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ASSESSMENT OF RED PHOSPHORUS IN THE ENVIRONMENT

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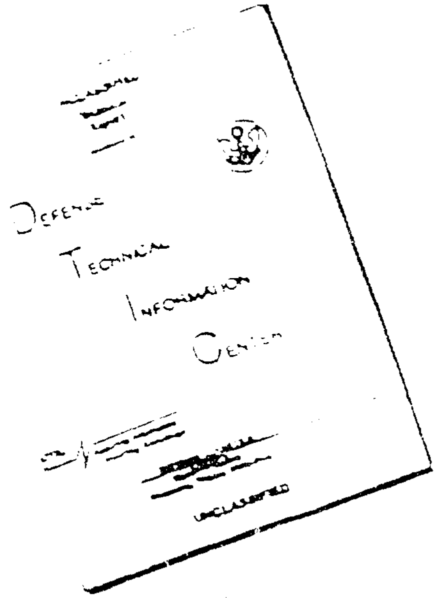
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This report is a brief critical review of the current literature relevant to the environmental and health effects of the use of red phosphorus in smoke and obscurant munitions by the Army. Properties of the element in its red allotropic form and its many combustion products, various oxyacids of phosphorus, are discussed within the context of their release to the environment in testing and military training operations. The possible consequences of increased environmental burdens of acid and phosphate deposition are considered, and toxicological effects are reviewed briefly.

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INTRODUCTION

The utilization of smokes and obscurants by the U.S. Army is essential for the achievement of tactical goals such as protection of potential targets and masking personnel and materiel movements. Toward that end and to ensure defense preparedness, large quantities of such munitions are used in military training areas throughout the United States and abroad. Environmental contamination associated with these munitions could occur as a result of their manufacture or their deployment. In view of present day concerns over risks associated with foreign substances in the environment, an understanding of the nature of such chemicals, their entry and fate in the environment, and their impact on living things is necessary to assess the degree of these risks realistically.

Elemental red phosphorus is a principal component in the formulation of several obscurant munitions produced and used by the U.S. Army. In grenades, mortar rounds, and a proposed howitzer shell, the element is deployed explosively over wide areas and burns rapidly to form oxides that can themselves react with water vapor to form aerosol particles of phosphoric acids. It is the purpose of this report to assess current literature regarding red phosphorus obscurant munitions as they relate to health and the environment.

PHYSICAL AND CHEMICAL PROPERTIES

Phosphorus is the 11th most common element in the earth's crust. It occurs commonly in the lithosphere in igneous, sedimentary, and metamorphic rock species and can be found as vast minable reserves in marine deposits [1]. In the biosphere [2] it is an essential nutrient in the formation of structural biomolecules such as membrane phospholipids, functional macromolecules like nucleic acids and adenosine triphosphate, and metabolic intermediates such as the sugar phosphates [3]. Human activities, such as the manufacture and use of detergents, fertilizers, and water softeners, contribute significant amounts of phosphorus to the environment [4]. However, in all of the above cases phosphorus exists in combination with other elements, whereas natural elemental phosphorus is not found free in the environment.

Depending upon the nature of interatomic bonds established during its formation, solid elemental phosphorus can occur in three major allotropic forms: black, white, or red. The black allotrope is the least reactive of the three due to its highly polymerized nature, and has no military application at this time. White phosphorus, the best known and commercially most important phosphorus allotrope, is considerably more reactive than the other solid forms, ignites spontaneously in air, and can be dissolved in various organic solvents. Its atoms exist as P_4 tetrahedra (figure 1a), accounting for its solubility and reactivity [5]. Because of its impact on health and the environment, white phosphorus has been reviewed recently in a context of its military applications [6].

