc.) or other flammable liquid storage tank	3.3×10^{-4}
Major spill from LNG storage tank	$<3 \times 10^{-4}$
Fire/explosion of LPG storage tank	3.3×10^{-6}
Fires and explosions at petroleum processing plants resulting in damage outside the plant property	1.4×10^{-4}
Failure of a tank containing nonflammable materials	2×10^{-5}

Source: Atallah, S., and E. M. Drake,



* Based on filling and leak-testing one shell

FIGURE 9. FAULT-TREE ANALYSIS OF LEAK TESTING

TABLE 37
DERIVATION OF PROBABILITY DATA

Event	Analogy	Probability
SHELL OVERFLOWS DURING FILLING	Shutdown device fails on demand. (Assume 10^3 demands/hr.)	1.0×10^{-4} /demand 1.0×10^{-1} /hr
SHELL LEAKS	Connection flange ruptures.	1.0×10^{-8} /hr
TESTER NOT WEARING GLOVES	General human error of omission.	1.0×10^{-2} /task
GLOVES FAIL	Electric motor fails	1.0×10^{-3} /demand
TESTER FAILS TO OBSERVE LACK OF PROTECTION	General human error of observance.	5.0×10^{-2} /task
FIRST AID DELAYED	Human error responding after major accident.	9.0×10^{-1} /event

5.2.3 Hazard Assessment

The production of WP-F and RP-BR screening smokes can be conducted with minimal risk to occupational safety and health and the surrounding environment if compliance with standard industrial hygiene and environmental controls is maintained. Pine Bluff Arsenal has established safe operating procedures including requirements for the use of personal protective equipment. In case of exposure, emergency eye wash and whole body drenching tubs are available. To prevent the development of chronic disease from long-term low-level phosphorus exposure, the Arsenal conducts a dental health surveillance program. In addition, the planned conversion to enclosed dry line operations will reduce emissions from production operations.

By reducing process water utilization, the dry line also reduces the potential for environmental impacts. More importantly, the development of a zero discharge pollution control system will eliminate the problems previously associated with process emissions.

Industrial hygiene, medical surveillance, and pollution control programs are vital aspects of WP-F and RP-BR production and, when strictly enforced, serve to control a variety of potential hazards.

5.3 Hazard Assessment for Training and Field Use

5.3.1 Hazard Identification

Reference should be made to Table 32 in Section 5.2.1 which includes potential hazards associated with the use of RP-BR and WP-F smokes under training and battlefield conditions.

5.3.2 Hazard Quantification

The Failure Mode and Effects Analysis (FMEA) for training or battlefield use of RP-BR and WP-F screening smokes shown in Table 38 identifies the hazard of leaking shells which is similar to the production hazard discussed in Section 5.2. In addition, hazards which occur during and after deployment of screening smokes such as troop or community exposure to airborne smoke or effects on flora and fauna from smoke deposition or smoke residuals are identified.

Fault-trees for hazardous events which may result from smoke deployment during training or on the battlefield have been developed. It should be noted that this analysis depends upon the interaction of two independent factors: troop movement and smoke dispersal. In order for the postulated hazardous exposure to occur, troops and high concentrations of smoke must be in the same place at the same time. Even when the location of troops and smoke are the same, exposure may be prevented by using respiratory protective equipment.

FAILURE MODE AND EFFECTS ANALYSIS-TRAINING/FIELD USE

Life Cycle Phase	Initiating Incident	Failure Mode	Possible Effect Of Failure	Assessment of Hazard Level (If Effect Occurs)*	Remarks
Shell Storage/Transport	Vibration or shock.	Phosphorus leaks from shell.	Troops handling shells have phosphorus skin contact. Phosphorus oxides in confined space. Air-borne phosphorus inhaled by troops.	2-3 1-2	Lack of immediate first aid results in severe burns. Confined spaces are unlikely in the field.
Deployment	Short fuse. Improper assessment of target.	Premature deployment. Deployment on friendly troops.	Troops exposed to concentrated smoke cloud. Troops exposed to concentrated smoke cloud.	1-2 1-2	Unlikely event, greater hazard from explosion and shrapnel. Only a limited area of the field will have harmful concentrations of phosphorus. Rapid dispersal reduces risk.
Post deployment	Troops enter smoke cloud. Incomplete combustion. Airborne smoke dispersal.	Respiratory protection not worn. Respiratory protection fails. Deposition of residual. Flora/fauna or local residents exposed.	" " Local toxic effects for flora/fauna. Minor respiratory or skin irritation.	1-2 1-2 4-5 1-2	" " During training deployment over limited target areas may result in large quantities of residual Minor irritation will not be acceptable to local communities. Training should be conducted in areas where community exposure is minimized.

* 1 - Minor injury
 2 - Multiple minor injury
 3 - Major injury
 4 - Multiple major injury or single fatality
 5 - Multiple fatality

Figure 10 is a fault-tree which describes the events leading up to the exposure of troops to hazardous concentrations of smoke. Probabilities for these events have been derived and their derivation is described in Table 39. Note that in this case the problem of troop and smoke interaction is addressed by assuming that troops will be in the smoke cloud ($p = 1$) so that the final assessment of risk is solely dependent upon the use of adequate respiratory protection. Estimates of the reliability of the protective equipment and the ability of the individuals exposed to use them are based upon analogies to industrial situations that are different in all aspects from the military situations where smoke is deployed. Thus their validity is problematic. The fault tree analysis does serve the purpose of pointing out the sensitivity of the hazard estimation procedure to variations in these two factors.

In order to assess community risks during training or field use of screening smokes, an additional dispersion calculation has been performed. This scenario is similar to the extended coverage scenario described in Chapter 3, except that interest is focused upon the maximum concentration of smoke at various distances for the deployment site. Furthermore, if it is assumed that populations may be found at these various distances, it is important to assess the risks which might be attributable to these population exposures. Table 40 shows the results of the dispersion calculation and Table 41 shows the relationship between selected distances, exposures, and health effects criteria.

