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Military Smokes And Obscurants Fate And Effects

A Literature Review Relative to Threatened and Endangered Species

Katherine von Stackleberg, Craig Amos,
Thomas Smith, Don Cropek, and Bruce
MacAllister

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Katherine von Stackleberg, Craig Amos, Thomas Smith, Don Cropek,
and Bruce MacAllister

*Engineer Research and Development Center
Construction Engineering Research Laboratory
PO Box 9005
Champaign, IL 61826-9005*

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ABSTRACT: As with many anthropogenic substances, there is concern about the potential impacts on ecosystems and their component species resulting from military training and testing exercises using chemical agents, obscurants, and other smokes. The purpose of this report is to provide a review and summary of literature and other reports on the fate and environmental effects of military smokes, obscurants, and other comparably used compounds.

Specifically, the focus is on species of high interest. Species of high interest include those species considered to be threatened and endangered as defined in the Endangered Species Act, and species found on United States Army and other military installations where smokes, obscurants, and riot control agents are used for military training and testing purposes.

This report provides a literature review of topics where literature is sufficient and an annotated bibliography for instances where the literature search revealed either a paucity of citations or largely inaccessible primary literature.

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Conversion Factors

U.S. standard units of measure can be converted to SI* units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
cubic inches	0.00001638706	cubic meters
degrees (angle)	0.01745329	radians
degrees Fahrenheit	$(5/9) \times (^\circ\text{F} - 32)$	degrees Celsius
degrees Fahrenheit	$(5/9) \times (^\circ\text{F} - 32) + 273.15$	kelvins
feet	0.3048	meters
gallons (U.S. liquid)	0.003785412	cubic meters
horsepower (550 ft-lb force per second)	745.6999	watts
inches	0.0254	meters
kips per square foot	47.88026	kilopascals
kips per square inch	6.894757	megapascals
miles (U.S. statute)	1.609347	kilometers
pounds (force)	4.448222	newtons
pounds (force) per square inch	0.006894757	megapascals
pounds (mass)	0.4535924	kilograms
square feet	0.09290304	square meters
square miles	2,589,998	square meters
tons (force)	8,896.443	newtons
tons (2,000 pounds, mass)	907.1847	kilograms
yards	0.9144	meters

* SI: *Système International d'Unités* (International System of Measurement).

Preface

This study was conducted for U.S. Army Corps of Engineers Research and Development Center/Construction Engineering Research Laboratory under A896, “Smokes and Obscurants”; Work Unit CNN-TO23, “Threatened and Endangered Species.” The Technical Monitor for this report was Mr. William E. Woodson, ACSIM.

The work was completed through the Ecological Processes Branch (CN-N) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Mr. Thomas Smith. Part of this work was done by the University of Illinois, Champaign, IL, under contract DACA 88-99-D-0002. The technical editor was Vicki A. Reinhart, Information Technology Laboratory. Mr. Stephen E. Hodapp is Chief, CEERD-CN-N, and Dr. John T. Bandy is Chief, CEERD-CN. The associated Technical Director was Dr. William D. Severinghaus, CEERD-CV-T. The Director of CERL is Dr. Alan W. Moore.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL James R. Rowan and the Director of ERDC is Dr. James R. Houston.

1 Introduction

Background

As with many anthropogenic substances, there is concern about the potential impacts on ecosystems and their component species resulting from military training and testing exercises using chemical agents, obscurants, and other smokes (referred to as S&Os in this report). The species present on military training and testing lands may be exposed to these smokes, obscurants, and other compounds during soldier training and testing exercises. A variety of smoke and obscurant materials have been used including fog oil, dyed smokes, hexachloroethane, titanium dioxide, and white phosphorus. Other materials such as brass and graphite are sometimes added for infrared and other wavelength blocking purposes. Additionally, compounds such as CS (tear gas) are used by the military as part of enemy personnel control training and could also result in exposure. The potential effects of any military S&O compounds released would depend on the inherent toxicity of the material and the overlap of the materials in the environment with the species of concern.

Objective

The purpose of this report is to provide a review and summary of literature and other reports on the fate and environmental effects of military smokes, obscurants, and other comparably used compounds. Specifically, the intention is to focus on species of high interest. Species of high interest include those species considered to be threatened and endangered as defined in the Endangered Species Act, and species found on United States Army and other military installations where smokes, obscurants, and riot control agents are used for military training and testing purposes. This review is intended to focus on ecological receptors. Therefore, information relating to laboratory animals or human health effects are not specifically addressed.

Approach

This report provides a literature review for topics where the literature is sufficient and an annotated bibliography for instances where the literature search revealed either a paucity of citations or largely inaccessible primary literature. In some cases, if neither an abstract nor a full citation was available, no summary of the citation is provided. The review and bibliography help to identify potential effects of smokes, obscurants, and other similar chemical agents on threatened and endangered species on or near military training areas, in accordance with the Endangered Species Act and implementing regulations (50 CFR).

Over 200 reports and other scientific papers were identified in this review. Every effort was made to identify the relevant literature through 2002. More recent information is included as it is known and appropriate. This review attempts to focus directly on primary military smoke and obscurant constituents. In general, information and literature on related chemical compounds has not been included. For example, there is a body of information on the fate, effects and other characteristics of petroleum products in natural and laboratory environments. This report does not address those types of broad-based topics but attempts to look at only the petroleum product fate and effects resulting from fog oil smoke generation.

This review attempts to provide a uniform level of review and discussion of each item of concern. However, due in part to varying amounts of information available for the constituents, this has not always been possible. In some instances the level of treatment differs because of subjective judgements made by the authors in determining what information to present, as well as judgements as to the current relative importance of the constituents to military training and other uses. A consideration in the level of discussion or detail presented has been not only the amount of data and information available, but also the relative or comparative apparent toxicity of the constituents addressed. In all instances we have attempted to address all relative and salient information. Relevant literature and reports are identified and summarized in this review. However, to ensure all relevant information in the reports is understood, the reader should consult the report and not rely solely on the review presented here.

The review focuses on potential toxicity to ecological receptors. The goal was to identify studies useful for assessing potential risks to threatened and endangered species. The typical primary route of chemical or environmental exposure is ingestion, and emphasis is given to those studies. However, because of the aerosol and/or gaseous characteristics, many of the studies on S&Os focused on the inhalation

pathway. Therefore, these studies are also included in the database (Table 1). All tables appear at the end of Chapter 4.

The review has five sections: Chapter 1 is this introductory section, Chapter 2 provides a summary discussion of the constituents of concern as well as the information sources consulted in developing the literature search, Chapter 3 provides details of the literature search for each of the categories and constituents, and Chapter 4 presents a discussion of the adequacy of the database with a focus on ecological risk assessment purposes, and the fifth section provides a listing of additional references.

Mode of Technology Transfer

This report will be made accessible through the World Wide Web (WWW) at URL: www.cecer.army.mil/tips.

2 Constituents of Concern

Constituents of Concern

This review focuses on the following eleven military smoke and obscurant categories and/or constituents of concern. These constituents of concern are the main topic headings and form the primary organizational basis of the review.

The list of constituents of concern includes:

- fog oil smoke
- hexachloroethane (HC) smoke
- white phosphorus (WP) smoke
- brass flakes/powder
- (2-chlorobenzal) malononitrile (CS)
- dibenz (b,f)-1,4-oxazepine (CR)
- titanium dioxide
- polyethylene glycol (PEG)
- graphite flakes/powder
- colored smokes
- terephthalic acid.

Data and Information Sources

The literature summary and review was compiled by searching available databases for:

- toxicity/toxic properties/characteristics, including any threshold levels
- environmental fate and transport
- degradation/breakdown and processes
- bioaccumulation in terrestrial and aquatic environments
- trophic transfer in terrestrial and aquatic environments
- pathways for biological exposure.

The literature search used three search engines: PUBMED, TOXLINE, and Cambridge Scientific Abstracts, as well as resources available from Oak Ridge National Laboratory.

This review organizes the information into the following categories:

- physical-chemical properties
- environmental fate and transport
- bioaccumulation and trophic transfer
- toxicity.

Table 1 provides a database summary of relevant articles. This database contains codes for each contaminant of concern addressed, the broad category that the citation applies to (e.g., physical and chemical properties, environmental fate and transformation, bioaccumulation and food chain transfer, or toxicity); whether or not an abstract (A), a complete primary reference (C), or neither (N) were obtained; a brief summary; and the full citation. Appendix A provides Material Safety Data Sheets (MSDS).

Smoke and Obscurant Overview

Historically, many types and combinations of obscurant smokes have been used by the military. In its early basic military applications, screening or obscuring smokes were generated by burning common combustible materials such as wood. In recent years three basic types of screening or obscurant smokes have received the most attention: fog oil, hexachloroethane (HC), and white phosphorus (WP) (Kroschwitz and Howe-Grant 1993, Shinn et al. 1987). Recent military usage of obscurant smoke is almost exclusively fog oil smoke. However, other types and formulations of smoke-producing compounds are available and have been deployed. For example, colored smokes are commonly used in military combat training and battlefield situations for signaling purposes. Also, additives such as brass or graphite are sometimes included during the smoke-generating process to facilitate visual and non-visual wavelength obscurance (Briere et al. 1992).

The known results and ecological impacts and effects of military S&O usage are comparatively limited. Ecological understanding of the effects of some formulations used by the military is better for some (fog oil smoke), than for others (CS). Even the human health effects of all of the S&O are not completely understood and toxicological profiles or summaries of many compounds are not available (for example ASTDR 2002).

Fog Oil Smoke

Fog oil smoke is a term used to describe an obscurant smoke generated by injecting mineral oil into a heated manifold. The oil vapor produced condenses when exposed to the atmosphere, producing small (1 μm to 7 μm) aerosolized droplets which interact with ecological elements through respiration, ingestion, deposition, or other processes (e.g. adsorption through aquatic media). The previous and current military specification (MILSPEC 1998) for fog oil specifies that the oil shall not demonstrate any toxic or potentially carcinogenic effect. As such, the currently used formulations are presumably less toxic and ecologically problematic than those produced prior to 1986.

While data information on ecological interactions of fog oil smoke are limited, this category of S&O has the best and most relevant data available. The studies and work supported by the U.S. Army and conducted by Driver et al. (2002a, 2002b, 2004) and Smith et al. (2004), support with a reasonable degree of certainty management's assumption of minimal or no individual, community, or population effects on three altricial avian species of small or medium size.

Hexachloroethane Smoke

Hexachloroethane smoke (HC), commonly referred to as HC smoke, is generated by burning a mixture of approximately equal amounts of HC and zinc oxide (ZnO) with some aluminum added. Any HC smoke toxicity is generally attributed to the resultant production of zinc chloride (ZnCl₂). As a military munition, HC has been used in field smoking devices, grenades, and projectiles (U.S. Army 1974).

Although the literature on hexachloroethane is more readily available than for many other S&O (ASTDR 1997a), there is a lack of information on the ecological fate and effects. Of those studies that have been reported, those of Cataldo et al. (1990), Schaeffer et al. (1988), Sadusky et al. (1993), and Fisher et al. (1993) are potentially the most relevant in that they address multiple ecological media exposure including soils, plants, and aquatic vertebrates and invertebrates.

White Phosphorus (WP) Smoke

White phosphorus (P₄) has been used as an obscurant smoke since the early 20th century. In military applications, it is typically used in mortar and artillery rounds for

down range soldier screening effects. In addition to its use in blocking visible light, it is also used to block infrared wavelengths or microwaves. White phosphorus is highly reactive at typical ambient air conditions. Therefore, it is the most effective S&O for defeating enemy thermal imagery systems. In addition to these screening effects, white phosphorus also can have certain anti-personnel effects because of its high reactivity.

Potential ecological fate and effects of white phosphorus smoke are not well documented. Elemental phosphorous has been known to cause mortality in fish (Jangaard 1972) and waterfowl (Racine et al. 1992).

Brass Flakes/Powder

Brass in flake or powdered form is used in smoke grenades as an infrared and other wavelength screening agent. Brass flakes are irregularly shaped particles approximately 2.1 to 2.3 μm in size and are commonly referred to as dust or powder. In military applications, it is used as a protection system against enemy range finders, thermal surveillance systems, and laser target identifiers. It is also used as obscurance and screening for armored vehicles (Briere et al. 1992). Brass performs poorly as a visual light band obscurant (Palmer 1992).

Brass is a compound of copper (Cu) and zinc (Zn) and its environmental effects are related to those two elements (see ASTDR 2002, 2003). Brass flakes are comparatively used very little in military training and testing applications. Among the most relevant research on brass particles done to date is that of Haley et al. (1988) and Guelta and Checkai (1998) who reported generally low aquatic toxicity and ecological risk for conventional military applications of flaked brass.

(2-Chlorbenzal) malononitrile

(2-Chlorbenzal)malononitrile (CS), also noted as o-Chlorbenzal malononitrile, is widely used as a riot control agent (Keller et al. 1986). In military applications, it is used to deny enemy personnel access to geographic features or to assist in the removal of enemy personnel from confined areas. More commonly, CS is used to train military personnel in the proper use of chemical, nuclear, biological (CNB) protective equipment.

In a strict sense CS is not a military S&O. However, through its use on military training installations, its known eye, nose, mouth, and respiratory irritation indicates potential negative effects on vertebrate and other ecological receptors. Information and data on ecological fate and effects of CS is sparse, although some indication of soil persistence has been noted (Keller et al. 1986).

Dibenz(b,f)-1,4-oxazepine

Like CS, dibenz(b,f)-1,4-oxazepine, commonly referred to as CR, is a riot control agent with peripheral sensory tract (i.e., eye, nose, mouth, skin, respiratory tract) irritation characteristics. Also like CS, CR is not strictly an S&O, and its military uses and application are in enemy personnel control and terrain denial. Also as with CS, CR can be used to train military personnel in the proper use of CNB protective equipment.

Ecological information on CR is also sparse. A certain degree of environmental stability has been noted (Keller et al. 1986). In military use, small quantities (i.e. < 1%) of CR are mixed with propylene glycol (PEG) and water (Biskup et al. 1975).

Titanium Dioxide

Titanium dioxide (TiO₂) is the major component of the proposed XM82 training smoke grenade. Military applications of titanium dioxide are those related to soldier screening and obscuring training. It has also been used as an obscurant, sometimes in conjunction with HC (Karlsson et al. 1986).

Potential ecological effects of the release of titanium dioxide as a part of U.S. Army and other military training actions are largely unknown. However, the apparent low level of use would seem to indicate little ecological concern.

Polyethylene Glycol

Polyethylene glycol (PEG) is a derivative of a paraffin (i.e. a waxy solid hydrocarbon). PEG has been investigated as a possible less-toxic replacement for fog oil since the smoke generated by PEG has similar obscurant qualities (Muhly 1983). However, with recent alterations in the formulation of fog oil (MILSPEC 1998), interest in PEG as a S&O has declined. Consequently, although ecological impacts and ef-

fects of PEG are largely unknown, little or no military-related exposure is taking place.

Graphite Flakes

The military application of graphite flakes or powder is as an S&O for enemy electromagnetic tracking and targeting systems. Graphite is a form of carbon (C) that is chemical inert and exists naturally.

Graphite used in military applications has a mass median diameter of 3 μm to 106 μm (Guelta et al. 1993). Because of this small aerodynamic size, flakes disperse and settle dependent on local meteorological conditions. The ecological effects of graphite exposure would be most related to inhalation because of its chemical inactivity.

Colored Smokes

Colored smokes are used primarily for local signaling purposes by the U.S. Army and other military services. A colored smoke munition/grenade is composed of a pyrotechnic mixture of fuel and dye. Typical training and other use consists of small hand held "grenades" which are released to mark specific sites. The release of colored S&O compounds is relatively limited in extent and amount. Also, colored S&O dissipates rapidly.

There are numerous colored S&O formulations, both in terms of color and/or chemical content. Red, yellow, and green are perhaps the most common, but other colors (e.g. purple) are used also. Recently, the formulas of colored smoke have been changed. For example, in new M18 grenades (the standard U.S. Army smoke grenade) sugar is used as a fuel instead of sulfur (Lundy and Eaton 1994). Table 5 lists the major combustion products of the new colored-smoke M18 grenades.

In part because of their limited spatial use, little investigation of ecological fate and effects has been done. The available information indicates very low practical ecological toxicity. Currently, the U.S. Army is supporting in-depth investigation of potential toxic effects of colored S&O on aquatic threatened and endangered species. To date, few reportable effects have been noted.

Terephthalic Acid

Terephthalic acid (TA) has been investigated and used by the U.S. Army as a munition (e.g. for use in M-83 smoke grenade and M-8 smoke pot) and as a soldier training replacement for the more toxic hexachloroethane smoke (Muse et al. 1997). TA is the main raw product used in the production of polyester packaging materials for a variety of common household products, such as those using linear crystalline polyester resins, fibers, and films (Sax and Lewis 1988). TA as used in those products, as well as in its typical physical form (i.e. crystalline powder) is not considered flammable but when burned, it produces dense white smoke with good obscuration qualities.

3 Results

Fog Oil Smoke

Fog oil smoke is produced by injecting middle distillate petroleum into a heated manifold of a smoke-generation machine mounted on military vehicles. The vaporized oil condenses upon contact with air forming a dense, white cloud composed of oil droplets of an approximate mass and median aerodynamic diameter of 1.3 μm (Driver et al. 2002b). The reviewed literature sometimes distinguished between *old* fog oil and *new* fog oil based on the chemical composition of the oils used. Old fog oils, referred to as SGF-1 (Standard Grade Fuel 1) were naphthentic oils and contained carcinogenic substances. These fog oil formulations were produced prior to formulation and specification changes in 1986 (see MILSPEC 1998). Those specification changes were designed to exclude any carcinogenic substances and are given the designation SGF-2. It is the primary oil currently used to produce fog oil smoke in military applications.

Physical/Chemical Properties

Table 2 provides the physical/chemical properties for fog oil smoke. Chemical and physical properties of fog oils are very similar to those of lubricating and petroleum-based cutting oils (NRC 1999). Other constituents are added in trace amounts to these oils to maintain desirable physical properties under extreme pressure and heat. The trace amount constituents are not expected to adversely impact potential toxicity (NRC 1997).

Katz, S., A. Snelson, R. Butler, R. Farlow, R. Welker and S. Mainer. 1980. Physical and chemical characterization of military smokes. Part 2: Fog Oils and Oil Fogs. DAMD17-78C-8085. ADA093205. IIT Research Institute, Chicago, IL.

This report provides a physical and chemical characterization of oil fogs and their precursor oils. Oils from three different sources were analyzed and three different fog generators were used in tests. All nine oil-generator combinations were sampled

and analyzed for particle size determination, aerosol aging, and chemical composition.

Average initial mass diameter for all oil fogs was 1.16 μm with a standard deviation of 0.14 μm . Aerosol aging involved droplet growth caused by collision, accompanied by a decrease in droplet concentration. Median droplet growth rarely exceeded 10% over a one-hour interval. Chemical analysis of oil fogs was based on liquid and gas chromatography fractionation, gas chromatography, and mass spectrometry identification. Oils and oil fogs were separated into class fractions of aliphatics, aromatics, alcohols, acids, and esters. Aliphatic and aromatic fractions predominated in both the oils and the oil fogs in near equal amounts and at 90% to 95% of the total. In general, aliphatic, aromatic, and ester fractions of the oil fogs appear to parallel the parent oil composition, suggesting only moderate alteration in the fog forming process. Several hundred chemical species identified with reasonable assurance are only a small fraction of the total number which were resolved but not identified. The high aromatic contents of both oils and oil fogs, at approximately 50% of the total, may represent a potential hazard.

Environmental Fate and Transport

Cataldo, D.A., P. Van Voris, M.W. Ligotke, R.J. Fellows and B.D. McVeety. 1989. Evaluate and Characterize Mechanisms Controlling Transport, Fate, and Effects of Army Smokes in and Aerosol Wind Tunnel: Transport, Formations, Fate and Terrestrial Ecological Effects of Fog Oil Obscurant Smokes: Final Report. 0AD-A20414. Pacific Northwest Laboratory, Richland, WA.

The terrestrial transport, chemical fate, and ecological effects of fog oil smoke obscurants were evaluated under controlled wind tunnel conditions. The primary objectives of this research program were to characterize and assess the impacts of smoke and obscurants on: (1) natural vegetation characteristic of U.S. Army training sites in the United States; (2) physical and chemical properties of soils representative of these training sites; and (3) soil microbiological and invertebrate communities. Impacts and dose/responses were evaluated based on an exposure scenario including exposure duration, exposure rate, and sequential cumulative dosing. Key to understanding the environmental impacts of fog oil smoke/obscurants is establishing the importance of environmental parameters, such as relative humidity and wind speed on airborne aerosol characteristics and deposition to receptor surfaces. Direct and indirect biotic effects were evaluated using five plant species and three soil types.

Cataldo D.A., M.W. Ligojke, H. Bolton, R.J. Fellows and P. Van Voris. 1990. Evaluate and Characterize Mechanisms Controlling transport, Fate, and Effects of Army Smokes in the Aerosol Wind Tunnel: Transport, Transformations, Fate and Terrestrial Ecological Effects of Hexachloroethane Obscurant Smokes. Final Report. Pacific Northwest Laboratory, Richland, WA.

The primary objective of this study was to characterize the fate and response of soil and biotic components of the terrestrial environment to aerosols, deposited brass, and brass in combination with fog oil. Important physical, chemical, and biotic aspects were investigated using an environmental wind tunnel. Air/surface deposition rates were determined for foliar and soil surfaces, both in the absence and presence of fog oil. Foliar contact toxicity was assessed using five different types of terrestrial vegetation representative of Army training sites and surrounding environments. The weathering and chemistry of brass aerosols deposited and amended to soils was assessed, along with the impacts of acid precipitation and moisture regimes on weathering rates. This citation is also included under *Brass Flakes*.

Chester, N.A. 1998. Review of Selected Army-Funded Research on Fog Oil Smoke Characteristics as Related to Clean Air Act Issues. - Final Report Oct 95-Oct 96. AD-A344 419/7. ERDEC-TR-475. Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

Potential violation of the Clean Air Act by use of fog oil has lead to a request for further understanding of technical data describing the characteristics and behavior of fog oil droplets, particles, and plumes. Selected sources of U.S. Army funded research have been reviewed and summarized in this report.

DeVaull G., W.E. Dunn, J.C. Liljegren, A.J. Policastro. 1990. Atmospheric Dispersion of Military Fog Oil Smoke. Argonne National Laboratory, Argonne, IL.

The authors describe an improved method for analysis of fog oil samples of both aerosol and vapor from field dispersion experiments. Using this method, fog oil is vaporized from a sample using heat, then the hot vapor is analyzed by gas chromatography.

DeVaull, G.E., D.F. Brown, W.E. Dunn and A.J. Policastro. 1990. Assessment and Computerized Modeling of the Environmental Deposition of Military

Smokes. - Final Report 1 Jul-30 Sep 90. AD-A246 942/7. Argonne National Laboratory, Argonne, IL.

This report presents the average and instantaneous concentration measurements from a series of atmospheric dispersion experiments conducted under both stable and unstable atmospheric conditions. The experiments were done at two different sites over both flat and complex terrain. Fog oil and hexachloroethane (HC) chemical smoke were the surface-level point aerosols used in these experiments. Depending on the site and atmospheric conditions, measurements of concentration at points along crosswind transects were taken over time periods of one hour at distances from 25 m to 3000 m from the source. These measurements included both aerosol photometer records for instantaneous concentration data and aspirated filter cassettes for average concentration data. This citation will also be included under *Fog Oil Smoke*.

Driver, C.J., M.W. Ligothke, E.B. Moore and J.F. Bowers. 1991. Generator, mechanical, smoke: For dual purpose unit, XM56, Yuma Proving Ground, Yuma, Arizona. Environmental Assessment. PNL-7781. Battelle Pacific Northwest Laboratories.

This environmental assessment evaluated the consequences of performing a field test of the XM56 smoke generator at the U.S. Army Yuma Proving Ground, AZ. The XM56 enables the use of fog oil in combination with other materials such as graphite flakes and is part of an effort to improve the efficiency of smoke generation and to extend the effectiveness of the resulting obscurant cloud to include the infrared spectrum. The planned field operation includes a road test and concurrent smoke-generation trials. Three M1037 vehicles with operation XM56 generators were road-tested for 100 h. Smoke was generated for 30 minutes from a single stationary XM56 four times during the road test, resulting in a total of 120 minutes of smoke generation. The total aerial release of obscurant materials during this test was expected to be 556 kg (1,220 lb) of fog oil and 547 kg (1,200 lb) of graphite flakes. This citation is also included under *Graphite Flakes*.

Getz, L.L., K.A. Reinbold, D.J. Tazik, T.J. Hayden and D.M. Cassels. 1996. Preliminary Assessment of the Potential Impact of Fog Oil Smoke on Selected Threatened and Endangered Species. Final Report. CERL-TR-96/38. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

This research provides a preliminary assessment of the environmental impacts of fog oil smoke used in training exercises based on available data and information (and assumptions stated in the report), especially as they might affect threatened and endangered species. This research also identifies specific data and information gaps that should be the focus of future research efforts.

Liljegren J.C., W.E. Dunn, G.E. DeVaul and A.J. Policastro. 1989. Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes: Field Study of Fog-Oil Smoke. AD-A205 344. Argonne National Laboratory, Argonne, IL.

The atmospheric dispersion of the military obscurant smoke produced from SGF-2 fog oil with the M3A3E3 prototype fog oil smoke generator was studied in a program of field trials carried out at Dugway Proving Ground, UT. Measurements of the mass rate of release, exit velocity and exit temperature were performed to define the smoke source. The smoke aerosol was physically characterized in terms of the particle size distribution. A description of the prevailing meteorology was obtained from measurements of the wind speed, wind direction, temperature, and dew point at five levels on each of two 32 m instrument towers located on the test site. Measurements of the average smoke concentration over the period of release were carried out at distances of 25 m to 800 m from the release point.

Maloney, D.M., A.J. Policastro, W.E. Dunn and D.F. Brown. 1993. Evaluation of Atmospheric Wind Field and Dispersion Models for Fog-Oil Smoke Dispersion in Complex Terrain: Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes. Argonne National Laboratory, Argonne, IL.

Three models used to predict the wind field and pollutant dispersion in complex terrain are compared with smoke dispersion data acquired as part of the AMADEUS field experiments in 1987 near Red Bluff, CA. The models evaluated were WADOCT, HOTMAC, and RAMS. The database for model testing included seven fog oil smoke releases from ground level under stable meteorological conditions.

Muhly, R.L. 1983. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 1. Fog Oil, Diesel Fuels, and Polyethylene Glycol (PEG 200). Department of Defense [DODXA], July 1983, 139p. ARCSL-EA-83001-VOL-1. AD-A134 846/5/INW. Prepared by Chemical Research and Development Center, Aberdeen Proving Ground, MD.

The environmental impacts associated with the use of petroleum distillate smokes for testing and training purposes were reviewed and compiled in this report. Based on the toxicological data gathered and the regulatory aspects associated with the use of these smoke/obscurants, it was concluded that this portion of the smoke program will not significantly affect the quality of the human environment. This citation is also included under *Polyethylene Glycol*.

Policastro, A.J. and W.E. Dunn. 1986. Survey and Evaluation of Field Data Suitable for Smoke Hazard Model Evaluation. ANL/ER-85-3. AD-A161 880. Argonne National Laboratory, Argonne, IL.

This report presents a summary and critical evaluation of the existing data on the dispersion of military smokes. Emphasis is on fog oil smokes in terms of the measurement of concentration, dosage, particle size distribution, and mass deposition rate.

Policastro A.J., D.M. Maloney, W.E. Dunn, J.C. Liljegren and G.E. Devaull. 1990. Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes: Evaluation of Atmospheric Dispersion Model for Fog-Oil Dispersion. Argonne National Laboratory, Argonne, IL.

This report provided an evaluation of four of the most promising mathematical models for the prediction of the dispersion of fog-oil smoke discharged from M3A3E3 or M3A4 smoke generators. The database used for model testing consists of seven data sets: three field trials conducted at Dugway Proving Ground, UT, during March/April 1985 and four field trials conducted at Camp Atterbury, IN, in November 1987. The results show that the four Gaussian puff models can predict within a factor of 2 to 3 under the convective and neutral conditions tested to distances of about 250 m.

Three D International, Inc. 1996. Environmental Fate of Fog Oil at Fort McClellan, Alabama. C7322.19. AD-A326 404/1. Prepared by Three D International, Inc., Cincinnati, OH, in cooperation with Harland Bartholomew and Associates, Inc., Chesterfield, MO for U.S. Army Corps of Engineers, Kansas City District.

A study of the environmental fate of fog oil was initiated at Fort McClellan, AL, to identify the environmental impacts of relocating the U.S. Army Chemical School and U.S. Army Military Police School to Fort Leonard Wood, MO. Fog oil smoke was

used at Fort McClellan for over 10 yrs. Researchers analyzed plant, bat, and fish tissue, soil, sediment, and surface water for a number of fog oil constituents. Selection of constituents, including PAH analytes was based on the known combustion products of both old and new fog oil formulations and their known environmental longevity.

One portion of the study involved collecting samples of fog oil smoke from M56 and M157 generators to determine the chemical composition. The study evaluated samples for volatiles, semi-volatiles, and thermal decomposition products. The authors identified the following chemicals: hexadecane, 1-methylfluorene, 2-ethylanthracene, and 9,10-dimethylanthracene in soil and water; hexadecane, phenanthrene, 2-ethylanthracene, and 3,6-dimethylphenanthrene in sediment; trace amounts of 1,3-dimethylnaphthalene, 2,3,5-trimethylnaphthalene and 9,10-dimethylanthracene in vegetation; and biphenyl, 2,6-dimethylnaphthalene, 1,3-dimethylnaphthalene, 1,2-dimethylnaphthalene, 2,3,4-trimethylnaphthalene, hexadecane, 4,4'-dimethylbiphenyl in bat tissue. There were no statistically significant differences between the site and reference areas for any constituents in insects, fish, and bat guano.

Fog oil smoke samples showed little change in chemical composition compared to parent fog oil. The authors were unable to detect any volatile or semi-volatile organics in the smoke samples. If volatilization of thermal decomposition occurs, they only form atmospheric gases or result in low concentrations of decomposition or volatilization products.

Bioaccumulation and Trophic Transfer

Driver C.J., M.W. Ligothke, J.L. Downs, B.L. Tiller and T.M. Poston. 1993. Environmental and Health Effects Review for Obscurant Fog Oil. AD-A271 244. Prepared for U.S. Army Chemical and Biological Defense Agency, Aberdeen Proving Ground, MD.

The health and environmental effects of fog oil smoke were reviewed and compared to predicted levels of fog oil materiel in the field during typical testing and training scenarios. The review found that fog oil is moderately harmful, chemically and physically, to plants and animals and can accumulate in food chains. Waterfowl are particularly vulnerable to adverse physical and chemical effects of lubricating oils and experience reproductive dysfunction at relatively low levels of exposure. However, specific information of SGF-2 impacts on avian or mammalian wildlife is lacking. Aquatic systems appear to be most vulnerable to fog oil toxicity and SFG-2 deposition in aquatic systems should be avoided.

Three D International, Inc. 1996. Environmental Fate of Fog Oil at Fort McClellan, Alabama. C7322.19. AD-A326 404/1. Prepared by Three D International, Inc., Cincinnati, OH, in cooperation with Harland Bartholomew and Associates, Inc., Chesterfield, MO, for U.S. Army Corps of Engineers, Kansas City District.

A study of the environmental fate of fog oil was initiated at Fort McClellan, AL, to identify the environmental impacts of relocating the U.S. Army Chemical School and U.S. Army Military Police School to Fort Leonard Wood, MO. Fog oil smoke was used at Fort McClellan for over 10 years. Researchers analyzed plant, bat, and fish tissue, soil, sediment, and surface water for a number of fog oil constituents. Selection of constituents, including PAH analytes was based on the known combustion products of both old and new fog oil formulations and their known environmental longevity.

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Toxicity

Aranyi, C., N. Rajendran, J. Bradof, J. Drummond and B. Levine. 1991. Inhalation Toxicity of Single Materials and Mixtures. Phase 3. Final Report. AD-A242 179/0/GAR. IIT Research Institute. August 28, 1991.

To investigate the potential inhalation hazard of obscurant materials to which military personnel may be exposed during field operations, a four-week whole-body inhalation toxicity study of aerosols of a petroleum-based liquid (PBL) fog oil, a solid particulate (graphite), or PBL/graphite aerosol mixtures was conducted in male F344

rats. Exposures were 4 hr/day, 4 days/week to aerosols of PBL alone (500 mg/m³ or 100 mg/m³), graphite alone (200 mg/m³) or PBL/graphite aerosol mixtures (500 mg/m³ or 1000 mg/m³ PBL, with 200 mg/m³ graphite). A sixth group was a filtered air control. Animals were monitored throughout the study for clinical signs, body weight gain, and food consumption. Selected biologic end points including histopathology, clinical pathology, pulmonary lavage, pulmonary function, pulmonary bactericidal activity, lung/body weight ratio and hepatic aryl hydrocarbon hydroxylase (AHH) activity were evaluated after the last exposure and again after a 3 week recovery period. This report is also included under *Graphite Flakes*.

DeJonge H., J.I. Freijer, J.M. Verstraten, J. Westerveld and F.W.M. Van der Wielen. 1997. Relation between bioavailability and fuel oil hydrocarbon composition in contaminated soils. *Environ Sci Technol.* 31(3):771-775.

Bioavailability of oil components in contaminated soils is an important regulating factor for biodegradation rates. Changes in the composition of mineral oil can provide information regarding the bioavailability restrictions in contaminated soils. The fate of oil components was studied in a lysimeter experiment and laboratory incubations. A shift in the n-alkane ratios in the range n-C16:n-C20 was observed around 4.0 g/kg, indicating that two different mechanisms control the bioavailability of the oil. At higher concentrations, the bioavailability was controlled by solubilization from a non-aqueous-phase liquid into the aqueous soil water phase. The ratios remained constant with decreasing oil concentration in this stage. Below 4.0 g/kg, desorption and diffusion became rate-limiting factors: a shift was observed in the n-alkane ratios, showing that biodegradation rates of n-alkanes increased with decreasing carbon number. The monitoring of n-alkane ratios can be used to improve the efficiency of bioremediation treatments.

Driver C., M. Ligothke, H. Galloway-Gorby, G. Dennis and K. Reinbold. 2002. Acute Inhalation Toxicity of Fog Oil Smoke in the Red-winged Blackbird, a Size-Specific Inhalation Surrogate for the Red-cockaded Woodpecker. ADA399210. ERDC/CERL-TR-02-6. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

The authors evaluated the acute toxicity and health risk of environmental releases of fog oil to avian wildlife. The Red-winged Blackbird (*Agelaius phoeniceus*) was used as a surrogate species for the Red-cockaded Woodpecker. Wild Red-winged Blackbirds were exposed to varying airborne concentrations of fog oil. The post-exposure response of the blackbirds was monitored for 28 days.

Compared to control birds, no mortality, body weight loss, clinical signs of toxicity, or behavioral abnormalities were observed in any of the fog oil-treated birds. The distribution and severity of gross and histopathological lesions were independent of the fog oil exposures and were typical of those found in wild bird populations. Although respiratory function data were limited, no major respiratory impairment or abnormalities were observed during the exposure or the post-exposure period.

Driver C., J. Ollero, Y.F. Su, R. Fulton, G. Dennis, B. Tiller, H. Balback and K. Beinbold. 2002. Effects of Fog Oil Smoke on the Hatchability and Fledgling Survival of the House Sparrow (*Passer domesticus*), a Nestling Surrogate for the Red-cockaded Woodpecker. ERDC/CERL TR-02-34. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

House Sparrows were used as a surrogate for fledgling Red-cockaded Woodpeckers. Sparrow eggs were exposed to several concentrations of fog oil smoke including that up to 450 mg/m³. Concentrations of fog oil inside the nests cavities were approximately 73% to 75% that of the outside air. Hatching success, fledgling success, and survivability of young was not significantly different between exposed and control groups.

Gardner, D.E., J.A. Harris, M.E. Hiteshow, D.W. Davies and E.C. Grose. 1984. Toxicological Studies of Smoke Obscurants. EPA-600/D-84-127. PB84-195288. U.S. Environmental Protection Agency - Health Effects Research Laboratory, in cooperation with Northrop Services, Inc.

An exposure facility was designed and constructed to support health effect studies of inhaled smoke obscurants generated from light lubricating oils. Concentrations were monitored using gravimetric filter sample analysis and continuous RAM-1 aerosol monitors. Chemical consistency of the test atmospheres was monitored by observing the relative stability of fractions of the oil as measured by high performance liquid chromatographic analysis of collected aerosol samples. Toxicological parameters investigated include: clinical chemistry, hematology immunology, pathology, and pulmonary physiology.

Li S.W., H. Bolton Jr., J.K. Fredrickson, P. Van Voris, D.A. Cataldo, R.J. Fellows, B.D. McVeety, M.W. Ligothke and K.W. McFadden. 1989. Influence of Fog Oil Obscurant Smoke on Microbial Activity. 89th Annual Meeting of the American Society for Microbiology, New Orleans, Louisiana. May 14-18, 1989.

Unable to obtain abstract or article.

Poston, T.M., K.M. McFadden, R.M. Bean, M.L. Clark and B.L. Thomas. 1986. Acute Toxicity of Smoke Screen Materials to Aquatic Organisms, White Phosphorous-Felt, Red Phosphorous-Butyl Rubber and SGF (Smoke Generator Fuel) No. 2 Fog Oil. Final Report 1983-1985. PNL-5584. AD-A167 900/0/GAR. Battelle Pacific Northwest Laboratories.

The acute toxicity of three obscurants was determined for nine fresh-water organisms. The materials tested were white -felt (WP-F) smoke, red -butyl rubber (RP-BR) smoke, and smoke generator fuel (SGF-2) fog oil (bulk and vaporized). The chemistry of WP-F and RP-BR smoke in water and the resulting effects on aquatic organisms were similar. Combustion of these two obscurants and their deposition in water leads to the formation of many complex oxy-phosphoric acids. Rates of hydrolysis of these complex products to ortho-phosphate were inconsistent and unpredictable over time.

These products acidify water and produce toxic effects after exhausting the buffering capacity of the water. The 96 hr median lethal concentration (LC₅₀) values for fish ranged from 3.9 to 5.1 pH units. The values for invertebrates ranged from 3.4 to 5.5. Algal growth was inhibited at pH levels less than 6.0. This citation is also included under *White Phosphorus Smoke*.

Poston T.M., R.M. Bean, D.R. Kalkwarf, B.L. Thomas and M.L. Clark. 1988. Photooxidation Products of Smoke Generator Fuel (SGF) No. 2 Fog Oil and Toxicity to *Hyallolella azteca*. *Env Toxicol Chem.* 7(9):753-762.

The authors investigated photooxidation of smoke generator fuel (SGF-2) fog oil to determine qualitative changes in the chemistry of the oil and the resulting acute toxicity to the freshwater amphipod *Hyallolella azteca*.

The 48-hour LC₅₀ was about 11.5 mg total oil/L for photooxidized fog oil. Toxicity was related to the greater solubility of photooxidized fog oil in that higher concentrations of total dissolved oil in oil/water mixtures were obtained after equivalent additions of photooxidized oil and nonphotooxidized oil. Photooxidation caused increases in carbonyl oxygen and the presence of alpha- and beta-unsaturated ketones and acetophenones in aqueous extracts. There was no evidence for the formation of phenolic compounds in the photooxidized fog oil or in oil/water mixtures.

Riis V., M. Stimming, D. Miethe and W. Babel. 1996. Investigations into the toxicity of persistent fractions of mineral oils. *Chemosphere*. 32(7):1435-1443.

This paper discusses whether toxicity could be a reason for the incomplete microbial degradation of mineral oils in the laboratory and the environment, especially in soils contaminated over a long period. The luminescence test showed inhibition by the nondegradable residues as well as by the water phase from degradation experiments. This most frequently applied test reaches its limits in the case of substances with very low solubility in water. Conclusions relating to the impact on the microbial community of a contaminated ecosystem are not admissible. Neither nondegradable residues from raffinates nor extracts from long-term contaminated soils showed inhibiting effects on the dehydrogenase activity of *Acetobacter methanolicus* and a mineral oil-adapted consortium. Inhibition of the respiration of the pure strain *A. methanolicus* and of the consortium growing on glucose and spindle oil respectively was not observed either. The residues evidently contain mainly highly stable compounds that withstand microbial attack. The toxicity of such compounds per se is unlikely. Moreover, toxicity investigations with aqueous phases from degradation experiments gave no indication of the formation of metabolites, which could be responsible for the stagnation of the process.

Schaeffer, D.J., W.R. Lower, S. Kapila, A.F. Yanders and R. Wang. 1986. Preliminary Study of Effects of Military Obscurant Smokes on Flora and Fauna During Field and Laboratory Exposures. Final Technical Report. December 1986. CERL-TR-86/22. AD-A176 328/3/GAR. U.S. Army Corps of Engineers - Construction Engineering Research Laboratory.

A preliminary biological and chemical study of smokes was conducted to determine whether tests could be developed to demonstrate measurable changes in organisms exposed to smokes and to evaluate whether short exposures to smokes produced measurable changes in the organisms tested. Fog oil, hexachloroethane, and tank diesel smokes were tested. This citation is also included under *Hexachloroethane Smoke*.

Selgrade M.K., G.E. Hatch, E.C. Grose, J.W. Illing, A.G. Stead, F.J. Miller, J.A. Graham, M.A. Stevens and J.F. Hardisty. 1987. Pulmonary Effects Due to Short-Term Exposure to Oil Fog. *J Tox Env Health*. 21(1-2):173-185.