The red allotropic form of elemental phosphorus is intermediate to the black and white varieties in reactivity, has military application as noted above, but has received considerably less attention in the literature than the white allotrope. Red phosphorus atoms are thought to form high polymers in which single bonds of phosphorus tetrahedra are broken and linked together forming chains and rings [7] (figure 1b). In this configuration, phosphorus is less reactive than in the white allotropic form and is insoluble in water as well as in organic solvents. Its greater stability (and insolubility) is explained by the necessity of breaking polymeric phosphorus bonds prior to the formation of new ones [8]. Nevertheless, red phosphorus can react slowly with oxygen and water vapor to evolve phosphine [9]. Moreover, since its oxidation is exothermic, spontaneous combustion has been noted in storage piles of this elemental form. Metallic impurities in the stored solid can catalyze the oxidation [5]. In addition to heating and exposure to oxidizing substances, ignition of red phosphorus can be accomplished by percussion, contact, and friction [5,10]. The chemical and physical properties of elemental red phosphorus are summarized in Table 1.

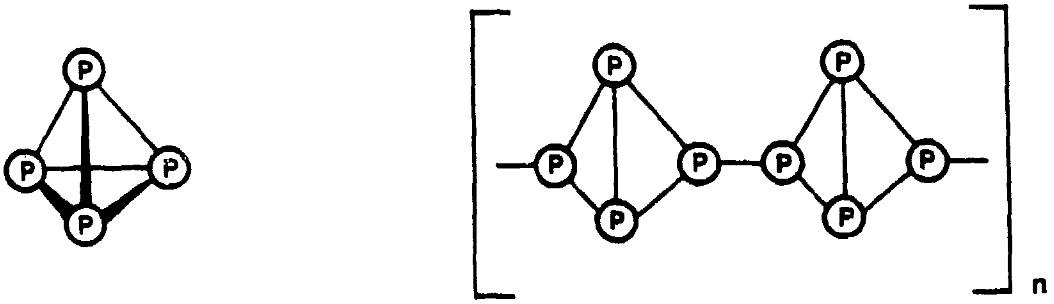

Figure 1. Three-dimensional structures of two of the allotropic forms of phosphorus: (a) white phosphorus tetrahedron; (b) red phosphorus chain

Table 1. Physical and Chemical Properties of Red Phosphorus

Property	Value	Reference
CAS NO.	7723-14-0	5
Formula	polymeric $(P4)_n$	7
Molecular Weight	$(123.9)_n$	11
Appearance	red-brown	11
Density	2.34 g/cm^3	11
Melting Point	sublimes at 416°C	11
Heat of Sublimation	19.7 kcal/mol	11
Ignition Temperature	280°C in air	11
Critical Temperature	589°C	11
Critical Pressure	43.1 atm	11
Heat Capacity	5.1 cal/deg/mol (P)	11
Solubility	insoluble in organic solvents, negligible in water	10
Uses	pyrotechnics, safety matches, fertilizers, pesticides, incendiaries, smoke bombs	10

As a Group VA element in the periodic table, with 5 electrons in its valence shell (3p), phosphorus commonly bonds three or four adjacent atoms forming molecules with three or five shared electrons. However, the element can also form stable compounds in which its oxidation number ranges from -3 to +5 owing to its capacity to fill s, p, and d orbitals [8,12]. Examples of elemental phosphorus and some of its more important compounds and their various oxidation states are given in Table 2.

Since the military application of red phosphorus as an obscurant involves combustion, its oxides (Table 2) are of practical importance in that they will be released directly to the environment. When combusted in a free supply of air, red phosphorus burns to form phosphorus pentoxide as a predominant combustion product. Alternatively, under conditions of oxygen deficiency, the formation of phosphorus trioxide is favored [8], and phosphorus tetroxide may also be present [13]. The phosphorus oxides themselves hydrolyze readily in water to form corresponding oxyacids, and in the case of phosphorus pentoxide, further condensation reactions result in the formation of polymeric phosphate products (Table 2). Thus, depending upon the availability of oxygen for combustion, water (or its vapor) for product dissolution, and heat to drive reactions, the burning of elemental phosphorus can result in complex mixtures of phosphorus compounds. Monomeric oxyacids such as phosphoric, phosphorous, and hypophosphorous acids and condensation products such as the linear pyro- and polyphosphates and cyclic metaphosphates can occur simultaneously in solution following combustion of the element [13-16].