Smoke yield increases with relative humidity. (See Appendix B.) At 50 percent humidity, five times the levels of phosphoric acid result, compared to smoke yield in dry atmospheres. The H_3PO_4 concentration at 5000 m becomes $4.8 \times 10^3 \mu\text{g}/\text{m}^3$. While the TLV is normally used to evaluate occupational exposures over an 8-hr work shift, it can also be used as a guideline for evaluating the potential impact of repeated short-term community exposures. If populations in the community are exposed over short durations of time to levels at or near the TLV, one would not expect toxic effects; however, it is possible that sensitive individuals would suffer from respiratory irritation. Therefore, it would be prudent to assure that an uninhabited buffer zone of greater than 5000 m be established between smoke training areas and local communities. In the continental US, it can be assumed that large-scale testing and training exercises will be conducted in remote areas set aside for such purposes, so exposures of local residents to concentrations of phosphorus screening smokes approaching the TLV would not be at all likely. However, if large-scale testing occurs in locations such as Pine Bluff Arsenal or during field maneuvers in Europe, local inhabitants may suffer from mild effects.

A "worst-case" assessment for deployment of WP-F smokes during training has been developed to examine the potential magnitude of environmental impacts. This assessment assumes the following:

- Training site area = $10,000 \text{ m}^2$ (2.47 acres).
- Frequency of use = 1 hr/week; 52 weeks/yr.
- Deployment criteria: Maintain obscuring smoke concentrations ($0.288 \text{ mg}/\text{m}^3$) for one hour.

FIGURE 10
FAULT-TREE ANALYSIS OF TROOP EXPOSURE

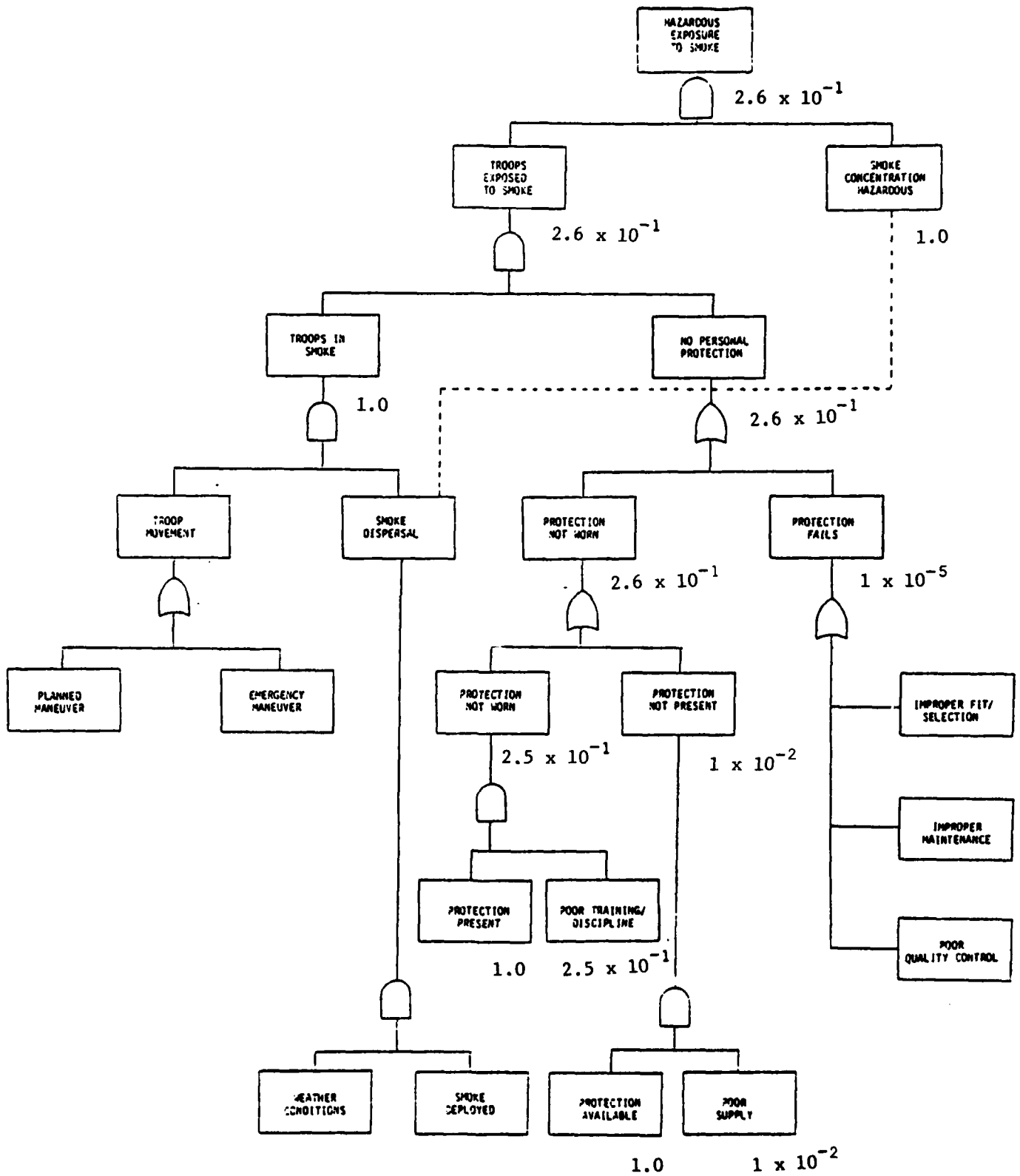


TABLE 39

DERIVATION OF PROBABILITY DATA

Effect	Analogy	Probability
TROOPS IN SMOKE	--	Assume 1.0
PROTECTION PRESENT	--	Assume 1.0
POOR TRAINING/ DISCIPLINE	General error rate at high stress activities that are occurring rapidly.	2.5×10^{-1} /task
PROTECTION AVAILABLE	--	Assume 1.0
POOR SUPPLY	General human error of omissions.	1.0×10^{-2} /task
PROTECTION FAILS	Relief valve fails to open on demand.	1.0×10^{-5} /demand
SMOKE CONCENTRATION HAZARDOUS	--	Assume 1.0

TABLE 40

COMMUNITY EXPOSURE TO FIELD TRAINING DEPLOYMENT

An area of 100m square is maintaining a concentration of $.288\mu\text{g}/\text{m}^3$ of P_2O_5 for neutral stability in a 3m/s wind, corresponds to an emission rate of 290.9g/s of P_2O_5 from the very center of the area source. Based on this emission rate, concentrations downwind can be calculated. Remember these concentrations will be extremely high because the initial concentration in the area is enough to obscure both visible and infrared electromagnetic radiation. The model's results are quasi-realistic because the distance downwind is measured from the center of the area source. The results are listed below.