The pulmonary effects of inhaled chemical smoke obscurants in male and female Crl:CD(SD)BR-rats were examined. Ten male and 10 female animals were exposed

to petroleum smoke concentrations ranging from 0.33 to 8.88 mg/L for 3.5 hr/day, 5 days/wk for 4 weeks in Hinners type chambers.

The LC₅₀ was 5.19 mg/L. Less than 15 % mortality occurred at 4 mg/L, while over 80% mortality occurred at 6 mg/l. No sex differences in sensitivity were noted. Histopathological analysis revealed a dose-dependent accumulation of macrophages within the alveolar lumen. Significant increases in cell number and pulmonary lavage fluid protein levels were observed in lung lavage fluids from animals exposed to 1.5 mg/L petroleum smoke. No changes in static lung volumes, ventilation distribution, or lung compliance were observed in any group. However, the amount of air left in the lungs after a normal breath was elevated in animals exposed to 1.5 mg/L petroleum smoke. Likewise, wet and dry lung weights were also elevated in these animals, although there were no differences in percent lung water.

Skyberg K., V. Skaug, B. Gylseth, J.R. Pedersen and O.H. Iversen. 1990. Subacute inhalation toxicity of mineral oils, C15-C20 alkylbenzenes, and polybutene in male rats. *Environ Res.* 53(1):48-61.

Male Wistar rats were exposed to mist and vapor of two mineral oils, two C15-C20 alkylbenzenes, and one polybutene at aerosol concentrations of 70 mg multiplied by m super(-3) and 700 mg multiplied by m super(-3) for 2 weeks. Of oil mist particles, 82 to 97% were respirable (< 4.7 µm). High-level exposure to polybutene was lethal to three of four animals, due to pulmonary edema. Elevated numbers of pulmonary macrophages and increased macrophage vacuolization were observed after exposure to the polybutene, both mineral oils, and one alkylbenzene. The same alkylbenzene produced body weight loss. Deposition analysis was performed for one mineral oil. No oil was detected in brain tissue, while retroperitoneal fat tissue contained 541 (401-702) µg oil/g tissue, half of this still present after an exposure free period of 2 weeks.

It was concluded that inhalation of the polybutene and one of the mineral cable oils tested here produces toxic effects in the lungs.

Smith J.H., M.G. Bird, S.C. Lewis, J.J. Freeman, G.K. Hogan and R.A. Scala. 1995. Subchronic feeding study of four white mineral oils in dogs and rats. *Drug Chem Toxicol.* 18(1):83-103.

Subchronic 90-day feeding studies were conducted on four highly refined white mineral oils to determine any potential for toxicity in Long-Evans rats (20 per sex per dose level) and beagle dogs (4 per sex per dose level). Each oil was fed at dietary

dose levels of 300 ppm and 1500 ppm (w/w). No treatment-related effects of toxicological importance were detected in daily observations of general health or in periodic assessments of food consumption and body weight, hematology, serum clinical chemistry, and urinalysis. Observations in dogs suggested that the white oils produced mild laxative effects. Gross and histopathologic examinations, as well as measurements of organ weights, did not reveal any macroscopic or microscopic changes which could be due to treatment. In addition, special staining by Oil Red O of liver, mesenteric lymph nodes, spleen, gastrointestinal tract, stomach, and kidneys indicated no evidence of oil or lipid deposition. A special re-examination of tissues from female and male rats, in response to more recent conflicting data from the Fischer 344 strain, found no histopathologic signs of macrophage accumulation and/or microgranuloma formation in liver, spleen, or mesenteric lymph nodes.

These data indicate that repeated exposure to relatively high levels of white mineral oils in the diets does not produce significant subchronic toxicity in Long-Evans rats or beagle dogs.

Yanders A.F., E.W. Novak, W.R. Lower, A.G. Underbrink and R. Wang. 1985. Mutagenic Testing of Obscurant Smokes. *Environ Mutagen.* 7(3):60.

Mutagenic tests of fog oil and hexachloroethane smokes were performed on plant and animal cells. Somatic cells and germ cells were the target analytes. Results were not available. This citation will also be included under *Hexachloroethane Smoke*.

Hexachloroethane (HC) Smoke

Hexachloroethane (C_2Cl_6) is a colorless solid sold under the trade names Avlothane, Distokal, Distopan, and Distopin that gradually evaporates when exposed to air. Hexachloroethane, the result of adding chlorine to tetrachloroethylene, is no longer made in the United States. Hexachloroethane is released to the air during military operations and training exercises using smoke-producing devices. Only small amounts (5% or less) remain after smoke has formed under typical applications. Hexachloroethane in air does not break down to other compounds but gradually escapes into the upper atmosphere. Small amounts of hexachloroethane found in surface water and soils will evaporate into the air while some will undergo anaerobic biodegradation by microscopic organisms. It takes approximately 4 days for 99% of the hexachloroethane in the soil to break down anaerobically while it can take 4 weeks or more aerobically. Hexachloroethane does not appear to significantly bioac-

cumulate in terrestrial food webs, but demonstrates a moderate bioaccumulation potential in aquatic food webs.

The Agency for Toxic Substances and Disease Registry (ATSDR) has published a toxicological profile for hexachloroethane (ATSDR 1997a). This profile summarizes all of the available information as of that date related to physical/chemical properties, environmental fate, bioaccumulation potential, toxicity, use and disposal of hexachloroethane.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for hexachloroethane smoke.

Environmental Fate and Transport

Summary

Hexachloroethane is quite stable in air. It is not expected to react with hydroxyl radicals or ozone in the atmosphere or to photodegrade in the troposphere (Callahan et al. 1979, Howard 1989). Hexachloroethane is expected to diffuse slowly into the stratosphere with a 30-year half-life. However, degradation by photolysis may occur in the stratosphere (ATSDR 1997a). The stability of hexachloroethane in air suggests that atmospheric transport is likely to occur (Class and Ballschmitter 1986; Singh et al. 1979).

Hexachloroethane is also relatively resistant to degradation in the aquatic environment. No hydrolysis of hexachloroethane in water was observed after 11 days at 85 °C at 3 pH levels (i.e. pH 3, 7, and 11) (Ellington et al. 1987, ATSDR, 1997). However, hexachloroethane may be reduced in aquatic systems in the presence of sulfide and ferrous ions (Kriegman-King and Reinhard 1991). The transformation rate of hexachloroethane to tetrachloroethylene under simulated groundwater conditions at 50 °C was evaluated without ferrous or sulfide ions, with minerals (biotite and vermiculite) providing ferrous ions, and with minerals and sulfide ions. Reported half-lives for hexachloroethane were 365 days for hexachloroethane alone, 57 days to 190 days with minerals present, and 0.45 day to 0.65 days in the presence of both minerals and sulfide. Photolysis of hexachloroethane in water has been reported, but degradation to carbon dioxide occurred at a temperature of 90 °C to 95 °C (Knoevenagel and Himmelreich 1976).

Biodegradation may represent an important removal process in ambient waters, but there is conflicting evidence regarding the significance of this fate process. Howard (1989) reports that less than 30% degradation of hexachloroethane occurred after a two week incubation period in activated sludge under aerobic conditions. Another study (Mrsny et al., 1978) reports that hexachloroethane had no effect on the growth rate of a mixed bacterial culture and was quantitatively recovered after incubation with the culture for 8 days. Hexachloroethane was only viable as a sole source of carbon after incubation for approximately six weeks. The authors concluded that hexachloroethane was nontoxic to and unmetabolizable by bacteria. However, there are other studies suggesting that biodegradation of hexachloroethane may occur. Tabak et al (1981) report 100% loss rate for hexachloroethane in a 7 day static-screening-flask test at 25 °C under aerobic conditions. Spanggord et al. (1985a) report significant volatilization losses under aerobic conditions. Under anaerobic conditions, 90% of hexachloroethane was removed from pond water in 18 days, while the authors observed no losses from sterile pond water (Spanggord et al. 1985a). Criddle et al. (1986) estimate a 40 day half-life for hexachloroethane in an unconfined sand aquifer. The authors also conducted laboratory studies with wastewater microflora cultures and aquifer material which provided evidence of microbial reduction of hexachloroethane to tetrachloroethylene under aerobic conditions.

Hexachloroethane released to water or soil may volatilize into air or adsorb onto soil and sediments. Volatilization appears to be the major removal mechanism for hexachloroethane in surface waters (Howard 1989). The volatilization rate from aquatic systems depends on specific conditions, including adsorption to sediments, temperature, agitation, and air flow rate. Volatilization is expected to be rapid from turbulent shallow water, with a half-life of about 70 hrs in a 2 m deep water body (Spanggord et al. 1985a). A volatilization half-life of 15 hrs for hexachloroethane in a model river 1 m deep, flowing 1 m/sec with a wind speed of 3 m/sec was calculated (Howard 1989). Measured half-lives of 40.7 min. and 45 min. for hexachloroethane volatilization from dilute solutions at 25 °C in a beaker 6.5 cm deep, stirred at 200 rpm, were reported (Dilling 1977, Dilling et al. 1975). Removal of 90% of the hexachloroethane required more than 120 min (Dilling et al. 1975). The relationship of these laboratory data to volatilization rates from natural waters is not clear (Callahan et al. 1979). Deposition of hexachloroethane from air to water, plants, and soil has been reported (Cataldo et al. 1989). Calculated soil adsorption factors ($\log K_{oc}$ of 2.24, 2.98, and 4.3) suggest that hexachloroethane has medium to low mobility in soil (Howard 1989) and moderate to slight adsorption to suspended solids and partitioning to sediments. There is moderate potential for leaching to groundwater. Results of studies with low organic carbon (0.02%) soil material indicate that sorption to aq-

uifer materials retards hexachloroethane migration in groundwater (Curtis et al. 1986).

Hexachloroethane may biodegrade in soil, but abiotic degradation processes are not expected to be significant. Hexachloroethane is biotransformed in soil under both aerobic and anaerobic conditions, but proceeds more rapidly in anaerobic soils (Spangford et al. 1985a). Loss of 99% of hexachloroethane was reported after 4 days of incubation anaerobically and after 4 weeks under aerobic conditions. Volatilization contributed to aerobic losses.

Cassel, G., S. Fredriksson and I. Faengmark. 1992. Zink-och Titanroek: Kemisk Sammansattning och Fysikaliska Egenskaper (Zinc and Titanium Smoke: Chemical Composition and Physical Characteristics). Technical Report. October 1992. FOA-C-40277-4.9, ETN-93-93759. National Defence Research Establishment, Umea (Sweden). NBC-Defence Dept.

Smoke generated from zinc/hexachloroethane and titanium dioxide/hexachloroethane pyrotechnical pictures in a closed space were investigated for the following parameters: smoke concentration, particle size distribution and chemical composition of the smoke. Zinc hydroxy acids, which are strong acids, are formed during combustion of the zinc munitions. The titanium tetrachloride formed in smoke from the titanium dioxide munitions will rapidly hydrolyze to hydrogen chloride and titanium dioxide. Several chlorinated organic substances are formed from both types of smoke munitions during combustion. Some of these substances have well-documented toxic and mutagenic effects including hexachlorobenzene, hexachlorobutadiene and chlorinated dibenzofurans and dibenzodioxins. The amount of byproducts formed is higher from the titanium dioxide/hexachloroethane munitions than from the zinc munitions. This citation will also be included under titanium dioxide.

Cataldo D.A., M.W. Ligothke, H. Bolton, R.J. Fellows and P. Van Voris. 1990. Evaluate and Characterize Mechanisms Controlling transport, Fate, and Effects of Army Smokes in the Aerosol Wind Tunnel: Transport, Transformations, Fate and Terrestrial Ecological Effects of Hexachloroethane Obscurant Smokes. Final Report. Pacific Northwest Laboratory, Richland, WA.

The terrestrial transport, chemical fate, and ecological effects of hexachloroethane (HC) smoke were evaluated under controlled wind tunnel conditions. Primary objectives of this research are to characterize and assess the impacts of smoke and ob-

scourants on: 1) natural vegetation characteristic of U.S. Army training sites in the U.S., 2) physical and chemical properties of soils representative of these training sites, and 3) soil microbiological and invertebrate communities. Impacts and dose/responses were evaluated based on exposure scenarios, including exposure duration, exposure rate, and sequential cumulative dosing. Key to understanding the environmental impacts of HC smoke/obscourants is establishing the importance of environmental parameters such as relative humidity and wind speed on airborne aerosol characteristics and deposition to receptor surfaces. Direct and indirect biotic effects were evaluated using 5 plant species and 2 soil types.

Cichowicz, J.J., 1984. Programmatic Life Cycle Environmental Assessment for Smoke/Obscourants. Volume 4. HC Smoke. ARCSL-EA-83007. Chemical Research and Development Center, US Army Armament, Munitions and Chemical Command, US Army Aberdeen Proving Ground, Edgewood, MD.

The objective of this report was to compile and review environmental assessment data including environmental impact data on HC smoke along its life cycle usage path from manufacturing to disposal so that mitigating controls may be instituted for the distribution and use of HC smoke until a suitable replacement is implemented into inventory supplies.

Davidson K.A., P.S. Hovatter and R.H. Ross. 1988. Water quality for hexachloroethane. ORNL-6469. Oak Ridge National Laboratory, Oak Ridge, TN.

A review of the available data regarding the environmental fate, aquatic toxicity, and mammalian toxicity of hexachloroethane (used in military screening smokes). U.S. EPA guidelines were used to generate water quality criteria for the protection of aquatic life, its uses, and human health.

DeVaul G.E., W.E. Dunn, J.C. Liljegren and A.J. Poliocastro. 1990. Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes: Analysis Methods and Results of Hexachloroethane Smoke Dispersion Experiments Conducted as Part of Atterbury-87 Field Studies. AD-A216048. Prepared by Argonne National Laboratory, Argonne, IL, for the U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Provides a description of the results of five dispersion experiments conducted using hexachloroethane (HC) smoke pots. The experiments included: (a) measurement of time-dependent release rate (four trials) and exit temperature (one trial), (b) meas-

urement of meteorological variables using a 10 m instrument tower and a 2 m mast upwind of the smoke source, (c) sampling of the particulate phase at four heights on 46 sampling masts organized into four transects located between 60 m and 500 m from the source, (d) twelve samples of the vapor phase which were chemically analyzed for four specific organic compounds and (e) determination of the particle size distribution at a single location using a quartz-crystal-microbalance cascade impactor. Chemical analysis methods for the particulate and vapor phases are described.

DeVaull, G.E., D.F. Brown, W.E. Dunn and A.J. Policastro. 1990. Assessment and Computerized Modeling of the Environmental Deposition of Military Smokes. - Final Rept. 1 Jul-30 Sep 90. AD-A246 942/7. Argonne National Laboratory, Argonne, IL.

This report presents the average and instantaneous concentration measurements from a series of atmospheric dispersion experiments conducted under both stable and unstable atmospheric conditions. The experiments were done at two different sites over both flat and complex terrain. Fog oil and hexachloroethane (HC) chemical smoke were the surface-level point aerosols used in these experiments. Depending on the site and atmospheric conditions, measurements of concentration at points along crosswind transects were taken over time periods of an hour at distances from 25 m to 3000 m from the source. These measurements included both aerosol photometer records for instantaneous concentration data and aspirated filter cassettes for average concentration data. This citation is also included under *Fog Oil Smoke*.

Gordon L., W.R. Hartley and W.C. Roberts. 1992. Hexachloroethane (HC). In: Drinking Water Advisory: Munitions. Lewis Publishers, Boca Raton, FL. Pp. 87-131.

This review of hexachloroethane focuses on the chemistry, use history, and degradation of hexachloroethane in the environment.

Nzengung V.A., L.N. Wolfe, D.E. Rennels, S.C. McCutcheon and C. Wang. 1999. Use of Aquatic Plants and Algae for Decontamination of Waters Polluted with Chlorinated Alkanes. *Int J Phytoremediation*. 1(3):203-226.

An investigation of the transformation of carbon tetrachloride (CT) and hexachloroethane (HC) by aquatic plants and freshwater algae was documented. Stressed, axenic, and physiologically healthy freshwater plants all transformed the two chlorinated alkanes, yielding similar breakdown products. Experiments conducted with dead plants were used to indirectly test the hypothesis that dead aquatic plants

maintain and possibly contribute to the dehalogenase activity observed in organic-rich sediments. After exposure of the aquatic plants and algae to HC and CT dosed solutions, a rapid sorption (or sequestration) step followed by a slow transformation lasting several hours was observed. The kinetics data were adequately described by two first-order rate equations; pseudo-first-order sorption rate coefficients were calculated for the initial rapid adsorption and transformation steps. The identified metabolites extracted from plants indicated that more than one pathway, possibly requiring different reactants, mediated the phytotransformation reactions. Mass balance estimations confirmed that >80% of the parent chemical was sequestered, transformed, and/or assimilated by the biomass. The metabolic activity observed with dead plants and algae suggests that photoautotrophs maintain this activity at death, and the active agents could become bound to the sediment-organic matrix as plants die, decay, and are buried in sediment.

The results of this study suggest the potential usefulness of aquatic plants and freshwater algae in the removal of chlorinated alkanes from water and remediation of aquatic environments.

Nzengung V.A. and P. Jeffers. 2001. Sequestration, Phytoreduction, and Phytooxidation of Halogenated Organic Chemicals by Aquatic and Terrestrial Plants. *Int J Phytoremediation*. 3(1):13-40.

Laboratory data from plant-mediated transformation of chlorinated and brominated alkanes, alkenes, and chlorinated pesticides, including phytotransformation data from field plants currently used in phytoremediation of trichloroethylene (TCE), were reviewed for the purpose of identifying important phytoprocesses and their respective roles in phytoremediation of halogenated organic compounds (HOCs). The results of the laboratory experiments indicated that the initial very rapid removal of hydrophobic HOCs from water or the gas phase by aquatic and terrestrial plants is primarily due to sequestration. The amount of HOC sequestered is controlled by the plant species and the physico-chemical properties (e.g., K_{ow} , aqueous solubility, volatility) of the contaminant. Phytodegradation studies conducted in both the gas and aqueous phases indicated that hexachloroethane (HC) is dechlorinated to the same metabolites by sterilized and axenically cultivated aquatic plants and an isolated plant dehalogenase factor.

Schaeffer D.J., S. Kapila, J.E. Meadows, E. Hinderberger and R. Wentzel. 1988. Chemical Characterization of Residues from Military HC Smokepots. *J Haz Mat*. 17(3):315-328.

The spent canister and deposited residue compositions from military HC smokepots were analyzed to determine the need for measures to reduce environmental contamination and exposure. The authors conclude that a single smokepot can increase soil concentration of aluminum, zinc, and chlorinated hydrocarbons by 3 µg/kg and the soil concentration of other inorganic constituents by 1 µg/kg, and that exposure to canisters and contaminated soils should be minimized.

Spangford R.J., T.W. Chou, T. Mill, W. Haag and W. Lau. 1985. Environmental Fate of Nitroguanidine, Diethyleneglycol Dinitrate, and Hexachloroethane Smoke. SRI International, Menlo Park, CA.

The authors studied the dominant pathways that control the movement of three chemicals either being produced or used by the Army, including the propellants nitroguanidine (NG), diethyleneglycol dinitrate (DEGDN), and hexachloroethane (HC).

Bioaccumulation and Trophic Transfer

Bioconcentration in fish has been reported and is expected to occur, but biomagnification through the food chain is unlikely. The U.S. Environmental Protection Agency (EPA) (1980) reports a bioconcentration factor (BCF) of 139 in bluegills. However, vertebrates appear to rapidly metabolize hexachloroethane, with estimated half-lives on the order of <1 day (Howard 1989). Oliver and Niimi (1983) report BCFs in rainbow trout of 510 and 1,200 at low (0.32 ng/l) and high (7.1 ng/l) exposure levels, respectively. Using an octanol-water partition coefficient (K_{ow}) and the molar solubility of the compound in octanol, Banerjee and Baughman (1991) calculated an apparent BCF of 245. Hexachloroethane has rarely been detected in ambient waters (ATSDR 1997) and appears to be rapidly metabolized, thus, significant bioaccumulation or biomagnification in the food chain is not expected.

Lien G.J., J.M. McKim, A.D. Hoffman and C.T. Jenson. 2001. A physiologically based toxicokinetic model for lake trout *Salvelinus namaycush*. *Aquat. Toxicol.* 51(3):335-350.

A physiologically based toxicokinetic (PB-TK) model for fish incorporating chemical exchange at the gill and accumulation in five tissue compartments was parameterized and evaluated for lake trout (*Salvelinus namaycush*). Individual-based model parameterization was used to examine the effect of natural variability in physiological, morphological, and physico-chemical parameters on model predictions. The PB-TK model was used to predict uptake of organic chemicals across the gill and accu-

mulation in blood and tissues in lake trout. To evaluate the accuracy of the model, a total of 13 adult lake trout were exposed to waterborne 1,1,2,2-tetrachloroethane (TCE), pentachloroethane (PCE), and hexachloroethane (HC) concurrently, for periods of 6, 12, 24 or 48 h. The measured and predicted concentrations of TCE, PCE and HC in expired water, dorsal aortic blood and tissues were generally within a factor of two, and in most instances much closer. Variability noted in model predictions, based on the individual-based model parameterization used in this study, reproduced variability observed in measured concentrations. The inference is made that parameters influencing variability in measured blood and tissue concentrations of xenobiotics are included and accurately represented in the model. This model contributes to a better understanding of the fundamental processes that regulate the uptake and disposition of xenobiotic chemicals in the lake trout. This information is crucial to developing a better understanding of the dynamic relationships between contaminant exposure and hazard to the lake trout.

Burkhard L.P., B.R. Sheedy, D.J. McCauley and G.M. DeGraeve. 1997. Bioaccumulation factors for chlorinated benzenes, chlorinated butadienes, and hexachloroethane. *Environ. Toxicol. Chem.* 16(8):1677-1686.

A field study was performed that measured bioaccumulation factors (BAFs) for chlorinated benzenes, chlorinated butadienes, and hexachloroethane in four species: mummichog (*Fundulus heteroclitus*), blue crabs (*Callinectes sapidus*), gulf menhaden (*Brevoortia patronus*), and Atlantic croaker (*Micropogonias undulatus*). The measured BAFs were not significantly different among the fishes. The measured BAFs for the *C. sapidus* were in good agreement with those measured for the fishes except for hexachloroethane (HC), E- and Z-1,1,2,3,4-pentachlorobuta-1,3-diene (E- and Z-PeCBD), and hexachlorobuta-1,3-diene (HCBd). Their measured BAFs were approximately an order of magnitude smaller than those measured for the fishes. The measured BAFs were also in good agreement with BAFs reported/derived from the literature and to BAFs predicted using two methods of the EPA except for HC, E- and Z-PeCBD, and HCBd in the blue crabs. These BAFs were much smaller than the reported/derived and predicted BAFs. The smaller BAFs for HC, E- and Z-PeCBD, and HCBd were consistent with the metabolism abilities for the blue crabs, and metabolism processes are believed to be the cause for the smaller BAFs. The predicted BAFs were within a factor of five of the measured BAFs for 90% and 94% using the two EPA methods.

Lien G.J., J.W. Nichols, J.M. McKim and C.A. Gallinat. 1994. Modeling the accumulation of three waterborne chlorinated ethanes in fathead minnows (*Pimephales promelas*): A physiologically based approach. *Environ. Toxicol. Chem.* 13(7):1195-1205.

A physiologically-based kinetic model was used to predict the accumulation of a homologous series of chlorinated ethanes in fathead minnows (*Pimephales promelas*). Uptake and accumulation of these compounds are described in terms of a few fundamental physiological, morphological, and physicochemical parameters. Chemical residues in 30 day old fathead minnows exposed to 1,1,2,2-tetrachloroethane, pentachloroethane, and hexachloroethane were used to evaluate model performance. The predicted and observed accumulations of the chlorinated ethanes were in close agreement. A quantitative assessment of the major factors regulating the exchange of these compounds indicates that the cutaneous surface may be an important route of uptake in small fish.

Toxicity

ATSDR. 1997. Toxicological Profile for Hexachloroethane. Prepared by the Agency of Toxic Substances and Disease Registry, Centers for Disease Control, Atlanta, GA.

This report contains information on the physical-chemical characteristics, environmental fate and transport, bioaccumulation potential, use, and disposal of hexachloroethane. The report emphasizes human health, but also provides summaries of all available animal studies.

Burton, D.T., D.J. Fisher and R.L. Paulson. 1990. Acute Toxicity of a Complex Mixture of Synthetic Hexachloroethane (HC) Smoke Combustion Products: 1. Comparative Toxicity to Freshwater Aquatic Organisms. *Environmental Toxicology and Chemistry*. 9:745-754.

The acute toxicity of a synthetic hexachloroethane (HC) smoke combustion products mixture to nine freshwater aquatic organisms was determined. Juvenile fish exposed to this mixture for 96 hours included: fathead minnow, bluegill, channel catfish, and rainbow trout. Invertebrates tested for 48 hours included: neonate water flea, early young amphipod, midge larva, and the mayfly larva. The effect of the mixture on the growth of the green alga (*Selenastrum capricornutum*) was also studied.

Eaton J.C., R.J. LoPinto and W.G. Palmer. 1994. Health Effects of Hexachloroethane (HC) Smoke. USABRD-TR-9402. Ad-A277838. U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, MD.

Soldier exposure to HC smoke and worker exposure to the volatile components of HC smoke munitions are reviewed. HC smoke is produced by the combustion of a mixture of hexachloroethane (HC), zinc oxide and aluminum. The major component of the smoke is zinc chloride. There are also several chlorinated organic compound in the smoke, some of which are documented potential human carcinogens. Exposure of unprotected soldiers to high concentrations of HC smoke for even a few minutes has resulted in injuries and fatalities. Therefore, it must be emphasized that this smoke should never be employed in enclosed areas and that all personnel must be compelled to mask when HC smokes are employed. In addition, HC (the organic component of the smoke mixture), even though it is not a major component of the smoke, has been recognized as a possible human carcinogen and has been shown to accumulate in the blood of exposed workers.

Elnabarawy M.T., A.N. Welter and R.R. Robideau. 1986. Relative Sensitivity of Three Daphnid Species to Selected Organic and Inorganic Chemicals. *Environ. Toxicol. Chem.* 5(4):393-398.

Static acute and renewal chronic tests were conducted with *Daphnia magna*, *Daphnia pulex*, and *Ceriodaphnia reticulata* to determine relative sensitivities to selected organic and inorganic chemicals: 2-chloroethanol, 2,4-pentanedione, pentachlorophenol, hexachloroethane, 2,2,2-trichloroethanol, 2-methyl-1-propanol, 2-methyl-2,4-pentadiol, Endrin(R), silver, lead, chromium, cadmium, copper, arsenic and mercury.

Fisher D.J., D.T. Burton and R.L. Paulson. 1990. Acute toxicity of a complex mixture of synthetic hexachloroethane (HC) smoke combustion products: I. Comparative toxicity to freshwater aquatic organisms. *Environ Toxicol. Chem.* 9(6):745-754.

The acute toxicity of a synthetic hexachloroethane (HC) smoke combustion product mixture to nine freshwater aquatic organisms was determined. Synthetic HC smoke combustion products are a complex mixture containing Zn, Cd, As, Pb, Al, CCl₄, C₂Cl₄, C₂Cl₆, C₆Cl₆, and HCl. Juvenile fish exposed to this mixture for 96 hours included: fathead minnow, bluegill, channel catfish and rainbow trout. Invertebrates tested for 48 hours included: neonate water flea, early young amphipod, midge larva and the mayfly larva. The effect of the mixture on the growth of the green alga *Selenastrum capricornutum* was also studied.

Fisher D.J., D.T. Burton and R.L. Paulson. 1990. Acute toxicity of a complex mixture of synthetic hexachloroethane (HC) smoke combustion prod-

ucts: II. Determination of component toxicity. *Environ Toxicol Chem.* 9(6):755-760.

Acute 48 hour static bioassays were conducted with neonate *Daphnia magna* to assess the toxicity of various individual components and mixtures of components of the synthetic HC smoke combustion products mixture. The tests showed that the metals, zinc in particular, were the major toxic component of the mixture. When the chlorinated organics were tested as a group, they caused only minimal toxicity to the daphnids.

Henry, M.C., J.J. Barkley and C.D. Rowlett. 1981. Mammalian Toxicologic Evaluation of Hexachloroethane Smoke Mixture and Red Phosphorus . Final Report 1978-1979. AD-A109 593/4/INW. Department of Defense [DODXA], Sep 81, 53p. Prepared by Litton Bionetics, Inc., Kensington, MD.

Four red phosphorus samples, three containing oil, were chemically analyzed for conformation to specifications. A hexachloroethane smoke mixture was burned in a laboratory apparatus to confirm that organic combustion products were present. The acute toxicity of one oiled red phosphorus sample was determined.

Karlsson N., G. Cassel, I. Fangmark and F. Bergman. 1986. A Comparative Study on the Acute Inhalation Toxicity of Smoke from TiO₂-Hexachloroethane and Zn-Hexachloroethane Pyrotechnic Mixtures. *Arch Toxicol.* 59(3):160-166.

This study determined the acute inhalation toxicity of smoke generated from pyrotechnic mixtures of titanium dioxide plus hexachloroethane, and zinc plus HC to rats. Female Sprague-Dawley-rats were exposed to smoke in a chamber in the static mode for 1.25 to 10 min., or to pure TiCl₂ gas or ZnCl₂ aerosol in an inhalation chamber in the dynamic mode for 10 min. TiO₂-HC smoke mixtures had low acute toxicity, but the smoke was irritating to eyes and nasal mucous membranes. Zn-HC was much more toxic. At the highest concentrations of Zn-HC, animals died after exposures of 1.25 min. and 2.5 min. Dyspnea developed within 10 to 15 min. post-exposure. Gross and microscopic pathological changes were found in the lungs; changes were more pronounced at higher doses. TiCl₄ exposure caused irritation, but no rats died after exposure. ZnCl₂ did not cause irritation, but signs of respiratory distress gradually developed. The aerosol was lethal at and above concentrations of 950 mg zinc/m³. Microscopic findings included atelectasis, hyperemia, hemorrhages, and edema. No clear dose response relationship was found. The authors concluded

that the difference between the two types of smoke is explained by the difference in toxicity of $TiCl_4$ and $ZnCl_2$. This citation is also included under *Titanium dioxide*.

Marrs T.C., W.E. Clifford and H.F. Colgrave. 1983. Pathological Changes Produced by Exposure of Rabbits and Rats to Smokes from Mixtures of Hexachloroethane and Zinc Oxide. *Toxicol Lett.* 19(3):247-252.

Rabbits and rats were exposed to single doses of hexachloroethane zinc smoke and observed for up to 14 days. Changes in the respiratory tract included acute inflammation and, in some cases, necrosis of the laryngeal and tracheal mucosa. Pulmonary edema and pneumonitis were observed in decedent animals. Animals that survived to the end of the experiment showed similar but less florid changes in the respiratory tract.

Marrs T.C., H.F. Colgrave, J.A.G. Edginton, R.F.R. Brown and N.L. Cross. 1988. The Repeated Dose Toxicity of a Zinc Oxide Hexachloroethane Smoke. *Arch Toxicol.* 62(2-3):123-132.

Mice, rats and guinea pigs were exposed to the smoke produced by ignition of a zinc oxide/hexachloroethane pyrotechnic composition, 1 hour/day, 5 days/wk, at three different dose levels, together with controls. The animals received 100 exposures except for the high-dose guinea pigs, which underwent 15 exposures because of high death rate during the first few days of exposure. The test material had very little effect on weight gain, but there was a high rate of early deaths in the top dose of mice.

Phipps, G.L. and G.W. Holcombe. 1985. Method for Aquatic Multiple Species Toxicant Testing: Acute Toxicity of 10 Chemicals to 5 Vertebrates and 2 Invertebrates. *Environ Poll.* 38(2):141-157.

A new method for conducting aquatic acute toxicity tests was produced so the resulting data would be directly comparable between species. This method produced LC_{50} data on several species at a fraction of the time and cost to produce them by using individual tests for each species. Species tested included: fathead minnows, goldfish, channel catfish, bluegill, rainbow trout, crayfish, snails, and chinook salmon. Compounds tested included pentachlorophenol, 2-chloroethanyl, 2,4-pentanedione, hexachloroethane, alpha-bromo-2',5'-dimethoxyacetophenone, benzaldehyde, 1,3-dichloro-4,6-dinitrobenzene, dursban, sevin, and cadmium chloride. The method as developed permits acute toxicity tests to be conducted on several species in different chambers of the same exposure tank. It allows an easy determination of the most sensitive

species and cuts cost of labor, materials, and chemical analyses for measured concentration tests.

Richards R.J., J. Atkins, T.C. Marrs and R.F.R. Brown. 1989. The Biochemical and Pathological Changes Produced by the Intratracheal Instillation of Certain Components of Zinc-Hexachloroethane Smoke. *Toxicology*. 54(1):79-88.

This study evaluates the combustion products of hexachloroethane smoke. Zinc chloride, formed by igniting a mixture of zinc oxide and hexachloroethane in the production of white smokes, has been shown to produce oedema when given to rats as a single instillation. As assessed by histopathology and measurements of alveolar surface protein in lavage fluid, the oedematous reaction is variable, dose-dependent, and maximal at 3 days but at sub-lethal doses it regresses after 7 days. The parent compound, zinc oxide, does not produce these effects. In some animals there is evidence of a fibrogenic response at 7 days post-exposure although it is currently unknown whether this effect is progressive.

Sadusky M.C., J.M. Skelly, M. Simini, R.T. Checkai and R.S. Wentzel. 1993. Hexachloroethane obscurant: Assessing tree foliage injury. *Environ Toxicol Chem*. 12(4):685-694.

Open-top chambers were used to determine the relationships between a hexachloroethane (HC) obscurant, zinc deposition, and foliar injury of tree species indigenous to military training facilities. Eight eastern U.S. tree species were exposed four times to three exposure regimens of the obscurant, measured as Zn, during the 1990 growing season. Plots received ambient or charcoal-filtered air for comparison purposes. Charcoal filtration did not affect severity of symptoms. Zinc deposition was positively correlated with most of the symptoms on black locust and black cherry.

Schaeffer, D.J., W.R. Lower, S. Kapila, A.F. Yanders and R. Wang. 1986. Preliminary Study of Effects of Military Obscurant Smokes on Flora and Fauna During Field and Laboratory Exposures. Final Technical Report. December 1986. CERL-TR-86/22. AD-A176 328/3/GAR. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

A preliminary biological and chemical study of smokes was conducted to determine if tests could be developed to demonstrate measurable changes in organisms exposed

to smokes, and to evaluate if short exposures to smokes produced measurable changes in the organisms tested. Fog oil, hexachloroethane, and tank diesel smokes were tested. This citation is also included under *Fog Oil Smoke*.

Yanders A.F., E.W. Novak, W.R. Lower, A.G. Underbrink and R. Wang. 1985. Mutagenic Testing of Obscurant Smokes. *Environ Mutagen.* 7(3):60.

Mutagenic tests of fog oil and hexachloroethane smokes were performed on plant and animal cells. Somatic cells and germ cells were the target analytes. Results were not available. This citation will also be included under *Fog Oil Smoke*.

White Phosphorus

Pure white phosphorus (P_4) (WP) is a colorless-to-white waxy solid, but commercial white phosphorus is usually yellow. WP is also known as phosphorus tetramer and can have a garlic-like smell. In air, it catches fire at temperatures 10 to 15 °C above room temperature. WP is generally stored under water because of its high reactivity with oxygen in air.

The U.S. Army uses at least two -based smoke/obscurants for training and testing activities (Shinn et al. 1985). These include white /felt (WP/F), and red /butyl rubber (Spangford et al. 1985). WP/F consists of 75 to 80% white phosphorus solidified into a cellulose (felt) matrix (20 to 25%).

The Agency for Toxic Substances and Disease Registry (ATSDR) has published a toxicological profile for white phosphorus (ATSDR 1997b). This profile summarizes all of the available information as of that date related to physical/chemical properties, environmental fate, bioaccumulation potential, toxicity, use, and disposal of white phosphorus.

Physical-Chemical Properties

Table 2 provides the physical and chemical properties of white phosphorus. Table 3 provides the physical-chemical properties of the primary combustion byproducts resulting from WP in air.

Environmental Fate and Transport

Combustion byproducts of white phosphorus/felt (WP/F) include oxidation and hydrolysis products of (e.g., pentoxide P_4O_{10} , and trioxide P_4O_6), as well as unburnt white phosphorous (WP), shown in Table 3. These oxides react with moisture in the air to form a number of phosphorus-containing acids, such as orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$), ortho acid (H_3PO_3), hypo acid (H_3PO_2), polyphosphoric acid of the general formula $H_{n+2}P_nO_{3n+1}$, where $n=2-8$, and a homologous series of linear and cyclic P6-P16 polyphosphates (Spanggord et al. 1983, Tolle et al. 1988). The composition of WP smoke changes with time (Spanggord et al. 1983). In the absence of stoichiometric quantities of oxygen, phosphine (PH_3) may form in WP/F smoke from hydrolysis of unreacted with moisture in air (Spanggord et al. 1983). The phosphine gas has a low water solubility and slow reactivity, thus, it is the byproduct with the longest half-life. Phosphine forms both in the presence and absence of air. However, since phosphine is a gas with a low water solubility, it either oxidizes or volatilizes rapidly from water (Lai and Rosenblatt 1977). At a WP concentration of 0.205 mg/L, approximately 6 to 9% of initial phosphorus was released as phosphine within 2 days (Lai and Rosenblatt 1977). Kinetic studies concluded that the rate of phosphine production is inversely proportional to the oxygen concentration, and thus is favored by low oxygen pressure (Spanggord et al. 1985). Phosphine in the presence of oxygen is highly reactive and is rapidly oxidized to phosphoric acid, among other things.

Wind tunnel studies showed levels of phosphine generated during a WP aerosol study at levels approaching the detection limit. The highest phosphine concentration observed was $70 \mu\text{g}/\text{m}^3$, representing 0.02% of the total phosphorus in the aerosol. The higher concentrations were more prevalent at higher relative humidities (Van Voris et al. 1987). Such a reaction is more likely in water and soil (EPA 1991). Of the several products formed during the use of WP/F obscurant/smoke, phosphine is especially important because of its toxicity (EPA 1991). The important process for the loss of phosphine in the atmosphere is most likely its reaction with hydroxyl radicals. Based on measured rates under simulated conditions, the estimated lifetime of phosphine in the troposphere due to reaction with hydroxyl radicals is <1 day (Fritz et al. 1982). The hydrogen abstraction reaction may produce PH_2 , which may react with ozone to produce H_2PO . Ultraviolet (UV) light can induce PH_3 (phosphine) to form PH_2 . H_2PO may produce hypo acid (H_2PO_2) as a result of a reaction with nitrogen dioxide in air and subsequent hydrolysis. The hypo acid is ultimately oxidized to phosphorus and phosphoric acid.

The persistence of WP in air is very short and may range from minutes to days. Particulate WP present as an aerosol may be coated with a protective layer of oxide and may have a longer half-life in air (Berkowitz et al. 1981). In addition to aerosol age, aerosol speciation is also affected by the humidity of the ambient environment (Van Voris et al. 1987). Washout and rainout processes transport both the reaction products of vapor phase and unreacted particles of phosphorus to water and land (Berkowitz et al. 1981).

Phosphorus enters water primarily as phosphate while smaller amounts enter as elemental phosphorus. Berkowitz et al. (1981) report that 90% of the phosphate in an aquatic system was partitioned to sediment and 10% was found in water. Unoxidized elemental phosphorus in water deposits in sediment via settling but a small amount remains in colloidal form in the water column. Elemental particles with diameters ranging from 0.015 μm to 3.0 μm were isolated from pond sediment samples of Eagle River Flats in Alaska (Bird 1991). The estimated soil sorption coefficient (K_{oc}) value of 3.05 indicates that both the water-soluble and colloidal forms of WP in the water phase may sorb moderately to particulate matter in water (Spangord et al. 1985b, Swarm et al. 1983). The particle-sorbed phosphorus is eventually transported to the sediment.

Volatilization from water to air is another potential pathway. The Henry's Law constant (H) of 2.11×10^{-3} atm m^3/mol (Spangord et al. 1985b) indicates that volatilization of elemental phosphorus from water is significant (Thomas 1982). The estimated volatilization half-life of WP from water is 48.5 min from a stream 4 ft deep, with an eddy diffusivity of 1 cm^2/sec (Spangord et al. 1985b). Under turbulent conditions, the rate of volatilization is faster and may be an important fate-determining process for white phosphorus.