Table 2. Phosphorus, Selected Phosphorus Compounds, and their Oxidation States

Substance				Oxidation State
Phosphines				
Phosphine	PH_3			-1
Diphosphine	P_2H_4			-2
Elemental Phosphorus				
White phosphorus	P_4			0
Red phosphorus	$(P_4)_n$			0
Oxides and their Oxyacids				
-		Hypophosphorous Acid	H_3PO_2	+1
Phosphorus trioxide	P_4O_6	Phosphorous Acid	H_3PO_3	+3
Phosphorus tetroxide	P_2O_4	Hypophosphoric Acid	$H_4P_2O_6$	+4
Phosphorus Pentoxide	P_4O_{10}	Orthophosphate (Phosphoric Acid)	H_3PO_4	+5
		Pyrophosphate (Diphosphoric Acid)	$H_4P_2O_7$	+5
		Polyphosphates (linear) (Triphosphoric Acid)	$H_5P_3O_{10}$	+5
		Tetraphosphoric Acid	$H_6P_4O_{13}$	
		Metaphosphates (cyclic) (Trimetaphosphoric Acid)	$H_3P_3O_9$	+5
		Tetrametaphophoric Acid	$H_4P_4O_{12}$	

Phosphine, a highly toxic gas, can be formed along with the above-described mixture of oxyacids from red phosphorus in oxidations taking place in the presence of water vapor and less than stoichiometric quantities of oxygen [13]. The reaction is extremely slow at normal temperatures and humidities [17] and it would not be a factor in the deployment of phosphorus munitions in military field exercises.

MANUFACTURE AND USE BY THE ARMY

The manufacture of white phosphorus from natural raw materials, its conversion to red phosphorus, and the many pollution problems associated with industrial phosphorus production and military white phosphorus processing have been described previously [5,6,18]. Since red phosphorus is not manufactured by the Army but is obtained commercially from sources abroad, production wastes are not a problem in this country [13]. However, blending and filling operations for red phosphorus munitions, as well as their testing, take place at Pine Bluff Arsenal (PBA), Arkansas. The principal munitions to be manufactured in the future will be smoke-forming grenades and mortar rounds.

There are currently 226,000 L8A1 grenades in the inventory [19]. This munition, which ignites while airborne, is designed to obscure vehicles from which grenade clusters are launched. The obscurant portion of the L8A1 grenade consists of 360 grams of a 95 to 5 mixture of red phosphorus and butyl rubber formulated in granules [11,20]. These grenades were originally obtained by the U.S. Army from Great Britain and were then produced at PBA until 1985, after which time their production was discontinued. In 1987, production began on the L8A3 grenade, a modification of the L8A1 that will eventually replace it [19]. The newer model is of similar design to the L8A1 but employs silica instead of talc as the granule coating material, to reduce phosphorus clumping and thereby improve its burning qualities [21]. During grenade production, red phosphorus is plasticized with butyl rubber in an organic solvent and extruded. The resulting granules are dried, pressed into pellets, and then inserted into the rubber sleeve of the grenade [11]. It has been estimated that at full production as many as 10,000 L8A3 grenades per month could be produced at PBA [22].

Red phosphorus is also the major smoke-generating ingredient in the XM819 mortar round. In this munition, it is compounded with sodium nitrate and an epoxy binder in an approximate ratio of 80:14:6 parts by weight, respectively [23]. Fill for the mortar rounds will be prepared by blending powdered red phosphorus, sodium nitrate, and epoxy binder with appropriate curing agents and solvents, granulating the resulting slurry, and pressing it into wedges for loading. During loading, mortar rounds will receive 28 wedges weighing approximately 43 grams each. The munition is designed so that following its detonation, ignited wedges will disperse both in the air and on the ground [23]. Consideration is also currently being given to the design and production of a third red phosphorus munition, the XM803 howitzer round, for even larger scale smoke generation [24].