<u>$\chi(\text{m})$</u>	<u>$\chi(\mu\text{g}/\text{m}^3)$</u>	<u>$\chi(\text{m})$</u>	<u>$\chi(\mu\text{g}/\text{m}^3)$</u>
100	1.46×10^5	850	1.17×10^4
150	9.50×10^4	900	1.10×10^4
200	6.98×10^4	950	1.03×10^4
250	5.61×10^4	1000	9.42×10^3
300	4.36×10^4	1050	8.88×10^3
350	3.56×10^4	1100	8.25×10^3
400	3.06×10^4	1150	7.80×10^3
450	2.67×10^4	1200	7.46×10^3
500	2.26×10^4	1250	7.01×10^3
550	2.09×10^4	1300	6.71×10^3
600	1.84×10^4	1350	6.43×10^3
650	1.66×10^4	1400	6.12×10^3
700	1.51×10^4	1450	5.79×10^3
750	1.39×10^4	1500	5.53×10^3
800	1.26×10^4	2000	3.86×10^3
		3000	2.19×10^3
		4000	1.47×10^3
		5000	9.63×10^2

Emission Rate = 290.9 g/s = Neutral stability; Wind Speed = 3m/s distance x (m) measured from center of area source. All concentrations in $\mu\text{g}/\text{m}^3$.

* Note that all concentrations are P_2O_5 NOT H_3PO_4 .

** Calculations of this type are rough and should be used for relative drop off rates.

TABLE 41

COMMUNITY EXPOSURE ESTIMATES

<u>Distance Downwind From Deployment</u>	<u>Maximum Concentrations (P₂O₅) ($\mu\text{g}/\text{m}^3$)</u>	<u>Health Effects</u>
100 m	1.46×10^5	Intolerable concentra- tion = $10^6 \mu\text{g}/\text{m}^3$ Minimum harassing concen- tration masks, mandatory = $7 \times 10^5 \mu\text{g}/\text{m}^3$
200 m	6.98×10^4	
300 m	4.36×10^4	Lowest toxic concentra- tion = $10^5 \mu\text{g}/\text{m}^3$
400 m	3.06×10^4	
500 m	2.26×10^4	
600 m	1.84×10^4	
700 m	1.51×10^4	
800 m	1.26×10^4	
900 m	1.10×10^4	
1000 m	9.42×10^3	
5000 m	9.63×10^2	Phosphoric Acid TLV = $10^3 \mu\text{g}/\text{m}^3$

- Deployment frequency: 1 shell/50 sec or 72 shells for the 1-hour training session.
- Shell fill weight: 5,980g smoke formulation (P₄).
- Deployment results in uniform distribution over the training area.
- Residual on the ground = 1% of the formulation.

Figure 11 illustrates the scenario and shows estimates of the residual dose to the training area. In actual practice it is not likely that the same target area will be used each week. Training with smoke screens will probably occur on large practice ranges in isolated parts of the country such as the National Training Center at Fort Irwin, California, or the Dugway Proving Ground in Utah. Since these installations cover thousands of acres (Fort Irwin is about the size of Rhode Island), repeated smoke deployment on the same site is unlikely during training maneuvers. On the other hand, testing sites with permanently installed monitoring devices will probably have repeated deployments over limited areas. In either case environmental impacts from residual smoke formulations will depend on the amount of residual, dilution factors, and any efforts taken to neutralize or clean-up the residual.

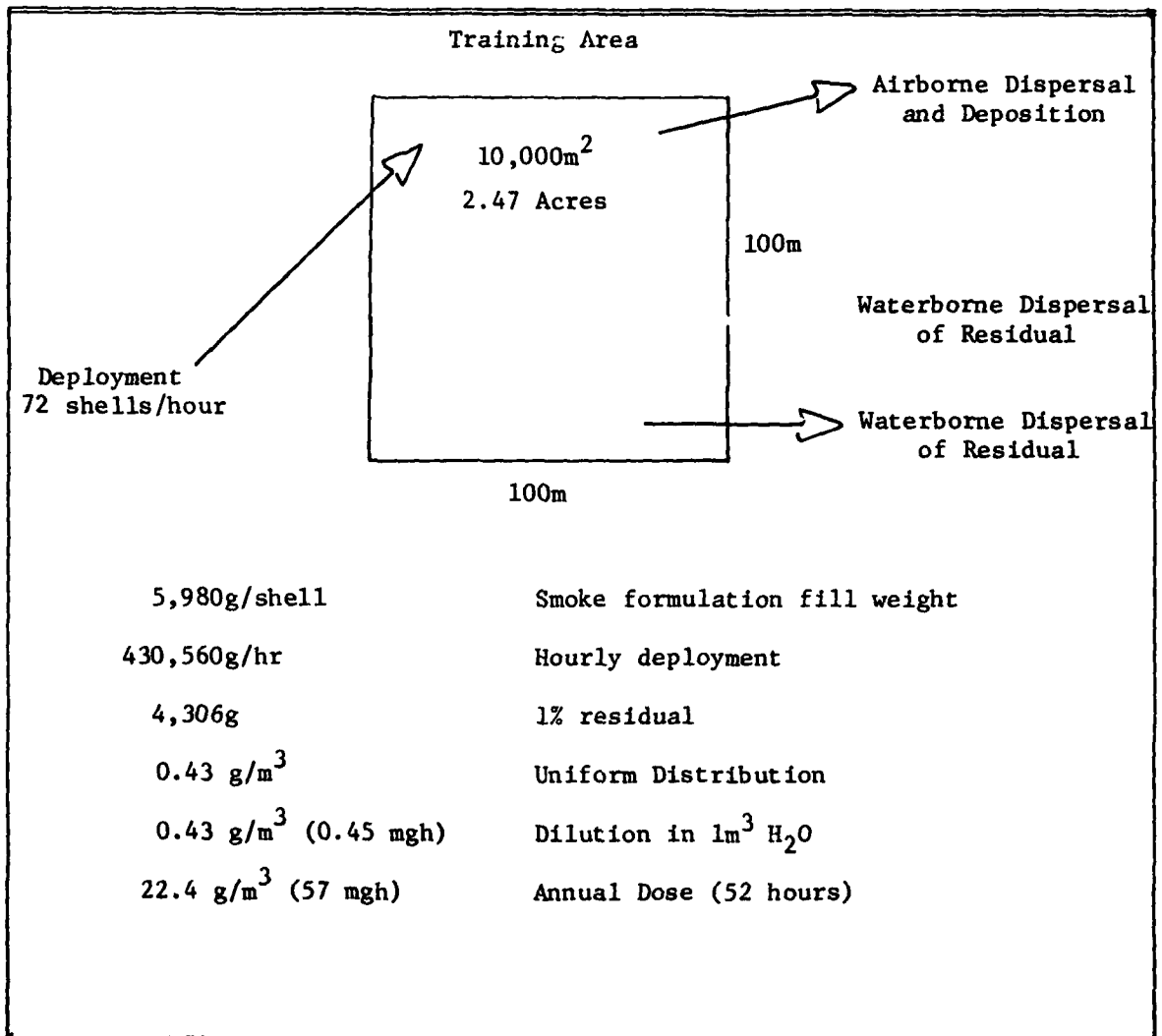
In the desert areas of the United States where training with and testing of smokes are most likely to be carried out, rainfall, though infrequent, can be torrential, causing a runoff of accumulated depositions into swollen streams, and from thence to the eventual receiving bodies or into aquifers which, in either case, could be located beyond the boundaries of even such vast posts as Fort Irwin and Dugway Proving Ground.