WP can exist in water as dissolved in amounts around 3 mg/L, in the colloidal state, as large particles of elemental at concentrations >3 mg/L, or in the particle-sorbed state (Bullock and Newlands 1969, EPA 1991). Elemental phosphorus can undergo oxidation and hydrolysis in water. The rate of reactions depends on the dissolved oxygen concentration, temperature, state of phosphorus in water (dissolved, sorbed, colloidal, or particle form), and possibly the pH of the solution. The rate of reaction grows faster as the temperature of the water increases (Lai and Rosenblatt 1977). At concentrations well below the solubility limit (3 mg/L), elemental phosphorus disappears from water by a first-order process with a half-life of 2 hrs at 10 $^{\circ}\text{C}$ and 0.85 hr at 30 $^{\circ}\text{C}$ (EPA 1991, Zitko et al. 1970). The rate of phosphorus disappearance in water increased with the oxygen (or air) concentration and the pH of water (Lai and Rosenblatt 1977). However, the faster initial disappearance half-life of 3.5 hours

(compared to distilled water at pH 4.2) observed in river water at 22 °C and a pH of 7.6 may have been due to the catalytic effects of ions present in the river water, rather than the pH effect (Lai and Rosenblatt 1977). The disappearance half-life of elemental phosphorus in water also depends on the physical state of phosphorus. For example, the disappearance half-life of colloidal was 80 hours at 30 °C and 240 hours at 0 °C at concentrations between 10 to 50 mg/L (Bullock and Newlands, 1969), compared to a half-life of 2 hours in solution form at 10 °C (Zitko et al. 1970). The half-life of white phosphorus in solution increased from 2 to 20 hours when the phosphorus was present in the sorbed state in sediment (Zitko et al. 1970). In anoxic water, the estimated half-life of a solid chunk of white phosphorus that was protectively coated due to oxidation/hydrolysis at the oxic zone was 2.43 years (Spanggard et al. 1985). The experiments discussed above determined the rate of disappearance and the half-life of elemental phosphorus in water in open systems. The phosphorus in these experiments disappeared due to hydrolysis/oxidation and evaporation. Spanggard et al. (1985) studied the loss of elemental phosphorus in sealed reaction flasks. In a closed reaction flask with argon-saturated water, the loss of WP can only be due to hydrolysis. The estimated half-life for hydrolysis at ambient temperatures was 84 hours (Spanggard et al. 1985). The estimated half-lives of WP at ambient temperatures due to a combination of hydrolysis and oxidation reaction were 42 hours in air-saturated water and 56 hours in nonair-saturated water (Spanggard et al. 1985).

The products of hydrolysis of WP are phosphine, hypo acid, phosphorus acid, and phosphoric acid. The oxidation products are oxides of phosphorus that produce hypo acid, phosphorus acid, and phosphoric acids in the presence of water (Spanggard et al. 1985). White phosphorus reacts rapidly with chlorine to form phosphorus trichloride, which finally hydrolyzes and oxidizes to form phosphoric acids (EPA 1991). Chlorination of water, therefore, further shortens the half-life of phosphorus in water.

No data on the biodegradation of WP in water under aerobic conditions were located. Considering the rapidity with which phosphorus disappears from aerated water as a result of a combination of evaporative and chemical processes, it is unlikely that aerobic biodegradation can compete with these loss processes. Anaerobic biodegradation studies have concluded that biotransformation of elemental phosphorus is not rapid in water (Spanggard et al. 1985). In most natural water, phosphine is very unstable and oxidizes even under anoxic conditions. Depending upon the redox potential of water, the oxidation products include diphosphine (P_2H_4), phosphorus, and phosphoric acid (Kumar et al. 1985). Based on soil studies (Berck and Gunther 1970, Hilton and Robison 1972), small amounts of phosphine may also be adsorbed (re-

versible sorption) or chemisorbed (irreversible sorption) to suspended solid and sediments in water. However, based on the estimated Henry's Law constant (H) of 0.09 atm·m³/mol and the expected volatility associated with various ranges of H, volatilization is expected to be the most important loss process for phosphine in water.

WP/F reacted rapidly in air with an estimated half-life of less than 5 minutes (Spanggard, et al. 1985b). However, the deployment of the military smoke/obscurant in the field may produce an estimated 10% of unburnt phosphorus (Spanggard et al. 1985b). Particle size from phosphorus obscurant aerosols is determined by the age of the particles and the amount of water vapor available in the atmosphere. In wind tunnel studies, particles increased in diameter by 1.3 times and increased in volume by 2.0 times at a relative humidity of 60%. Similar increases were observed with humidity levels higher than 60%. These increases are due to absorption of water vapor and to a lesser extent by coagulation of the particles. Therefore, in general particles that are smaller have been released more recently than larger particles (Van Voris et al. 1987). Since oxides of phosphorus are highly soluble in water, wet deposition removes them from air (Berkowitz et al. 1981). Particulate elemental phosphorus also reacts at most environmental pressures and at temperatures >5 °C (EPA 1989). The amount of phosphorus remaining in the particles has been observed to decrease with increasing relative humidity from a phosphorus percentage of 25% at low humidities to 15% for humidities near 90% (Van Voris et al. 1987). However, if the particulate phosphorus is coated with a protective layer of oxide, further oxidation may not occur (Berkowitz et al. 1981). This may increase the lifetime of elemental phosphorus in the air. Both wet and dry deposition remove the oxide-coated elemental phosphorus from the atmosphere with the wet deposition rate increasing with increasing relative humidity.

The two processes involved in the transport of elemental phosphorus from soil are volatilization and leaching. When 35 mg of elemental phosphorus was added to two soils, one acid and the other calcareous, 0.004% to 0.6% of the applied phosphorus was found at a depth of 10 cm volatilized as elemental phosphorus (not as oxides) in 3 days (Warnock 1972). The loss of a maximum amount of 0.6% phosphates was complete in 3 to 7 days. The amount of phosphorus volatilized appeared to be similar from both soils. The rate of volatilization decreased by increasing the depth to which the phosphorus was applied or by increasing soil moisture content; the rate did not go to zero. The transport of elemental phosphorus from soil by leaching depends on the K_{oc} value. The estimated K_{oc} value of 3.05 indicates that phosphorus may moderately sorb in soil. Therefore, moderate leaching of phosphorus may occur from the anaerobic soil zone where ele-

mental phosphorus will be stable toward chemical oxidation (EPA 1989, Richardson and Weston 1992).

The exposure of soil to phosphorus aerosols will upset the pH of the soil and create a more acidic layer of soil. This decrease in pH often can exceed the buffering capacity of the surface layer of the soil depending upon the amount of applied phosphorus. This process can be mitigated by a larger soil volume area so that phosphorus speciation on a field scale will be minimal. The interaction of metals with phosphorus condensates could lead to their leachability and possible trace metal migration from the soil (Van Voris et al. 1987).

Oxidation is the predominant route of loss of WP in soils to a depth that allows diffusion of oxygen (Bohn et al. 1970). The oxidation of phosphorus to its oxides is usually very rapid. WP oxidized within 2 days in soil at ambient temperatures (Rodriguez et al. 1972). A soil volatilization study found that the volatilization of elemental phosphorus stopped after 3 to 7 days (Warnock 1972). If the termination is attributed to oxide formation, it can be concluded that elemental phosphorus oxidized in soil within 3 to 7 days. However, the rate of oxidation will be slower if white phosphorus forms a protective coating (Bohn et al. 1970). The results of anaerobic biodegradation studies with soil and sediments are inconclusive (Spanggard et al. 1985b). Although WP transformed faster in some nonsterile than in sterile controls, the slower transformation in sterile soil could be attributed to a change in soil property due to autoclaving (Spanggard et al. 1985). The investigators found that the biotransformation microorganisms were difficult to grow under their test conditions. The lack of growth is an indication of lack of biodegradation. Therefore, in the absence of oxidation and biodegradation reactions in anaerobic zones of soil and sediment, the half-life of elemental phosphorus could be 10 to 10,000 years (Richardson and Weston 1992, Spanggard et al. 1985b). It should be mentioned that although microorganisms that biodegrade elemental phosphorus under anaerobic conditions could not be grown, both linear polyphosphates and cyclic metaphosphates could be microbially hydrolyzed to simpler phosphates in water and soil under aerobic and anaerobic conditions (Spanggard et al. 1985b). In sealed tubes, phosphine completely disappeared in less than 40 days from three different types of soil with varying amounts of moisture (Hilton and Robison 1972). The disappearance was attributed to initial sorption, and the subsequent biotic and abiotic oxidation of part of the sorbed compound. The rate of adsorption increased with decreasing moisture content and increasing organic soil content (Hilton and Robison 1972). The study showed that phosphine sorption in soil can occur by both physical and chemical sorption processes, and that the chemisorption process is higher in soils with a low organic matter and high mineral content (Berck and Gunther 1970). Chemisorption irre-

versibly binds phosphine in soil so that it is not available for volatilization. However, since phosphine is gaseous and is only slightly soluble in water, volatilization from soil may be the most important process by which phosphine is lost from soil when chemisorption is not occurring.

WP exposure to plants results in a variety of deleterious effects based on the species of plant, smoke concentration, duration of exposure, relative humidity, and wind speed. These effects can include leaf tip burn, leaf curl, leaf abscission and drop, floral abortion, chlorosis, necrotic spotting, wilting, dessication, and dieback. Other factors influencing the effects of WP on plants are whether there is a post-exposure rainfall and if the exposure is a large acute dose or several lower chronic doses (Van Voris et al. 1987).

Lawson, D.E., L.E. Hunter, S.R. Bigl, B.M. Nadeau and P.B. Weyrick. 1996. Physical System Dynamics and White Phosphorous Fate and Transport, 1994, Eagle River Flats, Fort Richardson, Alaska. Technical Report, August 1996. CRREL-96-9. ADA317 624/5. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, NH.

Eagle River Flats (ERF) is a subarctic estuarine salt marsh where human and natural forces are causing significant changes in the environment. ERF is also used as an artillery range by the U.S. Army, where past use has resulted in white phosphorous (WP) contamination of the sediments in ponds and mudflats. Bottom-feeding waterfowl ingest this WP, causing rapid death. This report documents analyses of the physical environment and describes the nature of the physical systems and factors controlling it. Data on sedimentation, erosion, and hydrology are included. The investigation provides knowledge necessary to design and evaluate remedial technologies. It also helps determine the capacity of the system to naturally attenuate the WP contamination.

Payne, M.P., R.O. Shillaker and A.J. Wilson. 1993. Phosphoric acid, phosphine, phosphonates, phosphates, phosphites, phosphonates, phosphonates, phosphonates. HSE Toxicity Review. V 30.

The toxicity, toxicokinetics, and metabolites of white phosphorous and white phosphorus combustion products are presented.

Spanggard R.J., R. Rewick, T.W. Chou, R. Wilson and R.T. Podoll. 1987. Environmental Fate of White Phosphorus Felt and Red Butyl Rubber Military Screening Smokes. DAMD17-82-C-2320. AD-176922. Prepared by SRI

International, Menlo Park, CA, for U.S. Army Medical Research and Development Command, Frederick, MD.

Investigations were conducted to identify the processes that control the loss and movement of white /felt (WP/F), red /butyl rubber (RP/BR), and their combustion products in air, soil, and aquatic environments. The fate of red phosphorous is controlled by oxidative transformation. In air and aerated water, half-lives of 1.8 years and approaching 3 years, respectively, were found to be dependent on both particle size and oxygen concentration. In soil the transformation was limited by oxygen diffusion, and half-lives into the thousands of years were projected. The oxidative transformation and combustion of WP/F and RP/BR lead to the formation of linear condensed polyphosphates, (P10-P22), phosphoric acid, phosphorous acid, hypophosphorous acid, and phosphine. The linear polyphosphates hydrolyze rapidly at low pH ($t_{1/2} = 2$ days), which is expected in the aerosol phase. In a neutralized state, the polyphosphates are subject to slow chemical hydrolysis ($t_{1/2} = 100$ days).

Walsh, M.E. and S. Taylor. 1993. Analytical methods for white residues in munitions-contaminated sediments. *Anal Chim Acta*. 282(1):55-61.

An analytical method is described to determine white phosphorus (WP) in sediments contaminated by smoke munitions. Experiments were performed to promote the extraction of WP from saturated sediment with a nonpolar solvent. WP extraction was enhanced by adding water to form a sediment/water slurry prior to shaking with isoctane for up to 24 hours. WP was determined with a portable capillary gas chromatograph equipped with a nitrogen- detector. A certified reporting limit of 0.88 $\mu\text{g}/\text{kg}$ was estimated.

Walsh, M.E., C.M. Collins and C.H. Racine. 1996. Persistence of white phosphorus (P₄) particles in salt marsh sediments. *Environ Tox Chem* 15(6):846-855.

Remediation of sediments at Eagle River Flats, AK, a salt marsh contaminated with solid particles of white phosphorus (P₄), may require severe alterations of the wetland by dredging, draining, or covering. However, some sediments may undergo decontamination naturally in areas that are seasonally subaerially exposed. The persistence of millimeter-size P₄ particles was studied in laboratory and field experiments. White phosphorus particles were found to be persistent in saturated sediments. In unsaturated sediments, loss was rapid (within 24 hrs) at 20 ° C, and was retarded by low temperatures.

Yon, R.L. 1984. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 2. Red, White, and Plasticized White phosphorus. ARCSL-EA-83004. Chemical Systems Laboratory, Chemical Research and Development Center, U.S. Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.

The environmental impacts associated with the use of phosphorus smoke compounds for testing and training purposes have been reviewed and compiled in this report. Based on the toxicological data gathered and the regulatory aspects associated with the use of these smoke/obscurants it was concluded that this portion of the smoke program will not significantly affect the quality of the environment.

Bioaccumulation and Trophic Transfer

White moderately bioconcentrates in aquatic organisms but is quickly depurated. The bioconcentration factors (BCF) for white in a few species of aquatic organisms are as follows: cod (*Gadus morhua*) whole body, 44, and muscle, 24; salmon (*Salmo salar*) muscle, 22 (Fletcher 1974); channel catfish (*Ictalurus punctatus*) muscle, 50 to 100; fathead minnow (*Pimephdes promelas*) muscle, 127 (Bentley et al. 1978); cod (*G. morhua*) muscle, 10 to 100 (Dyer et al. 1970); clams (*Mya arenaria*), 23; mussel (*Mytilus edulis*), 10; periwinkle (*Littorinu littoreu*), 42; starfish (*Asterius vulgaris*), 27; lobster (*Homurus americanus*) muscle, 23 to 34 (Fletcher 1971). It has been suggested that the BCF of elemental phosphorus in fish muscle may depend on the concentration in water. The BCF for cod muscle decreased with increasing water concentration, ranging from 34 at 4.4 µg/l to 10 at 29 µg/l (Maddock and Taylor 1976). Depuration was rapid once the contaminated fish were placed in clean water; no elemental phosphorus was observed from within hours to 7 days of exposure (Bentley et al. 1978, Fletcher 1971, Maddock and Taylor 1976).

Berglind, R. and C. Henriksson. 2000. Kvarlaemnad roekammunition med vit Fosfor(P4). Miljoerisker ur ett Langtidsperspektiv (Left Obscurant Ammunition Focusing on White phosphorus (P4) Environmental Effects in a Long-Term Perspective). Technical report. September 2000. FOA-R-00-01569-222-SE. PB2002-100659. Foersvarets Forskningsanstalt, Umea (Sweden). Avedelningen foer NBC Skydd.

This Swedish study investigated whether unexploded smoke shells containing white or red phosphorus could be a future environmental hazard. Red, violet and black elemental phosphorus are non-toxic modifications and not further investigated. White phosphorus is very toxic, very corrosive, and reacts intensively with oxygen-

giving oxides. The elemental white phosphorus is soft, waxy, and darkens in sunlight. The solubility of white phosphorus in water is low. White phosphorus ignites spontaneously when exposed to air. The half-life in water is longer than that in air (hours to days). Although the half-life in water is up to 24 hours, the risk for toxic effects in aquatic organisms such as fish and invertebrates is low. Particles of white phosphorus are inert for decades in water-saturated sediments. Small particles of white phosphorus deposited in shallow ponds may be mistaken for food by water birds such as mallards and swans that feed from sediments. At an artillery range where smoke obscurants have been used, white phosphorus-related mortality of waterfowl has been verified. Present study shows that small particles of white phosphorus are the modification presenting the main hazard to the environment. The presence of particulate elemental white phosphorus at Swedish artillery ranges must therefore be investigated and the hazard calculated in relation to the number of fired shells and remaining duds.

Johnston, J.J., D.A. Goldade, D.J. Kohler and J.L. Cummings. 2000. Determination of white phosphorus residues in ducks: an atomic emission detection/compound-independent calibration-based method of generating residue data for risk assessment and environmental monitoring. *Environ Sci Technol.* 34(9):1856-1861.

Analysis of phosphorous concentrations in the gizzards of ducks harvested from munitions sites was necessary to ascertain if acute phosphorus toxicity was the cause of death and to estimate potential secondary hazards to predators and scavengers, such as eagles that readily consume the dead ducks. Gas chromatography/atomic emission detection analysis permitted compound-independent quantification of white phosphorus standards following analysis of the stable phosphorus-containing compound triethyl phosphate. The white phosphorus standards were then used to quantify white phosphorus residues in duck gizzard extracts by gas chromatography/flame photometric detection analysis. For gizzards containing less than 0.01 μg of phosphorus, quantification was based on a three-point calibration curve. For gizzards containing 0.01 μg or more of white phosphorus, single-point calibration was used. Mean recoveries for phosphorus-fortified (0.03 μg to 3000 μg) gizzards ranged from 73 to 91%. The method limit of detection was 0.013 μg of phosphorus. This method was successfully applied to the quantification of white phosphorus in ducks collected from Eagle River Flats, AK. Potential applications to risk assessment and environmental monitoring are also discussed.

Milham, M.E., D.H. Anderson and R.H. Frickel. 1982. Infrared Optical Properties of Derived Smoke. *Appl Opt.* 21(14):2501-2507.

This report examines the atmospheric dispersion of -derived smoke. The reaction of elemental phosphorus with atmospheric oxygen and water vapor produces a highly visible white smoke; extinction spectra in the 7 μm to 14 μm infrared have been measured for such -derived smokes in varying environmental conditions. The extinction spectra show that the smoke particles are not homogeneous droplets of o-phosphoric acid. The dependence of -derived smoke extinction on relative humidity is described, and extinction spectra taken over a 280 min time period show that the smoke evolves toward an o-phosphoric acid aerosol. The relative humidity and time-dependent smoke extinction spectra are compared with o-phosphoric acid extinction spectra computed from Lorenz-Mie theory. The constants of the -derived smoke are found from the extinction spectra as functions of relative humidity and time.

Nam, S.I., B.D. Roebuck and M.E. Walsh. 1994. Uptake and loss of white phosphorus in American kestrels. *Environ Tox Chem* 13(4):637-641.

American kestrels (*Falco sparverius*) exposed to a diet containing white phosphorus (P_4) had detectable quantities of P_4 only in their fatty tissues. As early as 24 hours postdosing, P_4 was found in the fat depots and skin but not in other tissues such as the brain, heart, intestine, liver, kidney, and muscle. After 7 days of continuous exposure to P_4 -containing diet (6.4 μg P_4/g of diet), the skin but not the fat depots showed significant accumulation of P_4 . When P_4 -containing diet (6.4 μg P_4 per gram of diet) was fed for 2 days followed by 3 days of feeding a diet containing less P_4 (0.7 μg P_4 per gram of diet), P_4 was not detectable in the tissues. Upon refeeding with the higher dietary concentration of P_4 , P_4 was again detectable in skin and fat. This cyclic dosing regimen indicates that tissue levels are sensitive to dietary levels of P_4 .

Nam S.I., D.L. MacMillan and B.D. Roebuck. 1996. Translocation of white phosphorus from hen (*Gallus domesticus*) to eggs. *Environ Tox Chem* 15(9):1564-1569.

White phosphorus has been found in the egg of one herring gull (*Larus argentatus*) and in the yolks of some shorebirds at ERF. The presence of P_4 in eggs suggests potential toxic consequences for avian reproduction. This study was done to determine the magnitude and potential importance of P_4 translocation from the hen to the egg. Egg-laying hens (*Gallus domesticus*) were gavaged with a single dose of 1, 3, or 5 mg P_4/kg body weight or dosed with 1 mg P_4/kg body weight for 5 consecutive days. Eggs of dosed hens were collected daily. White phosphorus was extracted from the yolk and the white, individually, with isooctane and analyzed by gas chromatography. White phosphorus had no significant effect on chicken weight, egg weight, or shell thickness. However, laying frequency was significantly reduced ($p < 0.05$) in chick-

ens receiving 1 mg P₄/kg body weight for 5 days. For all treatments, P₄ was detected in the yolk and not in the white. It was first detected in the yolk approximately 1 to 2 days after P₄ exposure and became nondetectable 6 to 10 days after P₄ exposure. The total P₄ recovered from eggs of chickens treated with P₄ was less than 0.01% of the administered dose.

Spangford R.J., R. Rewick, T.W. Chou, R. Wilson and R.T. Podoll. 1987. Environmental Fate of White Phosphorus Felt and Red Phosphorus Butyl Rubber Military Screening Smokes. DAMD17-82-C-2320. AD-176922. Prepared by SRI International, Menlo Park, CA, for US Army Medical Research and Development Command, Frederick, MD.

The objective of this project was to review the literature for data that can be used to estimate the persistence of white and red phosphorus and their combustion products in air, soil, and aquatic environments and to identify gaps in the literature where data are lacking. The study reviewed the literature through on-line data files, including National Technical Information Service (NTIS), Chemical Abstracts, MEDLINE, TOXLINE, TOXBACK 74 and 65, and final reports on relevant -related contracts supported by the U.S. Army. Very few rate constants necessary for an environmental fate assessment have been reported. The authors conclude that oxidation will be an extremely important process for white and red phosphorus and that hydrolysis reaction will dominate the transformation of phosphorus oxides in the presence of moisture.

Sparling, D.W. and N.E. Federoff. 1997. Secondary poisoning of kestrels by white phosphorus. *Ecotoxicology*. 6(4):239-247.

Since 1982, extensive waterfowl mortality due to white phosphorous (P₄) has been observed at Eagle River Flats, a tidal marsh near Anchorage, AK. Ducks and swans that ingest P₄ pellets become lethargic and may display severe convulsions. Intoxicated waterfowl attract raptors and gulls that feed on dead or dying birds. To determine if avian predators can be affected by secondary poisoning, researchers fed American Kestrels (*Falco sparverius*) 10-day-old domestic chickens that had been dosed with white phosphorus. Eight of 15 kestrels fed intact chicks with a pellet of P₄ implanted in their crops died within seven days. Three of 15 kestrels fed chicks that had their upper digestive tracts removed to eliminate any pellets of white phosphorus also died.

Truhaut, R., J.R. Claude and J.M. Warnet. 1971. Study of the incorporation of 3-H-9-10 palmitic acid in the triglycerides and lipoproteins of rats poisoned by white phosphorus. *CR Hebd Seances Acad.* 272(18):2400-2403.

This study presents accumulation of white phosphorus metabolites in rat organs. White phosphorous, administered s.c. at doses of 10 mg/kg to adult male Wistar rats, provoke true hepatic steatosis with triglycerides. Their accumulation is produced in an unusual cellular compartment, with slow renewal, following the inhibition of liver triglyceride secretion in the plasma in the form of beta-lipoproteins.

Walsh, M.R., M.E. Walsh and C.M. Collins. 1999. Remediation methods for white phosphorus contamination in a coastal salt marsh. *Environ Conserv.* 26(2):112-124.

Natural remediation techniques are examined and compared with physical remediation techniques, such as dredging.

Toxicity

ATSDR. 1997. Toxicological Profile for White Phosphorus. Prepared for the Agency for Toxic Substances and Disease Registry.

This report contains information on the physical/chemical characteristics, environmental fate and transport, bioaccumulation potential, use, and disposal of white phosphorus. The report emphasizes human health but does provide summaries of all available animal studies.

Poston, T.M., K.M. McFadden, R.M. Bean, M.L. Clark and B.L. Thomas. 1986. Acute Toxicity of Smoke Screen Materials to Aquatic Organisms, White Phosphorous-Felt, Red Phosphorous-Butyl Rubber and SGF (Smoke Generator Fuel) No.2 Fog Oil. Final Report 1983-1985. PNL-5584. ADA167 900/0/GAR. Battelle Pacific Northwest Laboratories.

The acute toxicity of three obscurants was determined for nine freshwater organisms. The materials tested were white phosphorus-felt smoke, red phosphorus-butyl rubber smoke, and smoke generator fuel (SGF) No. 2 fog oil (bulk and vaporized). The chemistry of WP-F and RP-BR smoke in water and the resulting effects on aquatic organisms were similar. Combustion of these two obscurants and their deposition in water leads to the formation of many complex oxy-phosphoric acids. Rates of hydrolysis of these complex products to ortho-phosphate were inconsistent and

unpredictable over time. These products acidify water and produce toxic effects after exhausting the buffering capacity of the water. The 96 hour median lethal concentration (LC₅₀) values for fish ranged from 3.9 to 5.1 pH units. The values for invertebrates ranged from 3.4 to 5.5. Algal growth was inhibited at pH levels less than 6.0. This citation will also be included under *Fog Oil Smoke*.

Roebuck, B.D., S.I. Nam, D.L. MacMillan, K.J. Baumgartner and M.E. Walsh. 1998. Toxicology of white phosphorus (P₄) to ducks and risk for their predators: effects of particle size. *Environ Tox Chem* 17(3):511-518.

This study compared the properties of dissolved P₄ to particulate P₄. Farm-reared mallards (*Anas platyrhynchos*) were gavaged with P₄ (12 mg/kg body weight) dissolved in oil, large particles (1.87 mm mean diameter), or small particles (0.95 mm mean diameter). Signs of intoxication and time to convulsion were monitored. Individuals were autopsied at the onset of convulsions. P₄ in digestive tracts and body fat was analyzed by gas chromatography. For all 3 treatments, the behaviors of P₄, intoxication were similar to observations of wild ducks. There was no difference between treatments for onset of lethargy, vomiting, poor motor/muscle control, or the first convulsive event. At autopsy, P₄ was found throughout the digestive tracts with residual quantities of approximately 20% or less of the dose. Very little of the dissolved P₄ remained in gizzards; whereas, in the small and large particle groups, the gizzard contents contained 78 and 64%, respectively, of the total P₄, within the digestive tracts. Tissue concentrations of P₄ were small and did not appear to be a significant source of P₄ to predators. The conclusion was that intoxication from particles of P₄ was largely not a function of the size of the particles, but rather the dose. Residual P₄ in the digestive tracts represents a risk to secondary receptors. These relative risks of particulate P₄ to tissue P₄ are similar to poisoning from lead shot.

Sparling, D.W., R. Grove, E. Hill, M. Gustafson and L. Commerci. 1994. Toxicological studies of white phosphorus in waterfowl. Interagency Expanded Site Investigation: Evaluation of White phosphorus Contamination and Potential Treatability at Eagle River Flats, Alaska. FY93 Final Report, p. 133-151. (C.H. Racine and D. Cate, Eds.) Prepared by Cold Regions Research and Engineering Lab., Hanover, NH for U.S. Army Directorate of Public Works, Garrison, AK.

The acute median lethal dose for adult male and juvenile mallards exposed to P₄ dissolved in oil is 6.5 mg P₄/kg body weight (95% confidence interval = 5.8 - 6.9). Adult females were substantially less sensitive to P₄ than other age/sex classes. (The median lethal dose could not be calculated for this age/sex class.) Acute exposure to P₄

produced obvious clinical signs of (1) lethargy, ataxia and mild leg trembling (these could either recover or progress into more advanced stages); (2) more severe trembling and a stereotyped bill movement; and (3) severe convulsions terminating in death.

A characteristic very hard rigor mortis set in within 5 to 10 minutes after death in many cases. Some of the birds on repeated doses did not enter the convulsion phase and may have died from renal or liver failure. Gross necropsies and histopathology revealed that birds acutely dosed with > 5.2 mg/kg P₄ frequently had foci, necrosis and cellular vacuolations in the liver; damage to the proximal and distal convoluted tubules in the kidneys; and petechiae in the coronary fat band and pancreas. Brains of birds that died on dose often displayed mild to severe hemorrhaging or congestion. Duodena were also congested. Brain ChE activity was depressed in a dose-response manner in male mallards acutely exposed to P₄, but plasma ChE did not differ among doses. In contrast, the brain (ChE of females did not differ due to dose, but there was a depression in plasma ChE activity at higher dose levels. Cholinesterase depression may be a useful method of detecting P₄ exposure, but additional tests are required before this method can be recommended.

White phosphorus levels in acutely dosed mallards that died during the study ranged from below detection to 1.776 mg/kg for fat, 0.959 mg/kg in skin and 0.027 mg/kg in liver. We could not detect a linear relationship between P₄ residues and dosage. Birds that survived for a week had residue levels that were < 1/100 of those in birds that had died at the same doses. White phosphorus in the fat of dead birds remains the most reliable indicator of exposure, but its instability diminishes the value to determine exposure in living birds. The lowest-observed-effects level for acute mortality of mallards in this study was 4 mg/kg. However, organ damage was observed at the lowest dose used, 2 mg/kg.

Multiple daily exposures to P₄ over four days did not alter mortality above what would be expected by the acute levels of dosing solutions. There was a significant dose response in weight loss during treatment, probably due to malaise or inappetence, but this was transitory, and birds recovered their pretreatment weights within seven days after exposure.

Sparling, D.W., S. Vann and R.A. Grove. 1998. Blood changes in mallards exposed to white phosphorus. *Env Toxicol Chem.* 17(12):2521-2529.

This study was performed to determine the effects of experimental dosing on blood characteristics in game farm mallards (*Anas platyrhynchos*). In two experiments,

one employing single doses of 5.4 mg P₄ per kilogram body weight in corn oil and the other using daily repeated doses of pelletized P₄ at either 0.5 or 1.0 mg/kg, there were significant changes in aspartate aminotransferase, alanine aminotransferase, lactate dehydrogenase (LDH), inorganic P, hematocrit, and hemoglobin.

Tolle, D.A., M.F. Arthur, K.M. Duke and J. Chesson. 1990. Ecological effects evaluation of two phosphorus smoke-producing compounds using terrestrial microcosms. *ASTM Spec. Tech. Publ.*, ASTM, Philadelphia, PA. No. 1091, pp. 127-142.

An intact soil-core microcosm and static exposure system were used to evaluate the potential ecological effects of two obscurant smokes, red phosphorus/butyl rubber (RP/BR) and white phosphorus/felt (WP/F), used in the field during U.S. Army training exercises. Three plant species (white sweetclover, perennial ryegrass, and wheat) were used for both preliminary and microcosm tests. The stress-ethylene tests indicated that extremely high doses of either smoke would be required to elicit a response in the microcosm test. This information guided selection of microcosm test concentrations. Microcosms were exposed to either RP/BR or WP smoke at target concentrations of 0, 100, 300, 600, and 1500 mg/m. These concentrations bracket typical field concentrations. Minor ecosystem-level effects were detected in microcosms only at the highest smoke concentration.

Brass Flakes

Brass flakes, an alloy typically composed of approximately 70% copper and 30% zinc, are used to block detection of infrared waves. There are also trace amounts of aluminum (0.2%). Antimony (0.1%) and lead (0.1%) have been detected, and there may be other inorganic contaminants at concentrations close to or below typical detection limits (NRC, 1999). The predicted fate and effects of brass flakes depends not only on the form of the alloy, but the size of the individual particles and if specific coatings have been used. Typical coatings include palmitic and/or stearic acid, which make the powder float on water surfaces.

Many studies have documented that elevated concentrations of copper or zinc, in and of themselves, can have detrimental impacts on biological communities. Environmental fate and toxicity of brass flakes is regulated by the speciation of zinc and copper in the environment.

Physical-Chemical Properties

Table 2 provides the physical/chemical properties for brass flakes.

Environmental Fate and Transport

Cataldo, D.A., M.W. Ligothke, H. Bolton, R.J. Fellows and P. Van Voris. 1991. Evaluation and characterization of mechanisms controlling fate and effects of Army smokes. Transport, transformations, fate, and terrestrial ecological effects of brass obscurants, Final Report. PNL-7459, Pacific Northwest Laboratory, Richland, WA.

The primary objective of this study was to characterize the fate and response of soil and biotic components of the terrestrial environment to aerosols, deposited brass, and brass in combination with fog oil. Important physical, chemical, and biotic aspects were investigated using an environmental wind tunnel. Air/surface deposition rates were determined for foliar and soil surfaces, both in the absence and presence of fog oil. Foliar contact toxicity was assessed using five different types of terrestrial vegetation representative of Army training sites and surrounding environments. The weathering and chemistry of brass aerosols deposited and amended to soils was assessed, along with the impacts of acid precipitation and moisture regimes on weathering rates. This citation is also included under *Fog Oil Smoke*.

Guelta, M.A. and R.T. Checkai. 1998. Predictive Ecological Risk Assessment of Brass Infrared Wavelength Obscurant in a Terrestrial Environment. - Final Report October 1994 - December 1995. Technical Report. March 1998. ERDEC-TR-364. ADA342 600/4. Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

This report assessed and predicted the potential for ecological risk due to the use of brass infrared (IR) wavelength obscurant in the field. The report uses available environmental toxicity data, material fate and effects data, appropriate environmental fate modeling data and proposed field scenarios to predict the possibility of impact to the environment under study. These field use scenarios for brass flake obscurant materials are evaluated to predict the environmental impact on terrestrial ecosystems.

Haley, M.V. and C.W. Kurnas. 1993. Toxicity and Fate Comparison Between Several Brass and Titanium Dioxide Powders. ERDEC-TR-094. Edgewood Research, Development and Engineering Center, U.S. Army Ar-

mament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.

Brass flakes and four brands of titanium dioxide were tested to determine their toxicities to water flea (*Daphnia magna*), green algae (*Ankistrodesmus falcatus* and *Selenastrum capricornutum*). The fate of the brass material was determined in fresh water of varying hardness, in synthetic marine salt water (30 ppt), and in physiological saline solution (9 ppt). This citation is also included under *Titanium Dioxide*.

Landis, W.G., N.A. Chester, M.V. Haley, D.W. Johnson and W.T. Muse. 1988. Evaluation of the Aquatic Toxicity and Fate of Brass Dust Using the Standard Aquatic Microcosm. Department of Defense [DODXA], July 1988, 24p. Technical Report. CRDEC-TR-88116. ADA200 271/5/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

The impact of brass dust on a model aquatic ecosystem, the Standard Aquatic Microcosm (SAM), was investigated. The study included the interaction of trophic levels, community structure, and metabolism of nutrients, and chemical breakdown and dispersion of the brass dust.

Muse, W.T. 1988. Chemical Fate of Brass Dust in Waters of Varying Hardness Levels. Department of Defense [DODXA], Aug 1988, 27p. Technical Report. CRDEC-TR-88131. ADA199 598/4/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

The chemical fate of brass dust was examined at four levels of water hardness ranging from very soft to very hard water.

Bioaccumulation and Trophic Transfer

U.S. Army Corps of Engineers. 1993. A report of the accumulation of contaminants in soil samples from test area C52-A in connection with smoke weeks XIII and XIV, Eglin Air Force Base, FL. U.S. Army Corps of Engineers, Mobile, AL.

This study measured soil concentrations of several smoke materials, including brass smokes, at a training facility that provides testing for new smoke formulations. The study found that solid smoke materials do accumulate in the environment.

Toxicity

Armstrong, R.D. 1988. Spontaneous Activity and Passive Avoidance Behavior of Rats Exposed by Inhalation to Brass Dust (1 and 10 mg/m³). Department of Defense [DODXA], Jun 88, 27p. CRDEC-TR-88156. AD-A200 497/6/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

This report describes one part of a multilevel assessment of the subchronic toxicity of inhaled brass dust in rodents at 1 mg/m³ and 10 mg/m³. The behavior results are the subject of this report. There were no statistically significant dose-response or exposure duration effects on passive avoidance (step down) behavior or spontaneous activity. There was no evidence of any direct CNS effect in the rat related to the inhalation of brass dust. There was some evidence of residual recovery effects from exposure-related hyperpnea in the session SA of male rats.

Haley, M.V., D.W. Johnson, W.T. Muse and W.G. Landis. 1988. Aquatic Toxicity and Fate of Brass Dust. Aquatic Toxicology and Hazard Assessment. V. 10. American Society for Testing and Materials, Philadelphia, PA. Pp. 468-479.

A series of environmental bioassays and fate studies were performed on brass dust using the standardized aquatic microcosm (SAM), including *Daphnia magna* and green algae. Fate studies indicate that brass rapidly disassociates into Cu(++) and Zn(++) ions at low pH. At pHs above neutrality the disassociation is markedly slower.

Haley, M.V. and C.W. Kurnas. 1993. Toxicity and Fate Comparison Between Several Brass and Titanium Dioxide Powders. ERDEC-TR-094. Edgewood Research, Development and Engineering Center, U.S. Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.

Brass flakes and four brands of titanium dioxide were tested to determine their toxicities to water flea (*Daphnia magna*), green algae (*Ankistrodesmus falcatus* and *Selenastrum capricornutum*). The fate of the brass material was determined in fresh water of varying hardness, in synthetic marine salt water (30 ppt), and in physiological saline solution (9 ppt). This citation is also included under titanium dioxide.

Hardy, J.T., E.A. Crecelius, C.E. Cowan and R.S. Wentzel. 1988. Toxicity and metal speciation relationships for *Daphnia magna* exposed to brass powder. *Arch Environ Contam Toxicol.* 17(5):575-581.

The authors conducted a study to assess the fate and potential toxicity of brass powder deposited on water surfaces. They developed laboratory microcosms containing like water to quantify the effects of surface dose, pH, alkalinity, microbiota, and sediment binding on the availability and subsequent toxicity of Cu and Zn from brass powder. Eight days after deposition on the water surface, high concentrations of Cu and Zn remained in the aquatic surface microlayer (upper 33 μm). Concentrations of total Cu and Zn in the subsurface bulkwater were reduced by the presence of bottom sediment but were little affected by biota. Toxicity of brass powder to *Daphnia magna* increased with increasing surface deposition (dose) and decreased with increasing water pH and alkalinity. Little or no toxicity occurred at brass powder surface doses of 50 mg/m² and 1,000 mg/m² for low- and high-alkalinity environments, respectively. Geochemical modeling suggested that toxicity resulted from concentrations of both Cu²⁺ and Zn²⁺ ions in solution.

Landis, W.G., N.A. Chester, M.V. Haley, D.W. Johnson and W.T. Muse. 1988. Evaluation of the Aquatic Toxicity and Fate of Brass Dust Using the Standard Aquatic Microcosm. Department of Defense [DODXA], July 1988, 24p. Technical Report. CRDEC-TR-88116. AD-A200 271/5/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

The impact of brass dust on a model aquatic ecosystem, the Standard Aquatic Microcosm (SAM), was investigated. The study included the interaction of trophic levels, community structure, and metabolism of nutrients, and chemical breakdown and dispersion of the brass dust.

Wentzel, R.S. and M.A. Guelta. 1987. Toxicity of brass powder in soil to the earthworm *Lumbricus terrestris*. *Environ Toxicol Chem.* 6(10):741-745.

Brass powder applied to soil was shown to have sublethal effects on earthworms at concentrations of 120 $\mu\text{g/g}$ and above.

Wentzel, R.S. and M.A. Guelta. 1988. Avoidance of Brass Powder Contaminated Soil by the Earthworm *Lumbricus terrestris*. *Environ Toxicol Chem.* 7(3):241-244.

Tests of the avoidance of brass powder contaminated dust by the earthworm *Lumbricus terrestris* were conducted. Concentrations of brass powder ranged from 0 to 200 µg/g. Avoidance was significant ($p < 0.001$) at brass concentrations as low as 38 µg/g. The authors found avoidance to be a more sensitive indicator of brass powder impacts than sublethal effects measured by weight loss.

Yeh, H.C., M.B. Snipes, A.F. Eidson, C.H. Hobbs and M.C. Henry. 1990. Comparative Evaluation of Nose-Only Versus Whole-Body Inhalation Exposures for Rats: Aerosol Characteristics and Lung Deposition. *Inhal Toxicol.* 2(3):205-221.

Possible differences between two kinds of inhalation exposure systems, nose-only and whole-body, were investigated with consideration of exposure environment and lung burdens due to aerosol inhalation. Each of the two exposure atmospheres used had aerosol mass concentrations of about 100 mg/m³. The first was titanium dioxide (TiO₂) and the second was a respirable powder of brass. Using male and female F344-rats, both types of inhalation chambers were found to perform well; coefficients of variation were less than 10% for both temporal and spatial variations. The lung burden data for TiO₂ agreed well with literature values but those for the brass differed. Differences were also noticed between nose-only and whole-body exposures. This citation will also be included under *Titanium Dioxide*.

(2-Chlorobenzal)malononitrile (CS)

The riot control agent (2-Chlorobenzal)malononitrile (CS) (also noted as (o-Chlorobenzal)malonitrile) exists in both vapor and particulate form after use. The vapor phase degrades within approximately 100 hours, while the particulates are removed by both wet and dry deposition. CS is not particularly mobile in soils and sediments, and is expected to sorb to particles. Volatilization is unlikely. CS converts to free cyanide in the body via metabolism, and this conversion is largely responsible for observed toxicities.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for (2-Chlorobenzal)malononitrile.

Environmental Fate and Transport

If (2-chlorobenzal)malononitrile is released to air, a vapor pressure of 3.4×10^{-5} mm Hg at 20°C indicates it will exist in both the vapor and particulate phases in the ambient atmosphere. Vapor phase (2-chlorobenzal)malononitrile will be degraded in the atmosphere by reacting with photochemically produced hydroxyl radicals. The half-life for this reaction in air is estimated to be 110 hours. Particulate phase (2-chlorobenzal)malononitrile can be removed from the atmosphere by both wet and dry deposition.

If released to soil, (2-chlorobenzal)malononitrile is expected to have low mobility based upon an estimated K_{oc} of 1700. Analysis of snow samples near a detonation of a (2-chlorobenzal)malononitrile tear gas grenade in a Norwegian forest found detectable levels (0.3 ug) in snow 70 meters from the detonation site 29 days after the detonation. Dusts or powders of (2-chlorobenzal)malononitrile that have settled to the ground after use as a riot control agent can remain active for as long as 5 days. If the compound was formulated with a silicone water repellent, it may persist for as long as 45 days (Demek, 1970). Volatilization from moist soil surfaces is not expected to be an important fate process based upon an estimated Henry's Law constant of 1.0×10^{-8} atm-m³/mole. The vapor pressure suggests that (2-chlorobenzal)malononitrile will not volatilize from dry soil surfaces.