ANALYTICAL METHODS

While direct chemical analysis of elemental red phosphorus is not feasible due to its polymeric nature and insolubility, it is readily oxidized to the +5 state and then analyzed by standard gravimetric and volumetric [25], potentiometric [26], or colorimetric [27] methods for orthophosphate. For example, red phosphorus was first solubilized with aqua regia, oxidized with ammonium persulfate and sulfuric acid to orthophosphate, and then analyzed spectrophotometrically as a phosphomolybdate complex [28]. Alternatively, Spanggord [26] recently assayed red phosphorus by combusting it to completion, boiling the collected products in water to ensure conversion to orthophosphate, and measuring total phosphorus by titrating the one strongly ionized hydrogen present per phosphorus atom. Application of such methods to environmental samples containing elemental phosphorus would encounter interferences from naturally occurring phosphates and would not differentiate between the red and white allotropes. Conceivably, interfering phosphates could be removed from such samples by aqueous extraction (converted to a water soluble form if necessary) and white phosphorus could similarly be removed by extraction with an organic solvent prior to oxidation or combustion as described above.

In addition, phosphates can be assayed more rigorously and specifically by a number of fluorometric, radiological, atomic adsorption, and nuclear magnetic resonance techniques [13]. However, since the burning of phosphorus and dissolution of its oxides in water results in the formation of a variety of compounds, more general methods appropriate to the assay of phosphate mixtures have been developed. Paper, thin layer, and open-column chromatographic systems have been applied to the mixtures with varying degrees of success. One thin layer system, in which elution was conducted with acidic and then basic solvents, separated several of the monomeric phosphorus oxyacids, pyrophosphate, and a few meta- and polyphosphates. Similarly, open column ion exchange and gel chromatographic systems have resulted in partial separations of monomeric and condensed phosphate species in the mixtures [13]. More recently, high performance liquid chromatographic (HPLC) procedures coupling ion exchange columns to potentiometric or spectrophotometric detection systems have expanded phosphate separations (26,29-31]. Typically, Spanggord et al. [26] resolved ortho-, pyro-, tri-, and tetraphosphoric acids, as well as homologous linear condensed polyphosphates (P_6 to P_{16}) and several cyclic metaphosphate species by means of such columns eluted with sodium chloride gradients and quantified them as colored molybdate complexes. Likewise, modification of ion chromatographic systems has facilitated the differential analysis of lower oxyacids of phosphorus including separations of orthophosphate, phosphinate and phosphonate species [31,32].

Both paper strip and silica gel collector systems have been used for the colorimetric detection of phosphine. In the former case, mercuric chloride in methyl yellow was used as an indicator for HCl produced during the formation of $P(HgCl)_3$, whereas in the latter, color changes resulted from reaction of phosphine with impregnating $AuCl_3$ [13]. Gas chromatography has provided more sophisticated quantitative analysis of phosphine in combustion product vapors. Levels of 0.04 ppm and perhaps less have been demonstrated by means of isothermal analysis (75°, 80/100 mesh Porapak P columns) and nitrogen-phosphorus detection [26].

ENVIRONMENTAL EFFECTS AND FATE

Because of its unreactive polymeric nature, low vapor pressure, and insolubility, undisturbed red phosphorus is relatively inert in the environment. Its presence unchanged in soils as a consequence of Army operations is innocuous, with one important exception to be described shortly. Indeed, red phosphorus has been intentionally applied to soils experimentally as a possible fertilizer [33,34]. Surface films of oxides formed slowly (these have also been observed in the laboratory), but no further reaction or dissolution was found. However, as a consequence of both testing of munitions at PBA and deployment of grenades in military training exercises elsewhere, incompletely combusted clumps of oxide-coated red phosphorus have been observed and are believed to account for fires occurring at the training sites [19]. Thus the possible ignition of these residual clumps either spontaneously or by friction or other disturbance presents a potential threat for environmental damage from forest and grass fires.