Under the conditions described in Figure 12, the training area receives a dose of 0.43 mg/L during a training session or 22.4 mg/L on an annual basis. These concentrations exceed known toxicity thresholds for aquatic life. For example, while Yellow Lake at Pine Bluff Arsenal could support active finfish and waterfowl populations with a mean phosphorus concentration of 0.2-0.25 mg/L, the tributary creek was devoid of major life forms when the concentration was raised to 1-3mg/l. These data suggest that repeated deployment of screening smokes over limited areas will result in local impacts on the environment.

5.3.3 Hazard Assessment

The deployment of WP-F and RP-BR screening smokes in training or battle-field situations presents some hazards which, to a large extent, can be controlled with proper planning and utilization of protective equipment. Community risks can be eliminated by locating training sites in isolated areas. In wartime, community exposure cannot be well controlled; however, the hazards of screening smokes are negligible in comparison with other hazards of war.

FIGURE 11
TRAINING SCENARIO



If deployment is concentrated on a small area, environmental impacts are likely; however, they appear to be reversible as shown by the recovery of the area surrounding the production facility at Pine Bluff.

5.4 Discussion

The scope of work for this project required the collection of information for an initial estimate of the occupational and environmental hazards posed by the manufacture and use of white phosphorus-felt (WP-F) and red phosphorus-butyl rubber (RP-BR) screening smokes. Information was collected from a variety of sources including published literature, on-going research conducted by U.S. Army personnel and contractors, and site visits to Edgewood Arsenal, Aberdeen Proving Ground the Pine Bluff Arsenal. In addition, models were developed to characterize the environmental fates of the products of smoke deployment. All of this information was reviewed and served as a foundation for developing exposure scenarios and, subsequently, assessments of hazards.

The major problem associated with this logical series of tasks and a persistent theme throughout the report is the lack of a comprehensive precise data base.

From the perspective of hazard assessment, there are three basic areas where additional data are needed:

- (1) Characterization of emissions,
- (2) Evaluation of exposures, and
- (3) Utilization of protective measures.

On-going research at the Illinois Institute of Technology Research Institute (IITRI) is focusing on the identification of the products of screening smoke combustion. To date, little work has been conducted to evaluate exposures either in the occupational setting or in the field. During the information collection phase of the study only two industrial hygiene surveys at Pine Bluff Arsenal were identified. No attempts to measure personal exposure in the field were identified. Industrial hygiene sampling techniques should be applied to measure both worker and troop exposure.

Identification and evaluation of hazards is a necessary step in establishing standards and procedures both for the protection of workers and troops and for the protection of the environment.

6.0 REFERENCES *

Anon, American Conference of Governmental Industrial Hygienists (ACGIH): Methylene Chloride. Documentation of the TLVs for Substances = Workroom Air, 3rd Ed.: Cincinnati, OH (1976).

Anon, "Basic Smoke Characterization Test," U.S. Army Test and Evaluation Command, Aberdeen Proving Ground; 299 pp. (March, 1978) DTIC No. AD B031190.

Atallah, S., and E. M. Drake, "Safety Considerations in Siting Housing Projects," U.S. Department of Housing and Urban Development, HUD-PDR-161, (1976).

Ballantyne, B. *et al.*, "The Ophthalmic Toxicology of Dichloromethane," Toxicology 6:173 (1976), as cited. Mitre, 1976.

Balmer, M.F., F.A. Smith, L.J. Leach, and C.L. Yuile, "Effects in the Liver of Methylene Chloride Inhaled Alone and with Ethyl Alcohol," Am. Ind. Hyg. Assoc. J., 37:345 (1976).

Barker, E.A., E.A., Smuckler and E.P. Benditt, "Effects of Thioacetamide and Yellow Phosphorus Poisoning on Protein Synthesis *in vivo*," Lab. Invest., 12:955-960 (1963).

Beeson, P.B. and W. McDermott, ed., Textbook of Medicine; W.B. Saunders Company, Philadelphia, pp. 1452-1455, (1975).