The estimated K_{oc} suggests that (2-chlorobenzal)malononitrile will adsorb to sediments in the water column. Volatilization from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant. If released to water or soil, the major degradation process is expected to be hydrolysis. Aqueous hydrolysis experiments in seawater have determined hydrolysis half-lives of 281.7 min. at 0 °C and 14.5 min. at 25 °C. However, actual environmental degradation rates may be much slower because the rate at which (2-chlorobenzal)malononitrile dissolves in water can be very slow. (2-chlorobenzal)malononitrile released to water could float and travel for considerable distances before it dissolves.

Brooks, M.E., P.M. Davis and S. Sass. 1976. Demilitarization of CS I. Chemical Disposal of CS by Hydrolysis. NTIS. ADA-A033 469.

This study was focused on the chemical disposal of CS (tear gas or 2-chlorobenzal)malononitrile) by conversion to a salable product. Alkaline hydrolysis of CS was selected as the simplest means of converting CS to a salable product, o-chloro-benzaldehyde.

Forgang, J. and K.R. McIntosh. 1996. Case study: fate, transport, and remediation of tear gas chemicals in groundwater. Hazard Ind Wastes Proc Mid Atl Ind Waste Conf, Technomic Publ Co Inc, Lancaster PA. Pp. 351-358.

Extensive investigations of the fate and transport of buried mixture of CNS tear gas chemicals were carried out. This included investigation of chemical reaction and biodegradation of 2-chloroacetophenone, chloropicrin, and chloroform; hydraulic testing of fractured bedrock, and treatability studies for removal of the CNS tear gas constituents from groundwater. Monitoring data from the CNS disposal area are presented as an isoconcentration contour map for volatile organic compounds. The treatability studies showed that air stripping and additional activated carbon adsorption can be used to remove the tear gas constituents from groundwater.

Leadbeater, L., G.L. Sainsbury and C. Utley. 1973. Ortho-Chlorobenzylmalono nitrile: A metabolite formed from ortho-Chlorobenzylidenemalononitrile (CS). *Toxicol Appl Pharmacol.* 25(1):111-116.

Chlorobenzylmalononitrile (CSH₂) was identified by mass spectrometry as a metabolite of o-chlorobenzylidenemalononitrile. The reduction of the benzylidene double bond in CS decreases its toxicity. The LD₅₀ (i.v.) of CSH₂ in mice is 78.4 mg/kg, higher than that of CS. The irritancy of CSH₂ measured in the guinea pig blepharospasm test is 15 times less than that of CS. Evidence is presented that suggests the reduction of CS to CSH₂ in blood is catalyzed by an enzyme in the erythrocyte cytoplasm and that NADPH is a specific coenzyme.

Bioaccumulation and Trophic Transfer

As seen from Table 2, the predicted BCF of 30 suggests the potential for bioconcentration is low. Bioconcentration is not expected when (2-Chlorobenzal) malononitrile is present in the dissolved form as hydrolysis will occur rapidly (Demek, 1970). However, no empirical studies from the literature were identified that would support or refute that bioconcentration occurs.

Toxicity

Abram, F.S.H. and P. Wilson. 1979. The acute toxicity of o-chlorobenzylidene-malononitrile to rainbow trout (*Salmo gairdneri*). *Water Res.* 13(7):631-636.

A description of the acute toxicity of trout to CS and its two principal hydrolysis products (that appear to behave synergistically) is provided. CS gas pathways into the aquatic environment were also discussed.

Ballantyne, B. and S. Callaway. 1972. Inhalation toxicology and pathology of animals exposed to o-chlorobenzylidene-malononitrile. *Med Sci Law.* 12(1):43-65.

This study was conducted to determine the inhalation toxicity of CS smoke. Rats, rabbits, guinea pigs and mice were exposed to artificially high concentrations of smoke (about 4 g/m³) for periods of 5 to 20 minutes and also to lower concentrations (about 30 to 40 mg/m³) for 5 hr/day for several successive days.

Ballantyne, B., M.F. Gazzard, D.W. Swanston and P. Williams. 1974. The ophthalmic toxicology of o-chlorobenzylidene malononitrile (CS). *Arch Toxicol.* 32(3):149-168.

Rabbit eyes were contaminated with the riot control agent CS in solution (0.5 to 10% in polyethylene glycol 300), as a solid (0.5 to 5 mg), and as a pyrotechnically generated smoke (15 min exposure to 6 g/m³). CS caused lachrymation, blepharitis and conjunctival irritation by all the methods of contamination. The severity and duration increased with the amount of material applied. Effects were most severe with CS in solution, less with solid, and least marked with smoke. Mild and transient keratitis and iritis occurred with solutions containing 1% CS, being more severe and prolonged with the higher concentrations. Damage was due to CS, and not to its products of hydrolysis. Keratitis was not seen after exposure to smoke containing CS and superficial corneal damage of short duration occurred only in a few animals treated with 5 mg solid CS. A concentration-dependent increase in intraocular tension of less than one hour duration occurred with solutions of CS.

Ballantyne, B. and D.W. Swanston. 1978. The comparative acute mammalian toxicity of 1-chloroacetophenone (CN) and 2-chlorobenzylidene malononitrile (CS). *Arch Toxicol.* 75-96.

The comparative acute toxicity of two peripheral sensory irritant materials 1-chloroacetophenone (CN) and 2-chlorobenzylidene-malononitrile (CS), was investigated in several species of small mammal (rat, rabbit, mouse, guinea pig) using solutions in polyethylene glycol 300 for i.v., i.p. and oral administration, and as pure aerosols for inhalation exposure. The comparative potency for inducing primary contact dermatitis was studied. CN and CS were about equitoxic by i.v. and i.p. injection.

tion, but CS was significantly less toxic by the oral and inhalation routes and less likely to cause non-lethal tissue damage than CN.

Brewster, K., J.M. Harrison, L. Leadbeater, J. Newman and D.G. Upshall. 1987. The Fate of 2-Chlorobenzylidene-Malononitrile (CS) in Rats. *Xenobiotica*. 17(*):911-924.

The metabolic fate of 2-chlorobenzylidene-malononitrile (2698411) (CS) was investigated in rats and mice. Rats and mice given radio labeled CS, 2-chlorobenzyl-alcohol (17849386) (CB), and 2-chlorobenzyl-malononitrile (dihydro-CS) were placed in metabolism cages for 96 hours for the collection of urine, feces, and expired air. Radioactivity was determined by liquid scintillation counting, and identification of the purified metabolites was performed by gas liquid chromatography and mass spectrometry. Autoradiography was also performed on mice injected intravenously with radio labeled CS. The amount of CS excreted in the urine of rats ranged from 44 to 100 percent for doses of 0.08 to 159 micromoles per kilogram (micromol/kg) body weight. Approximately 95% of CB was excreted in the urine. Insignificant amounts of CS and CB were collected in the feces. The urine and feces accounted for approximately 80% and 18% of the dihydro-CS administered respectively. Dose related increases in urinary thiocyanate and malononitrile excretion were observed at CS doses of up to 159 micromole/kg. Autoradiography showed that within 1 hour of administration the majority of the radioactivity was confined to the gastrointestinal tract and urinary bladder. The authors conclude that CS is metabolized primarily to CB that is then oxidized to chlorobenzaldehyde and conjugated with glycine or reduced to 2-chlorobenzyl-alcohol and conjugated with cysteine.

Debarre, S., L. Karinthe, S. Delmanche, C. Fuche, P. Desforages and J.H. Calvet. 1999. Comparative acute toxicity of o-chlorobenzylidene malononitrile (CS) and oleoresin capsicum (OC) in awake rats. *Hum Exp Toxicol*. 18(12):724-730.

This study was performed to compare acute respiratory effects of o-chlorobenzylidene-malononitrile (CS), oleoresin capsicum (OC) and their respective solvents in awake rats, using an integrated system of nose-only exposure and multiple monitoring of breathing.

Delamanche, S., P. Desforages, S. Morio, C. Fuche and J.H. Calvet. 2001. Effect of oleoresin capsicum (OC) and ortho-chlorobenzylidene-malonitrile (CS) on ciliary beat frequency. *Toxicology*. 165(2-3):79-85.

This study evaluated the effects of ortho-chlorobenzylidene-malononitrile (CS) and oleoresin capsicum (OC) on ciliary beat frequency (CBF) of mouse tracheal rings.

Frankenberg, L. and B. Sorbo. 1973. Formation of cyanide from o-chlorobenzylidene-malononitrile and its toxicological significance. *Arch Toxicol.* 31(2):99-108.

Mice received o-chlorobenzylidene-malononitrile (CS) by i.p. injection (0.5 LD₅₀) or by aerosol exposure (20,000 mg/min/m³). Increased excretion of thiocyanate in the urine was observed indicating a transformation of CS to cyanide in vivo. Determinations of cyanide in whole blood after i.p. administration of CS verified a rapid transformation of the agent to cyanide. A correlation between the time course of cyanide levels and symptoms was observed. Toxicity of injected CS was significantly reduced by pretreatment with thiosulfate, slightly reduced by nitrite and not affected by CO₂EDTA. Thiocyanate excretion, blood cyanide levels and protective effect of antidotes were also evaluated after administration of 0.5 LD₅₀ of malononitrile and potassium cyanide. The importance of cyanide formation for the toxicity of CS was discussed.

Nagarkatti, M., P.S. Nagarkatti and C.D. Raghuveeran. 1981. Short-term Toxicity Studies of o-Chlorobenzylidene-Malononitrile on Humoral Immunity in Mice. *Toxicol Lett.* 8(1-2):461-465.

The effect of o-chlorobenzylidene-malononitrile (CS) on the immune system was studied in mice given 8 mg/kg and 16 mg/kg body weight i.p. of the compound daily for ten days.

Paradowski, M. 1979. Metabolism of toxic doses of o-chlorobenzylidene malononitrile in rabbits. *Pol J Pharmacol Pharm.* 31(6):563-572.

The authors quantitatively estimated the primary metabolic pathways of o-chlorobenzylidene-malononitrile (CS) in rabbits following i.v. administration of doses corresponding to 0.5 LD₅₀ - 1.0 LD₅₀. Concentration of CS and its basic metabolites in the blood in vivo and in vitro were determined by gas chromatography. CS was subjected to two independent reactions: hydrolysis (which is dominating) and reduction. The products of hydrolysis were o-chlorobenzaldehyde (o-CBAld) and malononitrile (MN). Because o-CBAld is more toxic than MN and CS, the toxic actions of CS can be ascribed to o-CBAld. The reduction of CS resulted in formation of o-chlorobenzyl-malononitrile (CSH₂) and represents an organismal detoxication process. Biotransformation of CS proceeds mainly in the blood, but the liver, in contrast

to kidneys, plays an important part in the CS biotransformation. CS and its basic metabolites: o-CBAld and CSH₂ seem to be reactive compounds in the rabbit body as judged from the short half-life times in the blood.

Rietveld, E.C., L.P.C. Delbressine, T.H.J.M. Waegemaekers and F. Seutter-Berlage. 1983. 2-Chlorobenzylmercapturic Acid, A Metabolite of the Riot Control Agent 2-Chlorobenzylidene-Malononitrile (CS) in the Rat. *Arch Toxicol.* 54(2):139-144.

The effects of 2-chlorobenzylidene-malononitrile (CS) were investigated in rats. CS was administered intraperitoneally (ip) once in a dose of 12.5 mg/kg to male Wistar-rats. Thin layer and preparative gas chromatography (GC) was performed on glass plates. Quantitative determination of mercapturic acid excretion in urine was made by injecting 12 rats ip with a single dose of CS. The Ames Salmonella/microsome assay for mutagenicity was performed with Salmonella-typhimurium TA-100. Bacterial toxicity was monitored by microscopic examination of the background lawn of test plates. After a single administration of CS i.p., only one mercapturic-acid could be detected. No mutagenic effect was detected using CS or any of the other compounds tested. At concentrations of CS higher than 1000 micrograms per plate, some bacterial toxicity appeared. With rat liver homogenate, the bacterial toxicity of CS was slightly stronger. The authors concluded that after a single i.p. administration of CS to rats in the urine, only mercapturic acid could be determined by GC in a small quantity.

Dibenz(b,f)-1,4-oxazepine (CR)

Dibenz(b,f)-1,4-oxazepine is a riot control agent with very similar properties as 2-chlorobenzalmalononitrile. However, there is little information available on the physical and chemical properties, fate and effects, potential for bioaccumulation, and chronic toxicity for this constituent. Most of the studies available for dibenz(b,f)-1,4-oxazepine focus on acute effects associated with inhalation exposures.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for dibenz(b,f)-1,4-oxazepine.

Harrison, J.M., T.D. Inch and D.G. Upshall. 1978. The synthesis and chemistry of (11-14C)-dibenz(b,f)-1,4-oxazepine. *J Labelled Compd Radiopharm.* 14(3):375-380.

The chemical makeup and synthesis reactions were presented in this report.

Environmental Fate and Transport

Haley, M.V., E.L. Vickers, T-C. Cheng, J. Defrank, T.A. Justus and W.G. Landis. 1989. Biodegradation and reduction in aquatic toxicity of the persistent riot control material 1-4-dibenzoxazepine. *Aquatic Toxicology and Risk Assessment*; 13th Symposium, Atlanta, Georgia. April 16-18, 1989.

Abstract or article was not available.

Bioaccumulation and Trophic Transfer

Table 2 provides the predicted BCF and Log K_{ow} for dibenz(b,f)-1,4-oxazepine. These values would suggest the potential for moderate bioconcentration, however, we did not identify any empirical studies that would support or refute this statement.

Toxicity

Balfour, D.J.K. 1978. Studies on the uptake and metabolism of dibenz(b,f)-1,4-oxazepine (CR) by guinea pig cornea. *Toxicology*. 9(1-2):11-20.

The uptake and metabolic fate of the sensory irritant dibenz(b,f)-1-4-oxazepine (CR) was tested on guinea pig cornea. Primary and final metabolites and toxicokinetics of the uptake and metabolism are also discussed.

Ballantyne, B., M.F. Gazzard, D.W. Swanston and P. Williams. 1975. The comparative ophthalmic toxicology of 1-chloroacetophenone (CN) and dibenz(b,f)-1,4-oxazepine (CR)). *Arch Toxicol*. 34(3):183-201.

Rabbit eyes were contaminated with 1-chloroacetophenone (CN) and dibenz (b,f)-1:4-oxazepine (CR) in solution (1-10% in polyethylene glycol 300), as a solid (0.1 mg to 5 mg), and as aerosols (15 min exposure to 360 mg/m³ to 719 mg/m³). In solution, CN caused marked and persistent inflammatory effects, the severity and duration being related to the concentration used. Corneal damage was marked and persistent with 5% and 10% solutions; the lowest concentration causing just detectable keratitis in a small proportion of animals was 2%. Solid CN was even more damaging to the eye than similar amounts in solution. In marked contrast, CR in solution caused mild to moderate inflammatory effects, usually of only a few days duration, even at the higher concentrations. With 1% and 2%, these effects were just detectable to mild,

lasting for 24 hours or less. Just detectable keratitis of usually only a few days duration was caused by 10% CR. The lowest concentration causing just detectable keratitis in a small proportion of treated animals was 5%. Solid CR merely caused minor irritation of the conjunctivae and eyelids for about 1 hour. Aerosols of CN and CR did not damage the eye, but irritation of the lids and conjunctivae was more marked and persistent with CN. Solutions of CN and CR caused concentration-related increases in corneal thickness and intraocular tension, being more marked and sustained with CN.

Ballantyne, B. 1977. The acute mammalian toxicology of dibenz(b,f)-1,4-oxazepine. *Toxicology*. 8(3):347-380.

Dibenz(b,f)-1,4-oxazepine (CR), a potent peripheral sensory irritant material, has a very low acute lethal and sub-lethal toxicity by i.v., i.p., oral, percutaneous and inhalation routes to several species of laboratory mammal (rats, rabbits, guinea pigs, mice). There was no organ-specific (liver, spleen, adrenal, thymus, kidney, lung) pathology. Comparison of the acute toxicity of CR with that of two other peripheral sensory irritants, 1-chloroacetophenone (CN) and 2-chlorobenzylidene malononitrile (CS), shows CR to be significantly less toxic than either of them. Pyrotechnically generated CR smoke was more toxic than pure (thermally generated) aerosols of CR. This was due to the presence of pyrotechnic decomposition products in the atmosphere from the burning of the smoke-generating composition. The median lethal toxicity of pyrotechnically generated CR smoke was significantly less than that of either pyrotechnically generated CN or CS smokes. Short-term cumulative toxicity did not occur following multiple oral dosing with CR. The acute toxicology of three ether intermediates encountered in the synthesis of CR from 1-chloro-2-nitrobenzene and sodium phenoxide (2-nitrodiphenyl ether, 2-aminodiphenyl ether and 2-formamidodiphenyl ether) was investigated. All three ethers were less acutely toxic than CR itself.

French, M.C., J.M. Harrison, T.D. Inch, L. Leadbeater, J. Newman, D.G. Upshall and G.M. Powell. 1983. The Fate of Dibenz(b,f)-1,4-oxazepine in the Rat, Rhesus Monkey, and Guinea Pig. Part I. Metabolism in Vivo. *Xenobiotica*. 13(6):345-359.

The authors studied the metabolism of dibenz(b,f)-1,4-oxazepine (CR) in rats, monkeys, and guinea-pigs. Blood, urine, feces, and expired air samples were collected and assayed to determine the disposition of CR.

French, M.C., J.M. Harrison, J. Newman, D.G. Upshall and G.M. Powell. 1983. The Fate of Dibenz(b,f)-1,4-oxazepine in the Rat. Part III. The Intermediary Metabolites. *Xenobiotica*. 13(6):373-381.

The authors evaluated the fate of dibenz(b,f)-1,4-oxazepine (CR) metabolites in rats. The authors conclude that the major metabolic fate of CR in the rat is oxidation of the lactam, followed by ring hydroxylation, sulfation, and urinary elimination.

Furnival, B., J.M. Harrison, J. Newman, D.G. Upshall. 1983. The Fate of Dibenz(b,f)-1,4-oxazepine in the Rat. Part II. Metabolism in Vitro. *Xenobiotica*. 13(6):361-372.

The authors evaluated in vitro metabolism of dibenz(b,f)-1,4-oxazepine (CR) in rats.

Husain K., P. Kumar and R.C. Malhorta. 1991. A comparative study of biochemical changes induced by inhalation of aerosols of o-chloroacetophenone and dibenz(b,f)-1,4-oxazepine in rats. *Indian J Med Res Sect B*. 94:76-79.

The biochemical changes in blood samples of rats at several intervals after O-chloroacetophenone (CN) and dibenz (b,f)-1,4 oxazepine (CR) were studied. After a single subacute (1/10 LC50) exposure, both the compounds induced hyperglycaemia that was abolished within 24 hours. The level of plasma urea was unaltered. CR exposed animals did not show any significant changes in plasma GOT, acid and alkaline phosphatase activities at different intervals. However, in CN exposed animals, a significant elevation of the activities of GOT, GPT, acid and alkaline phosphatase was observed at different intervals. All the parameters became normal within seven days after the exposure. It was concluded that inhalation of CN aerosols can lead to tissue damaging effects in rats.

Johnson, D.W., M.V. Haley and W.G. Landis. 1989. The aquatic toxicity of the sensory irritant and riot control agent dibenz(b,f)-1,4-oxazepine (CR). *Aquatic Toxicology and Risk Assessment*; 13th Symposium, Atlanta, Georgia. April 16-18, 1989.

No abstract or article was available.

Kumar, P., R. Vijayaraghaven, S.C. Pant, A.S. Sachan and R.C. Malhotra. 1995. Effects of Inhaled Aerosol of 1-Chloroacetophenone (CN) and

Dibenz(b,f)-1,4-oxazepine (CR) on Lung Mechanisms and Pulmonary Surfactants in Rats. *Hum Exper Toxicol.* 14(5):404-409.

The effects of 1-chloroacetophenone (CN) and dibenz(b,f)-1,4-oxazepine (CR) on lung mechanics and pulmonary surfactant production were studied in rats. Male Wistar-rats were exposed to 0 or 0.0626 milligram per liter (mg/l) CN or 1.4061 mg/l CR aerosols for 24 hours. They were then killed and the lungs were removed and weighed. The dynamic surface tension of the lungs was measured. Some lungs were perfused and changes in phospholipid concentration and composition in the perfusates were determined. Other lungs were inflated and total lung capacity, volume of air at 0 and 5 centimeters water pressure, and lung compliance were determined. The lungs were examined for histomorphological changes. Both CN and CR induced transient respiratory distress lasting about 2 hours after the start of exposure. Relative lung weights were not affected by either agent. CN, but not CR, significantly increased dynamic surface tension. CN significantly increased lung compliance and CR significantly decreased lung compliance. CN significantly decreased total lung phospholipid and sphingomyelin concentrations. CR did not affect total phospholipid concentration, but significantly increased sphingomyelin concentration and significantly decreased phosphatidylcholine and ethanolamine concentrations. CN induced bronchiolar epithelial cell degeneration and alveolar septal wall thickening that was accompanied by an influx of mononuclear cells into the alveoli. CR induced enlarged air spaces and mild perivascular edema. The authors conclude that CN demonstrates more inhalation toxicity than CR. The pulmonary toxicity of CN is probably due to lung damage.

Kumar, P. and A.S. Sachan. 1998. Evaluation of 1-chloroacetophenone (CN) and dibenz(b,f)-1,4-oxazepine (CR) induces respiratory tract sensory irritation following a simple inhalation exposure method in mice. *Biomed Environ Sci.* 11(2):171-178.

Sensory irritation of the upper respiratory tract was induced in mice by inhalation of vapors, generated under thermal stress of two tear gases: 1-chloroacetophenone (CN) and dibenz (b, f)-1,4 oxazepine (CR).

Upshall, D.G. 1974. Effects of dibenz(b,f)-1,4-oxazepine (CR) upon rat and rabbit embryonic development. *Toxicol Appl Pharmacol.* 29:301-311.

The effects of dibenz b, f (1,4) oxazepine on the embryonic development of rats and rabbits were evaluated. Pregnant rats and rabbits were exposed to CR aerosols at concentrations of approximately 2, 20, and 200 mg/m³ for 5 to 7 minutes on days 6-

15 and 6-18 of pregnancy, respectively. In addition, rats and rabbits were dosed intragastrically with CR solutions on alternate days throughout the period of organogenesis at doses of 0.2 mg/kg -100 mg/kg. Rabbits were injected i.v. on three consecutive days with 0.33 mg/kg of the acute i.v. LD₅₀. No teratogenic response that could be attributed to CR was noted in any case, and only in the i.v. studies were embryolethal effects observed. These effects may have been due to precipitation of CR from the saturated solution upon injection.

Titanium Dioxide

Titanium dioxide particles are used to block detection of light waves in the visible portion of the electromagnetic spectrum (NRC, 1999). Titanium tetrachloride is formed in smoke from titanium dioxide munitions that rapidly hydrolyze to hydrogen chloride and titanium dioxide.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for titanium dioxide.

Environmental Fate and Transport

Cassel, G., S. Fredriksson and I. Faengmark. 1992. Zink-och Titanroek: Kemisk Sammansaettning och Fysikaliska Egenskaper (Zinc and Titanium Smoke: Chemical Composition and Physical Characteristics). Technical Report. October 1992. FOA-C-40277-4.9, ETN-93-93759. National Defense Research Establishment, Umea (Sweden). NBC-Defense Dept.

Smoke generated from zinc/hexachloroethane and titanium dioxide/hexachloroethane pyrotechnical pictures in a closed space were investigated for the following parameters: smoke concentration, particle size distribution, and chemical composition of the smoke. Zinc hydroxy are strong acids formed during combustion of the zinc munition. The titanium tetrachloride formed in smoke from the titanium dioxide munition will rapidly hydrolyze to hydrogen chloride and titanium dioxide. Several chlorinated organic substances are formed from both types of smoke munitions during combustion. Some of these substances have well-documented toxic and mutagenic effects; for example: hexachlorobenzene, hexachlorobutadiene, and chlorinated dibenzofurans and dibenzodioxins. The amount for byproducts formed is higher from the titanium dioxide/hexachloroethane munition than from the zinc munition. This citation is also included under *Hexachloroethane*.

Haley, M.V. and C.W. Kurnas. 1993. Toxicity and Fate Comparison Between Several Brass and Titanium Dioxide Powders. ERDEC-TR-094. Edgewood Research, Development and Engineering Center, US Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.

Brass flakes and four brands of titanium dioxide were tested to determine their toxicities to *Daphnia magna* (water flea), *Ankistrodesmus falcatus* (green algae), and *Selenastrum capricornutum* (green algae). The fate of the brass material was determined in fresh water of varying hardness, in synthetic marine salt water (30 ppt), and in physiological saline solution (9 ppt). This citation is also included under *Brass Flakes*.

da Silva, E.M., M.F.T. Navarro, A.F. Barros, M.F.V. Mota and C.B.A. Chastinet. 2000. Metals in the sediments of Jaua Lake (Camacari, Bahia, Brazil) following an episode of industrial contamination. *Aquat Ecosyst Health Manage.* 3(4):509-514.

The contamination of sediments caused by the deposition of industrial residues from titanium dioxide production in sand dunes near a wetland was assessed through atomic absorption spectrometry.

Bioaccumulation and Trophic Transfer

Coulon, J., M. Truchet and R. Martoja. 1987. Chemical features of mussels (*Mytilus edulis*) in situ exposed to an effluent of the titanium dioxide industry. *Ann Inst Oceanogr.* 63(2):89-100.

Levels of contaminants in mussels located near a titanium dioxide plant effluent discharge were analyzed.

Toxicity

Bellmann, B., H. Muhle, O. Creutzenberg, S. Takenaka and W. Koch. 1987. Untersuchungen ueber den Einfluss nicht-toxischer Staeebe auf die Lungenreinigung und die Funktion der Alveolarmakrophagen. Schlussbericht. (Investigation of the influence of 'nuisance' dust inhalation on lung clearance and function of alveolar macrophages. Final report). TIB/A90-81062INW. Prepared for Bundesministerium fuer Forschung und Tech-

nologie, Bonn (Germany, F.R.) by Fraunhofer-Inst. fuer Toxikologie und Aerosolforschung, Hanover (Germany, F.R).

The effect of three different nuisance dusts on rats was investigated. Test materials were titanium dioxide, PVC powder, and iron powder with the densities 4.3 g/cm, 1.3 g/cm, and 8 g/cm (3), respectively. Female Fischer rats were exposed "nose-only" for 25 hours per week.

BIBRA Working Group. 1990. Titanium Dioxide. Toxicity Profile. The British Industrial Biological Research Association.

Toxicological profile for titanium dioxide.

Haley, M.V. and C.W. Kurnas. 1993. Toxicity and Fate Comparison Between Several Brass and Titanium Dioxide Powders. ERDEC-TR-094. Edgewood Research, Development and Engineering Center, U.S. Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.

Brass flakes and four brands of titanium dioxide were tested to determine their toxicities to *Daphnia magna* (water flea), *Ankistrodesmus falcatus* (green algae), and *Selenastrum capricornutum* (green algae). The fate of the brass material was determined in fresh water of varying hardness, in synthetic marine salt water (30 ppt), and in physiological saline solution (9 ppt). This citation is also included under *Brass Flakes*.

Hilaski, R.J., J.D. Bergmann, J.C. Carpin, W.T. Muse, Jr. and S.A. Thomson. 1992. Acute Inhalation Toxicity Effects of Explosively Disseminated XM82 Grenade Titanium Dioxide. CRDEC-TR-363. Chemical Research, Development and Engineering Center, US Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.

The purpose of this study was to determine acute toxicological effects in rats exposed by inhalation to explosively disseminated TiO₂ and the resultant by-products present in the aerosol. Groups of male, Fisher 344 rats were exposed by nose-only inhalation to three concentrations of TiO₂ dust for 30 minutes. The highest concentration was used as the "worst case" field concentration. Two other concentrations were selected to produce a "no adverse effect" level. Air-exposed and fuse/fuel exposed rats served as controls.

Karlsson, N., G. Cassel, I. Fangmark and F. Bergman. 1984. The Inhalation Toxicity of Screening Smokes. *J Toxicol Clin Toxicol.* 23(4-6).

This citation is included in Proceedings of the XI International Congress of the European Association of Poison Control Centers, Stockholm, Sweden, June 17-20, 1984. No abstract was available.

Karlsson N., G. Cassel, I. Fangmark and F. Bergman. 1986. A Comparative Study on the Acute Inhalation Toxicity of Smoke from TiO₂-Hexachloroethane and Zn-Hexachloroethane Pyrotechnic Mixtures. *Arch Toxicol.* 59(3):160-166.

This study determined the acute inhalation toxicity to rats of smoke generated from pyrotechnic mixtures of titanium-dioxide plus hexachloroethane (HC), and zinc plus HC. Female Sprague-Dawley-rats were exposed to smoke in a chamber in the static mode for 1.25 to 10 minutes or to pure TiCl₂ gas or ZnCl₂ aerosol in an inhalation chamber in the dynamic mode for 10 minutes. TiO₂-HC smoke mixtures had low acute toxicity, but the smoke was irritating to eyes and nasal mucous membranes. Zn-HC was much more toxic; at the highest concentrations of Zn-HC, animals died after exposures of 1.25 and 2.5 minutes. Dyspnea developed within 10 to 15 min post-exposure. Gross and microscopic pathological changes were found in the lungs; changes were more pronounced at higher doses. TiCl₄ exposure caused irritation, but no rats died after exposure. ZnCl₂ did not cause irritation, but signs of respiratory distress developed gradually. The aerosol was lethal at and above concentrations of 950 milligrams zinc/cubic meter (mg/m³). Microscopic findings included atelectasis, hyperemia, hemorrhages, and edema. No clear dose response relationship was found. The authors conclude that the difference between the two types of smoke is explained by the difference in toxicity of TiCl₄ and ZnCl₂. This citation is also included under *Hexachloroethane*.

Vincent, J.H., A.D. Jones, A.M. Johnston, C. McMillan, R.E. Bolton and H. Cowie. 1987. Accumulation of Inhaled Mineral Dust in the Lung and Associated Lymph Nodes: Implications for Exposure and Dose in Occupational Lung Disease. *Ann Occup Hyg.* 31(3):375-393.

The accumulation of inhaled mineral dust in the lungs and associated lymph nodes was studied in rats. Male SPF-Wistar-rats were exposed to respirable fractions of titanium-dioxide or quartz at concentrations of 1 mg/m³ to 90 mg/m³ and 0.1 mg/m³ to 30 mg/m³, respectively, for 7 hours daily 5 days per week for 222 or 684 days. The rats were killed at various times up to 38 days after the last exposure, and lungs as

well as hilar and mediastinal lymph nodes were removed for analysis for titanium dioxide or quartz. The data were fit to a kinetic model for deposition and clearance. For both quartz and titanium dioxide, lung burden increased linearly with exposure time, except for a nonlinear phase occurring early in the exposure period. No quartz or titanium dioxide was detected in lymph nodes at low lung dust burdens. Lymph dust burdens did not significantly increase until a substantial increase in lung burden occurred. The lymph burden of both dusts increased slightly with inhaled dust concentration and exposure time but was generally less than 10% of the lung burden. The data were fit to a model that involved evoking a sequestration compartment in addition to the usual lung, lymph node, and mucociliary compartments. The sequestration compartment described the permanent retention of inhaled dust such that it could not be cleared by way of the mucociliary escalator. The authors conclude that chronic exposure to constant levels of respirable dust results in progressive increase in the lung burden due to sequestration, that transport to the lymph nodes from the deep lung is only significant above a threshold level of lung burden, and that the rate of this transport is proportional to deep lung burden in excess of this threshold level.

Vincent, J.H. and K. Donaldson. 1990. A dosimetric approach for relating the biological response of the lung to the accumulation of inhaled mineral dust. *Inst Occup Med.* 47(5):302-307.

Results from studies of the retention of contrasting mineral dusts inhaled by rats (for periods of up to three months) and the resultant changes in the phagocyte defense system of the deep lung were examined. The dusts used were titanium dioxide (relatively innocuous) and quartz (relatively toxic). The parameters assessed included the accumulation of material in the lung and lymph nodes during chronic exposure and the associated leukocyte response as assessed by bronchoalveolar lavage. The principal findings were that: (a) low level exposure to titanium dioxide produced no measurable inflammation (as indicated by neutrophil recruitment) but higher concentrations (30, 50, and 90 mg/m³) caused the transfer of dust to lymph nodes and first evidence of inflammation; and (b) for quartz, there was a more prominent response and earlier transfer of material to the lymph nodes. The suggested relation between changes in the neutrophil population and dust accumulation was discussed.

U.S. Environmental Protection Agency. 1975. Literature Study of Selected Potential Environmental Contaminants, Titanium Dioxide. Final Report. ADL-C-77354, EPA-68-01-2688, EPA/560/2-75-001. Prepared by Arthur D. Little, Inc., Cambridge, MA for USEPA Office of Toxic Substances, Washington, D.C.

Findings of a comprehensive review of the literature on titanium dioxide are reported. Focus is given to physical and chemical properties of titanium dioxide, environmental exposure factors related to its consumption and use, health and environmental results of exposure, and regulations and standards governing its use.

Yeh, H.C., M.B. Snipes, A.F. Eidson, C.H. Hobbs and M.C. Henry. 1990. Comparative Evaluation of Nose-Only Versus Whole-Body Inhalation Exposures for Rats: Aerosol Characteristics and Lung Deposition. *Inhal Toxicol.* 2(3):205-221.

Possible differences between two kinds of inhalation exposure systems, nose only and whole body, were investigated with consideration of exposure environment and lung burdens due to aerosol inhalation. Each of the two exposure atmospheres used had aerosol mass concentrations of about 100 mg/m³. The first was titanium-dioxide and the second was a respirable powder of brass. Using male and female F344-rats, both types of inhalation chambers were found to perform well; coefficients of variation were less than 10% for both temporal and spatial variations. The lung burden data for TiO₂ agreed well with literature values but those for the brass differed. Differences were also noticed between nose only and whole body exposures. This citation will also be included under *Brass Flakes*.

Polyethylene Glycol

Polyethylene glycols (PEG) are viscous, colorless liquids with varying molecular weights. PEG generally has a low acute and chronic toxicity in animals. Toxic effects to the kidney have occurred from high doses, but studies have found little risk from exposure to PEG at low concentrations (Silverstein, et al. 1984). PEG degrades rapidly under anaerobic conditions, but has longer environmental longevity under aerobic conditions.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for polyethylene glycol.

Environmental Fate and Transport

Dwyer, D.F. and J.M. Tiedje. 1983. Degradation of ethylene glycol and polyethylene glycol by methanogenic consortia. *Appl Environ Microbiol.* 46(1):185-190.

Methanogenic enrichments were isolated from sewage sludge and used to degrade polyethylene glycol. Degradation products and intermediaries were analyzed and recorded.

Muhly, R.L. 1983. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants, Volume 1. Fog Oil, Diesel Fuels, and Polyethylene Glycol (PEG 200). Department of Defense [DODXA], July 1983, 139p. ARCSL-EA-83001-VOL-1. AD-A134 846/5/INW. Prepared by Chemical Research and Development Center, Aberdeen Proving Ground, MD.

The environmental impacts associated with the use of petroleum distillate smokes for testing and training purposes have been reviewed and compiled in this report. Based on the toxicological data gathered and the regulatory aspects associated with the use of these smoke/obscurants it was concluded that this portion of the smoke program will not significantly affect the quality of the human environment. This citation will also be included under *Fog Oil Smoke*.

Watson, G.K. and N. Jones. 1977. The biodegradation of polyethylene glycol by sewage bacteria. *Water Res.* 11(1):95-100.

Several strains of bacteria able to degrade polyethylene glycols (PEG) were isolated from sewage effluent and the effect of molecular weight on biodegradability was determined.

Bioaccumulation and Trophic Transfer

No information is available for this constituent.

Toxicity

Phillips, S.F., A.F. Hofmann and V.S. Chadwick. 1997. Measurements of intestinal permeability using low molecular weight polyethylene glycol (PEG 400). 1. Chemical analysis and biological properties of PEG 400. *Gastroenterology.* 73:241-246.

The biological properties, kinetics of intestinal absorption behavior as a permeability probe, metabolic fate and renal excretion of polyethylene glycol 400 (PEG 400), 1 to 15 g given orally to normal subjects, and the renal excretion of 2 g given i.v. to a dog are reported. The GLC analysis of PEG 400 after its extraction from urine, stool water, or intestinal perfusion fluid is also described. In toxicity studies, 10 times the

maximum dose/kg (0.3 g/kg) was given i.v. to 3 different species of laboratory animals without ill effects. No side effects were noted by subjects who ingested up to 20 g of PEG 400. PEG 400 is nontoxic, not degraded by intestinal bacteria, not metabolized after absorption, and rapidly excreted in urine. The different sized molecular components cross the intestinal epithelium at different rates, allowing characterization of the passive permeability properties of the mucosa.

Silverstein, B.D., P.S. Furcinitti, W.A. Cameron, J.E. Brower and O. White. 1984. Biological Effects Summary Report: Polyethylene Glycol. DE84007984/INW. BNL-51745. Department of Energy [DE], Jan 84, 27p. Prepared by Brookhaven National Laboratory, Upton, NY.

An evaluation of the health effects of polyethylene glycol (PEG) was made to assess its potential use as a substitute for di(2-ethylhexyl) phthalate, which is used as test aerosol in quantitative fit testing of respirators. Toxicological studies were reviewed in this report.

Yamaoka, T., Y. Tabata and Y. Ikada. 1995. Fate of water-soluble polymers administered via different routes. *J Pharm Sci.* 84:349-354.

To investigate the effects of injection site and molecular weight of polymers on the excretion of polymers, mice received either polyethylene glycol or polyvinyl alcohol of varying molecular weights as intraperitoneal (i.p.), subcutaneous (s.c.), or intramuscular (i.m.) injections; blood samples were taken frequently and analyzed for pharmacokinetic parameters. Elimination from the injection sites and translocation from the injection site into the circulation were analyzed.

Graphite Flakes

Graphite flakes are used as an infrared wavelength obscurant, typically as an additive for fog oil smoke. Driver et al. (1993) found little risk, chemically and mechanically, to aquatic or terrestrial systems from obscurant graphite flakes.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for graphite flakes.

National Technical Information Service. 1984. Graphite Powder. June, 1970-October, 1984 (Citations from the NTIS Database). Report for Jun 70-Oct 84. October 1984. PB84-877364.

This bibliography contains citations concerning the properties and characteristics of graphite powder, flakes and particles used alone as well as in combination with other substances.

Environmental Fate and Transport

Driver, C.J., M.W. Ligothke, E.B. Moore and J.F. Bowers. 1991. Generator, mechanical, smoke: For dual-purpose unit, XM56, Yuma Proving Ground, Yuma, Arizona. Environmental Assessment. PNL-7781. Battelle Pacific Northwest Laboratories.

This environmental assessment evaluated the consequences of performing a field test of the XM56 smoke generator at the U.S. Army Yuma Proving Ground, AZ. The XM56 enables the use of fog oil in combination with other materials such as graphite flakes, and is part of an effort to improve the efficiency of smoke generation and to extend the effectiveness of the resulting obscurant cloud to include the infrared spectrum. The planned field operation includes a road test and concurrent smoke-generation trials. Three M1037 vehicles with operation XM56 generators will be road-tested for 100 hours. Smoke will be generated for 30 minutes from a single stationary XM56 four times during the road test, resulting in a total of 120 minutes of smoke generation. The total aerial release of obscurant materials during this test is expected to be 556 kg (1,220 lb) of fog oil and 547 kg (1,200 lb) of graphite flakes. This citation is also included under *Fog Oil*.

Driver, C.J., M.W. Ligothke, W.G. Landis, J.L. Downs and B.L. Tiller. 1993. Environmental and health effects review for obscurant graphite flakes. Final report, 1991 July–1993 May. PNL-8585. DE93040324. Battelle Pacific Northwest Laboratories and U.S. Department of Energy.

The health and environmental effects of obscurant graphite flakes were reviewed and compared to predicted levels of graphite flake material in the field during typical testing and training scenarios. Graphite flake dispersion and deposition for simulated mechanical and pyrotechnic releases were determined using a modified Gaussian atmospheric plume-dispersion model. The potential for wind resuspension of graphite flakes is controlled by weathering processes and incorporation rates in soil.

Guelta, M.A. and R.T. Checkai. 1995. Predictive Ecological Risk Assessment of Graphite Infrared Wavelength Obscurant in a Terrestrial Environment. - Final rept. Oct 93-Dec 94. Technical Report. March 1995. ERDEC-TR-240. AD-A294 363/7. Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

The purpose of this report is to demonstrate the application and utility of employing Ecological Risk Assessment methodologies to predict the environmental impact of proposed testing with graphite flake obscurant materials.

Bioaccumulation and Trophic Transfer

No information is available for this constituent.

Toxicity

Aranyi, C., N. Rajendran, J. Bradof, J. Drummond and B. Levine. 1991. Inhalation Toxicity of Single Materials and Mixtures. Phase 3. Final Report. AD-A242 179/0/GAR. IIT Research Institute. August 28, 1991.

To investigate the potential inhalation hazard of obscurant materials to which military personnel may be exposed during field operations, a four-week whole-body inhalation toxicity study of aerosols of a petroleum-based liquid (PBL) fog oil, a solid particulate (graphite), or PBL/graphite aerosol mixtures was conducted in male F344 rats. Exposures were 4 hours/day, 4 days/week to aerosols of PBL alone (500 mg/m³ or 1000 mg/m³), graphite alone (200 mg/m³) or PBL/graphite aerosol mixtures (500 mg/m³ or 1000 mg/m³ PBL, with 200 mg/m³ graphite). A sixth group was a filtered air control. Animals were monitored throughout the study for clinical signs, body weight gain, and food consumption. Selected biologic end points including histopathology, clinical pathology, pulmonary lavage, pulmonary function, pulmonary bactericidal activity, lung weight/body weight ratio, and hepatic aryl hydrocarbon hydroxylase (AHH) activity were evaluated after the last exposure and after a three week recovery period. This report is also included under *Fog Oil*.