The environmental impact of the combustion products of red phosphorus was an important consideration. Laboratory analyses have shown that essentially the same products result from burning of either the red or white allotrope: oxides of phosphorus which in the presence of atmospheric moisture form complex mixtures of polymeric phosphoric acids and other oxyacids of phosphorus. In the environment the polymeric oxyacids are known to break down both chemically and microbiologically with increasing time to the ultimate product, orthophosphoric acid [16,26,30,31]. Two possible adverse effects then needed to be evaluated: an increase in acid deposition and an increase in phosphate levels in the local waters. It can be generally concluded that pH effects in water will be of little consequence unless the buffering capacity of the system is exceeded. For experimental aquatic systems, a relationship between buffering capacity, pH, and total phosphorus has been developed which indicates that excessive smoke deposition is necessary to bring about pH changes [31]. Specifically, a pond (3000 m^2 x 1.5 m) containing 4.5 x 10^6 L of water at an alkalinity of 100 mg/L $CaCO_3$ would require the deposition of approximately 230 kg of total combusted phosphorus to lower the pH to 6. As a matter of perspective, such a change would require the complete combustion and total obscurant deposition in the system of somewhat more than 700 L8-series grenades.

On the other hand, it has been shown that combustion products of phosphorus can stimulate algal growth in experimental systems at levels which do not significantly acidify poorly buffered growth media. Optimal phosphorus-phosphate for growth of green algae occurs in the range of 0.02 to 0.5 mg/L whereas that for blue-green species occurs at higher levels of up to 3.0 mg/L [31]. Because of these growth responses at low phosphate levels, relatively small amounts of red phosphorus combustion products could affect algal levels without producing detectable pH changes. As part of the lake eutrophication process, the excessive input of phosphorus to water systems leading to nuisance algal blooms is well known [35]. Thus the repeated high level deposition of red phosphorus obscurant combustion products to aqueous systems, either directly or as a result of runoff, has the potential to decrement surface water quality. Even then, however, the degree to which such an effect would be manifested would be a function of the nature of the receiving body, its trophic state, and the time of the year. For example, an algal bloom would more likely be encountered in a small lake with a low flushing rate during spring when phosphorus is limiting than in a rapidly moving stream in summer and fall when nitrogen may be deficient [36].

Analysis of soils following the experimental burning of red (and white) phosphorus in two different microcosm systems has defined no more than minor ecological effects [24,37]. In neither study were significant pH effects noted even at high aerosol concentrations. However, in the first study, nutrient losses (particularly calcium) in leachates were detected after the application of phosphorus smokes at concentrations far exceeding those anticipated during field use (1500 mg/m^3), but were attributed to biological and not physicochemical processes. Similarly, in the second study, transient mobility of trace elements was noted following repeated applications of phosphorus smokes and was attributed to their interactions with various phosphates formed after deposition. Such mobility was shown to decrease with the soil volume in the microcosm studies, and for that reason has been suggested to be minimal on a field scale.

In terrestrial microcosm studies little effect has been noted on total respiration of environmental microorganisms in soil even after exposure to extremely high concentrations of smokes [37]. On the other hand, exposure of some soils to elevated smoke concentrations can reduce nitrification and microbial dehydrogenase activity, ostensibly due to acidification, and depress levels of microbial phosphatase activity, possibly as a result of orthophosphate end product inhibition [39]. Even then, however, it has been concluded that the effects occur predominantly at soil surfaces, and in the case of nitrification are transient [24]. For plant species including sweet clover, rye-grass, and wheat exposed to concentrations several times higher than typical field levels (50-400 mg/m^3), no more than minor adverse effects were detected; and it has been concluded based on these and similar results that repeated deployment of the smokes at or below 600 mg/m^3 for a period of eight weeks should be possible without adverse ecological effects [37]. Moreover, toxic effects noted at high mass loadings on other plant species including pine seedlings, bushbeans, blando bromegrass, and sagebrush were, with the exception of the bromegrass, reported to be transient and could be ameliorated by rainfall [24]. For aquatic organisms including several fish, invertebrates, and an algal species, combustion products of phosphorus were not toxic except at high concentrations, in which case the effects were related to acidification of water after its buffering capacity was exhausted rather than to the phosphates themselves [31].