Ben-Hur, N., A. Giladi, L. Neuman, B. Shugerman, J. Appelbaum, "Phosphorus Burns: A Pathophysiological Study," Br. J. Plast. Surg. 25(3):238-244 (1972).

Ben-Hur, N., J. Appelbaum, "Biochemistry, Histopathology and Treatment of Phosphorus Burns: An Experimental Study," Isr. J. Med. Sci. 9(1):40-48, (1973).

Berkowitz, J. *et al.*, "Literature Review - Problem Definition Studies on Selected Chemicals, Vol II," Final Report, Contract No. DAMD17-77-C-7037 to U.S. Army Medical Research and Development Command, Ft. Detrick, MD 21701 (June, 1978).

Bornmann, G. and A. Loeser, "Chronic Toxic Effect of Dichloromethane," Z. Lebensm. - Unters. Forsch. 136:14-18, (1967). Abstract.

Bowen, T.E., T.J. Whelan, Jr., T.G. Nelson, "Sudden Deaths After Phosphorus Burns: Experimental Observations Of Hypocalcemia, Hyperphosphatemia and Electrocardiographic Abnormalities Following Production of a Standard White Phosphorus Burn," Annals Surgery 174:779-784, (1971).

*USAMRDC - US Army Medical Research and Development Command
USAMBRDL - US Army Medical Bioengineering Research and Development
Laboratory

EPA - Environmental Protection Agency

DTIC - Defense Technical Information Center, Alexandria, VA 22314

WTIS - National Technical Information Service, Springfield, VA 22161

Broughton, W.E., "Epoxy Resins in Industry - The Hazards and Their Control," Ann. Occup. Hyg., 8:131-142, (1965).

Brown, B.J., J.T. Weimer, G.E. Affleck, R.L. Farrand, D.H. Heitkamp and F.K. Lee, "The Acute Effects of Single Exposures to White Phosphorus Smoke in Rats and Guinea Pigs," Chemical Systems Laboratory Technical Report ARCSL-TR-80013, U.S. Army Armament Research and Development Command, Aberdeen Proving Ground, MD, March 1980a.

Brown, B.J., et al., "The Subchronic Effects of Repeated Exposure to White Phosphorus/Felt Screening Smokes in Rats," Chemical Systems Laboratory Report ARCSL-TR-80068, May 1981.

Buchanan, D.J., M.V. Sigal, C.S. Robinson, F. Pope, M.F. Ferguson, J.B. Thomison, "Studies of Phosphorus Intoxication," Arch. Ind. Hy. Occup. Med., 9(1):1-8, (1954).

Burrows, D., J.C. Dacre, "Mammalian Toxicology and Toxicity to Aquatic Organisms of White Phosphorus and "Phossy Water, A Water Borne Munitions Manufacturing Waste Pollutant - A Literature Evaluation, Contract No. DAD17-73-C-3170, U.S. Army Medical Research and Development Command DTIC No. AD 777901 (Nov. 1973).

Calder, K.L., "Atmospheric Diffusion of Particulate Material Considered as a Boundary Value Problem," J. Meteorol., 18(3):413-416 (1961).

Ciba Geigy, Scientific Tables, 7th Ed. p663 (1971)

Chan, T.L. and M. Lippmann, "Experimental Measurements and Empirical Modelling of the Regional Deposition of Inhaled Particles in Humans," Am. Ind. Hyg. Assoc., 41:399-409 (1980).

Cooper, A.E. and E.J. Owens, "A Review of the Toxicology of Screening Smokes," Private document provided by USAMBRDL, Fort Detrick, MD 21701.

Cotton and Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Interscience Publishers, John Wiley & Sons, New York, 1972.

Cullumbine, H., "The Burning Power and Harassing Effects of White Phosphorus," Military Intelligence Division, Great Britain, Report No. 2604, March 17, 1944.

Dalhamn, T. and B. Holma, "Animal Experiments on the Spread of Inhaled Radioactive Red Phosphorus in the Body," Arch. Ind. Health, 20:429-431 (1959).

Dearden, W.F., Brit. Med. J. 2:408 (1901), as cited by Miles, (1972).

Dianzani, M.U., "Liver Steatosis Induced by White Phosphorus," Morgagni, 1:1-23 (1972).

Diaz-Rivera, R.S., P.J. Collazo, E.R. Pons, M.V. Torregrosa, "Acute Phosphorus Poisoning in Man, A Study of 56 Cases," Medicine, 29: 269-298, (1950).

DiVincenzo, G.D., F.J. Yanno, and B.D. Astill, "Human and Canine Exposures to Methylene Chloride Vapor," Am. Ind. Hyg. Assoc. J., 33:125-35 (1972).

DiVincenzo, G.D., M.L. Hamilton, "Fate and Disposition of (14 C) Methylene Chloride in the Rat," Toxicol. Appl. Pharmacol., 32:385-93 (1975).

Drivas, Peter J., Fredrick H. Shair, "Dispersion of an Instantaneous Cross-wind Line Source of Tracer Released from an Urban Highway," Atmos. Environ. 8:475-485 (1974).

Edzwald, J.D., "Phosphorus in Aquatic Systems: The Role of the Sediments," in Fate of Pollutants in the Air and Water Environments, Part 1, I. H. Suffet (ed.), pg. 183, John Wiley & Sons, New York, 1977.

Filippova, L.M., O.A. Pan'shin and R.G. Kostyanovskii, "Chemical Mutagens. IV. Genetic Activity of Geminal Systems," Genetika, 8: 134-148, (1967), as cited in Kirk-Othmer Encyclopedia of Chemical Technology 2nd ed., Vol. 5, Wiley, New York, p. 111-119, 1965.

Fleming, R.B.L., J.W. Miller, and V.R. Swayne, Jr., "Some Recent Observations on Phosphorus Toxicology," J. Ind. Hyg. Toxicol., 24:154-158 (1942).

Fodor, G.G. and A. Roscovanu, "Increased Blood- Co- Content in Humans and Animals by Incorporated Halogenated Hydrocarbons," Zentralbl Bakteriol. pp. 34-40, (1976). Abstract.