Bowser, L.K., C.T. Phillips and R.S. Wentzel. 1990. Toxicity of Graphite Flakes in Soil to Earthworms. - Final rept. Jun 88-Oct 89. Technical Report. June 1990. CRDEC-TR-129. AD-A224 244/4. Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

Graphite flakes were tested for their toxicity to the earthworm (*Eisenia foetida*). The graphite flakes were tested at 0% (control), 0.05%, 0.10%, 0.50%, and 1.00% concentrations by weight. These concentrations were used in the study by thoroughly incorporating the graphite flakes into an artificial soil mixture composed of sphagnum peat (10%), kaolinite clay (20%), fine sand (69%), and calcium carbonate (1%).

Landis, W.G., N.A. Chester, M.V. Haley, D.W. Johnson and R.M. Tauber. 1988. Evaluation of Graphite for Environmental Toxicity Using the Standard Aquatic Microcosm. Department of Defense [DODXA], Aug 88, 21p. CRDEC-TR-88133. AD-A199 722/0/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

The impact of a graphite dust on an aquatic ecosystem model, the Standard Aquatic microcosm (SAM), was investigated. Graphite dust produced effects that resembled eutrophication in that diversity decreased, ammonia increased, and a photosynthesis/respiration ratio of less than one was observed in the highest concentration. Compared to brass dust, graphite has much less potential to adversely impact aquatic ecosystems.

Colored Smoke

Colored smokes consist of various kinds of dyes. Many of these dyes are used for other purposes, such as cosmetics or for food additives, while others are unique to the military and considerably more hazardous. There are “old” and “new” colored smoke formulations. In the new smoke formulations, several constituents (e.g., benzanthrone, Vat Yellow 4) were replaced by other dyes. Table 4 provides the primary constituents in both the old and new smoke formulations. For the purposes of this survey, and following NAS (1999), the following individual constituents were considered:

- Vat Yellow 4
- 1,4-diaminoanthraquinone
- Benzanthrone
- Solvent Yellow 33
- Solvent Green 33
- Solvent Red 1
- Disperse Red 9
- Disperse Red 11
- 1,4-Diamino-2,3-Dihydroanthraquinone

Dyes are categorized according to their chemical structure and include azo (N=N), anthraquinone, quinoline, and disperse dyes.

Combustion of colored smokes is regulated by adjusting the proportions of oxidant versus combustible material and by using a number of coolants. Tables 5 and 6 provide the expected byproducts from combustion of colored smokes.

Physical-Chemical Properties

Table 2 provides the physical-chemical properties for a number of colored smokes.

Baughman, G.L. and T.A. Perenich. 1988. Fate of dyes in aquatic systems. I. Solubility and partitioning of some hydrophobic dyes and related compounds. *Environ Toxicol Chem.* 7(3):183-200.

The authors combined solubilities and vapor pressures from the literature with calculated octanol-water partition coefficients to assess the expected environmental behavior of nearly 50 dyes. Most of the older disperse dyes in use for decades have solubilities on the order of 10^{-7} to 10^{-6} . This solubility suggests the potential for a 30- to 150-fold concentration enhancement in sediments and approximately thousand fold bioconcentration factors in the absence of metabolism. The data also indicate that solubilities computed from K_{ow} may be significantly overestimated and that the product of subcooled liquid solubility and estimated K_{ow} for disperse dyes is 10 to 100 times smaller than reported for most other compounds. Henry's Law Constants calculated from solubility and vapor pressure show that disperse and vat dyes will be entirely gas-phase-controlled in their rate of volatilization from water and that this process will be extremely slow. No definitive conclusions can be drawn about the behavior of more recently developed disperse dyes. Available physical constants are compiled along with structures, Color Index number, CAS number and names.

Buchanan, M.V. and C.Y. Ma. 1988. Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Chemical Characterization of Colored Signal Smokes. ORNL/TM-1195. Ad A209 379. Oak Ridge National Laboratory, Oak Ridge, TN.

The chemical compositions of four colored smoke mixes: red, violet, green, and yellow, were characterized to assess possible changes in composition due to the combustion of these materials as smoke grenades. The smoke mixes and combusted products were fractionated using high performance liquid chromatography and then characterized using combined gas chromatography/mass spectroscopy, direct probe mass spectrometry, and laser desorption Fourier transform mass spectrometry. Structures were confirmed using ^{13}C nuclear magnetic resonance and Fourier trans-

form infrared spectroscopy. The red and violet smoke mixes appeared to undergo more extensive chemical transformation than the green and yellow grenades. Two of the components in the combusted violet smoke mix have previously been shown to exhibit bacterial mutagenicity.

Buchanan, M.V., C.L. Ma, J.H. Moneyhun and M.R. Guerin. 1988. Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Smoke Generation and Characterization Part 2, Colored Smoke Grenades. Oak Ridge National Laboratory, Oak Ridge, TN.

The purpose of this project is to chemically characterize the chemical constituents of four colored signal smokes to assess whether chemical transformations occur upon combustion of these materials as smoke grenades. These studies center on the characterization of the major components in the four original dye mixes, the generation and collection of both the volatile and particulate components of the combusted dye smokes, and the characterization of the major components of the combusted dyes. The four smoke grenades, red, yellow, violet, and green, are composed of organic dyes and inorganic components. The red dye is a mixture of Solvent Red 1 and Disperse Red 11. The violet dye is Disperse Red 11 and Disperse Blue 3. The yellow dye is Chinoline Yellow (Solvent Yellow 33) and the green dye contains Solvent Green 3 and Chinoline Yellow.

Chin, A. 1986. Investigation of the Effluents Produced during the Functioning of Black and White Colored Smoke Devices. Department of Defense [DODXA], 31 Jan 86, 18p. Technical Report. NWSC/CR/RDTR-242. AD-A167 468/8/INW. Prepared by Applied Sciences Dept., Naval Weapons Support Center, Crane, IN.

The qualitative and quantitative analyses on the combustion effluents from black and white colored smoke devices were completed. Techniques for qualitative identification of the structures from combustion effluents were basically similar to that described in the previous paper. Quantitative analyses were completed by obtaining the smoke settling curve at first. Only the amount of smoke collected within the range of the smoke settling curve plateau was used to calculate the quantities of each combustion product. Quantification for most of the combustion effluents was accomplished by comparing the areas of HPLC and GC spectra with that of the standard compounds which are commercially available. Others were estimated by total ion counts or single ion monitoring methods using a mass spectrometer with or without internal standards.

Dacre, J.C., W.D. Burrows, C.W.R. Wade, A.F. Hegyeli, T.A. Miller and D.R. Cogley. 1979. Problem definition studies on potential environmental pollutants V. Physical, chemical, toxicological and biological properties of seven chemicals used in pyrotechnic compositions. Prepared by U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.

This report provides a literature survey of physical and chemical properties, purity of substances, analytical methods, mammalian toxicology, and environmental considerations. It identifies data gaps and provides recommendations for further studies. The report focuses on the following seven chemicals: auramine, auramine hydrochloride, benzthron, 1,4-di-p-toluidinoanthraquinone, 1,4-diamino-2,3-dihydroanthraquinone, 1-methylaminoanthraquinone, Vat Yellow 4, and hexachloroethane. All of the dyes demonstrated high melting points, and were insoluble in both water and alkaline media. All of the dyes were more soluble in alcohols, ethers, aromatic solvents, chlorinated solvents, and concentrated sulfuric acid. The authors found that these compounds may contain as much as 23% in unidentified impurities, further confounding studies on fate and effects. Most of the available toxicological studies at that time focused on inhalation studies, or occupational exposure studies. The literature at that time provided no evidence of studies on in vitro and in vivo fates of these materials.

Higuchi, M.A. and D.W. Davies. 1990. Inhalation Toxicology of Red and Violet Dye Mixtures, Chamber Concentration and Particle Size Distribution Report. - Rept. for 1 Jan-21 Dec 90. AD-A237 664/8. Health Effects Research Lab., Research Triangle Park, NC.

An inhalation exposure facility was developed at the U.S. Environmental Protection Agency, Research Triangle Park, NC, to conduct inhalation exposures of rodents and guinea pigs to dye mixtures used by the U.S. Army in the manufacture of smoke munitions. Initially, an evaluation of the prototype chamber aerosol homogeneity was conducted to determine the uniformity and reproducibility of the concentration and particle size of dye aerosol throughout the breathing zone of the test animals. The red grenade mixture was formulated by combining the anthraquinone dye Disperse Red 11 (DR11) and the azo dye Solvent Red 1 (SR1); the violet grenade mixture was formulated from DR11 and Disperse Blue 3 (DB3), another anthraquinone dye. The three dyes, DR11, SR1, and DB3, were chemically analyzed for purity and optically examined for size and shape. All pure dyes appeared to be stable at room temperature except DB3, which decomposes if not stored at 4 °C.

Rubin, I.B. and M.V. Buchanan. 1983. **Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures. Chemical Characterization of Army Colored Smoke: Inventory Smoke Mixes (Red, Violet, Yellow, and Green).** ORNL/TM-8956. AD A134777. Oak Ridge National Laboratory, Oak Ridge, TN.

Red, violet, yellow, and green inventory smoke mixes were fractionated by vacuum sublimation, differential solubility and liquid chromatography. Two unique components, benzantrone and dibenzochrysenedione were purified by the same methods. Major components of the smoke mixes were isolated and identified by comparison to the pure dyes using a variety of instrumental techniques. A number of contaminants at very minor levels were identified by gas chromatography/mass spectroscopy. All of the smoke mixes contained relatively large quantities (10 to 25%) of chloroform insoluble or non-volatile undifferentiated carbonaceous material.

Environmental Fate and Transport

Adams, R.L., E.J. Weber and G.L. Baughman. 1994. **Photolysis of smoke dyes on soils.** *Environ Toxicol Chem.* 13(6):889-896.

The authors investigated photolysis of an azo, a quinophthalone, and several anthraquinone smoke dyes on soil surfaces. Initially, rapid photodegradation of each dye occurred, followed by a period of much slower loss rate, indicating that the remaining fraction of the dye was photochemically protected. The average mean depths of photolysis ranged from 0.33 mm to 0.68 mm for outdoor studies and from 0.42 to 0.74 mm for lab studies. The magnitude of the mean depths of photolysis suggests that photodegradation of the dyes occurs through indirect photochemical processes. Photolysis products for only two of the dyes could be identified. Photolysis of Disperse Red 9 resulted in the formation of 1-aminoanthraquinone, whereas Solvent Yellow 33 photodegraded to give 2-carboxyquinoline and phthalic anhydride. Reaction mechanisms involving sensitized photo-oxidation by singlet oxygen were consistent with the formation of these reaction products.

Baughman, G.L., E.J. Weber, R.L. Adams and M.S. Brewer. 1992. **Fate of Colored Smoke Dyes. Supported by US Army Biomedical Research and Development Laboratory. Army Project No. 88PP8863.**

The study was designed to provide part of the data necessary for environmental assessment. The project consisted of seven tasks addressing three basic goals: (1) purification and characterization of study compounds, (2) measurement of reaction rates

and (3) identification of products for the most probable transformation products as typified by the anilines. Five pathways or processes were identified that were expected to be important for the environmental fate of the smoke dyes: (1) partitioning from water to soil/sediment and biota, (2) assessment of metal complexation, (3) photolysis on soil, (4) transformation in anaerobic sediments, and (5) transformation of aromatic amines.

The authors measured the water solubility, octanol-water partition coefficient and entropy of fusion for the smoke dyes and other disperse and solvent dyes. Based on these data, they examined three regression approaches for use in estimating water solubilities and octanol-water partition coefficients. The data showed that the smoke dyes will partition strongly to sediments and soils and they have potential bioconcentration factors that range from 100 to well over a million.

The authors concluded that Solvent Yellow 33 is a good complexing agent for divalent metals and probably undergoes cation exchange with sediments. However, the authors were not able to predict the extent of metal complexation for Solvent Red 1. Based on fundamental chemical considerations and the absence of data for metal complexes, they concluded that complexation of Disperse Red 9, Disperse Violet 1, and Disperse Red 11 in the environment would likely be insignificant.

Photolysis studies on soil indicated that all of the dyes were readily photodegraded to some extent. None of the dyes were completely photolyzed due to light attenuation by soil particles. The magnitude of mean depths of photolysis, the dependence of the mean depth of photolysis on soil depth and solution phase photolysis studies suggested that photodegradation of the dyes was occurring primarily through photoxygenation via reaction with singlet oxygen. Except for Solvent Green 3, none of the dyes resulted in photolysis products that were expected to persist in the environment.

The authors measured degradation rate constants in anaerobic sediments. Half-lives varied from 0.1 to 140 days or approximately 1000 fold. Only Disperse Blue 3, Disperse Blue 14, and Solvent Yellow 33 had half-lives greater than a few days. Solvent Yellow 33 was the least reactive but is predicted to have a half-life in anaerobic sediment of approximately six months. The azo dyes, Disperse Red 5 and Solvent Red 1, showed that reduction of the azo linkages and the nitro group resulted in the formation of substituted anilines. Reduction of Disperse Red 9 resulted in the formation of anthrones. The 1,4-diaminoanthraquinones, Disperse Violet 1 and Disperse Red 11, undergo more complex reactions. It is probable that multiple products result from reduction and replacement of the amino groups with OH. De-

methylation of Disperse Red 11 also occurs, resulting in the formation of a product that accumulates.

Finally, the authors also evaluated the mechanisms by which aromatic amines sorb to soil and sediment surfaces. They found the rate and extent of sorption to increase with the pKa of the aniline. Decreasing pH enhanced the sorption of the 4-substituted anilines in a silt-clay. Other studies have shown the sorption of aniline was pH independent. Sequential extraction studies with ¹⁴C-aniline suggest that reversible cation exchange processes do not significantly contribute to aniline sorption in natural sediment-water systems and that irreversible covalent binding to the organic matter of the sediment matrix dominates the sorption process. Treatment of a sediment-water system with 2,4-DNP or hydroxylamine 24 hours prior to the addition of 4-methoxyaniline effectively blocked the sorption of the aniline, suggesting the importance of covalent binding through nucleophilic addition to carbonyl groups in the sediment matrix. Although the authors only examined a small number of anilines, they concluded that such compounds will be rendered highly immobile in soil or sediment systems.

Baughman, G.L. and E.J. Weber. 1994. Transformations of Dyes and Related Compounds in Anoxic Sediment: Kinetics and Products. *Environ. Sci. Technol.* 28:267-276.

The authors studied the reactions of several azo, anthraquinone, and quinoline dyes in settled sediments. Several 1-substituted anthraquinones were lost from sediment with half-lives less than 10 days. For monosubstituted 1-amino and 1-methylamino (Disperse Red 9) compounds, the most stable product is the intramolecularly hydrogen-bonded anthrone. The 1,4-diaminoanthraquinone (Disperse Violet 1) and 1,4-diamino-2-methoxyanthraquinone (Disperse Red 11) were lost without formation of detectable products except for a dimethylation product of the latter. Both the anthrone from Disperse Red 9 and the demethylation product of Disperse Red 11 reacted with half-lives of a few months, but other products were not detected. An azo dye, (Solvent Red 1) and a quinoline dye (Solvent Yellow 33) were transformed with half-lives of a few days and months, respectively. The azo dye reacted by reductive cleavage of the azo bond.

Buchanan, M.V., I.B. Rubin and J.H. Moneyhun. 1983. Compositional Changes in Red and Violet Smoke Mixes After Combustion. Oak Ridge National Laboratory, Oak Ridge, TN.

Anthraquinone-derived dyes are commonly used in colored dye mixes prepared for signal smoke grenades. Biological studies have shown, however, that a number of these dyes exhibit bacterial mutagenicity. In addition, these dyes are similar in structure to several polycyclic aromatic hydrocarbons that are known carcinogens. The grenades contain not only anthraquinone-derived dyes, but also a pyrotechnic fuel and cooling and starting mixes consisting primarily of potassium chlorate and nitrate, sodium bicarbonate, and sulfur. These dyes are volatilized at temperatures up to 550 °C during the detonation of the grenade, which could subject the dyes to oxidative and pyrolytic reactions that could result in a variety of reaction by-products. As part of a program to investigate possible environmental and occupational risks of the colored smoke dyes in signal grenades, two colored smoke mixes, red and violet, have been studied both before and after detonation to evaluate any differences.

Dacre, J.C., W.D. Burrows, C.W.R. Wade, A.F. Hegyeli, T.A. Miller and D.R. Cogley. 1979. Problem definition studies on potential environmental pollutants V. Physical, chemical, toxicological and biological properties of seven chemicals used in pyrotechnic compositions. Prepared by U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.

This report provides a literature survey of physical and chemical properties, purity of substances, analytical methods, mammalian toxicology, and environmental considerations. It identifies data gaps and provides recommendations for further studies. The report focuses on the following seven chemicals: auramine, auramine hydrochloride, benzothrone, 1,4-di-p-toluidinoanthraquinone, 1,4-diamino-2,3-dihydroanthraquinone, 1-methylaminoanthraquinone, Vat Yellow 4, and hexachloroethane. All of the dyes demonstrated high melting points, and are insoluble in both water and alkaline media. All of the dyes are more soluble in alcohols, ethers, aromatic solvents, chlorinated solvents, and concentrated sulfuric acid. The authors found that these compounds may contain as much as 23% in unidentified impurities, further confounding studies on fate and effects. Most of the available toxicological studies at that time focused on inhalation studies, or occupational exposure studies. The literature at that time provided no evidence of studies on in vitro and in vivo fates of these materials.

Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Disperse Red 9. Final Report. July 1987. ORNL-6356. AD-A183 369/8/GAR. Oak Ridge National Laboratory.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of Disperse Red 9 (1-methylaminoanthraquinone), an organic dye used in pyrotechnic smoke signals. The U.S. Environmental Protection Agency (USEPA) guidelines were used in an attempt to generate water quality criteria for the protection of aquatic life and its uses and of human health. No data are available concerning the toxic effects of Disperse Red 9 on aquatic organisms; therefore, a Criterion Maximum Concentration and a Criterion Continuous Concentration cannot be calculated. Toxicity studies following the USEPA guidelines are recommended. Because non-threshold and threshold toxicity data were insufficient, a water quality criterion for the protection of human health could not be calculated according to the USEPA guidelines.

Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Colored Smokes: Solvent Green 3: Final Report. Department of Energy [DE], Dec 87, 96p. Technical Report. ORNL-6409. DE88003303/INW. Prepared by Oak Ridge National Laboratory, TN.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of Solvent Green 3, an anthraquinone dye used in colored smoke grenades. The U.S. Environmental Protection Agency guidelines were used in an attempt to generate water quality criteria for the protection of human health and of aquatic life and its uses. Sufficient data to determine the toxicity of Solvent Green 3 in freshwater aquatic organisms are lacking. The 96 hour TL_{50} for *Pimephales promelas* is >100 mg. Solvent Green 3, at a concentration of 10 mg/l, causes a transient reduction in growth of the green alga *Selenastrum capricornutum*. No data are available concerning the chronic toxicity or bioaccumulation of Solvent Green 3 in aquatic organisms. No data are available on any of the toxicity parameters for Solvent Green 3 in humans. No data on the pharmacokinetics of Solvent Green 3 administered orally in laboratory animals are available.

Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Colored Smokes: Solvent Yellow 33, Final Report. Department of Energy [DE], Nov 87, 110p. Technical Report. ORNL-6383. DE88002682/INW. Prepared by Oak Ridge National Laboratory, TN.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of Solvent Yellow 33, a quinoline dye used in colored smoke grenades. The U.S. Environmental Protection Agency guidelines were used in an attempt to generate water quality criteria for the protection of human health and aquatic life. Colored smoke grenades are formulated and loaded at the Pine Bluff

Arsenal, AR. During typical production of pyrotechnic items, approximately 1 to 2% of the smoke formulation is released into the aquatic environment. The primary aquatic system receiving these discharges is the Arkansas River and associated drainages.

Loda, R.T. and T.P. Parr. 1984. Real-Time Fluorescence Analysis of the Controlled Incineration of Army Colored Smoke Compositions. Department of Defense [DODXA], Dec 1984, 84p. Technical Report. NWC-TP-6559. AD-A152 479/2/INW. Prepared by Naval Weapons Center, China Lake, CA.

Polynuclear aromatic hydrocarbons can be produced during the thermal destruction of unserviceable colored smoke compositions. Because some of these compounds are carcinogenic, there is a need to monitor their possible release into the environment. The real-time monitoring of stack gases during the incineration testing of several U.S. Army colored smoke formulations is the subject of this report.

Bioaccumulation and Trophic Transfer

Anliker, R. and P. Moser. 1987. The limits of bioaccumulation of organic pigments in fish: Their relation to the partition coefficient and the solubility in water and octanol. *Ecotox Env Safe* 13:43-52.

Because of the extremely low water solubilities of most organic pigments, reliable experimental determination of partition coefficients is difficult. The authors calculated K_{ow} values and water solubility values for several organic pigments and disperse dyes. Calculated K_{ow} values were high, suggesting bioaccumulation factors greater than 100. The low water solubilities indicate that despite the high predicted bioaccumulation factors, concentrations of pigments are not expected to accumulate in fish.

Anliker, R., P. Moser and D. Poppinger. 1988. Bioaccumulation of dyestuffs and organic pigments in fish. Relationships to hydrophobicity and steric factors. *Chemosphere* 17(8):1631-1644.

The authors calculated and/or measured octanol-water partition coefficients ($\log K_{ow}$) for 23 disperse dyestuffs and 2 organic pigments. They chose the molecular weight and the second largest van der Waals diameter of the molecule. None of the disperse dyestuffs, even the highly lipophilic ones with $\log K_{ow}$ greater than 3, accumulated in fish to any significant degrees. The authors argue that the large molecu-

lar size effectively prevents permeation through biological membranes and thus prevents uptake.

Baughman, G.L. and T.A. Perenich. 1988. Fate of dyes in aquatic systems. I. Solubility and partitioning of some hydrophobic dyes and related compounds. *Environ Toxicol Chem.* 7(3):183-200.

The authors combined solubilities and vapor pressures from the literature with calculated octanol-water partition coefficients to assess the expected environmental behavior of nearly 50 dyes. Most of the older disperse dyes in use for decades have solubilities on the order of 10^{-7} to 10^{-6} . This solubility suggests the potential for a 30 to 150 fold concentration enhancement in sediments and approximately thousand-fold bioconcentration factors in the absence of metabolism. The data also indicate that solubilities computed from K_{ow} may be significantly overestimated and that the product of subcooled liquid solubility and estimated K_{ow} for disperse dyes is 10 to 100 times smaller than reported for most other compounds. Henry's Law Constants calculated from solubility and vapor pressure show that the disperse and vat dyes will be entirely gas-phase-controlled in their rate of volatilization from water and that this process will be extremely slow. No definitive conclusions can be drawn about the behavior of more recently developed disperse dyes. Available physical constants are compiled along with structures, Color Index number, CAS number and names.

Baughman, G.L., E.J. Weber, R.L. Adams, and M.S. Brewer. 1992. Fate of Colored Smoke Dyes. Supported by U.S. Army Biomedical Research and Development Laboratory. Army Project No. 88PP8863.

The present study was designed to provide part of the data necessary for environmental assessment. The project consisted of seven tasks addressing three basic goals: (1) purification and characterization of study compounds, (2) measurement of reaction rates and (3) identification of products for the most probable transformation products as typified by the anilines. Five pathways or processes were identified that were expected to be important for the environmental fate of the smoke dyes: (1) partitioning from water to soil/sediment and biota, (2) assessment of metal complexation, (3) photolysis on soil, (4) transformation in anaerobic sediments, and (5) transformation of aromatic amines.

The authors measured water solubility, octanol-water partition coefficient and entropy of fusion for the smoke dyes and other disperse and solvent dyes. Based on these data, they examined three regression approaches for use in estimating water

solubilities and octanol-water partition coefficients. The data showed that the smoke dyes will partition strongly to sediments and soils and they have potential bioconcentration factors that range from 100 to well over a million.

Toxicity

Bice, D.E., Y.S. Cheng, J.S. Dutcher, F.F. Hahn and T.C. Marshall. 1984. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Phase III, Studies: Four-Week Inhalation Exposures of Rats to Dye Aerosols. Department of Energy [DE], 10 Sep 84, 68p. AD-A156 698/3/INW. Prepared by Inhalation Toxicology Research Inst., Lovelace Biomedical and Environmental Research Inst., Albuquerque, NM.

The USAMBRDL has an interest in the potential inhalation toxicity of yellow dye (SY) and a yellow/green dye mixture (SY) used in colored smoke munitions. Rats were exposed by inhalation to aerosols of SY or SY/SG generated in a respirable particle size range for 6 hour/day, 5 days/week for four weeks. Nominal exposure concentrations selected for both dye exposures were 0, 10, 50, and 250 mg/m³. Animals exposed to the highest concentration of SY (230mg/m³) showed only a slight decrease in weight gain (8%) and mild respiratory function changes, with no observable histopathological lesions. Exposure to the lower concentrations of SY dye elicited no observed response. Animals exposed to the highest level of SY/SG dye (210 mg/m³) displayed signs of pulmonary inflammation with histopathological evidence of mild Type II pulmonary epithelial cell hyperplasia and proliferation of foamy alveolar macrophages.

Buchanan, M.V. and C.Y. Ma. 1988. Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Chemical Characterization of Colored Signal Smokes. ORNL/TM-1195. Ad A209 379. Oak Ridge National Laboratory, Oak Ridge, TN.

The chemical compositions of four colored smoke mixes: red, violet, green, and yellow, have been characterized to assess possible changes in composition due to the combustion of these materials as smoke grenades. The smoke mixes and combusted products were fractionated using high performance liquid chromatography and then characterized using combined gas chromatography/mass spectroscopy, direct probe mass spectrometry and laser desorption Fourier transform mass spectrometry. Structures were confirmed using ¹³C nuclear magnetic resonance and Fourier transform infrared spectroscopy. The red and violet smoke mixes appeared to undergo more extensive chemical transformation than the green and yellow grenades. Two of

the components in the combusted violet smoke mix have previously been shown to exhibit bacterial mutagenicity.

Cichowicz, J.J. and R.S. Wentzel. 1983. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 5. Dye/Colored Smokes. Department of Defense [DODXA], July 1983, 110p. ARCSL-EA-83010. AD-A141 973/8/INW. Prepared by Chemical Research and Development Center, Aberdeen Proving Ground, MD.

Colored smokes/dyes have been used extensively in the past to satisfy signaling and communication needs of the Armed Forces and will continue to be used as vital elements of the national defense posture. Associated with the need for colored smoke is the concern for noncarcinogenicity, nonmutagenicity, and minimal (reversible/nonincapacitating) toxicity to handling and user personnel and the environment. The environmental impacts and data relevant to the life cycle use of the standard dyes and the recommended replacement of safer dyes for future use are compiled in this report. With controlled distribution and use of the colored smokes, that is adherence to safety aspects and regulations, and the implementation of suggested mitigation, minimal adverse impacts to the quality of the human environment is predicted. The conclusion is that proposed on-going smoke programs will not significantly affect the quality of the environment. Use of Benzanthrone and Vat Yellow 4 have been discontinued.

Dacre, J.C., W.D. Burrows, C.W.R. Wade, A.F. Hegyeli, T.A. Miller and D.R. Cogley. 1979. Problem definition studies on potential environmental pollutants V. Physical, chemical, toxicological and biological properties of seven chemicals used in pyrotechnic compositions. Prepared by U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.

This report provides a literature survey of physical and chemical properties, purity of substances, analytical methods, mammalian toxicology, and environmental considerations. It identifies data gaps and provides recommendations for further studies. The report focuses on the following seven chemicals: auramine, auramine hydrochloride, benznthrone, 1,4-di-p-toluidinoanthraquinone, 1,4-diamino-2,3-dihydroanthraquinone, 1-methylaminoanthraquinone, Vat Yellow 4, and hexachloroethane. All of the dyes demonstrated high melting points, and are insoluble in both water and alkaline media. All of the dyes are more soluble in alcohols, ethers, aromatic solvents, chlorinated solvents, and concentrated sulfuric acid. The authors found

that these compounds may contain as much as 23% in unidentified impurities, further confounding studies on fate and effects. Most of the available toxicological studies at that time focused on inhalation studies, or occupational exposure studies. The literature at that time provided no evidence of studies on in vitro and in vivo fates of these materials.

Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Disperse Red 9. Final Report. July 1987. ORNL-6356. AD-A183 369/8/GAR. Oak Ridge National Laboratory.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of Disperse Red 9 (1-methylaminoanthraquinone), an organic dye used in pyrotechnic smoke signals. The U.S. Environmental Protection Agency (USEPA) guidelines were used in an attempt to generate water quality criteria for the protection of aquatic life and its uses and of human health. No data are available concerning the toxic effects of Disperse Red 9 on aquatic organisms; therefore, a Criterion Maximum Concentration and a Criterion Continuous Concentration cannot be calculated. Toxicity studies following the USEPA guidelines are recommended. Because non-threshold and threshold toxicity data were insufficient, a water quality criterion for the protection of human health could not be calculated according to the USEPA guidelines.

Davidson, K.A., P.S. Hovatter and R.H. Ross. 1988. Water Quality Criteria for Colored Smokes: 1,4-Diamino-2,3-Dihydroanthraquinone: Final Report. Department of Energy [DE], Jan 88, 70p. ORNL-6410. DE88004328/INW. Prepared by Oak Ridge National Laboratory, TN.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of 1,4-diamino-2,3-dihydroanthraquinone (DDA), and anthraquinone dye used in violet-colored smoke grenades, were reviewed. The US Environmental Protection Agency (USEPA) guidelines were used in an attempt to generate water quality criteria for the protection of human health and of aquatic life and its uses. DDA will readily oxidize to 1,4-diaminoanthraquinone (DAA) in air or during combustion of the smoke grenade. The dye is insoluble in water; however, no information is available concerning its transformation or transport in soil, water, and sediments. No data are available concerning the toxic effects of DDA in aquatic organisms; therefore, a Criterion Maximum Concentration and a Criterion Continuous Concentration cannot be determined. Toxicity studies following the USEPA guidelines are recommended. DDA is a weak mutagen in the Salmonella Reversin Assay, but the combustion or oxidation product, DAA, is a strong mutagen.

Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Colored Smokes: Solvent Green 3: Final Report. Department of Energy [DE], Dec 87, 96p. Technical Report. ORNL-6409. DE88003303/INW. Prepared by Oak Ridge National Lab., TN.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of Solvent Green 3, an anthraquinone dye used in colored smoke grenades. The U.S. Environmental Protection Agency (USEPA) guidelines were used in an attempt to generate water quality criteria for the protection of human health and of aquatic life and its uses. Sufficient data to determine the toxicity of Solvent Green 3 in freshwater aquatic organisms are lacking. The 96-hr TL₅₀ for *Pimephales promelas* is >100 mg. Solvent Green 3, at a concentration of 10 mg/l, causes a transient reduction in growth of the green alga *Selenastrum capricornutum*. No data are available concerning the chronic toxicity or bioaccumulation of Solvent Green 3 in aquatic organisms. No data are available on any of the toxicity parameters for Solvent Green 3 in humans. No data on the pharmacokinetics of Solvent Green 3 administered orally in laboratory animals are available.

Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Colored Smokes: Solvent Yellow 33, Final Report. Department of Energy [DE], Nov 87, 110p. Technical Report. ORNL-6383. DE88002682/INW. Prepared by Oak Ridge National Lab., TN.

The authors reviewed the available data on the environmental fate, aquatic toxicity, and mammalian toxicity of Solvent Yellow 33, a quinoline dye used in colored smoke grenades, were reviewed. The U.S. Environmental Protection Agency guidelines were used in an attempt to generate water quality criteria for the protection of aquatic life and its uses and of human health. Colored smoke grenades are formulated and loaded at the Pine Bluff Arsenal, Arkansas. During typical production of pyrotechnic items, approximately 1 to 2 percent of the smoke formulation is released into the aquatic environment. The primary aquatic system receiving these discharges is the Arkansas River and associated drainages.

Dwivedi, N., M. Das and S.K. Khanna. 2001. Role of biological antioxidants in benzanthrone toxicity. *Arch Toxicol* 75: 221-226.

Previous studies indicate that benzanthrone, an anthraquinone dye intermediate, caused significant depletion of ascorbic acid (AsA). In this investigation, the effect of benzanthrone on the status of different forms of AsA and other bio-antioxidants such as glutathione (GSH) was studied. Oral administration of benzanthrone (50, 125 or

250 mg/kg body weight) resulted in a significant increase of urinary AsA levels with a concomitant decrease in the urinary dehydroascorbic acid (DHA) content in both rats and guinea-pigs. Benzanthrone caused a dose-dependent decrease in hepatic, adrenal and serum AsA levels with a subsequent increase in DHA and diketogulonic acid (DKA) levels in both rats and guinea pigs. Following benzanthrone treatment, rats showed an increase in the scorbutic index (to 1.01 to 1.21) of the liver, adrenal glands and serum compared to controls (0.12 to 0.24). The scorbutic indices of liver, adrenal glands and serum were also substantially increased (to 3.61 to 11.20) in benzanthrone-treated guinea pigs compared to controls (0.16 to 0.38). Single oral administration of benzanthrone to guinea pigs caused a dose-dependent depletion of GSH in liver (15 to 51%), adrenal glands (27 to 64%) and serum (32 to 86%). Furthermore, the depletion of GSH by benzanthrone in rats was of a lesser degree. This suggests that continued exposure of guinea pigs to benzanthrone may lead to scurvy type changes in this animal species but not to the same extent in rats, since the latter has the enzymatic capacity to synthesize AsA. Therefore, it can be hypothesized that benzanthrone per se, or its metabolites, interact with reduced GSH thereby causing its depletion. Furthermore, in order to replenish the depleted GSH levels, AsA might be oxidized to DHA and hence the decrease in AsA with the simultaneous increase in DHA was observed.

Henderson, R.F., Y.S. Cheng, J.S. Dutcher, T.C. Marshall and J.E. White. 1984. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Final Report for Phase I Studies. Generation and Characterization of Dye Aerosol. Department of Energy [DE], 1 Feb 84, 59p. AD-A142 491/0/INW. Prepared by Inhalation Toxicology Research Inst., Lovelace Biomedical and Environmental Research Inst., Albuquerque, NM.

The authors developed a method for generation of respirable size particles of yellow dye and a yellow/green dye mixtures for inhalation toxicity studies.

Henderson, R.F., J.S. Dutcher, F.F. Hahn, D.E. Bice and T.C. Marshall. 1985. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Phase II Studies: Range Finding and Toxicokinetics Studies of Inhaled Dye Aerosols. Department of Defense [DODXA], 15 Mar 85, 84p. AD-A163 267/8/INW. Prepared by Army Medical Research and Development Command, Fort Detrick, MD.

The USAMBRDL has an interest in the potential inhalation toxicity of yellow dye (SY) and a yellow/green dye mixture (SY/SG) used in colored smoke munitions. In the range finding studies, no mortalities or life-threatening lesions were observed in

rats exposed for as long as 6 hours per day for 5 days to airborne concentrations greater than 1 g/cu m of either SY or SY/SG. The particle size of the aerosols employed was about 5 micrometers MMAD. In the toxico-kinetic studies, rats inhaled pure 14C-SY aerosols or 14 micrometers C-SY aerosols in combination with SG (a 0.6 ratio of yellow to green by weight). SY was rapidly cleared from the respiratory tract ($T_{1/2}$ approximately 3 hr). SG, however, was retained for a longer time ($T_{1/2} > 22$ days). The major pathway for excretion of SY metabolites was the feces, but some metabolites were also excreted in urine. There was no effect of SG on the kinetics of distribution and elimination of SY. The rapid absorption, distribution, and excretion of SY contributes to a lower observed toxicity.

Henderson, R.F., Y.S. Cheng, F.F. Hahn, J.L. Mauderly and J.A. Pickrell. 1985. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Phase 4. 90-Day Inhalation Exposures of Rats to Dye Aerosols. Department of Defense [DODXA], Oct 85, 300p. AD-A170 446/9/INW. Prepared by Inhalation Toxicology Research Inst., Lovelace Biomedical and Environmental Research Inst., Albuquerque, NM.

The U.S. Army has an interest in the potential inhalation toxicity of yellow dye (SY) and a yellow/green dye mixture (SY) used in colored smoke munitions. Rats were exposed by inhalation to aerosols of SY or SY/SG generated in a respirable particle size range (2.1-4.2 micrometers mass median aerodynamic diameter) for 6 hrs/day, 5 days/wk for a period of 90 days. The objective was to determine an exposure concentration that produced no observable adverse effects. Nominal exposure concentration produced no observable adverse effects. Nominal exposure concentrations selected for both dye exposures were 0, 1, 10, and 100 mg/m³. Actual concentrations were within 10% of these nominal concentrations. Animals exposed to the highest concentration of SY (100 mg/m³) had only a slight decrease in body weight gain of 4% compared to control animals and an accumulation of foamy macrophages in lungs. Exposure to the lower concentrations of SY dye elicited no observed response.

Jaskot, R.H. and D.L. Costa. 1994. Toxicity of an anthraquinone violet dye mixture following inhalation exposure, intratracheal instillation, or gavage. *Fundamental and Applied Toxicology* 22(1):103-112.

The authors investigated the effects of a prototype violet dye mixture (VDM) consisting of 92.9% Disperse Red 11 (DR11), (1,4-diamino-2-methoxy-anthraquinone) and 7.1% Disperse Blue 3 (DB3) 11-methylamino-4-hydroxyethylamino-anthraquinone) on F344 male and female rats. Fischer-344-rats were exposed whole body to VDM aerosols at concentrations of 10, 40, 70, 100, 300, or 1,000 mg/m³ or nose only to 300

mg/m³ for 6 hours. Other rats were exposed whole body to 40 mg/m³ of VDM aerosol 6 hours daily for 5 days or up to 1,000 micrograms VDM once by intratracheal instillation. Additional rats were gavaged once with 800 mg/kg VDM or its components DR11 or DB3. The rats were observed for clinical signs of toxicity. Rats were killed 1, 3, or 7 days after exposure and necropsied. Single whole body exposure to 500 and 1,000 mg/m³ VDM caused 100% mortality. VDM given for 5 days caused 50% mortality. The deaths were due to severe liver damage. Necrosis of the nasal olfactory epithelium was also seen in these groups. Serum glutamic-pyruvic-transaminase (SGPT) and lactate-dehydrogenase (LDH) activities were also significantly elevated. In rats exposed whole body to 100 mg/m³ VDM, moderate degeneration and necrosis of centrilobular hepatocytes and nasal olfactory epithelial necrosis were observed. Lower doses caused a dose related increase in nasal olfactory epithelial degeneration and necrosis but no liver damage. Surviving rats exposed to 40 mg/m³ VDM for 5 days had significantly elevated SGPT and LDH activities. No pathological changes were seen in the lungs. Intratracheal instillation of VDM caused no treatment related pathological changes. VDM given by gavage caused significant increases in SGPT, LDH, isocitrate-dehydrogenase, succinate-dehydrogenase, glutathione-reductase and other enzymes indicative of glutathione metabolism, NADPH-cytochrome-c-reductase, and glutathione-S-transferase. DR11 and DB3 caused only minimal changes in these enzymes. The authors conclude that DR11 and DB3 appear to be minimally toxic when administered individually to rats. When combined in VDM, they induce significant hepatotoxicity and cause damage to olfactory epithelial cells.

Marrs, T.C., H.F. Colgrave, N.L. Cross, J.A.G. Edginton and B.C. Morris. 1988. Inhalation Toxicity of a Coloured Smoke and the Mutagenicity of Its Constituent Dyes, Solvent Yellow 33 (CI 47,000) and Disperse Orange 11 (CI 60,700) in the Ames Test. *Jnl Haz Mat* 17(3):269-285.

The inhalation toxicity and mutagenicity of smoke generated from a pyrotechnic mixture was studied. Female Porton-SPF-mice, female Porton-Wistar-rats, and female Dunkin-Hartley-guinea pigs were allocated randomly to control, low, medium, and high exposure groups. Smoke was generated at three concentrations from smoke composition ignited on heated wire. The animals were exposed for 1 hour per day for 5 days per week for 200 exposures (75 exposures for high dose guinea pigs). Animals showing signs of ill health and those alive after 17 months were killed and necropsied. No great differences in survival were found in rats or mice. Guinea pigs showed more deaths in the test groups, including 22 out of 46 of the high exposure group in the fourth month of study. Decedent mice and rats of the test groups had lung histological changes. Decedent guinea pigs frequently had mild alveolitis. During expo-

sure, statistically significant reductions of weight occurred in all test groups, but these were largely reversed after cessation of exposure. Relative lung weights in mice tended to increase with dose; this was statistically significant for high dose animals. Surviving mice showed a large variety of histological changes in the lungs, including macrophage infiltration and peribronchial and perivascular lymphocyte infiltration. Organ specific toxicity was mainly confined to the respiratory tract in all three species and was primarily attributed to non-dye constituents of smoke. The dyes used in the smoke, Solvent Yellow 33 (8003223) and Disperse Orange 11 (82280), were tested for mutagenic activity. Both were mutagenic in the Ames test with *Salmonella typhimurium* (TA-1537R+), with or without S9 mix. Neither dye was mutagenic for strains (TA-98), (TA-100), or (TA-1537), with or without S9. The authors concluded that the colored smoke is notably lacking in organ specific toxicity outside the respiratory tract, but that the genotoxic potential of the dyes gives rise to concern.