TOXICITY

Little if any significant toxicity appears to be associated with elemental red phosphorus unless it is contaminated with the white allotropic form [38]. When applied under patches to the intact or abraded skin of rabbits at doses of 0.5 g per site, no dermal irritation was noted following 24 hours of exposure to red phosphorus. Similarly, dermal application of the element to guinea pigs resulted in no skin irritation or sensitization responses, and interdermal injection resulted in only slight irritation with no skin sensitization. Doses of 100 mg did not result in rabbit eye irritation. Even at oral doses of 10,000 mg/Kg, lethality in Fischer 344 male and female rats was less than 20% of the experimental subjects after 14 days, and the oral LD50 was reported as being greater than 10g/kg [28].

For phosphorus combustion products, studies have been conducted both to establish toxicity levels for laboratory animals and humans and to estimate toxic effects on environmental fauna. Phosphorus smoke toxicity levels for mammalian species have been listed recently [38] and extensively discussed in a context of the manufacture and military use of red and white phosphorus obscurant munitions [11]. Recent results of rat aerosol exposure studies indicate that the concentration of phosphorus smokes is a much more important factor in determining mortality than is the duration of exposure [40]. With the exception of guinea pigs, which are highly susceptible to the smokes, data for laboratory animals (mice, rats, dogs, and goats) for one hour exposures indicate that the critical concentration for LC_{50} for most species is in the vicinity of 2000 mg/m^3 [11]. Lethal effects were both acute and chronic in nature and were accompanied by symptoms of respiratory distress, most commonly including pulmonary congestion, edema, and atelectasis [16,41]. In contrast, repeated short term exposures (8 minutes per day during 5 day periods for 12 weeks) of mice, rats, and rabbits to phosphorus smokes at anticipated field concentrations resulted in no irreversible toxic effects and no latent toxicity, tumor formation or reproductive defects [20]. Toxicity levels for man are unavailable; however, exposure of volunteers to concentrations of between 100 and 700 mg/m^3 for between 2 and 15 minutes resulted in significant but reversible respiratory distress symptoms, as well as mucus membrane and eye irritation [38,41]. It is estimated that human exposure to concentrations in the neighborhood of 2000 mg/m^3 for longer than 15 minutes would result in increasing deaths; concentrations of 1000 mg/m^3 are considered intolerable and 700 mg/m^3 is the minimum harassing concentration, or that concentration at which masking is mandatory [11,41].

An apparent exception to the mammalian scenario summarized above has just been published [42]. A laboratory study on two species of wildlife, rock doves and black-tailed prairie dogs, reported that these remarkable creatures survived several multiple 80 minute exposures to extremely high concentrations of up to 4000 mg/m^3 phosphorus smoke. Transient adverse behavioral and physiological responses were noted, and the birds were the more vulnerable of the two species.

CONCLUSIONS AND RECOMMENDATIONS

Except for its possible association with grass and forest fires and its potential to produce phosphine in confined spaces, elemental red phosphorus has not been demonstrated to pose a threat to the environment or health. In the former case, new red phosphorus munitions, particularly mortar rounds and howitzer shells designed to ignite close to the ground, should be thoroughly evaluated in the light of their fire hazard potential. In the latter case, the U.S. Army should determine if phosphine production and worker exposure exist at red phosphorus munitions facilities and, if so, define the steps necessary to obviate the problem. For the military burning of phosphorus during obscurant generation, it should be emphasized that levels of phosphate entering the environment are minute in comparison to those from other sources such as agricultural runoffs and natural leaching. However, the potential exists at local levels for problems resulting from the heavy and repeated use of phosphorus munitions. In that context and in the light of the extensive environmental effects data for phosphates and phosphorus smokes cited in this report, a future U.S. Army effort could be the establishment of practical site-specific guidelines for phosphorus munitions usage to preclude local environmental damage.

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