Ghoshal, A.K., E.A. Porta, W.S. Hartroft, "Isotopic Studies on the Absorption and Tissue Distribution of White Phosphorus in Rats," Exp. Mol. Pathol., 14(2):212-219, (1971).

Gleason, M.N., R.E. Gosselin, D.C. Hodge, R.P. Smith, Clinical Toxicology of Commercial Products, 3rd Edition, Williams & Wilkins Co., Baltimore, 1969.

Haun, C.C., E.S. Harris, and K.I. Darmer, Jr., "Continuous Animal Exposure to Methylene Chloride," NTIS, AD 751432, (1971).

Heimann, H., "Chronic Phosphorus Poisoning," J. Ind. Hyg. Toxicol. 28(4):142-150 (1946).

Heppel, L.A., P.A. Neal, T.L. Perrin, M.L. Orr, V.T. Porterfield, "Toxicology of Dichloromethane (Methylene Chloride)--I. Studies on Effects of Daily Inhalation," J. Ind. Hyg. Toxicol., 26:8-16 (1944).

Hilado, C.J., M.T. Lopez, "Relative Toxicity of Pyrolysis Products of some Elastomers," J. Combustion Toxicol., 4(1):61-68 (1977).

Hughes, J.P.W., R. Baron, D.H. Buchland, M.A. Cooke, J.D. Craig, D.P. Duffield, A.W. Grosart, P.W.J. Parkes, A. Porter, "Phosphorus Necrosis of the Jaw: A Present Day Study," Br. J. Ind. Med., 19 (2):83-99 (1962).

Hunter, D., The Diseases of Occupations; 2nd ed., English University Press, London, 1957, as cited in Hughes et al. (1962).

Industrial Hygiene Survey No. 35-036-75/76, Pine Bluff Arsenal; Pine Bluff, Arizona (April 7 - 15, 1975).

Industrial Hygiene Special Study No. 35-0112-78, "Preoperational Survey of White Phosphorus (WP) Fill Line," Pine Bluff Arsenal, Arizona (Dec. 5 - 9, 1977).

JANAF Thermochemical Tables; 2nd ed., National Bureau of Standards, Printing Office (1971).

Johnson, Morris C. and P.D. Forney, "The Effectiveness of Obscuring Smokes," U.S. Army Munitions Command, Operations Research Group, Edgewood Arsenal, Maryland (Sept., 1972).

Jongen, W.M.F., G.M. Alink, and J.H. Loeman, "Mutagenic Effect of Dichloromethane on Salmonella Fythimurium," Mutat. Res., 56:245-248 (1978).

Kennon, R., J.W. Hallam, "Modern Phosphorus Caries and Necrosis," Brit. Dental J., 76(12):321-330 (1944).

Kitchens, J.F., W.E. Harvard, D.M. Lauter, R.S. Wentzel and R.S. Valentine, "Preliminary Problem Definition Study of 48 Munitions-Related Chemicals, Vol. III Pyrotechnic-Related Compounds," Contract No. DAMD 17-77-C-7057, Report to U.S. Army Medical Research and Development Command, Ft. Detrick, Maryland (April, 1978) DTIC No. AD A066308.

Lee, C., J.V. Dilley, J.R. Hodgson, D.O. Helton, W.J. Wiegand, D.N. Roberts, B.S. Anderson, L.M. Halfpap, L.D. Kurtz, N. West, "Mammalian Toxicity of Munition Compounds, Phase I. Acute Oral Toxicity, Primary Skin and Eye Irritation, Dermal Sensitization, and Disposition and Metabolism," Report No. 1, Prepared for U.S. Army Medical Research and Development Command, Ft. Detrick, Maryland 21701 (July 22, 1975) DTIC No. AD B011150L.

Leong, K.J., H.N. MacFarland, "Hazards from Thermodecomposition of Epoxy Resins," Arch. Environ. Health, 7:675-681 (1963).

MacEwen, J.D., E.H. Vernet, and C.C. Haun, "Continuous Animal Exposure to Methylene Chloride," Aerospace Medical Research Labs, Wright Patterson Air Force Base, Contract No. NASA Order T-80498 (1972), NTIS, AD 746295 (1972).

Marchetti, Robert M., A Transport and Diffusion Model for Smoke Munitions; U.S. Army Material Systems Analysis Activity. Technical Report No. 272, Aberdeen Proving Ground, Maryland (August, 1977) DTIC No. AD A079489.

Maruo, T., "Poisoning Due to Gas of Phosphorus. Part I. The Hemogram of Rabbits," Fukuoka Acta Med. 46:604-615 (1955).

Merck Index, 9th ed., Merck & Co., Rahway, New Jersey (1976).

Miles, A.E.W., "Phosphorus Necrosis of the Jaw: Phossy Jaw," Brit. Dental J., 133(5):203-206 (1972).

Milham, M.E., et al., New Findings on the Nature of WP/RP Smokes, Chemical Systems Laboratory Rep. #ARCSL-TR-77067, Partial Report (July, 1977).

Miller, V.L., R.R. Engel and M.W. Anders, "In Vivo Metabolism of Dihalomethanes to Carbon Monoxide," The Pharmacologist, 15:190 (1973).

Milly, George H., Atmospheric Diffusion and Generalized Munitions Expenditures; Operations Research Group Study No. 17, U.S. Army Chemical Corps., Army Chemical Center, Maryland (May, 1958).

Mitre, "Air Pollution Assessment of Methylene Chloride," Report by Mitre Corporation to the U.S. EPA MITRE Technical Report MTR-7334 (Sept., 1976).

Mod. Paint Coat, 6(42):68 (1977).

Moskowitz, S. and H. Shapiro, "Fatal Exposure to Methylene Chloride Vapor," Arch. Ind. Hyg. Occup. Med., 6:116-23 (1952).

NAS, Drinking Water and Health; National Academy of Sciences, Washington, DC 1977.

Neubauer, E., O. Porges, "Adrenal Insufficiency in Phosphorus Poisoning," Biochem. Z., 32:290-307 1911 (German).

NIOSH, "Criteria for a Recommended Standard . . . Occupational Exposure to Methylene Chloride," National Institute for Occupational Safety and Health, March 1976.