Marrs, T.C., H.F. Colgrave, P. Rice, J.A.G. Edginton and B. Morris. 1989. The Repeated Dose Toxicity of a Smoke Containing Disperse Blue 180, and Anthraquinone Dye Mixture. *J Haz Mat.* 21(1):73-88.

The toxicity of repeated doses of smoke from a pyrotechnic composition containing the anthraquinone dye mixture Disperse-Blue-180 was investigated in mice, rats and guinea pigs. Female Porton-mice, Porton-rats and Dunkin-Hartley-guinea pigs were exposed to freshly generated smoke obtained from a pyrotechnic composition containing Disperse-Blue-180. The animals were exposed to the smoke for 1 hour/day, 5 days/week, until they had experienced 200 exposures at concentrations of 50, 160, or 500 mg/m³. There was a partially reversible effect on growth, particularly in mice, but it was not possible to establish a no effect level. There was no statistically significant difference in deaths in the dosed animals over the corresponding controls. A significantly elevated frequency of alveogenic carcinomas was noted in the high dose group of mice. Even though this study was not designed as a carcinogenesis bioassay, this finding has provided evidence of experimental carcinogenicity in mice. Mutagenicity in the Ames *Salmonella typhimurium* test was noted as dependent on the frameshift indicator strain (TA-1537R+), a strain particularly sensitive to anthraquinone dyes. The substitution indicator strains, (TA-1535) and (TA-100), did not show a mutagenic response. Macrophage infiltration was observed in the rats and to a lesser extent in the other two species.

Medinsky, M.A., Y-S Cheng, S.J. Kampcik, R.F. Henderson and J.S. Dutcher. 1986. Disposition and metabolism of 14C-solvent yellow and solvent green aerosols after inhalation. *Fundam Appl Toxicol.* 7(1):170-178.

Solvent yellow (2-(2'-quinolinyl)-1,3-indandione) and solvent green (1,4-di-p-toluidinoanthraquinone) are components of colored smoke munitions and may be inhaled by workers during manufacture. The authors exposed male F344/N rats to super(14)C-solvent yellow aerosols (160 nmol solvent yellow/liter air) or a mixture of super(14)C-solvent yellow and unlabeled solvent green (340 nmol solvent yellow and 370 nmol solvent green/liter air) for 60 minutes. After either exposure, solvent yellow was rapidly cleared from the respiratory tract, with a $T_{1/2}$ of 2 to 3 hours. Solvent green was retained in the lungs with a minimum estimated $T_{1/2}$ for clearance of 22 days. Solvent green was not detected in other tissues during the 70 hour post-exposure period. Analysis of tissues extracts indicated 40 to 75% of the super(14)C in liver and kidney consisted of solvent yellow metabolites.

National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants. Volume 3. National Academy Press, Washington, D.C.

This volume summarizes the available literature on physical-chemical properties and health effects of several individual constituents of colored smokes. The emphasis is on protecting and recommending inhalation exposure levels for military personnel in training and for the general public residing or working near military training facilities. The subcommittee on military smokes and obscurants concluded that the available toxicity database for the combustion products of both old and new smoke formulations is inadequate for use in assessing the potential health risk of exposure to these smokes.

Paulson, R.L., D.J. Fisher and D.T. Burton. 1989. Comparative Toxicity of Solvent Yellow 33 (2-(2'-quinolinyl)-1,3-indandione) and Solvent Green 3 (1,4-Di-p-toluidino-anthaquinone) Dyes to Freshwater Organisms. *Chemosphere*. 19(12):1959-1970.

The toxicity of Solvent Yellow 33 and Solvent Green 3 mixtures used as components of smoke munitions by the military was studied. The acute toxicity of the dyes to an array of nine freshwater aquatic organisms from various trophic levels was determined. Fish exposed to the two dyes for 96 hours included the fathead minnow (*Pimephales promelas*), bluegill (*Lepomis macrochirus*), channel catfish (*Ictalurus punctatus*) and rainbow trout (*Salmo gairdneri*). Invertebrates, which were exposed for 48 hours, included the water flea (*Daphnia magna*), amphipod (*Gammarus pseudolimnaeus*), midge larva (*Paratanytarsus parthenogeneticus*) and the mayfly larva (*Hexagenia bilinata*). Growth of the green alga *Selenastrum capricornutum* was also determined for both dyes. Solvent Yellow 33 and a Solvent Green 3 mixture (30:70

mixture of Solvent Yellow 33 and Solvent Green 3) were not acutely toxic to seven of nine freshwater species when tested at the solubility limits of the dyes in freshwater. A solubility limit solution of the Solvent Green 3 mixture killed 50% of the rainbow trout tested for 96 hours but was nontoxic when diluted by 50%. Both dyes caused a reduction in green algal growth at solubility limits. The Solvent Green 3 mixture was the most detrimental causing a 98-99% reduction in growth after five days of exposure.

Smith, S.H., G.L. Doyle, J.C. Kreuger, K.A. Mellon and D.A. Mayhew. 1986. Dermal, Eye and Oral Toxicological Evaluations. Phase IV with Disperse Red 11, Disperse Blue 3, Solvent Red 1, and Red and Violet Mixtures. Prepared by American Biogenics Corporation, Decatur, IL, for US Army Medical Research and Development Command, Fort Detrick, MD.

Six test articles were evaluated to establish their eye and skin irritation potential and their oral and dermal toxicity. The test articles evaluated were as follows: (1) Disperse Red 11 - Lot 1; (2) Disperse Red 11 - Lot 2; (3) Disperse Blue 3 - Lot 3; (4) Violet Mixture - 35 parts Disperse Red 11 - Lot 1:5 parts Disperse Blue 3; (5) Solvent Red 1; and (6) Red Mixture - 33.4 parts Solvent Red 1:6.6 parts Disperse Red 11 - Lot 1. Oral studies were conducted using the Fischer-344 albino rat as the test system; all other studies utilized the New Zealand White Albino Rabbit as the test system.

Disperse Red 11: Lot 1 was found to be a moderate skin irritant; tested negative for eye irritation, had a dermal LD₅₀ greater than 2 g/kg. The authors were unable to calculate an oral LD₅₀ for males but estimate that it is between 708 mg/kg and 891 mg/kg. The oral LD₅₀ for females is at least 5 g/kg.

Disperse Red 11: Lot 2 was found to be a mild skin irritant; tested negative for eye irritation, had a dermal LD₅₀ greater than 2 g/kg; and oral LD₅₀ of 1042.7 mg/kg in males, and greater than 5 g/kg in females.

Disperse Blue 3 was found to be practically non-irritating to the skin; tested negative for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ greater than 5 g/kg.

Violet Mixture: 35 parts Lot 1 Disperse Red 11 to 5 parts Disperse Blue 3 was found to be a mild skin irritant; tested negative for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ of between 794 mg/kg and 1000 mg/kg for

males, between 1,413 mg/kg and 1,778 mg/kg for females, and 1052 mg/kg for combined sexes.

Solvent Red 1 was found to be non-irritating to the skin; tested positive for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ greater than 5 g/kg.

Red Mixture: 33.4 parts Solvent Red 1 to 6.6 parts Lot 1 Disperse Red 11 was found to be nonirritating to the skin; tested positive for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ greater than 5 g/kg.

Sun, J.D., R.F. Henderson, T.C. Marshall, Y-S Cheng, J.S. Dutcher, J.A. Pickrell, J.L. Mauderly, F.F. Hahn, D.A. Banas, F.A. Seiler and C.H. Hobbs. 1987. The Inhalation Toxicity of Two Commercial Dyes: Solvent Yellow 33 and Solvent Green 3. *Fundamental and Applied Toxicology*, 8(3):358-371.

The potential inhalation toxicity of two commercial dyes, 2-(2'-quinolyl)-1,3-indandione (8003223) (solvent yellow 33) (SY) and 1,4-di-p-toluidinoanthraquinone (128803) (solvent green 3) (SG), was studied in a series of *in-vivo* experiments using F344-rats as the animal model. The dyes are said to be used in the manufacture of M18 colored smoke grenades, where workers may be exposed to the compounds. Male and female F344/N-rats were exposed to a 30:70 weight/weight mixture of SY/SG in aerosol form for four to 13 weeks, at a rate of 6 hours/day, 5 days/week. The concentrations used in the four week exposure were SY/SG aerosols at 11, 49, or 210 mg/m³, and SY aerosols at 10, 51, or 230 mg/m³. For 13 week experiments, SY aerosols at concentrations of 1.0, 10.8, or 100 mg/m³, and SY/SG mixture at 1.1, 10.2, or 101 mg/m³ were used. Exposures for 4 weeks caused a body weight reduction of 7 to 8% compared to controls at the highest concentrations of the dyes tested. Also noted were pulmonary effects including mild inflammation, airflow obstruction, decreased gas exchange efficiency, proliferation of vacuolated alveolar macrophages, and mild type II pulmonary epithelial cell hyperplasia. In 13 week exposures, at the highest concentrations tested, body weight reduction of about 5 to 9% was seen, with accompanying pulmonary inflammation, type II pulmonary cell hyperplasia, and accumulation by vacuolated alveolar macrophages in the lungs. The clearance of SY from the lungs was very rapid, but the clearance of SG was slower, with a half life of roughly 280 days after the 13 week exposures. The authors conclude that neither dye is highly toxic following inhalation. The relatively higher toxicity of the SY/SG mixture over SY alone is suggested to be due to the slow clearance of SG from the lungs. The authors recommended conducting tests with longer observation periods, to establish long term effects of these dyes.

Terephthalic Acid

Physical-Chemical Properties

Technical grade terephthalic acid takes the form of white crystals or powder. It has a low volatility and is not considered flammable. Terephthalic acid has been used in the production of polyester products. Table 2 provides the physical-chemical properties for terephthalic acid.

Anon. 1988. Terephthalic acid. *Dangerous Properties of Industrial Materials Report*. 8(4): 68-71.

Terephthalic acid, a chemical with various industrial applications, is mildly irritating in direct contact exposure. Protective clothing is recommended when handling the material. Because of potential irritation to the respiratory tract when inhaled, protective filter masks are also recommended.

Anthony JS, CL Crouse, WT Muse, SA Thompson. Characterization of pyrotechnically disseminated terephthalic acid as released from the M8 smoke pot. Edgewood Research, Development, and Engineering Center, Aberdeen Proving Ground, MD.

M8 training smoke pots were detonated in the field to characterize the major by-products contained in the generated smoke. Previous studies on the M83 grenades had shown certain organic compounds to be present, specifically benzene and formaldehyde. With the dissemination of a larger amount of material from the pot (25 lb as compared to 360 g), organic vapor concentrations were also going to be higher. At the 8 ft sampling line, the concentrations of formaldehyde, benzene, toluene, carbon monoxide, and carbon dioxide were 34, 63, 1.2, 791, and 190 ppm respectively. However, using molecular modeling, concentrations were calculated to 50 ft. This distance is specified in the operational Standard Operating Procedure as the minimal distance that must be maintained from the pot when performing routine work. All concentrations of organic combustion products at this 50 ft distance were below their respective threshold limit values, therefore supporting the idea that the M8 is currently the safest training grenade.

United States Environmental Protection Agency (USEPA). 1983. AP-42, Fifth Edition, Volume. Chapter 6: Organic Chemical Process Industry.

The USEPA AP-42 provides the manufacturing and refinement processes for producing terephthalic acid.

Environmental Fate and Transport

Atmospheric TA was found in both the vapor and particulate phase, and had an estimated atmospheric half-life of 58 days (HSDB 2003). Vapor phase TA is expected to photochemically react with hydroxyl radicals and undergo transport to remote areas based on the estimated half-life (HSDB 2003).

Soil suspension biodegradation tests found that TA will completely degrade from aerated soils within two days (HSDB 2003). TA has an estimated K_{oc} of 290, indicating moderate mobility in soil (HSDB 2003) that may result in TA leaching to anaerobic zones in the soil column. Anaerobic degradation of TA occurs at a slower rate than aerobic degradation. Studies on anaerobic degradation of TA focus primarily on the treatment of wastewaters from TA production facilities. Kleerebezem et al. (1997) found that terephthalate-mineralizing bacteria mixtures have a slow growth rate, with a maximum removal capacity of 3.9 g COD/l/day in a lab-scale Up-flow Anaerobic Sludge Bed (UASB) reactor. Macarie et al. (1992) found a maximum removal capacity of 74.5% COD over 3.4 days in a downflow tubular fixed film reactor treatment system. The primary degradation products were identified as m-hydroxybenzoic acid and protocatechuic acid (He and Zhang 1992). Treatment of TA production facility wastewaters involves pre-treatment and bacterial mixture inoculations, which does not apply directly to natural degradation in anaerobic soils, but does highlight that TA will degrade under anaerobic conditions. Due to the slow anaerobic degradation rate, TA is expected to accumulate in anaerobic soils.

In aquatic systems, TA is expected to biodegrade or be adsorbed to suspended solids in the water column, based on screening level studies on the aquatic fate of TA and the estimated K_{oc} of 290 (HSDB 2003).

He X, Z Zhang, S MA. 1992. Study on biodegradability of terephthalic acid. *China Journal of Environmental Science*. 13(3):18-24.

A study on the biodegradability of terephthalic acid (TA) aiming at clarifying its biodegradation characteristics, biodegradation rate and metabolic pathways, by activated sludge was carried out. The results showed that terephthalic acid can be biodegraded rapidly by microorganisms. The relationship between biodegradation rate and the concentration of TA can be fitted into Michaelis-Menten model. The biodegraded products from terephthalic acid by activated sludge were identified as m-

hydroxybenzoic acid and protocatechuic acid and a metabolic pathway of terephthalic acid was accordingly proposed.

HSDB. 2003. Hazardous Substances Databank. A Database of the National Library of Medicine's TOXNET System.

<http://toxnet.nlm.nih.gov>. Accessed December 17, 2003.

Kleerebezem, R., Mortier, J., Hulshoff Pol, L.W. and Lettinga, G. 1997. Anaerobic pre-treatment of petrochemical effluents: Terephthalic acid wastewater. IAWQ International Conference on Pretreatment of Industrial Wastewaters, Athens (Greece), 16-18 Oct 1996.

During petrochemical production of purified terephthalic acid (PTA, 1,4-benzene dicarboxylic acid), a large quantity of concentrated effluent is produced. Main polluting compounds in this wastewater are terephthalic acid, acetic acid, and benzoic acid in decreasing order of concentration. Acetic acid and benzoic acid are known to be rapidly degraded in high rate anaerobic treatment systems, such as Upflow Anaerobic Sludge Bed (UASB) reactors. Concerning the kinetics of anaerobic mineralization of terephthalic acid, however, no information was available in literature. Therefore, the work focused on the anaerobic degradation of neutralized terephthalic acid (disodium terephthalate) in laboratory scale UASB-reactors and batch reactors. It was found that high rate anaerobic treatment of terephthalate was difficult to obtain due to the low growth rate (μ approximately 0.04/day) of the terephthalate mineralizing mixed culture. The maximum removal capacity of a lab-scale UASB-reactor was found to be 3.9 g COD/l/day at a loading rate of 4.5 g COD/l/day and a hydraulic retention time of 24 hours. Terephthalate was used as sole carbon source during these experiments. Addition of small amounts of sucrose (co-substrate) to the influent, as a source of reducing equivalents, was found to have a negative influence on the anaerobic degradation of terephthalate. Also benzoate was found to inhibit the mineralization of terephthalate. Batch-toxicity experiments showed that terephthalate is not toxic to any of the species involved in its mineralization. Based on these observations, a staged anaerobic reactor system is suggested for the anaerobic pre-treatment of PTA-wastewater.

Macarie, H., Noyola, A. and Guyot, J.P. 1992. Anaerobic treatment of a petrochemical wastewater from a terephthalic acid plant. *Water Science and Technology* 25(7): 223-235.

Anaerobic treatment of terephthalic acid plant wastewater was tested using two UASB reactors (T and U) and a downflow tubular fixed film reactor. UASB T was inoculated with sludge sampled from an anaerobic stabilization pond receiving waste activated sludge from a petrochemical industry treatment plant, UASB U and the fixed film reactor were inoculated with anaerobically adapted activated sludge from a municipal plant. Raw effluent had to be settled and neutralized before reactor feeding. Sedimentation resulted in 70% TSS and 37% COD removal. UASB digesters presented comparable treatment efficiencies with rather low COD removals: the best results were 46.4% for UASB T at 2.6 kg COD/m²d and a hydraulic retention time (θ) of 2.7 days and 43.9% for UASB U at 2.2 kg COD/m²d and θ of 3.2 days. The performance of the tubular reactor was much higher: 74.5% COD removal at 1.89 kg/m²d and θ of 3.4 days. The better efficiencies of this last digester are explained mainly by a higher VSS content and a better resistance to toxicity caused by the aromatics present in the wastewater. A primary settling-anaerobic-aerobic process is proposed as an alternative to the conventional aerobic process for treating terephthalic wastewater, but disposal of solids from primary sedimentation and cost of neutralization have to be considered before application.

Bioaccumulation and Trophic Transfer

TA has an estimated BCF of 19, indicating potential for bioaccumulation is low (HSDB 2003). Moffit et al. (1975) found no significant quantities of radio-labeled TA to accumulate in tissues following oral, intratracheal, dermal, and ocular dosing to rats and rabbits. Most TA was excreted in urine and feces within 48 hours of dosing. Yao et al. (2001) found excretion rates of TA in urine from rats were about 50%, 52% and 53% in 0-24 hours, 0-48 hours, and 0-72 hours, respectively, after administration. Tremaine and Quebbemann (1985) found that approximately 85% of radio-labeled TA was excreted unchanged in urine. Considering the low estimated BCF and toxicokinetics studies, TA is not expected to bioaccumulate in tissues or be transferred through trophic levels.

Moffitt, A.E., Jr., Clary, J.J., Lewis, T.R., Blanck, M.D. and Perone, V.B. 1975. Absorption, distribution and excretion of terephthalic acid and dimethyl terephthalate. *Am Ind Hyg Assoc J.* 36(8): 633-641.

Data from a radiotracer study in rabbits and rats to determine the absorption, distribution, and excretion of terephthalic acid (TA) and dimethyl terephthalate (DMT) following oral, intratracheal, dermal and ocular administration indicate the following: (1) a rapid absorption and excretion of ¹⁴C-TA and ¹⁴C-DMT with no evidence of tissue accumulation in rats following single or repeated oral and intratracheal ad-

ministration; (2) no evidence of skin irritation in rats after a single or repeated dermal application of 80 mg of ^{14}C -TA or ^{14}C -DMT and no significant skin absorption of ^{14}C -TA; (3) recovery of approximately 11% of a single dose and 13% of five repeated cutaneous doses of ^{14}C -DMT from the urine and feces of rats within 10 days after initial dosing; (4) no significant absorption of ^{14}C -TA when applied to the conjunctival sac of one eye of eight rabbits; (5) excretion of approximately 33% of a single ocular dose (50 mg) of ^{14}C -DMT in the urine and feces of rabbits within 10 days after instillation with no evidence of tissue accumulation or ocular damage. These results suggest that TA and DMT are rapidly absorbed and excreted and that no significant quantities of these compounds accumulate in the tissues following single or repeated oral, intratracheal, dermal, or ocular administration to laboratory animals.

Tremaine, L.M. and Quebbemann, A.J. 1985. The renal handling of terephthalic acid. *Toxicol Appl Pharmacol.* 77(1): 165-174.

By use of the Sperber in-vivo chicken preparation method (1948, Ann. R. Agric. Coll. Swed. 15, 317-349), infusion of radiolabeled terephthalic acid (^{14}C]TPA) into the renal portal circulation revealed a first-pass excretion of the unchanged compound into the urine. This model was used further to characterize the excretory transport of ^{14}C]TPA and provide information on the structural specificity in the secretion of dicarboxylic acids. At an infusion rate of 0.4 nmol/min., 60% of the ^{14}C]TPA that reached the kidney was directly excreted. An infusion rate of 3 or 6 $\mu\text{mol}/\text{min}$ resulted in complete removal of ^{14}C]TPA by the kidney. These results indicate that TPA is both actively secreted and actively reabsorbed when infused at 0.4 nmol/min and that active reabsorption is saturated with the infusion of TPA at higher concentrations. The secretory process was saturated with the infusion of TPA at 40 $\mu\text{mol}/\text{mn}$. The excretory transport of TPA was inhibited by the infusion of probenecid, salicylate, and m-hydroxybenzoic acid, indicating that these organic acids share the same organic anion excretory transport process. m-Hydroxybenzoic acid did not alter the simultaneously measured excretory transport of p-aminohippuric acid (PAH), suggesting that there are different systems involved in the secretion of TPA and PAH. The structural specificity for renal secretion of dicarboxylic acids was revealed by the use of o-phthalic acid and m-phthalic acid as possible inhibitors of TPA secretion. m-Phthalate, but not o-phthalate, inhibited TPA excretory transport, indicating that there is some specificity in the renal secretion of carboxy-substituted benzoic acids. TPA was actively accumulated by rat and human cadaver renal cortical slices.

Yao, H., Wang, X., Wang, D. and Dai, J. 2001. [Toxicokinetics of terephthalic acid]. *Wei Sheng Yan Jiu.* 30(1): 23-24.

In order to study the toxicokinetics of terephthalic acid (TPA) in rats, and provide scientific basis for its biological exposed index (BEI), the concentrations of urine TPA in rats after single oral administration in dose of 100 mg/kg BW were determined by high pressure liquid chromatography. The toxicokinetic parameters were computed by using 3P97 program. The results showed that the first-order kinetics and two-compartment model were noted on the elimination of TPA. The main toxicokinetic parameters were as follows: $K_a = 0.51/\text{hr}$, $T_{1/2ka} = 0.488 \text{ hr}$, $T_{1/2 \text{ alpha}} = 2.446 \text{ hrs}$, $T_{\text{peak}} = 2.160 \text{ h}$, $K_u = 0.143/\text{h}$, $T_{1/2 \text{ beta}} = 31.551 \text{ hrs}$, $X_u(\text{max}) = 10.00 \text{ mg}$. The excretion rates of TPA in urine were about 50%, 52% and 53% in 0 to 24 hrs, 0 to 48 hrs and 0 to 72 hrs, respectively, after administration. TPA is well absorbed when given orally and rapidly eliminated via urine. Urine TPA at the end of work shift should be considered as a biomarker of exposure for the occupational workers.

Toxicity

Brooks, A.L., Seiler, F.A., Hanson, R.L. and Henderson, R.F. 1989. In vitro genotoxicity of dyes present in colored smoke munitions. *Environ. Mol. Mutagen.* 13(4): 304-313.

Genetic toxicology studies were conducted on organic dyes and mixtures used in colored smoke munitions. The dyes studied included Solvent Red 1; two different batches (Lot 1 and Lot 2) of Disperse Red 11; terephthalic acid; and a mixture of 25 parts Solvent Red 1, 5 parts Disperse Red 11, and 16 parts terephthalic acid. The dyes were evaluated for their ability to produce mutations in *Salmonella* bacterial strains and in Chinese hamster ovary (CHO) cells. The dyes were also tested in CHO cells to determine cytotoxicity and the induction of sister chromatid exchanges and chromosome aberration. None of the dyes were genotoxic in the standard Ames assay using bacterial strain TA1535 or TA100 with or without the addition of S-9 or in TA98 and TA1538 without S-9. With S-9, Disperse Red 11 (Lot 2) showed significant mutagenic activity in TA98 and TA1538 that increased as a function of S-9 concentration. However, the maximum level of mutagenic activity detected was low (3.8 revertants/micrograms). The azo dye Solvent Red 1 was also negative in a pre-incubation assay designed to reduce azo compounds to free amines. Solvent Red 1 was cytotoxic to mammalian cells, caused a significant increase in SCE, but was not mutagenic or clastogenic. Disperse Red 11 (Lot 1 and Lot 2) were not cytotoxic or clastogenic but produced an increase in cell cycle time and SCE frequency. Only Disperse Red 11 (Lot 2) increased mutations in the CHO/hypoxanthine-guanine phosphoribosyltransferase (HGPRT) assay. The mutagenic activity of the dye mixture was not significant, suggesting no synergistic interaction between the dyes. These studies demonstrated that none of the dyes was clastogenic and that a con-

taminant in Disperse Red 11 (Lot 2) may be responsible for the weak mutagenic activity in both mammalian and bacterial cell systems.

Hall I.H., O.T. Wong, D.J. Reynolds, R. Simlot, J.J. Chang. 1993. Terephthalic acid in Sprague-Dawley rats as a hypolipidemic agent. *Arch. Pharm.* 326:5-13.

The effects of terephthalic acid on liver and intestinal mucosa lipid metabolism in rats, its acute toxicity in mice, and LDL and HDL receptor activity as they relate to the enzymes that regulate lipid metabolism in rat and human cells were described. Results indicate that terephthalic acid has potential as a hypolipidemic agent. The acute toxic studies indicate no serious problems with its use in mice.

Kim, M.N., Lee, B.Y., Lee, I.M., Lee, H.S. and Yoon, J.S. 2001. Toxicity and biodegradation of products from polyester hydrolysis. *J Environ Sci Health Part A Tox Hazard Subst Environ Eng.* 36(4): 447-463.

Toxicity of products from polyester hydrolysis such as succinic acid (SA), adipic acid (AA), mandelic acid (MA), terephthalic acid (TA), 1,4-butanediol (1,4-B), ethylene glycol (EG), styrene glycol (SG) and 1,4-cyclohexane dimethanol (1,4-C) was evaluated by phytotoxicity test on germination of young radish seeds and by cytotoxicity test on HeLa cells. The phytotoxicity test revealed $SG > MA > 1,4-C > AA$ approximately $SA > TA$ approximately $EG > 1,4-B$ in order of decreasing toxicity taking into consideration the growth behavior after germination as well as the percentage of germination. Toxicity on HeLa cells decreased in slightly different order compared to that on young radish seeds, i.e. $SG > 1,4-C > MA > TA > SA > AA > EG > 1,4-B$. Tests for the phytotoxicity and for cytotoxicity indicated that the aromatic compounds were more harmful than the aliphatic ones. Each group of 4 strains which grew most rapidly on each agar plate containing SA, AA, MA, TA, 1,4-B, EG, SG and 1,4-C respectively as a sole carbon source was identified by the fatty acid methyl esters analysis. The modified Sturm test was carried out using the single isolated strain, an activated sludge or a mixed soil to measure the rate of mineralization of the compounds into carbon dioxide. The aliphatic compounds were mineralized more easily than the aromatic compounds. 1,4-C showed the most exceptionally slow degradation. A scrutiny of residual 1,4-C after degradation is required before polyesters containing 1,4-C could be classified as compostable because 1,4-C has detrimental effects on young radish seeds and HeLa cells and has a tendency to accumulate in the environment due to its slow degradability.

Muse, W.T., Jr., Anthony, J.S., Bergmann, J.D., Burnett, D.C., Crouse, C.L., Gaviola, B.P. and Thomson, S.A. 1997. Chemical and toxicological evaluation of pyrotechnically disseminated terephthalic acid smoke. *Drug Chem Toxicol.* 20(4): 293-302.

The terephthalic acid (TPA) smoke obscurants (M-83 grenade and M-8 smoke pot) were developed by the U.S. Army for training purposes to replace the more toxic hexachloroethane (HC) smoke. Inhalation toxicity testing and chemical characterization of pyrotechnically-generated TPA was conducted to assess the health hazard potential of TPA and its combustion products. Fisher 344 rats were subjected to acute and repeated exposures to TPA smoke generated from the M-83 grenade. Acute exposure levels ranged from 150 mg/m³ to 1,900 mg/m³ for 30 min and repeated dose exposures ranged from 128 mg/m³ to 1,965 mg/m³ for 30 min/day for 5 days. Exposed and control rats were evaluated for toxic signs, and histopathologic changes. During exposure, the rats exhibited slight to moderate lacrimation, rhinorrhea, lethargy and dyspnea, that reversed within one hour post-exposure. No deaths occurred, even at the highest smoke concentrations. Histopathological changes were confined to exposure related nasal necrosis and inflammation in both the acute and repeated dose exposures at levels above 900 mg/m³. Chemical characterization of the M-83 grenade and the M-8 smoke pot showed that formaldehyde, benzene and carbon monoxide were the major organic vapor by-products formed. These by-products were above their respective ACGIH threshold limit values at various concentrations, but should not pose a hazard if the smoke is deployed in an open area. Overall, TPA is a safer training smoke to replace the HC smoke.

The authors concluded that despite the lack of substantial acute toxicity following exposure to pyrotechnically disseminated TA, the manifestation of histopathologic alteration in the nasal cavity raises concern regarding TA as devoid of any inhalation hazard.

Ryan BM, NS Hatoum, JD Jernigan. 1990. A segment II inhalation teratology study of terephthalic acid in rats. *Toxicologist* 10(1):40.

Purified Terephthalic Acid (PTA) is a monomer component of polyester with a variety of applications including adhesives, tire cord, beverage bottles and magnetic recording tapes. In an effort to assess its teratogenic potential, PTA was administered as a particulate aerosol by inhalation at target concentrations of 0, 1.0 mg/m³, 5.0 mg/m³, and 10.0 mg/m³ to four groups of 22 to 25 timed-pregnant primiparous Sprague-Dawley rats. The rats were exposed 6 hours/day, on gestation days 6 through 15. The time-weighted average concentrations were 0, 0.9 mg/m³, 4.7 mg/m³, and 10.4

mg/m³ for the filtered air control, low, medium, and high exposure groups, respectively. No deaths occurred and no signs of maternal toxicity were observed during the study. No statistically significant differences in mean dam body or uterus weights, litter weights, dam body weight gain or pup viability were detected in the PTA-exposed rats compared to filtered air controls. External and soft tissue examinations failed to show any significant increase in the incidence of fetal malformations or abnormalities in the PTA-exposed litters compared to the controls. A statistically significant increase in the incidence of fetuses with rib anomalies was detected in the 5.0 mg/m³ group only when all rib anomalies were collapsed together. However, this increase was not considered a teratogenic event since the anomalies seen were common variations that were not elevated in a dose-related manner, were consistent with in-house historical control values, and no other signs of embryotoxicity were evident in the PTA-exposed groups. Therefore, exposure to 1.0 mg/m³, 5.0 mg/m³, or 10.0 mg/m³ of PTA did not result in significant toxic or teratogenic effects in the dam or fetus.

Shi, A., Wang, D., Wang, X. and Xu, X. 2000. [Changes of pulmonary surfactant in the rat lung exposed to terephthalic acid]. *Wei Sheng Yan Jiu.* 29(2): 71-72.

The contents of phospholipids in the lung surfactant in bronchoalveolar lavage fluid (BALF) of rats inhaled terephthalic acid (TPA) dust were analysed with high pressure liquid chromatography (HPLC). The average geometric concentrations of TPA dust in experimental groups were 8.93 mg/m³, 274.45 mg/m³ and 618.12 mg/m³ respectively. The results showed that phosphatidylcholine (PC), phosphatidyl glycerol (PG), and phosphatidylinositol (PI) of the rats exposed to TPA at the middle and high concentrations were decreased when compared with those in the control (P < 0.001). It was suggested that the functions of producing and secreting pulmonary surfactant in type II epithelial cells were damaged after inhaling TPA dust.

Article not available in English.

Yao, H., Wang, X., Xu, X. and Shi, A. 2002. [Study on the injury of liver induced by terephthalic acid ethylene glycol and/or dowtherm A in rats]. *Wei Sheng Yan Jiu.* 31(1): 12-14.

The joint injury actions and mechanisms of terephthalic acid (TPA), ethylene glycol (EG) and/or dowtherm A (DOW) on liver in rats were investigated. A subchronic toxicity study was designed by a 2(3) factorial method. Some enzymes, biochemical and morphologic indices reflecting the injury of liver were studied. The results showed

that serum ALT and serum total bile acid (TBA) of rats in the combined intoxication groups were significantly higher than those in the groups with single toxic agent and control group. The results of factorial analysis showed that the joint action induced by TPA, EG and/or DOW were characterized as additive (TPA + EG), synergistic (EG + DOW), synergistic (TPA + DOW) and additive (TPA + EG + DOW) actions. The deduction was identified by morphologic observations.

Article not available in English.

Smokes and Obscurants - General

The following citations contain either general information about smokes and obscurants, or did not identify the smokes and obscurants discussed in the text.

Physical-Chemical Properties

Stewart, C.E. and J.B. Sullivan, Jr. 1992. Military Munitions and Antipersonnel Agents. Hazardous Materials Toxicology, Clinical Principles of Environmental Health. Williams and Wilkins, Baltimore, Maryland.

Several smokes and obscurants were reviewed in this report, including white , CR gas, and CS gas. Chemical composition and toxicities of these compounds are reviewed.

Environmental Fate and Transport

Leitner, P. 1986. Environmental Fate of Phosphates, Chlorides, and Organic Residuals from Combusted Military Smoke Materials: Final Report. Department of Energy [DE], 15 Jul 86, 20p. UCRL-15875. DE87006725/INW. Prepared by Dept. of Biology, Saint Mary's College, Moraga, CA.

This report summarized the results and conclusions of data base assessment studies carried out on the environmental fate of residuals from combusted military smoke materials. The work described is organized as follows: (1) identification of residuals; (2) environmental fate and transport; (3) estimation of toxicities; (4) biota at test facilities; and (5) outline of a short course on preparation of environmental assessment documents.

Vroblesky, D.A., T.M. Yanosky and F.R. Siegel. 1992. Increased Concentrations of Potassium in Heartwood of Trees in Response to Groundwater Contamination. *EGWSEI*. 19(2):71-74.

The wood of tulip trees (*Liriodendron tulipifera* L.) growing above groundwater contamination from a hazardous waste landfill in Maryland contained elevated concentrations of potassium (K). The groundwater contamination also contained elevated concentrations of dissolved K, as well as arsenic (As), cadmium (Cd), chloride (Cl), iron (Fe), manganese (Mn), zinc (Zn), and organic solvents. The dissolved K is derived from disposed smoke munitions. The excess K in the tulip trees is concentrated in the heartwood, the part of the xylem most depleted in K in trees growing outside of the contamination. These data show that the uptake and translocation of K by tulip trees can be strongly influenced by the availability of K in groundwater contamination and suggest the utility of this species as a real indicator of groundwater contamination.

Smith, T.S. 2004. Methods for Field Studies of Effects of Military Smokes, Obscurants, and Riot Control Agents on Threatened and Endangered Species. Volume 1: Background, Overview, Issues, and Recommendations. ERDC/CERL-TR-04-5. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

Sample, B.E., T.L. Ashwood, B.A. Carrico, L.A. Kszos and M.S. Nazerias. 1997. Methods for Field Studies of Effects of Military Smokes, Obscurants, and Riot-Control Agents on Threatened and Endangered Species. Volume 2: Methods for Assessing Ecological Risks. USACERL TR-97/140. AD-A333 828/2. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

Cassels, D.M., A.J. Krzysik and K.A. Reinbold. 2001. Methods for Field Studies of the Effects of Military Smokes, Obscurants, and Riot-Control Agents on Threatened and Endangered Species. Volume 3. Statistical Methods. ERDC/CERL-TR-01-59. ADA395028. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

Nam, S., M.E. Walsh, J. Day and K.A. Reinbold. 1999. Methods for Field Studies of the Effects of Military Smokes, Obscurants, and Riot-Control Agents on Threatened and Endangered Species. Volume 4. Chemical Analytical Methods and Appendices. USACERL-TR-99/56. ADA368050INW. Pre-

pared by U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.

This series of reports (4 volumes) provided information and methods on developing field programs for evaluating the potential effects of military smokes, obscurants, and riot-control agents on ecological receptors, with a particular emphasis on threatened and endangered species. The series reviews statutory and other legal requirements, provides information on selected smoke and obscurant compounds, reviews sampling and statistical methods potentially applicable to smoke and obscurant investigations, and reviews chemical and laboratory analytical methods for determining and analyzing smoke and obscurant compounds

Shinn, J.H., S.A. Martins, P.L. Cederwall and L.B. Gratt. 1985. Smokes and Obscurants: A Health and Environmental Effects Data Base Assessment. A First-Order, Environmental Screening and Ranking of Army Smokes and Obscurants. Phase1. Department of Defense [DODXA], Mar 85, 121p. UCID-20931. AD-A185 377/9/INW. Prepared by Lawrence Livermore National Lab., CA. Environmental Sciences Div.

The report provided an initial environmental screening and ranking for each U.S. Army smoke and obscurant depending on the smoke type and smoke-generating device. This was done according to the magnitude of the impact area, the characteristic environmental concentration, the relative inhalation toxicity, the relative toxicity when ingested by animals, the aquatic toxicity, the environmental mobility when freshly deposited, and the ultimate mobility and fate in the environment. The major smoke types considered were various forms of white , red , hexachloroethane-derived smokes, fog oil, diesel fuel smokes, and some infrared obscuring agents.

Bioaccumulation and Trophic Transfer

Information for specific constituents is included in the appropriate sections.

Toxicity

National Research Council, Subcommittee on Military Smokes and Obscurants. 1997. Toxicity of Military Smokes and Obscurants. Volume 1. National Academy Press, Washington, D.C.

National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants. Volume 2. National Academy Press, Washington, D.C.

National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants. Volume 3. National Academy Press, Washington, D.C.

This series of reports (3 volumes) summarized toxicity information on a number of military smoke and obscurant compounds. The focus is on human health effects and human exposures. Volume 1 deals with diesel fuel smoke, fog oil smoke, red phosphorous smoke, and hexachloroethane smoke. Volume 2 deals with white phosphorous smoke, brass smoke, titanium dioxide smoke, and graphite smoke. Volume 3 addresses potential toxicity of colored smoke formulations and colored smoke dyes.

4 Adequacy Of Database

This Section provides a review of the adequacy of the database (Section 4) for the identified S&O constituents (Section 3) for threatened and endangered species and ecological management, conservation, recovery, and risk assessment purposes (Table 7).

Fog Oil Smoke

Fog oil smoke is produced by injecting middle distillate petroleum into a heating element of a smoke-generation machine typically mounted on small and rapidly mobile military vehicles. Smoke-generating equipment can also be mounted and employed on weapons systems and carriers such as tanks and armored personnel carriers. The heated oil vaporizes and subsequently condenses upon contact with air forming a dense, white cloud composed of oil droplets of an approximate mass and median aerodynamic diameter of 1.3 μm (Driver et al. 2002). The reviewed literature sometimes distinguished between “old” fog oil and “new” oil based on the chemical composition of the oils used. Old fog oils, generally referred to as SGF 1 (Standard Grade Fuel 1), were naphthentic oils and contained carcinogenic substances. The fog oil formulation was changed in 1986 to exclude any carcinogenic substances and given the designation SGF 2 (or SFG No.2), which is the primary oil currently used to produce fog oil smoke. However, fog oil is nonetheless composed of many different types of chemicals, predominately aliphatic hydrocarbons with low levels of non-carcinogenic hydrocarbons (Brubaker et al. 1992).

There is little information on the health effects of fog oils, but potential toxicity can be estimated using data from lubricating and mineral oils. Specifically, fog oils are expected to behave similarly to insoluble cutting oils composed of mineral oils with only small amounts of additives.

Environmental Fate and Transport

Studies have been conducted on the environmental fate and transport of fog oil both under laboratory and field conditions (Cataldo et al. 1989, DeVaul et al. 1990a, 1990b, 3D 1996). The field studies evaluated concentrations in the environment following long-term use of fog oils. Both the laboratory and field studies consider fog oil alone as well as together with additives such as graphite flakes, brass flakes, and polyethylene glycol.

Several authors have modeled fog oil dispersion both alone and together with additives to determine particle size distributions and deposition velocities for use in predicting the likely impact area resulting from training and maneuver exercises. A recent study by Battelle with two smoke generators, the M56 and M157A2, were conducted in July 1998 at Dugway Proving Ground, UT. Battelle set up samplers at varying distances from the generators in order to capture and analyze elements in the fog oil smoke and the generators' exhaust. An inert tracer gas (SF6) was used to monitor plume meander and migration and allow identification and determination of the emission rate of the chemicals of concern in the exhaust and fog oil smoke. The exhaust and smoke samples were subjected to detailed chemical analysis, the results of which were used in an air dispersion model to predict fog oil smoke concentrations under a variety of meteorological conditions. The model was tailored for the topography, meteorological conditions, and scheduled training scenarios to be conducted at Fort Leonard Wood, MO. The study showed that under the right environmental conditions, the fog oil plume could persist longer than the duration of the training exercise and can migrate according to local meteorological conditions (summary available on the Web at:

<http://www.battelle.org/Environment/publications/EnvUpdates/Special2000/article4.html>).

The fate of fog oil once in the environment is less well understood. Fog oil (particularly when combined with additives such as graphite and brass flakes) is composed of numerous individual constituents, each of which behaves differently in the environment. Fog oils are expected to behave similarly to insoluble cutting oils and light mineral oils, but there are few field studies to validate this information. Therefore, availability of atmospheric dispersion information is excellent, and information on degradation pathways, transfer between environmental compartments (e.g., soil to plant), and other aspects of environmental fate and transport is adequate for predicting environmental concentrations of fog oil.

Bioaccumulation and Trophic Transfer

The evidence for bioaccumulation and trophic transfer is mixed. A field study at Fort McClellan, AL, found no evidence of concentrations of hydrocarbons in tissue samples. The authors conclude that no bioaccumulation of fog oil from fog oil smoke is occurring at Fort McClellan (3D 1996). However, Driver et al. (1993) found that the fog oil formulation under evaluation in that study did show some evidence of bioaccumulation. The physical-chemical properties of fog oil would suggest that fog oil constituents have a moderate potential for bioaccumulation, but this has not been verified in field or laboratory studies.

The database is inadequate for evaluating the bioaccumulation and trophic transfer potential of fog oil in terrestrial environments. There is more information available for aquatic environments and for this purpose the database is adequate.

Toxicity

There are not many toxicity studies for fog oil. The available studies have primarily evaluated inhalation effects and those are much better understood than ingestion or dermal absorption. In addition, most of the studies have focused on short-term inhalation exposures as opposed to long term exposures.

It is known that fog oil, at least as previously produced (i.e. before 1986), can contain several possible carcinogens, including 1,3-butadiene, benzene, and quinoline, in addition to causing systemic effects. Fog oil composition can vary depending on the additives and the way in which the fog oil is administered. Most toxicity estimates have been developed for inhalation exposures. Longer term ingestion toxicity estimates are based on toxicity studies conducted on mineral oils rather than fog oil per se. The database is inadequate for deriving toxicity reference values for mammals, amphibians and reptiles, and aquatic invertebrates, but is adequate for avian, soil invertebrate, and plant receptors. However, although some data is available on ingestion, none of the avian studies focused on ingestion as a pathway but rather on fog oil smoke inhalation and fog oil smoke settling into nesting cavities.

Hexachloroethane (HC) Smoke

Hexachloroethane is released to the air during military operations and training exercises using smoke-producing devices. Under typical military training generation applications, only small amounts (less than 5%) remain after smoke has formed. HC

smoke is produced by the combustion of a mixture of hexachloroethane (HC), zinc oxide, and aluminum. These mixtures are used in smoke producing devices such as smoke pots, grenades, and projectiles. The major component of the smoke is zinc chloride. There are also several chlorinated organic compounds in the smoke, some are documented potential human carcinogens. Hexachloroethane is also used commercially in the production of fluorocarbons and as an ingredient in some lubricants, pesticides, plastics, and cellulose (ATSDR 1997a).

Environmental Fate and Transport

Hexachloroethane is relatively resistant to degradation in the aquatic environment. No hydrolysis of hexachloroethane in water was observed after 11 days at 85 °C at pH levels of 3, 7, and 11 (Ellington et al. 1987, ATSDR 1997a). However, hexachloroethane may be reduced in aquatic systems in the presence of sulfide and ferrous ions (Kriegman-King and Reinhard 1991). The transformation rate of hexachloroethane to tetrachloroethylene under simulated groundwater conditions at 50 °C was evaluated without ferrous or sulfide ions, with minerals (biotite and vermiculite) providing ferrous ions, and with minerals and sulfide ions. Reported half-lives for hexachloroethane were 365 days for hexachloroethane alone, 57 days to 190 days with minerals present, and 0.45 days to 0.65 days in the presence of both minerals and sulfide. Photolysis of hexachloroethane in water has been reported, but degradation to carbon dioxide occurred at a temperature of 90 °C to 95 °C (Knoevenagel and Himmelreich 1976).

Biodegradation may represent an important removal process in ambient waters, but there is conflicting evidence regarding the significance of this fate process. Howard (1989) reports that less than 30% degradation of hexachloroethane occurred after a 2 week incubation period in activated sludge under aerobic conditions. Another study (Mrsny et al. 1978) reports that hexachloroethane had no effect on the growth rate of a mixed bacterial culture and was quantitatively recovered after incubation with the culture for 8 days. Hexachloroethane was only viable as a sole source of carbon after incubation for approximately 6 weeks. The authors concluded that hexachloroethane was nontoxic to and unmetabolizable by bacteria. However, there are other studies suggesting that biodegradation of hexachloroethane may occur. Tabak et al (1981) report 100% loss rate for hexachloroethane in a seven day static-screening-flask test at 25 °C under aerobic conditions. Spanggard et al. (1985a) report significant volatilization losses under aerobic conditions. Under anaerobic conditions, 90% of hexachloroethane was removed from pond water in 18 days, while no losses were observed from sterile pond water (Spanggard et al. 1985a). Criddle et al. (1986) estimate a 40 day half-life for hexachloroethane in an unconfined sand aquifer. Labo-

ratory studies were also conducted with wastewater microflora cultures and aquifer material that provided evidence of microbial reduction of hexachloroethane to tetrachloroethylene under aerobic conditions.

Hexachloroethane released to water or soil may volatilize into air or adsorb onto soil and sediments. Volatilization appears to be the major removal mechanism for hexachloroethane in surface waters (Howard 1989). The volatilization rate from aquatic systems depends on specific conditions, including adsorption to sediments, temperature, agitation, and airflow rate. Volatilization is expected to be rapid from turbulent shallow water, with a half-life of about 70 hours in a 2 m deep water body (Spangord et al., 1985a). A volatilization half-life of 15 hours for hexachloroethane in a model river 1 m deep, flowing 1 m/sec with a wind speed of 3 m/sec was calculated (Howard 1989). Measured half-lives of 40.7 minutes and 45 minutes for hexachloroethane volatilization from dilute solutions at 25 °C in a beaker 6.5 cm deep, stirred at 200 rpm, were reported (Dilling 1977; Dilling et al. 1975). Removal of 90% of the hexachloroethane required more than 120 minutes (Dilling et al. 1975). The relationship of these laboratory data to volatilization rates from natural waters is not clear (Callahan et al. 1979). Deposition of hexachloroethane from air to water, plants, and soil has been reported (Cataldo et al. 1989). Calculated soil adsorption factors (log K_{oc} of 2.24, 2.98, and 4.3) suggest that hexachloroethane has medium to low mobility in soil (Howard 1989) and moderate to slight adsorption to suspended solids and partitioning to sediments. There is moderate potential for leaching to groundwater. Results of studies with low organic carbon (0.02%) soil material indicate that sorption to aquifer materials retards hexachloroethane migration in groundwater (Curtis et al. 1986).

Hexachloroethane may biodegrade in soil, but abiotic degradation processes are not expected to be significant. Hexachloroethane is biotransformed in soil under both aerobic and anaerobic conditions, but proceeds more rapidly in anaerobic soils (Spangord et al., 1985a). Loss of 99% of hexachloroethane was reported after 4 days of incubation anaerobically and after 4 weeks under aerobic conditions. Volatilization contributed to aerobic losses.

The database is adequate for evaluating the fate of hexachloroethane in both aquatic and terrestrial environments.

Bioaccumulation and Trophic Transfer

Bioconcentration in fish has been reported and is expected to occur, but biomagnification through the food chain is unlikely. EPA (1980) reports a bioconcentration fac-

tor (BCF) of 139 in bluegills. However, vertebrates appear to rapidly metabolize hexachloroethane, with estimated half-lives on the order of <1 day (Howard 1989). Oliver and Niimi (1983) report BCFs in rainbow trout of 510 and 1,200 at low (0.32 ng/l) and high (7.1 ng/l) exposure levels, respectively. Using an octanol-water partition coefficient (K_{ow}) and the molar solubility of the compound in octanol, Banerjee and Baughman (1991) calculated an apparent BCF of 245. Hexachloroethane has rarely been detected in ambient waters (ATSDR 1997a) and appears to be rapidly metabolized, thus, significant bioaccumulation or biomagnification in the food chain is not expected.

Cataldo et al. (1989) conducted numerous studies evaluating the potential for transport, transformation, fate and potential terrestrial ecological effects of hexachloroethane obscurant smokes. The evaluation was conducted for soil microbial communities, one earthworm study, and several plant studies, but did not evaluate the potential for bioaccumulation in higher order receptors (e.g., consumers of plants and soil invertebrates).

The database is adequate for evaluating the potential for bioaccumulation in aquatic environments but is inadequate for terrestrial environments.

Toxicity

The toxicity of hexachloroethane smokes have been more extensively evaluated in aquatic environments (e.g., acute and chronic toxicity tests using a variety of fish and invertebrates) than in terrestrial environments. The literature summary identified two plant studies (Sadusky et al. 1993, Schaeffer et al. 1986) and one soil invertebrate study (Cataldo et al. 1989). There are numerous inhalation studies (e.g. Karlsson et al. 1986, Marrs et al. 1983, 1988, Richards et al. 1989) but the literature review did not identify any ingestion studies.

The database is adequate for evaluating toxicity in plants, aquatic invertebrates, birds, and mammals, but inadequate for fish, amphibians, and reptiles.

White Phosphorous (WP) Smoke

The fate of WP smoke is similar to the fate of reaction products of WP vapor in air. White phosphorus vapor in air reacts with oxygen and transforms to relatively harmless chemicals within minutes. However, these particles often have a protective coating that contributes to their unreactivity. In water, WP again reacts primarily

with the oxygen and may stay in water for hours to days. Low oxygen levels in water, soils, and sediment contribute to longer half-lives. WP may react with water to form phosphine under low oxygen conditions. Phosphine is a highly toxic gas and quickly volatilizes from water to air.

WP has a low to moderate bioaccumulation potential, but because it is known to accumulate in anaerobic soil and sediment layers it can be a significant source to the food web. For example, in arctic or sub-arctic environments (e.g. Eagle Flats [Fort Richardson] AK), WP has been observed accumulating in sediment. Numerous studies have shown these accumulated deposits have adversely impacted local flora and fauna.

Environmental Fate and Transport

White phosphorus reacts rapidly in air with an estimated half-life of less than 5 min (Spanggord et al. 1985b). However, the deployment of the military smoke/obscurant in the field may produce an estimated 10% of unburnt phosphorus (Spanggord et al. 1985b). Particle size from phosphorus obscurant aerosols is determined by the age of the particles and the amount of water vapor available in the atmosphere. In wind tunnel studies particles increased in diameter by 1.3 times and increased in volume by 2.0 times at a relative humidity of 60%. Similar increases were observed with humidity levels higher than 60%. These increases are due to absorption of water vapor and to a lesser extent by coagulation of the particles.

Oxides of phosphorus are highly soluble in water, and wet deposition removes them from air (Berkowitz et al. 1981) more rapidly. Particulate elemental phosphorus also reacts at most environmental pressures and at temperatures $>5^{\circ}\text{C}$ (EPA 1989). The amount of phosphorus remaining in the particles has been observed to decrease with increasing relative humidity from a phosphorus percentage of 25% at low humidity to 15% for humidity near 90% (Van Voris et al. 1987). However, if the particulate phosphorus is coated with a protective layer of oxide, further oxidation may not occur (Berkowitz et al. 1981). This may increase the lifetime of elemental phosphorus in the air. Both wet and dry deposition remove the oxide-coated elemental phosphorus from the atmosphere with the wet deposition rate increasing with increasing relative humidity.

The exposure of soil to phosphorus aerosols will upset the pH of the soil and create a more acidic layer of soil. This decrease in pH often can exceed the buffering capacity of the surface layer of the soil depending upon the amount of applied phosphorus. This process can be mitigated by a larger soil volume area so that phosphorus speci-

ation on a field scale will be minimal. The interaction of metals with phosphorus condensates could lead to their leachability and possible trace metal migration from the soil (Van Voris et al. 1987).

In soils, oxidation is the predominant route of loss of white phosphorus up to a depth that allows diffusion of oxygen (Bohn et al. 1970). The oxidation of phosphorus to its oxides is usually very rapid. White phosphorus oxidized within 2 days in soil at ambient temperatures (Rodriguez et al. 1972). A soil volatilization study found that the volatilization of elemental phosphorus stopped after 3 to 7 days (Warnock 1972). If the termination is attributed to oxide formation, it can be concluded that elemental phosphorus oxidized in soil within 3 to 7 days. However, the rate of oxidation will be slower if white phosphorus forms a protective coating (Bohn et al. 1970). The results of anaerobic biodegradation studies with soil and sediments are inconclusive (Spanggord et al. 1985b). Although white phosphorus transformed faster in some nonsterile than in sterile controls, the slower transformation in sterile soil could be attributed to a change in soil property due to autoclaving (Spanggord et al. 1985b). The investigators found that the biotransformation microorganisms were difficult to grow under their test conditions. The lack of growth is an indication of lack of biodegradation. Therefore, in the absence of oxidation and biodegradation reactions in anaerobic zones of soil and sediment, the half-life of elemental phosphorus could be 10 yrs to 10,000 yrs (Richardson and Weston 1992, Spanggord et al. 1985b). It should be mentioned that although microorganisms that biodegrade elemental phosphorus under anaerobic conditions could not be grown, both linear polyphosphates and cyclic metaphosphates could be microbially hydrolyzed to simpler phosphates in water and soil under aerobic and anaerobic conditions (Spanggord et al. 1985b). In sealed tubes, phosphine completely disappeared in less than 40 days from three different types of soil with varying amounts of moisture (Hilton and Robison 1972). The disappearance was attributed to initial sorption, and the subsequent biotic and abiotic oxidation of part of the sorbed compound. The rate of adsorption increased with decreasing moisture content and increasing organic soil content (Hilton and Robison 1972). The study showed that phosphine sorption in soil can occur by both physical and chemical sorption processes, and that the chemisorption process is higher in soils with a low organic matter and high mineral content (Berck and Gunther 1970). Chemisorption irreversibly binds phosphine in soil so that it is not available for volatilization. However, since phosphine is gaseous and is only slightly soluble in water, volatilization from soil may be the most important process by which phosphine is lost from soil when chemisorption is not occurring.

The two processes involved in the transport of elemental phosphorus from soil are volatilization and leaching. When 35 mg of elemental phosphorus was added to two soils, one

acid and the other calcareous, 0.004% to 0.6% of the applied found at a depth of 10 cm volatilized as elemental (not as oxides) in 3 days (Warnock 1972). The loss of a maximum amount of 0.6% phosphates was complete in 3 to 7 days. The amount of phosphorus volatilized appeared to be similar from both soils. The rate of volatilization decreased by increasing the depth to which the phosphorus was applied or by increasing soil moisture content; the rate did not go to zero. The transport of elemental phosphorus from soil by leaching depends on the K_{oc} value. The estimated K_{oc} value of 3.05 indicates that phosphorus may moderately sorb in soil. Therefore, moderate leaching of phosphorus may occur from the anaerobic soil zone where elemental phosphorus will be stable toward chemical oxidation (EPA 1989, Richardson and Weston 1992).

Phosphorus enters water mainly as phosphate; smaller amounts enter as elemental phosphorus. Berkowitz et al. (1981) report that 90% of the phosphate in an aquatic system was partitioned to sediment and the remaining 10% was found in water. Unoxidized elemental phosphorus in water deposits in sediment via settling but a small amount remains in colloidal form in the water column. Elemental phosphorus particles with diameters ranging from 0.015 to 3.0 mm were isolated from pond sediment samples of Eagle River Flats, AK (Bird 1991). The estimated soil sorption coefficient (K_{oc}) value of 3.05 indicates that both the water-soluble and colloidal forms of white phosphorus in the water phase may sorb moderately to particulate matter in water (Spanggard et al. 1985b, Swarm et al. 1983). The particle-sorbed phosphorus is eventually transported to the sediment.

Volatilization from water to air is another potential pathway. The Henry's Law constant (H) of 2.11×10^{-3} atm m³/mol (Spanggard et al. 1985b) indicates that volatilization of elemental phosphorus from water is significant (Thomas 1982). The estimated volatilization half-life of white phosphorus from water is 48.5 min from a stream 4 feet deep, with an eddy diffusivity of 1 cm²/second (Spanggard et al. 1985b). Under turbulent conditions, the rate of volatilization is faster and may be an important fate-determining process for white phosphorus.

The database is excellent for evaluating the fate and transport of white phosphorus in the environment.

Bioaccumulation and Trophic Transfer

White phosphorus moderately bioconcentrates in aquatic organisms but is quickly depurated. The bioconcentration factors for white in a few species of aquatic organisms are as follows: cod (*Gadus morhua*) whole body, 44, and muscle, 24; salmon

(*Salvo salur*) muscle, 22 (Fletcher 1974); channel catfish (*Ictalurus punctatus*) muscle, 50-100; fathead minnow (*Pimephdes promelas*) muscle, 127 (Bentley et al. 1978); cod (*G. morhua*) muscle, 10-100 (Dyer et al. 1970); clams (*Mya arenaria*), 23; mussel (*Mytilus edulis*), 10; periwinkle (*Littorinu littroreu*), 42; starfish (*Asterius vulgaris*), 27; lobster (*Homurus americanus*) muscle, 23-34 (Fletcher 1971). It has been suggested that the bioconcentration factor (BCF) of elemental phosphorus in fish muscle may depend on the concentration in water. The BCF for cod muscle decreased with increasing water concentration, ranging from 34 at 4.4 µg/l to 10 at 29 µg/l (Maddock and Taylor 1976). Depuration was rapid once the contaminated fish were placed in clean water; no elemental phosphorus was observed from within hours to 7 days of exposure (Bentley et al. 1978, Fletcher 1971, Maddock and Taylor 1976).

There are several studies evaluating the potential for uptake and transfer in avian receptors (Nam et al. 1994, 1996, Sparling and Federoff 1997) but only one study in mammals (Truhaut et al. 1971).

The database is excellent for evaluating bioaccumulation in aquatic environments and adequate for terrestrial environments.

Toxicity

There are numerous inhalation studies and several subchronic ingestion studies in mammals (primarily laboratory rats and mice) but very few field studies (ATSDR 1997). Ingested white phosphorous is considered to be highly toxic, as are high concentrations (e.g. >3,000 mg/m³) of white phosphorous smoke (as H₃PO₄) (NRC 1999a).

White exposure to plants results in a variety of deleterious effects based on the species of plant, smoke concentration, duration of exposure, relative humidity, and wind speed. These effects can include leaf tip burn, leaf curl, leaf abscission and drop, floral abortion, chlorosis, necrotic spotting, wilting, desiccation, and dieback. Other factors influencing the effects of white phosphorus on plants include if there is a post-exposure rainfall and if the exposure is a large acute dose or several lower chronic doses (Van Voris et al. 1987).

The database is adequate for deriving ingestion-based toxicity reference values for ecological receptors, although there were no documented studies of white phosphorus toxicity in higher order mammalian receptors (either aquatic or terrestrial) or any field studies for the mammalian receptors.

Brass Flakes/Powder

Brass flakes, an alloy typically composed of approximately 70% copper (Cu) and 30% zinc (Zn), are used to block detection of infrared waves. Trace amounts of aluminum (Al) (0.2%), antimony (Sb) (0.1%), and lead (Pb) (0.1%) have also been detected, but there may be other inorganic contaminants at concentrations close to or below typical detection limits (NRC 1999a). The predicted fate and effects of brass flakes depends not only on the form of the alloy, but the size of the individual particles and if specific coatings have been used. Typical coatings include palmitic and/or stearic acid that make the powder float on water surfaces.

Many studies have documented that elevated concentrations of copper and or zinc, in and of themselves, can have detrimental impacts on biological communities. Environmental fate and toxicity of brass flakes is regulated by the speciation of zinc and copper in the environment.

Environmental Fate and Transport

The environmental fate and transport of copper and zinc are reasonably well understood, although speciation in the environment is highly site-specific and depends on a number of soil and sediment parameters such as pH, redox potential, presence of specific bacteria, and other factors. However, the database is adequate for evaluating fate and transport.

Bioaccumulation and Trophic Transfer

The database for evaluating the potential bioaccumulation in aquatic and terrestrial environments has been reviewed both for brass flakes as well as copper and zinc individually. Again, the form of the metal in the environment will dictate the bioaccumulation potential, but the database is adequate for determining this potential on a site-specific basis.

Toxicity

The potential effects of brass flakes, specifically in terms of their usage as a U.S. Army obscurant, have been evaluated in detail for earthworms (Wentzel and Guelta 1987, 1988) and through aquatic toxicity tests (Landis et al. 1988, Hardy et al. 1988). No studies were identified in the literature review evaluating the potential toxicity of brass obscurants in other ecological receptors, but there are numerous

studies available for zinc and copper individually. Although the individual toxicity estimates do not capture the possible synergistic or antagonistic toxicity of the combined mixture, it is still possible to develop toxicity reference values for ecological receptors for zinc and copper. The database is evaluated as adequate.

(2-Chlorobenzal)malonitrile (CS)

The riot-control agent (2-Chlorobenzal)malonitrile (CS) exists in both vapor and particulate form after use. The vapor phase will degrade within approximately 100 hours, while the particulates will be removed by both wet and dry deposition. CS is not particularly mobile in soil and sediments and is expected to sorb to particles. Volatilization is unlikely. CS converts to free cyanide in the body via metabolism, and this conversion is largely responsible for limited toxic observations.

Environmental Fate and Transport

The database is inadequate for characterizing the environmental fate and transport of CS.

Bioaccumulation and Trophic Transfer

The predicted bioconcentration factor (BCF) of 30 for CS suggests the potential for bioconcentration is low. Bioconcentration is not expected when CS is present in the dissolved form because hydrolysis will rapidly occur (Demek 1970). However, the literature review did not identify any empirical studies on bioaccumulation in terrestrial or aquatic environments. Therefore, the database is evaluated as inadequate.

Toxicity

There are several inhalation studies available (Ballantine and Callaway 1972, Ballantine et al. 1974, Ballantine and Swanston 1978) and one study in laboratory rats (Rietveld et al 1983) using i.p. injection. CS is known to cause acute inhalation effects by design. However, the database is inadequate with respect to characterizing potential toxicity to ecological receptors.

Dibenz(b,f)-1,4-oxazepine (CR)

Dibenz(b,f)-1,4-oxazepine (CR) is a riot control agent with properties very similar to CS. However, there is little information available on the physical and chemical

properties, fate and effects, potential for bioaccumulation, and chronic toxicity for this constituent. Most of the studies available for CR focus on the acute effects associated with inhalation exposures.

Environmental Fate and Transport

The database is inadequate for characterizing the fate and transport of CR.

Bioaccumulation and Trophic Transfer

The literature review did not identify any studies or information on the potential for bioaccumulation in terrestrial and aquatic environments. Therefore, the database is evaluated as inadequate.

Toxicity

As with CS, there are several inhalation studies for CR. CR is known to cause acute inhalation effects by design. However, the database is inadequate with respect to characterizing potential toxicity to ecological receptors.

Titanium Dioxide

Titanium dioxide is used as an obscurant in military applications. It is also used topically for nonmilitary uses.

Environmental Fate and Transport

In 1975 the USEPA conducted a literature review of the fate and effects of titanium dioxide (USEPA 1975) but that literature review identified very few other studies.

Cassel et al. (1992) investigated a smoke generated from zinc/hexachloroethane and titanium dioxide/hexachloroethane pyrotechnical pictures in a closed space for the following parameters: smoke concentration, particle size distribution, and chemical composition of the smoke. Zinc hydroxy acids, which are strong acids, are formed during combustion of the zinc munition. The titanium tetrachloride formed in the smoke from the titanium dioxide munition will rapidly hydrolyze to hydrogen chloride and titanium dioxide. Several chlorinated organic substances are formed from both types of smoke munitions during combustion. Some of the substances have well-documented toxic and mutagenic effects; for example: hexachlorobenzene, hexa-

chlorobutadiene, and chlorinated dibenzofurans and dibenzodioxins. The amount of byproduct formed is higher from the titanium dioxide/hexachloroethane munition than from the zinc munition.

The database is inadequate for quantifying the environmental fate and transport of titanium dioxide.

Bioaccumulation and Trophic Transfer

The literature review identified one study evaluating concentrations of titanium dioxide in sediments and mussels near a titanium dioxide production facility (da Silva et al. 2000). In that study, some accumulation was noted. However, the literature summary did not identify any other studies on the bioaccumulation potential of titanium dioxide in aquatic or terrestrial ecosystems. Therefore, the database is deemed inadequate for the purpose of ecological risk assessment.

Toxicity

Most of the available studies for titanium dioxide focus on inhalation exposures in rats and the potential for carcinogenic effects. Generally these studies have indicated apparent minimal effects, although high long term exposures (e.g. 250 mg/m³, 24 mo) have been shown to produce carcinogenic effects (NRC 1999a). The literature survey did not identify any studies relevant to ecological risk assessment. Therefore the database is evaluated as inadequate.

Polyethylene Glycol (PEG)

Polyethylene glycols (PEG) are viscous, colorless liquids with varying molecular weights. PEG generally has a low acute and chronic toxicity in animals. Toxic effects to the kidney have occurred from high doses, but studies found little risk from exposure to PEG at low concentrations (Silverstein et al. 1984). PEG degrades rapidly under anaerobic conditions, but has longer environmental longevity under aerobic conditions.

Environmental Fate and Transport

The literature survey did not identify any relevant studies on the fate and transport of PEG. The database is inadequate for characterizing potential fate and transport in the environment, although the behavior of PEG in air is well-understood.

Bioaccumulation and Trophic Transfer

The literature survey did not identify any studies for quantifying bioaccumulation in terrestrial or aquatic environments; therefore, the database is evaluated as inadequate.

Toxicity

A few inhalation studies are available (HSDB 2003), but there are no data available for developing toxicity reference values for ecological receptors. The toxicity of PEG has been considered relatively low (Muhly 1983).

Graphite Flakes

Graphite flakes are used as an infrared wavelength obscurant, typically as an additive for fog oil smoke. Driver et al. (1993) found little risk, chemically and mechanically, to aquatic or terrestrial systems from obscurant graphite flakes.

Environmental Fate and Transport

Little is known about the potential environmental fate and transport of graphite flakes (Driver et al. 1993). The flakes have a small enough aerodynamic diameter that they could be incorporated into soil, but little is known about factors affecting bioavailability and uptake into plants and soil invertebrates. Consequently, the database for determining the environmental fate and transfer of graphite flakes contains virtually no data and is inadequate for the purposes of risk assessment.

Bioaccumulation and Trophic Transfer

We were unable to identify any data on the potential for bioaccumulation and trophic transfer in terrestrial and aquatic environments. Therefore, the database is inadequate for ecological risk assessment.

Toxicity

There are a number of inhalation studies (laboratory and primarily short term) available but very few ingestion or direct contact studies. These studies indicate minimal effects in laboratory mammals (NCR 1999a). Graphite in military application is used in conjunction with fog oil and synergistic effects are possible. Although

graphite has been demonstrated to accumulate in lungs, overt toxicological effects of long term (e.g. up to 13 wks) graphite and fog oil exposure has not been shown (Aranyi et al. 1992). The literature review identified one earthworm study (Bowser et al. 1990) and a 64 day standard aquatic microcosm test (Landis et al. 1988). Driver et al. (1993) state that "consumption of graphite flakes while foraging unlikely to cause effects" but do not provide any references to support that statement. Therefore, the database is inadequate for the purposes of ecological risk assessment for higher order mammalian and avian receptors, although some, but still inadequate, data is available for soil invertebrates and plants (Guelta and Checkai 1995).

Colored Smokes

Colored smoke grenades contain a combination of colored smoke mixtures and pyrotechnic mixtures. The dye components of the colored smoke grenades (approximately 42%) represent the bulk of the chemicals in the mixture (NRC 1999b). Most of the dyes contain anthraquinone and/or one of its derivatives. It is soluble in alcohol, ether, acetone, and insoluble in water.

Environmental Fate and Transport

The fate of colored smokes and dyes has been better studied in aquatic environments than in terrestrial environments, but the potential fate of the numerous constituents in the dyes is poorly understood. The database for aquatic environments is adequate, but it is inadequate for air and terrestrial environments.

Bioaccumulation and Trophic Transfer

Anliker and Moser (1987) estimated K_{ow} values and water solubility values for several organic pigments and disperse dyes. Calculated K_{ow} values were high, suggesting bioaccumulation factors greater than 100. The low water solubilities indicate that despite the predicted high bioaccumulation factors, concentrations of pigments were not expected to accumulate in fish. The following year, Anliker et al. (1988) calculated and/or measured octanol-water partition coefficients ($\log K_{ow}$) for 23 disperse dyestuffs and two organic pigments. The molecular weight and the second largest van der Waals diameter of the molecule was chosen. None of the disperse dyestuffs, even the highly lipophilic ones with $\log K_{ow}$ greater than 3, accumulated in fish to any significant degree. The authors argue that the large molecular size effectively prevents permeation through biological membranes and thus, uptake.

Baughman and Perenich (1988) combined solubilities and vapor pressures from the literature with calculated octanol-water partition coefficients to assess the expected environmental behavior of about 50 dyes. Most of the older disperse dyes in use for decades had solubilities on the order of 10^{-7} to 10^{-6} . This solubility suggests the potential for a 30- to 150-fold concentration enhancement in sediments and approximately a thousand-fold bioconcentration factor in the absence of metabolism. The data also indicate that solubilities computed from K_{ow} may be significantly overestimated and that the product of subcooled liquid solubility and estimated K_{ow} for disperse dyes is 10 to 100 times smaller than reported for most other compounds. Baughman et al. (1992) examined three regression approaches for use in estimating water solubilities and octanol-water partition coefficients for a large number of dyes. The data showed that the smoke dyes will partition strongly to sediments and soils and have potential bioconcentration factors that range from 100 to over a million.

No studies were found that evaluated potential bioaccumulation in terrestrial systems.

The database is adequate for evaluating bioaccumulation potential in aquatic systems, although the theoretical bioconcentration and bioaccumulation predicted from physical/chemical properties has only limited empirical verification. The database is inadequate for evaluating bioaccumulation in terrestrial systems due to the lack of data.

Toxicity

There are several inhalation studies of colored smokes, but the literature survey identified only one study that evaluated the potential for oral toxicity. Smith et al. (1986) evaluated six test articles to establish eye and skin irritation potential and the oral and dermal toxicity. The test articles evaluated included:

- (1) Disperse Red 11 - Lot 1;
- (2) Disperse Red 11 - Lot 2;
- (3) Disperse Blue 3 - Lot 3;
- (4) Violet Mixture - 35 parts Disperse Red 11 - Lot 1:5 parts Disperse Blue 3;
- (5) Solvent Red 1; and
- (6) Red Mixture - 33.4 parts Solvent Red 1:6.6 parts Disperse Red 11 - Lot 1.

Oral studies were conducted using the Fischer-344 albino rat as the test system; all other studies used the New Zealand White Albino Rabbit as the test system. Results were as follows:

Disperse Red 11: Lot 1 was found to be a moderate skin irritant; tested negative for eye irritation, had a dermal LD₅₀ greater than 2 g/kg. The authors were unable to calculate an oral LD₅₀ for males but estimate that it is between 708 mg/kg and 891 mg/kg. The oral LD₅₀ for females is at least 5 g/kg.

Disperse Red 11: Lot 2 was found to be a mild skin irritant; tested negative for eye irritation, had a dermal LD₅₀ greater than 2 g/kg; and oral LD₅₀ of 1042.7 mg/kg in males, and greater than 5 g/kg in females.

Disperse Blue 3 was found to be predominantly nonirritating to the skin; tested negative for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ greater than 5 g/kg.

Violet Mixture: 35 parts Lot 1 Disperse Red 11 to 5 parts Disperse Blue 3 was found to be a mild skin irritant; tested negative for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ of between 794 mg/kg and 1000 mg/kg for males, between 1,413 mg/kg and 1,778 mg/kg for females, and 1052 mg/kg for combined sexes.

Solvent Red 1 was found to be nonirritating to the skin; tested positive for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ greater than 5 g/kg.

Red Mixture: 33.4 parts Solvent Red 1 to 6.6 parts Lot 1 Disperse Red 11 was found to be nonirritating to the skin; tested positive for eye irritation; had a dermal LD₅₀ greater than 2 g/kg; and an oral LD₅₀ greater than 5 g/kg.

The only oral toxicity studies identified from the literature summary focused on death as the endpoint, which is less relevant to evaluating long-term potential effects for ecological risk assessment. Therefore, the database is inadequate for developing toxicity reference values for ecological receptors.

Terephthalic Acid

Terephthalic acid (TA) is formed by hydrolysis of *p*-xylene in the presence of acetic acid and a catalyst such as manganese or cobalt acetate and sodium bromide (EPA 1983). TA is the main raw product used in the production of polyester packaging materials for a variety of common household products, as well as an additive to poultry feeds (Anon 1988). TA sublimates at 402 °C, forming a dense white smoke, which is used by the military in the M-83 smoke grenade and M-8 smoke pot. The U.S.

Army developed these TA munitions as training-scenario replacements for the more toxic hexachloroethane smoke munitions (Muse et al. 1997).

Environmental Fate and Transport

Atmospheric TA has been found in both the vapor and particulate phase, and had an estimated atmospheric half-life of 58 days (HSDB 2003). Vapor phase TA is expected to photochemically react with hydroxyl radicals and undergo transport to remote areas based on the estimated half-life (HSDB 2003). Following combustion, formaldehyde, benzene, and toluene are among the compounds formed (Muse et al. 1997). The database for air, aquatic, and terrestrial environments is deemed adequate.

Bioaccumulation and Trophic Transfer

TA has an estimated BCF of 19, indicating potential for bioaccumulation is low (HSDB, 2003). Moffit et al. (1975) found no significant quantities of radio-labeled TA to accumulate in tissues following oral, intratracheal, dermal, and ocular dosing to rats and rabbits. Most TA was excreted in urine and feces within 48 hours of dosing. Yao et al. (2001) found excretion rates of TA in urine from rats were about 50, 52, and 53% in 0-24 hours, 0-48 hours, and 0-72 hours respectively, after administration. Tremaine and Quebbemann (1985) found that approximately 85% of radio-labeled TA was excreted unchanged in urine. Considering the low estimated BCF and toxicokinetics studies, TA is not expected to bioaccumulate in tissues or be transferred through trophic levels.

The database is inadequate for modeling bioaccumulation in terrestrial and aquatic environments.

Toxicity

Muse et al. (1997) evaluated the toxicity of pyrotechnically disseminated TA smoke to rats over a wide range of smoke concentrations (150 mg/m³ to 1900 mg/m³). TA smoke was generated using the M-83 smoke grenade and M-8 smoke pot. The rats exhibited moderate levels of lacrimation, rhinorrhea, lethargy, and moderate-to-severe dyspnea at the highest smoke concentrations. No mortalities occurred from acute exposure within 14 days post-exposure, or after repeated exposures within a 3 month post-exposure period (Muse et al., 1997). TA was found to be non-genotoxic in standard Ames assays (Brooks 1989). A comparative toxicity study of products from polyester hydrolysis found TA to be moderately phytotoxic to young radish seeds and

moderately cytotoxic to HeLa cells (Kim et al. 2001). Shi et al. (2000) suggested that the production and secretion functions of epithelial cells in lungs were damaged after inhalation of TA dust because reduced levels of bronchoalveolar lavage fluids were found in rats exposed to TA. TA was found to damage liver cells of rats significantly more when acting synergistically with other toxicants (Yao et al. 2002). In a similar study, TA was found to present no serious toxicity to mice (Hall et al. 1993). Ryan et al. (1990) found that TA did not result in significant toxic effects in the fetus or litters of rats exposed to aerosolized TA.

The toxicological and toxicokinetic data suggests that TA is mildly toxic. Exposure to raw TA and TA smoke caused mild acute symptoms with no significant mortality. TA is excreted unchanged at high percentages in all evaluated exposure scenarios. TA also has a number of uses outside the military, including an additive to poultry feed. However, the database is inadequate for developing toxicity reference values for ecological receptors.

Key for Table 1

Categories	
P	Physical / Chemical Properties
E	Environmental Fate and Transport
T	Toxicity
B	Bioaccumulation
Agents	
DNB	1,3-Dinitrobenzene
DNP	2,4-Dinitrophenol
DNT	Dinitrotoluene and isomers
HMX	High Melting Point Explosive
NB	Nitrobenzene and isomers
NG	Nitroglycerin
NP	Nitrophenol and isomers
PETN	Pentaerythritol Tetranitrate
RDX	Cyclotrimethylenetrinitramine
TA	Terephthalic Acid
TET	Trinitrophenylmethylnitramine (Tetryl)
TNB	1,3,5-Trinitrobenzene
TNT	Trinitrotoluene
UG	Unspecified or General
Status	
A	Abstract Available
C	Complete Citation Available
N	No Abstract or Citation Available

Table 1. Database summary of relevant articles.

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
BF	T	A	Subchronic toxicity of inhaled brass dust in rodents	Armstrong, R.D. 1988. Spontaneous Activity and Passive Avoidance Behavior of Rats Exposed by Inhalation to Brass Dust (1 and 10 mg/m(sup 3)). Department of Defense [DODXA], Jun 88, 27p. CRDEC-TR-88156. AD-A200 497/6/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A200 497/6/INW
BF	E	A	Ecological risk assessment of brass obscurant	Guelta, M.A. and R.T. Checkai. 1998. Predictive Ecological Risk Assessment of Brass Infrared wavelength Obscurant in a Terrestrial Environment. - Final Report October 1994 - December 1995. Technical Report. March 1998. ERDEC-TR-364. AD-A342 600/4. Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A342 600/4
BF	ET	A	Fate and toxicity of brass powder deposited on water surfaces to aquatic invertebrates and algae	Haley, M.V., D.W. Johnson, W.T. Muse and W.G. Landis. 1988. Aquatic Toxicity and Fate of Brass Dust. Aquatic Toxicology and Hazard Assessment. V. 10. American Society for Testing and Materials, Philadelphia, PA. Pp. 468-479.	
BF	ET	C	Fate and toxicity of brass powder deposited on water surfaces to aquatic invertebrates	Hardy, J.T., E.A. Crecelius, C.E. Cowan and R.S. Wentzel. 1988. Toxicity and metal speciation relationships for Daphnia magna exposed to brass powder. Arch Environ Contam Toxicol. 17(5):575-581.	
BF	E	A	Effects of brass dust on standard aquatic microcosm	Landis, W.G., N.A. Chester, M.V. Haley, D.W. Johnson and W.T. Muse. 1988. Evaluation of the Aquatic Toxicity and Fate of Brass Dust Using the Standard Aquatic Microcosm. Department of Defense [DODXA], Jul 88, 24p. Technical Report. CRDEC-TR-88116. AD-A200 271/5/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A200 271/5/INW
BF	PE	A	Chemical composition and fate of brass at varying water hardness levels	Muse, W.T. 1988. Chemical Fate of Brass Dust in Waters of Varying Hardness Levels. Department of Defense [DODXA], Aug 88, 27p. Technical Report. CRDEC-TR-88131. AD-A199 598/4/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A199 598/4/INW
BF	B	A	Soil measurements at a training facility	US Army Corps of Engineers. 1993. A report of the accumulation of contaminants in soil samples from test area C52-A in connection with smoke weeks XIII and XIV. Eglin Air Force Base, Eglin, FL. US Army Corps of Engineers, Mobile, AL.	
BF	T	C	Toxicity of brass powder to earthworms	Wentzel, R.S. and M.A. Guelta. 1987. Toxicity of brass powder in soil to the earthworm Lumbricus terrestris. Environ Toxicol Chem. 6(10):741-745.	
BF	E	C	Brass powder contaminated soils	Wentzel, R.S. and M.A. Guelta. 1988. Avoidance of Brass Powder Contaminated Soil by the Earthworm Lumbricus terrestris. Environ Toxicol Chem. 7(3):241-244.	

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
BF FO	ET	C	Dispersion, deposition, biotic response and fate of brass associated with fog oil	Cataldo, D.A., M.W. Ligothke, H. Bolton, R.J. Fellows and P. Van Voris. 1991. Evaluation and characterization of mechanisms controlling fate and effects of Army smokes. Transport, transformations, fate, and terrestrial ecological effects of brass obscurants, Final Report. PNL-7459, Pacific Northwest Laboratory, Richland, WA.	
BF FO	E	A	Ecological survey of smoke testing ground	Downs JL, LE Eberhardt, RE Fitzner, LE Rogers. 1991. Ecological survey of M-field, Edgewood area Aberdeen Proving Ground, Maryland. Tech Rep Batelle Pac Northw Lab. Contract AC06-76RL01830.	
FO	ETB	C	Literature review on fog oil smoke	Liss-Suter, D. and J.E. Villaume. 1978. A Literature Review-Problem Definitions Studies on Selected Toxic Chemicals. Volume 8 of 8. Environmental Aspects of Diesel Fuels and Fog Oils SGF No. 1 and SGF No. 2 and Smoke Screens Generated from Them. Final Report. Franklin Insitute Research labs, Philadelphia.	ADA-056021
BF TD	ET	A	Toxicity testing on aquatic organisms	Haley, M.V. and C.W. Kurnas. 1993. Toxicity and Fate Comparison Between Several Brass and Titanium Dioxide Powders. ERDEC-TR-094. Edgewood Research, Development and Engineering Center, US Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.	
BF TD	T	A	Lung deposition study in rats and comparison between two exposure routes	Yeh, H.C., M.B. Snipes, A.F. Eidson, C.H. Hobbs and M.C. Henry. 1990. Comparative Evaluation of Nose-Only Versus Whole-Body Inhalation Exposures for Rats: Aerosol Characteristics and Lung Deposition. <i>Inhal Toxicol.</i> 2(3):205-221.	
CR	T	A	Uptake and metabolism of CR by guinea pig cornea	Balfour, D.J.K. 1978. Studies on the uptake and metabolism of dibenz(b,f)-1,4-oxazepine (CR) by guinea pig cornea. <i>Toxicology.</i> 9(1-2):11-20.	
CR	T	A	Acute mammalian toxicology of CR	Ballantyne, B. 1977. The acute mammalian toxicology of dibenz(b,f)-1,4-oxazepine. <i>Toxicology.</i> 8(3):347-380.	
CR	T	A	Rabbit eye exposure to smoke and liquid CR	Ballantyne, B., M.F. Gazzard, D.W. Swanson and P. Williams. 1975. The comparative ophthalmic toxicology of 1-chloroacetophenone (CN) and dibenz(b,f)-1,4-oxazepine (CR). <i>Arch Toxicol.</i> 34(3):183-201.	
CR	T	A	Metabolism and fate of CR in rats	French, M.C., J.M. Harrison, J. Newman, D.G. Upshall and G.M. Powell. 1983. The Fate of Dibenz(b,f)-1,4-oxazepine in the Rat. Part III. The Intermediary Metabolites. <i>Xenobiotica.</i> 13(6):373-381.	
CR	T	A	Metabolism and fate of CR in rats, monkeys, and guinea pigs	French, M.C., J.M. Harrison, T.D. Inch, L. Leadbeater, J. Newman, D.G. Spshall and G.M. Powell. 1983. The Fate of Dibenz(b,f)-1,4-oxazepine in the Rat, Rhesus Monkey, and Guinea Pig. Part I. Metabolism in Vivo. <i>Xenobiotica.</i> 13(6):345-359.	
CR	T	A	Metabolism and fate of CR in rats	Furnival, B., J.M. Harrison, J. Newman, D.G. Upshall. 1983. The Fate of Dibenz(b,f)-1,4-oxazepine in the Rat. Part II. Metabolism in Vitro. <i>Xenobiotica.</i> 13(6):361-372.	