Pani, P., E. Gravela, C. Mazzarino, E. Burdino, "On the Mechanism of Fatty Liver in White Phosphorus Poisoned Rats," Exptl. Mol. Pathol., 16:201-209 (1972).

Patty, F.A. (ed.), Industrial Hygiene and Toxicology; Interscience Publishers, New York, 1963 (Second Revised Edition).

Price, P.J., C.M. Hassett, and J.L. Mansfield, "Transforming Activities," In Vitro, 14(3):290-293 (1978).

Rasmussen, H., et al., "Reactor Safety Study--An Assessment of Accident Risks in U.S. Commercial Nuclear Power Plants," U.S. Atomic Energy Commission Report No. WASH-1400 (1974).

Ratney, R.S., D.H. Wegman, H.B. Elkins, "In Vivo Conversion of Methylene Chloride to Carbon Monoxide," Arch. Environ. Health, 28: 223-26 (1974).

Registry of Toxic Effects of Chemical Substances, 1975 and 1978 edition, U.S. Dept. of H.E.W. Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, Ohio (1979).

Rodkey, F.L. and H.A. Collison, "Biological Oxidation of (14c) Methylene Chloride to Carbon Monoxide and Carbon Dioxide by the Rat," Toxicol. Appl. Pharmacol., 40:33-38 (1977).

Rubel, G.O., "Predicting the Droplet Size and Yield Factors of a Phosphorus Smoke as a Function of Droplet Composition and Ambient Relative Humidity under Tactical Conditions," report to Chemical Systems Lab., Aberdeen Proving Ground, MD., Report No. ARCSL-TR-78057 (1978) DTIC No. AD A064076.

Roth, R.P., R.T. Drew, R.J. Lo, and J.R. Fouts, "Dichloromethane Inhalation, Carboxyhemoglobin Concentrations, and Drug-Metabolizing Enzymes in Rabbits," Toxicol. Appl. Pharmacol., 33(3):427-437, (1975).

Sax, I., Dangerous Properties of Industrial Materials, Van Nostrand Reinhold Co., 5th ed., (1979).

Schwetz, B.A., B.K.J. Leong, P.J. Gehring, "The Effect of Maternally Inhaled Trichlorethylene, Perchloroethylene, Methyl Chloroform and Methylene Chloride on Embryonal and Fetal Development in Mice and Rats," Toxicol. Appl. Pharmacol., 32:85-96, (1975).

Science Applications, Inc., 1200 Prospect St., LaJolla, CA 92037 "LNG Terminal Risk Assessment Study for Los Angeles, California," Report for Western LNG Terminal Company, December 1975.

Simmon, V.F., K. Kauhanen, and R.C. Tariff, "Mutagenic Activity of Chemicals Identified in Drinking Water," Paper Presented at Second International Environmental Mutagen Society Meeting, Edinboro, Scotland (1977).

Sittig, M., Hazardous and Toxic Effects of Industrial Chemicals; Noyes Data Corp., Park Ridge, New Jersey (1979).

Slade, David H., "Meteorology and Atomic Energy 1968," Air Resources Laboratories, Environmental Science Services Administration, Report to the U.S. Atomic Energy Commission, July 1968.

Snelson, A., Personal Communication; ITT Research Institute, Chicago, Illinois 60616.

Snelson, A. and S. Katz, "Physical and Chemical Characterization of Military Smokes. Part II. Fogs, Oils and Oil Fogs" Contract No. DAMD 17-78-C-8085, ITT Research Institute to USAMBRDL, Ft. Detrick, Maryland 21701 (June, 1980).

Sollmann, T., "Studies of Chronic Intoxications on Albino Rats; VIII., Yellow Phosphorus," J. Pharm. Exp. Ther. 24:119-122 (1925).

Stewart, F.M. and H.D. McKinney, "Summary Report on New White Phosphorus (WP) Dry Fill Line," Paper presented to Sixth Quadrupartite Ammunition Conference, Naval Weapons Center, Yorktown, Virginia (Oct. 6, 1977).

Stewart, R.D., T.N. Fisher, M.J. Hosko, J.E. Peterson, E.D. Baretta, H.C. Dodd, "Experimental Human Exposure to Methylene Chloride," Arch. Environ. Health, 25:342-48 (1972a).

Stewart, R.D., T.N. Fisher, M.J. Hosko, J.E. Peterson, E.D. Baretta, and H.C. Dodd, "Carboxyhemoglobin Elevation after Exposure to Dichloromethane," Science, 176:295-296 (1972b).

Stewart, R.D. and C.L. Hake, "Paint-remover Hazard," JAMA, 235: 398-401 (1976).

Sullivan, J., H.D. Putnam, M.A. Keirn, B.C. Pruitt, J.C. Nichols, and J.T. McClare, "A Summary and Evaluation of Aquatic Environmental Data in Relation to Establishing Water Quality Criteria for Munitions-Unique Compounds, Part 3: White Phosphorus Final Report," USAMRDC Contract N01 DAMD 17-77-C-7027, Ft. Detrick, MD 21701 (1979).

Summerlin, W.T., A.I. Walder, J.A. Moncrief, "White Phosphorus Burns and Massive Hemolysis," J. Trauma, 7(3):476-484, (1967).

Sutton, O.G., "A Theory of Eddy Diffusion in the Atmosphere," Proc. Roy. Soc., A, 135:143-165 (1932).

Sutton, O.G. Micrometeorology; McGraw-Hill Book Company, New York (1953).

Talley, R.C., J.W. Linhart, A.J. Trevino, L. Moore, A.M. Beller, "Acute Elemental Phosphorus Poisoning in Man: Cardiovascular Toxicity," Amer. Heart J., 84:139-140 (1972).

Tarnove, T.L., "Studies of the Chemistry of the Formation of Phosphorus Derived Smokes and Their Implication for Phosphorus Smoke Munitions," Chemical Systems Lab, Munitions Division, ARCSL-TR-8004, 53pp. (1980).

Task Group on Lung Dynamics, "Deposition and Retention Models for Internal Dosimetry of the Human Respiratory Tract," Health Physics 12:173-207 (1966).

Theiss, J.C., G.D. Stoner, M.B. Shimkin and E.K. Weisburger, "Test for Carcinogenicity of Organic Contaminants of United States Drinking Waters by Pulmonary Tumor Response in Strain A Mice," Cancer Res. 37:2717-2720, (1977).

Truhaut, R., J.R. Claude, M. Thevenin, R. Podevin and J.M. Warnet. "Explanation of the Biochemical Mechanism of the Rat Hepatic Steatosis Induced by White Phosphorus. . ." Eur. J. Toxicol. Enviro. Hyg., 7(3):167-176 (1974).

Turner, D.B., Workbook of Atmospheric Dispersion Estimates, Air Resources Field Research Office, Environmental Science Services Administration, Public Health Service Publication No. 999-AP-26, (1970). NTIS, 5285 Port Royal Rd., Springfield, VA 22161 PB-191 482.

U.S. EPA, "Criterion Document - Halomethanes," Interim Draft No. 1, U.S. Environmental Protection Agency, Washington, DC (Nov., 1977).

Van Wazar, J.R., Phosphorus and Its Compounds, Volume I: Chemistry; Interscience Publishers, Inc., New York, 954 pg. 1958.

Voxovaya, M.A., L.K. Malyarova, and R.M. Enikeeva, "Methylene Chloride Content in Maternal and Fetal Tissue during Pregnancy and Nursing of Female Workers at a Rubberware Plant," Gig. Tr. Prof. Zabol., 4:42-43, 1974.

Walker, J., Jr., M. Galdston, J. Wexler, M.L. Hill, G. Midgely, "WP Casualties at Edgewood Arsenal. Medical Division Report No. 103," Edgewood Arsenal, Maryland (1947). DTIC No. AD 824420.

Walker, J., Jr., J. Wexler and M.L. Hill, "Quantitative Analysis of Phosphorus-Containing Compounds Formed in WP Burns," Edgewood Arsenal Special Publication, 1969, (original printing in 1945), DTIC No. AD 687270.

Wasti, K., K.J.R. Abaidoo, J.E. Villaume and P.N. Craig, "a Literature Review - Problem Definition Studies on Selected Toxic Chemicals, Vol. 2, Occupational Health and Safety Aspects of Phosphorus Smoke Compounds," Final Report to U.S. Army Medical Research and Development Command, Ft. Detrick, MD. 21701, Contract No. DAMD 17-77-C-7020, 93pp. (April, 1978), DTIC No. AD A056019.

Weimer, J.T., G. Affleck, J. Preston, J. Lucey, J. Manthei, and F. Lee, "The Acute Effects of Single Exposures to United Kingdom Red Phosphorus Screening Smoke in Rats, Guinea Pigs, Rabbits, and Dogs," Technical Report ARCSL-TR-77052. U.S. Army Armament Research and Development Command, Aberdeen Proving Ground, Maryland (August, 1977).

Weinstein, R.S., D.D. Boyd, and K.C. Back, "Effects of Continuous Inhalation of Dichloromethane in the Mouse--Morphologic and Functional Observations," Toxicol. Appl. Pharmacol., 23:660-79 (1972).

Welker, J.R. et al., "Fire Safety Aboard LNG Vessel," U.S. Dept. of Trans., U.S. Coast Guard Report No. CG-D-94-76 (Jan., 1976).

Whalen, J.P., N. O'Donohue, L. Crook, E.A. Nunez, "Pathogenesis of Abnormal Remodeling of Bones: Effects of Yellow Phosphorus in the Growing Rat," Anat. Rec., 177(1):15-22 (1973).

White, S.A., C.C. Armstrong, "White Phosphorus Smoke Bombs: Irritating Concentration for Man and its Toxicity for Small Animals After One-Hour Exposures," Project A5.2-1 War Department. Chemical Warfare Service, Edgewood Arsenal, Maryland (1935), as cited by Wasti, et al., 1978.

Winneke, G., "Behaviorial Effects of Methylene Chloride and Carbon Monoxide As Assessed by Sensory and Psychomotor Performance in Xintaras," C. Johnson, B.L. DeGroot, (eds.), Behavioral Toxicology--Early Detection of Occupational Hazards; Publication HEW No. (NIOSH) 74-126, U.S. H.E.W, Public Health Service, Center for Disease Control, Nat. Ins. for Occupational Safety and Health (1974), pp.130-144.

Wolff, R.K., D.G. Brownstein, R.L. Carpenter, J.L. Mauderly, "Toxicity of 0.4- and 0.8 μ m Sulfuric Acid Aerosols in the Guinea Pig," J. Toxicol. Environ. Health, 5:1037-1047 (1979).

Yant, W.P., H.W. Shoaf and J. Chronyak, "Observations on the Possibility of Methylchloride Poisoning by Ingestion with Food and Water," Public Health Reports, 45:19 (1930), as cited in MITRE, 1976.

Yesair, D.W., D. Jaques, P. Schepis and R.H. Liss, "Dose-related Pharmacokinetics of ¹⁴C- Methylene Chloride in Mice," Fed. Proc. 36:998 (1977).

7.0 ACKNOWLEDGMENT

The authors gratefully acknowledge the help and advice provided by the project officer, James C. Eaton, Jr., and other members of the USAMBRDL staff and by personnel in the Office of the Project Manager for Smoke and Obscurants and Chemical Systems Laboratory, both at Aberdeen Proving Ground, MD, and by Mr. Joseph Janski and others at Pine Bluff Arsenal, Pine Bluff, AK.

8.0 TASK ORDER #5 SUPPORT

1. Personnel

<u>Name</u>	<u>Degree</u>
Rosalind C. Anderson	Ph.D.
Joan B. Berkowitz	Ph.D.
Anthony J. Colella	B.S.
Warren J. Lyman	Ph.D.
Alan L. Preston	M.S.
William D. Steber	M.S.
Richard G. Thomas	M.S.
Robert G. Vranka	Ph.D.
G. Stewart Young	M.P.A.

2. Publications

No external publications were supported by this Task Order.

3. Degrees

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