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
CR	ET	N	Biodegradation and reduction of aquatic toxicity of CR	Haley, M.V., E.L. Vickers, T-C. Cheng, J. Defrank, T.A. Justus and W.G. Landis. 1989. Biodegradation and reduction in aquatic toxicity of the persistent riot control material 1-4-dibenzoxazepine. Aquatic Toxicology and Risk Assessment; 13th Symposium, Atlanta, Georgia. April 16-18, 1989.	
CR	P	A	Synthesis and chemistry of CR	Harrison, J.M., T.D. Inch and D.G. Upshall. 1978. The synthesis and chemistry of (11-14C)-dibenz(b,f)-1,4-oxazepine. J Labelled Compd Radiopharm. 14(3):375-380.	
CR	T	A	Biochemical changes in rats after exposure to CR	Husain K., P. Kumar and R.C. Malhorta. 1991. A comparative study of biochemical changes induced by inhalation of aerosols of o-chloroacetophenone and dibenz(b,f)-1,4-oxazepine in rats. Indian J Med Res Sect B. 94:76-79.	
CR	T	N	Aquatic toxicity of CR	Johnson, D.W., M.V. Haley and W.G. Landis. 1989. The aquatic toxicity of the sensory irritant and riot control agent dibenz(b,f)-1,4-oxazepine (CR). Aquatic Toxicology and Risk Assessment; 13th Symposium, Atlanta, Georgia. April 16-18, 1989.	
CR	T	A	Inhalation toxicity in mice	Kumar, P. and A.S. Sachan. 1998. Evaluation of 1-chloroacetophenone (CN) and dibenz(b,f)-1,4-oxazepine (CR) induces respiratory tract sensory irritation following a simple inhalation exposure method in mice. Biomed Environ Sci. 11(2):171-178.	
CR	T	A	Inhalation effects of CR on rat lungs	Kumar, P., R. Vijayaraghaven, S.C. Pant, A.S. Sachan and R.C. Malhotra. 1995. Effects of Inhaled Aerosol of 1-Chloroacetophenone (CN) and Dibenz(b,f)-1,4-oxazepine (CR) on Lung Mechanisms and Pulmonary Surfactants in Rats. Hum Exper Toxicol. 14(5):404-409.	
CR	T	C	Effects of CR on rat and rabbit embryo development	Upshall, D.G. 1974. Effects of dibenz(b,f)-1,4-oxazepine (CR) upon rat and rabbit embryonic development. Toxicol Appl Pharmacol. 29:301-311.	
CR CS	PT	A	Review of toxicity, chemistry, and effects of tear gasses	Olajos EJ and H Salem. 2001. Riot Control Agents: Pharmacology, Toxicology, Biochemistry and Chemistry. J Appl Toxicol. 21(5):355-391.	
CS	ET	A	Toxicity and exposure pathways of CS to fish	Abram, F.S.H. and P. Wilson. 1979. The acute toxicity of o-chlorobenzylidene malononitrile to rainbow trout (<i>Salmo gairdneri</i>). Water Res. 13(7):631-636.	
CS	T	A	Mammalian toxicology of CS	Ballantyne, B. and D.W. Swanston. 1978. The comparative acute mammalian toxicity of 1-chloroacetophenone (CN) and 2-chlorobenzylidene malononitrile (CS). Arch Toxicol. 75-96.	
CS	T	A	Inhalation toxicity of CS in rats, mice, rabbits, and guinea pigs	Ballantyne, B. and S. Callaway. 1972. Inhalation toxicology and pathology of animals exposed to o-chlorobenzylidene malononitrile. Med Sci Law. 12(1):43-65.	
CS	T	A	Rabbit eye exposure to smoke and liquid CS	Ballantyne, B., M.F. Gazzard, D.W. Swanston and P. Williams. 1974. The ophthalmic toxicology of o-chlorobenzylidene malononitrile (CS). Arch Toxicol. 32(3):149-168.	
CS	T	A	Fate of CS in rats	Brewster, K., J.M. Harrison, L. Leadbeater, J. Newman and D.G. Upshall. 1987. The Fate of 2-Chlorobenzylidene Malononitrile	

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				(CS) in Rats. <i>Xenobiotica</i> . 17(*):911-924.	
CS	PE	A	Studies on chemical conversion and disposal of CS	Brooks, M.E., P.M. Davis and S. Sass. 1976. Demilitarization of CS I. Chemical Disposal of CS by Hydrolysis. NTIS. ADA-A033 469.	
CS	T	A	Acute toxicity tests on rats	Debarre, S., L. Karinthe, S. Delmanche, C. Fuche, P. Desforges and J.H. Calvet*. 1999. Comparative acute toxicity of o-chlorobenzylidene malononitrile (CS) and oleoresin capsicum (OC) in awake rats. <i>Hum Exp Toxicol</i> . 18(12):724-730.	
CS	T	A	Inhalation toxicity and effects on respiratory tract	Delamanche, S., P. Desforges, S. Morio, C. Fuche and J.H. Calvet*. 2001. Effect of oleoresin capsicum (OC) and ortho-chlorobenzylidene malonitrile (CS) on ciliary beat frequency. <i>Toxicology</i> . 165(2-3):79-85.	
CS	E	A	Fate, transport, and remediation of CS in groundwater	Forgang, J. and K.R. McIntosh. 1996. Case study: fate, transport, and remediation of tear gas chemicals in groundwater. Hazard Ind Wastes Proc Mid Atl Ind Waste Conf, Technomic Publ Co Inc, Lancaster PA. Pp. 351-358.	
CS	T	A	Cyanide formed by CS transformation in mice	Frankenberg, L. and B. Sorbo. 1973. Formation of cyanide from o-chlorobenzylidene malononitrile and its toxicological significance. <i>Arch Toxicol</i> . 31(2):99-108.	
CS	T	A	Blood transformations of CS in guinea pigs	Leadbeater, L., G.L. Sainsbury and C. Utley. 1973. Ortho-Chlorobenzylmalononitrile: A metabolite formed from ortho-Chlorobenzylidenemalononitrile (CS). <i>Toxicol Appl Pharmacol</i> . 25(1):111-116.	
CS	T	A	CS effects on immune system in mice	Nagarkatti, M., P.S. Nagarkatti and C.D. Raghuvveeran. 1981. Short-term Toxicity Studies of o-Chlorobenzylidene Malononitrile on Humoral Immunity in Mice. <i>Toxicol Lett</i> . 8(1-2):461-465.	
CS	T	A	Metabolism of CS in rabbits	Paradowski, M. 1979. Metabolism of toxic doses of o-chlorobenzylidene malononitrile in rabbits. <i>Pol J Pharmacol Pharm</i> . 31(6):563-572.	
CS	T	A	Metabolism of CS in the rat	Rietveld, E.C., L.P.C. Delbressine, T.H.J.M. Waegemaekers and F. Seutter-Berlage. 1983. 2-Chlorobenzylmercapturic Acid, A Metabolite of the Riot Control Agent 2-Chlorobenzylidene Malononitrile (CS) in the Rat. <i>Arch Toxicol</i> . 54(2):139-144.	
DB	T	A	Toxicity of Disperse Blue 180 to rats, mice and guinea pigs	Marrs, T.C., H.F. Colgrave, P. Rice, J.A.G. Edginton and B. Morris. 1989. The Repeated Dose Toxicity of a Smoke Containing Disperse Blue 180, and Anthraquinone Dye Mixture. <i>J Haz Mat</i> . 21(1):73-88.	
DB DR SR	T	C	Oral and inhalation toxicity to rats and rabbits	Smith, S.H., G.L. Doyle, J.C. Kreuger, K.A. Mellon and D.A. Mayhew. 1986. Dermal, Eye and Oral Toxicological Evaluations. Phase IV with Disperse Red 11, Disperse Blue 3, Solvent Red 1, and Red and Violet Mixtures. Prepared by American Biogenics Corporation, Decatur, IL for US Army Medical Research and Development Command, Fort Detrick, MD.	
DR	ET	A	Water quality criteria	Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Disperse Red 9. Final Report. July 1987. ORNL-6356. AD-A183 369/8/GAR. Oak Ridge National Laboratory.	AD-A183 369/8/GAR

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DR	T	N	Metabolism of benzanthrone	Dwivedi, N., M. Das and S.K. Khanna. 2001. Role of biological antioxidants in benzanthrone toxicity. Arch Toxicol 75: 221-226.	
DR DV DB	T	N	Toxicity study	Jaskot, R.H. and D.L. Costa. 1994. Toxicity of an anthraquinone violet dye mixture following inhalation exposure, intratracheal instillation, or gavage. Fundamental and Applied Toxicology 22(1):103-112.	
DR DV SR SY	E	N	Degradation kinetics and products of dyes in anoxic sediments	Baughman, G.L. and E.J. Weber. 1994. Transformations of Dyes and Related Compounds in Anoxic Sediment: Kinetics and Products. Environ Sci Technol 28:267-276. Updated Citation: Baughman, G.L. and E.J. Weber. 1994. Transformation of Dyes and Related Compounds in Anoxic Sediment: Kinetics and Products. Environmental Protection Agency [EPAORD], 1994, 12p. Prepared by: Environmental Research Lab., Athens, GA. Office of Research and Development. EPA/600/J-94/116.	PB94-15553INW
FO	PE	A	Atmospheric dispersion of fog oil smokes	Barad ML and B Shorr. 1954. Field Studies of the Diffusion of Aerosols. Am Ind Hyg Assoc Quart. 15(2):136-140.	
FO	E	C	Terrestrial transport, fate, and ecological effects	Cataldo, D.A., P. Van Voris, M.W. Ligothe, R.J. Fellows, B.D. McVeety, S.W. Li, H. Bolton, Jr. and J.K. Frederickson. 1989. Evaluate and Characterize Mechanisms Controlling Transport, Fate, and Effects of Army Smokes in an Aerosol Wind Tunnel: Transport, Transformations, Fate and Terrestrial Ecological Effects of Fog Oil Obscurant Smokes: Final Report. OAD-A20414. DE89006573. PNL-6799. Prepared by Pacific Northwest Laboratory, Richland, WA for U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.	
FO	PE	A	Review of fog oil particles and plumes studies	Chester, N.A. 1998. Review of Selected Army-Funded Research on Fog Oil Smoke Characteristics as Related to Clean Air Act Issues. - Final rept. Oct 95-Oct 96. AD-A344 419/7. ERDEC-TR-475. Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A344 419/7
FO	ET	A	Bioavailability of fuel oil components in soils	DeJonge H., J.I. Freijer, J.M. Verstraten, J. Westerveld and F.W.M. Van der Wielen. 1997. Relation between bioavailability and fuel oil hydrocarbon composition in contaminated soils. Environ Sci Technol. 31(3):771-775.	
FO	PE	A	Atmospheric dispersion of fog oil smokes	DeVaul G., W.E. Dunn, J.C. Liljegren, A.J. Policastro. 1990. Atmospheric Dispersion of Military Fog Oil Smoke. Argonne National Laboratory, Argonne, IL.	
FO	T	C	Effects of fog oil smoke on sparrows	Driver C., J. Ollero, Y.F. Su, R. Fulton, G. Dennis, B. Tiller, H. Balback and K. Beibold. 2002. Effects of Fog Oil Smoke on the Hachability and Fledgling Survival of the House Sparrow (Passer domesticus), a Nestling Surrogate for the Red-cockaded Woodpecker. ERDC/CERL. TR-02-34.	

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FO	T	C	Toxicity to endangered avian species	Driver C., M. Ligothke, H. Galloway-Gorby, G. Dennis and K. Reinbold. 2002. Acute Inhalation Toxicity of Fog Oil Smoke in the Red-Winged Blackbird, a Size-Specific Inhalation Surrogate for the Red-Cockaded Woodpecker. - Draft rept. ADA399210. ERDC/CERL-TR-02-6. Engineer Research and Development Center, Construction Engineering Research Lab. (Army), Champaign, IL.	
FO	ETB	C	Review of health and environmental effects of fog oil	Driver C.J., M.W. Ligothke, J.L. Downs, B.L. Tiller, T.M. Poston, E.B. Moore Jr., D.A. Cataldo. 1993. Environmental and Health Effects Review for Obscurant Fog Oil. Pacific Northwest Laboratory, Richland, WA.	AD-A271 244
FO	T	A	Inhalation studies	Gardner, D.E., J.A. Harris, M.E. Hiteshew, D.W. Davies and E.C. Grose. 1984. Toxicological Studies of Smoke Obscurants. EPA-600/D-84-127. PB84-195288. U.S. Environmental Protection Agency - Health Effects Research Laboratory, in cooperation with Northrop Services, Inc.	PB84-195288
FO	E	C	Assessment of risk of fog oil to threatened and endangered species	Getz, L.L., K.A. Reinbold, D.J. Tazik, T.J. Hayden and D.M. Cassels. 1996. Preliminary Assessment of the Potential Impact of Fog Oil Smoke on Selected Threatened and Endangered Species. Final Report. January 1996. CERL-TR-96/38. U.S. Army Corps of Engineers - Construction Engineering Research Laboratory.	AD-A306 219/GAR
FO	E	A	Environmental fate and risk assessment to endangered species	Guelta, M.A. and R.T. Checkai. 2001. Methodology for Measurement of Fog Oil Smoke Penetration into a Red-Cockaded Woodpecker Nest Cavity. - Final rept. Sep 1995-Jan 1997. Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD. Technical Report. March 2001. ECBC-TR-152.	AD-A389 229
FO	PE	C	Physical and chemical characterization of fog oils	Katz, S, A Snelson, R. Butler, R. Farlow, R Welker and S. Mainer. 1980. Physical and chemical characterization of military smokes. Part 2: Fog Oils and Oil Fogs. Final Report Oct 78 - Feb 80. DAMD17-78C-8085. Ad-A093205. IIT Research Institute, Chicago, IL.	
FO	T	N	Fog oil effects on microbial activity	Li S.W., H. Bolton Jr., J.K. Fredrickson, P. Van Voris, D.A. Cataldo, R.J. Fellows, B.D. McVeety, M.W. Ligothke and K.W. McFadden. 1989. Influence of Fog Oil Obscurant Smoke on Microbial Activity. 89th Annual Meeting of the American Society for Microbiology, New Orleans, Louisiana. May 14-18, 1989.	
FO	PE	A	Atmospheric dispersion of fog oil smokes	Liljegren J.C., W.E. Dunn, G.E. Devaull and A.J. Policastro. 1989. Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes: Field Study of Fog-Oil Smoke. AD-A205 344. Argonne National Laboratory, Argonne, IL.	
FO	PE	A	Dispersion model of fog oil	Lozar, R.C. 2002. Web Interface for Modeling Fog Oil Dispersion During Training. - Final rept. U.S. Army Corps of Engineers - Construction Engineering Research Laboratory. Technical Report. August 2002. ERDC/CERL-TR-02-16.	ADA406751

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FO	PE	A	Review of models used to predict dispersion	Maloney, D.M., A.J. Policastro, W.E. Dunn and D.F. Brown. 1993. Evaluation of Atmospheric Wind Field and Dispersion Models for Fog-Oil Smoke Dispersion in Complex Terrain: Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes. Argonne National Laboratory, Argonne, IL.	
FO	PE	A	Atmospheric dispersion of fog oil smokes	Policastro A.J., D.M. Maloney, W.E. Dunn, J.C. Liljegren and G.E. Devaull. 1990. Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes: Evaluation of Atmospheric Dispersion Model for Fog-Oil Dispersion. Argonne National Laboratory, Argonne, IL.	
FO	PE	A	Summary and review of existing dispersion data	Policastro, A.J. and W.E. Dunn. 1986. Survey and Evaluation of Field Data Suitable for Smoke Hazard Model Evaluation. ANL/ER-85-3. AD-A161 880. Argonne National Laboratory, Argonne, IL.	
FO	T	A	Toxicity of fog oil and photooxidized fog oil to amphipods	Poston T.M., R.M. Bean, D.R. Kalkwarf, B.L. Thomas and M.L. Clark. 1988. Photooxidation Products of Smoke Generator Fuel (SGF) No. 2 Fog Oil and Toxicity to <i>Hyallela azteca</i> . <i>Env Toxicol Chem.</i> 7(9):753-762.	
FO	ET	A	Toxicity of persistent fractions of mineral oil	Riis V., M. Stimming, D. Miethe and W. Babel. 1996. Investigations into the toxicity of persistent fractions of mineral oils. <i>Chemosphere.</i> 32(7):1435-1443.	
FO	T	C	Toxicity of lubricating oils: surrogate for fog oil	Hartung, R. and G. Hunt. 1966. Toxicity of some oils to waterfowl. <i>Journal of Wildlife Management.</i> 30(3):564-570.	
FO	T	A	Short term exposure effects	Selgrade M.K., G.E. Hatch, E.C. Grose, J.W. Illing, A.G. Stead, F.J. Miller, J.A. Graham, M.A. Stevens and J.F. Hardisty. 1987. Pulmonary Effects Due to Short-Term Exposure to Oil Fog. <i>J Tox Env Health.</i> 21(1-2):173-185.	
FO	T	A	Inhalation toxicity of mineral oils to rats	Skyberg K., V. Skaug, B. Gylseth, J.R. Pedersen and O.H. Iversen. 1990. Subacute inhalation toxicity of mineral oils, C15-C20 alkylbenzenes, and polybutene in male rats. <i>Environ Res.</i> 53(1):48-61.	
FO	T	A	Subchronic white mineral oil feeding toxicity tests on dogs and rats	Smith J.H., M.G. Bird, S.C. Lewis, J.J. Freeman, G.K. Hogan and R.A. Scala. 1995. Subchronic feeding study of four white mineral oils in dogs and rats. <i>Drug Chem Toxicol.</i> 18(1):83-103.	
FO	E	C	Environmental fate and risk assessment to endangered species	Three D International, Inc. 1996. Environmental Fate of Fog Oil at Fort McClellan, Alabama. C7322.19. AD-A326 404/1. Prepared by Three D International, Inc., Cincinnati, OH in cooperation with Harland Bartholomew and Associates, Inc., Chesterfield, MO for US Army Corps of Engineers - Kansas City District.	AD-A326 404/1
FO	T	A	Literature review of fog oil smoke toxicity	U.S. Army in cooperation with Parsons Engineering Science, Inc. 1997. Evaluation of Human Health Risks Associated with Fog Oil Training at Fort Leonard Wood, Missouri Preliminary Risk Evaluation Report. (Revision). - Final Report. Prepared by: Bartholomew (Harland) and Associates, Jacksonville, FL.	AD-A326 407/4

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FO GF	T	A	Toxicity of fog oil with graphite	Aranyi, C., N. Rajendran, J. Bradof, J. Drummond and B. Levine. 1991. Inhalation Toxicity of Single Materials and Mixtures. Phase 3. Final Report. AD-A242 179/0/GAR. IIT Research Institute. August 28, 1991.	AD-A242 179/0/GAR
FO GF	E	A	Environmental assessment of fog oil with graphite flake generator field test	Driver, C.J., M.W. Ligothke, E.B. Moore and J.F. Bowers. 1991. Generator, mechanical, smoke: For dual-purpose unit, XM56, Yuma Proving Ground, Yuma, Arizona. Environmental Assessment. PNL-7781. Battelle Pacific Northwest Laboratories.	DE92001826/GAR
FO HC	PE	A	Atmospheric dispersion and deposition of smokes	DeVaull, G.E., D.F. Brown, W.E. Dunn and A.J. Policastro. 1990. Assessment and Computerized Modeling of the Environmental Deposition of Military Smokes. - Final rept. 1 Jul-30 Sep 90. AD-A246 942/7. Argonne National Laboratory, Argonne, IL.	AD-A246 942/7
FO HC	P	N	Physical and chemical characterization	EPA/OTS. Physical and Chemical Characterization of Fog Oil Smoke and Hexachloroethane Smoke. 2000. Doc #40-8038022.	
FO HC	PTB	C	Toxicity of military smokes and obscurants review	National Research Council, Subcommittee on Military Smokes and Obscurants. 1997. Toxicity of Military Smokes and Obscurants. Volume 1. National Academy Press, Washington, D.C.	
FO HC	PT	A	Preliminary assessment of smoke effect on flora and fauna of training sites	Schaeffer, D.J., W.R. Lower, S. Kapila, A.F. Yanders and R. Wang. 1986. Preliminary Study of Effects of Military Obscurant Smokes on Flora and Fauna During Field and Laboratory Exposures. Final Technical Report. December 1986. CERL-TR-86/22. AD-A176 328/3/GAR. U.S. Army Corps of Engineers - Construction Engineering Research Laboratory.	AD-A176 328/3/GAR
FO HC	T	N	Mutagenic testing of FO and HC smokes	Yanders A.F., E.W. Novak, W.R. Lower, A.G. Underbrink and R. Wang. 1985. Mutagenic Testing of Obscurant Smokes. Environ Mutagen. 7(3):60.	
FO PEG	E	C	Environmental impacts of petroleum distillate smokes	Muhly, R.L. 1983. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 1 of 5. Fog Oil, Diesel Fuels, and Polyethylene Glycol (PEG 200). July 1983. 139p. ARCSL-EA-83001-VOL-1. AD-A134 846/5/INW. Prepared by Chemical Research and Development Center, Aberdeen Proving Ground, MD for Project Manager Some/Obscurants - U. S. Army Armament Munitions & Chemical Command.	AD-A134 846/5/INW
FO WP	P	A	Chemical characterization	Brazell, R.S., R.W. Holmberg and J.H. Moneyhun. 1983. Chemical Characterization of Selected Military Obscurants. Chemical Systems Laboratories conference on obscuration and aerosol research, Aberdeen Proving Ground, MD, USA, June 20, 1983. Oak Ridge National Laboratory. CONF-8306196-1.	DE84003202/GAR
FO WP	T	A	Toxicity to freshwater organisms	Poston, T.M., K.M. McFadden, R.M. Bean, M.L. Clark and B.L. Thomas. 1986. Acute Toxicity of Smoke Screen Materials to Aquatic Organisms, White Phosphorous-Felt, Red Phosphorous-Butyl Rubber and SGF (Smoke Generator Fuel) No.2 Fog Oil. Final Report 1983-1985. PNL-5584. AD-A167 900/0/GAR. Battelle Pacific Northwest	AD-A167 900/0/GAR

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				Laboratories.	
G R V Y	PT	C	Chemical composition and toxicity of four colored smoke mixes	Buchanan, M.V. and C.Y. Ma. 1988. Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Chemical Characterization of Colored Signal Smokes. ORNL/TM-11195. Ad A209 379. Prepared by Oak Ridge National Laboratory, Oak Ridge, TN for US Army Medical Research and Development Command, Fort Detrick, Frederick, MD.	
G R V Y	PT	A	Chemical composition and toxicity of four colored smoke mixes	Buchanan, M.V., C.L. Ma, J.H. Moneyhun and M.R. Guerin. 1988. Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Smoke Generation and Characterization Part 2, Colored Smoke Grenades. Oak Ridge National Laboratory, Oak Ridge, TN.	
G R V Y	P	A	Chemical composition of four colored smoke mixtures	Rubin, I.B. and M.V. Buchanan. 1983. Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures. Chemical Characterization of Army Colored Smoke: Inventory Smoke Mixes (Red, Violet, Yellow, and Green). ORNL/TM-8956. AD A134777. Oak Ridge National Laboratory, Oak Ridge, TN.	
GF	T	C	Toxicity tests on earthworms	Bowser, L.K., C.T. Phillips and R.S. Wentzel. 1990. Toxicity of Graphite Flakes in Soil to Earthworms. - Final rept. Jun 88-Oct 89. Technical Report. June 1990. CRDEC-TR-129. AD-A224 244/4. Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A224 244/4
GF	T	C	Effects of graphite flakes on plants	Phillips, C.T. and R.S. Wentzel. 1990. The Effects of Graphite Flakes in Soil on Terrestrial Plants. Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	ADA-227281
GF	ETB	C	Review of health and environmental effects of graphite flakes	Driver, C.J., M.W. Ligothe, W.G. Landis, J.L. Downs, B.L. Tiller, E.B. Moore Jr. and D.A. Cataldo. 1993. Environmental and health effects review for obscurant graphite flakes. Final report, 1991 July--1993 May. ERDEC-CR-056. PNL-8585. DE93040324. Prepared by Pacific Northwest Laboratory, Richland, WA for Edgewood Research, Development & Engineering Center, U.S. Army Chemical and Biological Defense Agency, Aberdeen Proving Ground, MD.	DE93040324
GF	E	A	Ecological risk assessment of graphite obscurant	Guelta, M.A. and R.T. Checkai. 1995. Predictive Ecological Risk Assessment of Graphite Infrared Wavelength Obscurant in a Terrestrial Environment. - Final rept. Oct 93-Dec 94. Technical Report. March 1995. ERDEC-TR-240. AD-A294 363/7. Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A294 363/7

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GF	T	A	Toxicity of graphite to aquatic microcosm	Landis, W.G., N.A. Chester, M.V. Haley, D.W. Johnson and R.M. Tauber. 1988. Evaluation of Graphite for Environmental Toxicity Using the Standard Aquatic Microcosm. Department of Defense [DODXA], Aug 88, 21p. CRDEC-TR-88133. AD-A199 722/0/INW. Prepared by Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.	AD-A199 722/0/INW
GF	P	A	Literature review of graphite properties and characteristics	National Technical Information Service. 1984. Graphite Powder. June, 1970-October, 1984 (Citations from the NTIS Database). Report for Jun 70-Oct 84. October 1984. PB84-877364.	PB84-877364
HC	T	C	Toxicological profile	ATSDR. 1997. Toxicological Profile for Hexachloroethane. Prepared for Agency of Toxic Substances and Disease Registry.	
HC	B	C	Field study of bioaccumulation factors of HC on aquatic organisms	Burkhard L.P., B.R. Sheedy, D.J. McCauley and G.M. DeGraeve. 1997. Bioaccumulation factors for chlorinated benzenes, chlorinated butadienes, and hexachloroethane. Environ Toxicol Chem. 16(8):1677-1686.	
HC	ET	A	Toxicity of HC and its combustion products	Burton, D.T., D.J. Fisher and R.L. Paulson. 1990. Acute Toxicity of a Complex Mixture of Synthetic Hexachloroethane (HC) Smoke Combustion Products: 1. Comparative Toxicity to Freshwater Aquatic Organisms. Environmental Toxicology and Chemistry. 9:745-754.	AD-A299 929/0
HC	ET	C	Dispersion, deposition, biotic response and fate of HC smoke	Cataldo D.A., M.W. Ligothke, H. Bolton, R.J. Fellows, P. Van Voris, B.D. McVeety, S.W. Li and K.M. McFadden. 1989. Evaluate and Characterize Mechanisms Controlling Transport, Fate, and Effects of Army Smokes in the Aerosol Wind Tunnel: Transport, Transformations, Fate and Terrestrial Ecological Effects of Hexachloroethane Obscurant Smokes. Final Report. PNL-7166. DE90002923. September 1, 1989. Prepared by Pacific Northwest Laboratory, Richland, WA for U.S. Army Medical Research and Development Command, Fort Detrick, MD.	
HC	E	A	Environmental impacts of HC smoke	Cichowicz, J.J., 1984. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 4. HC Smoke. ARCSL-EA-83007. Chemical Research and Development Center, US Army Armament, Munitions and Chemical Command, US Army Aberdeen Proving Ground, Edgewood, MD.	
HC	ET	A	Water quality for HC	Davidson K.A., P.S. Hovatter and R.H. Ross. 1988. Water quality for hexachloroethane. ORNL-6469.	
HC	PE	A	Dispersion model of HC smoke	DeVaull G.E., W.E. Dunn, J.C. Liljegren and A.J. Polioastro. 1990. Field Measurement and Model Evaluation Program for Assessment of the Environmental Effects of Military Smokes: Analysis Methods and Results of Hexachloroethane Smoke Dispersion Experiments Conducted as Part of Atterbury-87 Field Studies. AD-A216048. Prepared by Argonne National Laboratory, Argonne, IL, for the US Army Medical Research and Development Command, Fort Detrick, Frederick, MD.	

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HC	T	A	Health effects of HC smoke; including toxicity, bioaccumulation, chemical composition	Eaton J.C., R.J. LoPinto and W.G. Palmer. 1994. Health Effects of Hexachloroethane (HC) Smoke. USABRD-TR-9402. AD-A277838. US Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, MD.	
HC	T	A	Toxicological profile	Eisenmann, C., J.M. Donohue and C. Smith-Simon. 1997. Prepared by Research Triangle Institute, in cooperation with Sciences International, Inc. and Life Systems, Inc.. Prepared for Agency for Toxic Substances and Disease Registry - Division of Toxicology. Technical Report. September 1997.	PB98-101041
HC	T	A	Toxicity tests on aquatic invertebrates	Elnabarawy M.T., A.N. Welter and R.R. Robideau. 1986. Relative Sensitivity of Three Daphnid Species to Selected Organic and Inorganic Chemicals. Environ Toxicol Chem. 5(4):393-398.	
HC	ET	A	Toxicity of HC and its combustion products	Fisher D.J., D.T. Burton and R.L. Paulson. 1990. Acute toxicity of a complex mixture of synthetic hexachloroethane (HC) smoke combustion products: I. Comparative toxicity to freshwater aquatic organisms. Environ Toxicol Chem. 9(6):745-754.	
HC	ET	A	Toxicity of HC and its combustion products	Fisher D.J., D.T. Burton and R.L. Paulson. 1990. Acute toxicity of a complex mixture of synthetic hexachloroethane (HC) smoke combustion products: II. Determination of component toxicity. Environ Toxicol Chem. 9(6):755-760.	
HC	PE	A	Chemical characterization and environmental fate	Gordon L., W.R. Hartley and W.C. Roberts. 1992. Hexachloroethane (HC). In: Drinking Water Advisory: Munitions. Lewis Publishers, Boca Raton, FL. Pp. 87-131.	
HC	T	A	Mammalian toxicity testing	Henry, M.C., J.J. Barkley and C.D. Rowlett. 1981. Mammalian Toxicologic Evaluation of Hexachloroethane Smoke Mixture and Red. Final Report 1978-1979. AD-A109 593/4/INW. Department of Defense [DODXA], Sep 81, 53p. Prepared by Litton Bionetics, Inc., Kensington, MD.	AD-A109 593/4/INW
HC	EB	A	Uptake and bioaccumulation model development and testing for HC effects on fish	Lien G.J., J.M. McKim, A.D. Hoffman and C.T. Jenson. 2001. A physiologically based toxicokinetic model for lake trout <i>Salvelinus namaycush</i> . Aquat Toxicol. 51(3):335-350.	
HC	B	A	Modeling uptake and bioaccumulation in Fathead Minnow	Lien G.J., J.W. Nichols, J.M. McKim and C.A. Gallinat. 1994. Modeling the accumulation of three waterborne chlorinated ethanes in fathead minnows (<i>Pimephales promelas</i>): A physiologically based approach. Environ Toxicol Chem. 13(7):1195-1205.	
HC	T	A	Dose toxicity testing on mice, rats, and guinea pigs	Marrs T.C., H.F. Colgrave, J.A.G. Edginton, R.F.R. Brown and N.L. Cross. 1988. The Repeated Dose Toxicity of a Zinc Oxide Hexachloroethane Smoke. Arch Toxicol. 62(2-3):123-132.	
HC	T	A	Toxicity to rats and rabbits	Marrs T.C., W.E. Clifford and H.F. Colgrave. 1983. Pathological Changes Produced by Exposure of Rabbits and Rats to Smokes from Mixtures of Hexachloroethane and Zinc Oxide. Toxicol Lett. 19(3):247-252.	

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HC	E	A	Degradation by terrestrial and aquatic plants	Nzengung V.A. and P. Jeffers. 2001. Sequestration, Phytoreduction, and Phytotoxicity of Halogenated Organic Chemicals by Aquatic and Terrestrial Plants. <i>Int J Phytoremediation</i> . 3(1):13-40.	
HC	EB	A	Uptake and transformation of HC by aquatic plants and algae	Nzengung V.A., L.N. Wolfe, D.E. Rennels, S.C. McCutcheon and C. Wang. 1999. Use of Aquatic Plants and Algae for Decontamination of Waters Polluted with Chlorinated Alkanes. <i>Int J Phytoremediation</i> . 1(3):203-226.	
HC	T	A	Toxicity tests on aquatic vertebrates and invertebrates	Phipps, G.L. and G.W. Holcombe. 1985. Method for Aquatic Multiple Species Toxicant Testing: Acute Toxicity of 10 Chemicals to 5 Vertebrates and 2 Invertebrates. <i>Environ Poll.</i> 38(2):141-157.	
HC	T	A	Toxicity of HC combustion products to rats	Richards R.J., J. Atkins, T.C. Marrs and R.F.R. Brown. 1989. The Biochemical and Pathological Changes Produced by the Intratracheal Instillation of Certain Components of Zinc-Hexachloroethane Smoke. <i>Toxicology</i> . 54(1):79-88.	
HC	T	A	Effects of HC smoke on tree foliage	Sadusky M.C., J.M. Skelly, M. Simini, R.T. Checkai and R.S. Wentzel. 1993. Hexachloroethane obscurant: Assessing tree foliage injury. <i>Environ Toxicol Chem.</i> 12(4):685-694.	
HC	PE	A	Analysis of residues from HC smokepots	Schaeffer D.J., S. Kapila, J.E. Meadows, E. Hinderberger and R. Wentzel. 1988. Chemical Characterization of Residues from Military HC Smokepots. <i>J Haz Mat.</i> 17(3):315-328.	
HC	E	C	Transformations and fate of HC smoke	Spanggord R.J., T.W. Chou, T. Mill, W. Haag and W. Lau. 1987. Environmental Fate of Nitroguanidine, Diethyleneglycol Dinitrate, and Hexachloroethane Smoke. Final Report, Phase II. Prepared by SRI International, Menlo Park, CA for U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.	
HC	E	C	Transformations and fate of HC smoke	Spanggord R.J., T.W. Chou, T. Mill, R.T. Podoll, J.C. Harper and D.S. Tse. 1985. Environmental Fate of Nitroguanidine, Diethyleneglycol Dinitrate, and Hexachloroethane Smoke. Final Report, Phase I. Prepared by SRI International, Menlo Park, CA for U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.	
HC TD	P	A	Concentration, particle size, chemical composition of smoke	Cassel, G., S. Fredriksson and I. Faengmark. 1992. Zink-och Titanroek: Kemisk Sammansaettning och Fysikaliska Egenskaper (Zinc and Titanium Smoke: Chemical Composition and Physical Characteristics). Technical Report. October 1992. FOA-C-40277-4.9, ETN-93-93759. National Defence Research Establishment, Umea (Sweden). NBC-Defence Dept.	N94-20552/3
HC TD	T	A	Acute inhalation toxicity on rats	Karlsson N., G. Cassel, I. Fangmark and F. Bergman. 1986. A Comparative Study on the Acute Inhalation Toxicity of Smoke from TiO ₂ -Hexachloroethane and Zn-Hexachloroethane Pyrotechnic Mixtures. <i>Arch Toxicol.</i> 59(3):160-166.	
HC TD	T	A	Inhalation toxicity	Karlsson, N., G. Cassel, I. Fangmark and F. Bergman. 1984. The Inhalation Toxicity of Screening Smokes. <i>J Toxicol Clin Toxicol.</i>	

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				23(4-6). Updated Citation: Karlsson, N., G. Cassel, I. Fangmark and F. Bergman. 1984. The Inhalation Toxicity of Screening Smokes. National Defense Research Institute, S-901 82 Umea and University of Umea, Dept. of Pathology, S-901 82 Umea, Sweden.	
KW	P	A	Combustion effluent from black and white colored smoke devices	Chin, A. 1986. Investigation of the Effluents Produced during the Functioning of Black and White Colored Smoke Devices. Department of Defense [DODXA], 31 Jan 86, 18p. Technical Report. NWSC/CR/RDTR-242. AD-A167 468/8/INW. Prepared by Applied Sciences Dept., Naval Weapons Support Center, Crane, IN.	AD-A167 468/8/INW
PEG	E	A	Degradation by methanogens	Dwyer, D.F. and J.M. Tiedje. 1983. Degradation of ethylene glycol and polyethylene glycol by methanogenic consortia. Appl Environ Microbiol. 46(1):185-190.	
PEG	P	A	Crystalization of PEG	Gines JM, MJ Arias, JR Moyano, PJ Sanchez-Soto. 1996. Thermal investigation of crystalization of polyethylene glycols in solid dispersion containing oxazepam. Int J Pharm. 143:247-253.	
PEG	T	A	Intestinal permeability of low molecular weight PEG	Phillips, S.F., A.F. Hofmann and V.S. Chadwick. 1997. Measurements of intestinal permeability using low molecular weight polyethylene glycol (PEG 400). 1. Chemical analysis and biological properties of PEG 400. Gastroenterology. 73:241-246.	
PEG	T	A	Summary of biological effects	Silverstein, B.D., P.S. Furcinitti, W.A. Cameron, J.E. Brower and O. White. 1984. Biological Effects Summary Report: Polyethylene Glycol. DE84007984/INW. BNL-51745. Department of Energy [DE], Jan 84, 27p. Prepared by Brookhaven National Lab., Upton, NY.	DE84007984/INW
PEG	E	A	Degradation by sewage bacteria	Watson, G.K. and N. Jones. 1977. The biodegradation of polyethylene glycol by sewage bacteria. Water Res. 11(1):95-100.	
PEG	T	A	Metabolism of PEG in mice	Yamaoka, T., Y. Tabata and Y. Ikada. 1995. Fate of water-soluble polymers administered via different routes. J Pharm Sci. 84:349-354.	
R V	ET	A	Combustion products of red and violet smoke mixes	Buchanan, M.V., I.B. Rubin and J.H. Moneyhun. 1983. Compositional Changes in Red and Violet Smoke Mixes After Combustion. Oak Ridge National Laboratory, Oak Ridge, TN.	
R V	PT	A	Inhalation toxicity, particle size, and particle concentration study	Higuchi, M.A. and D.W. Davies. 1990. Inhalation Toxicology of Red and Violet Dye Mixtures, Chamber Concentration and Particle Size Distribution Report. - Rept. for 1 Jan-21 Dec 90. AD-A237 664/8. Health Effects Research Lab., Research Triangle Park, NC.	AD-A237 664/8
RDX	E	C	Degradation and degradation products of RDX	Adrian, N.R. and Chow, T. 2001. Identification of hydroxylamino-dinitroso-1,3,5-triazine as a transient intermediate formed during the anaerobic biodegradation of hexahydro-1,3,5-trinitro-1,3,5-triazine. Environ Toxicol Chem. 20(9): 1874-1877.	

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SG	ET	A	Water quality criteria	Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Colored Smokes: Solvent Green 3: Final Report. Department of Energy [DE], Dec 87, 96p. Technical Report. ORNL-6409. DE88003303/INW. Prepared by Oak Ridge National Lab., TN.	DE88003303/INW
SG SY	T	A	Toxicity and metabolism of solvent yellow and green	Bice, D.E., Y.S. Cheng, J.S. Dutcher, F.F. Hahn and T.C. Marshall. 1984. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Phase III, Studies: Four-Week Inhalation Exposures of Rats to Dye Aerosols. Department of Energy [DE], 10 Sep 84, 68p. AD-A156 698/3/INW. Prepared by Inhalation Toxicology Research Inst., Lovelace Biomedical and Environmental Research Inst., Albuquerque, NM.	AD-A156 698/3/INW
SG SY	ET	A	Combustion products and toxicity to freshwater organisms	Fisher, D.J., D.T. Burton and R.L. Paulson. 1987. Toxicity of DEDGN (Diethyleneglycol Dinitrate), Synthetic-HC Smoke Combustion Products, Solvent Yellow 33 and Solvent Green 3 to Freshwater Aquatic Organisms. Department of Defense [DODXA], 15 Jan 87, 80p. Prepared by: Johns Hopkins Univ., Shady Side, MD. Environmental Sciences Group. Technical Report.	AD-A188 766/0/INW
SG SY	T	A	Toxicity and metabolism of colored smoke dyes	Henderson, R.F., J.S. Dutcher, F.F. Hahn, D.E. Bice and T.C. Marshall. 1985. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Phase II Studies: Range Finding and Toxicokinetics Studies of Inhaled Dye Aerosols. Department of Defense [DODXA], 15 Mar 85, 84p. AD-A163 267/8/INW. Prepared by Army Medical Research and Development Command, Fort Detrick, MD.	AD-A163 267/8/INW
SG SY	T	A	Inhalation toxicity of dyes and dye mixtures	Henderson, R.F., Y.S. Cheng, F.F. Hahn, J.L. Mauderly and J.A. Pickrell. 1985. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Phase 4. 90-Day Inhalation Exposures of Rats to Dye Aerosols. Department of Defense [DODXA], Oct 85, 300p. AD-A170 446/9/INW. Prepared by Inhalation Toxicology Research Inst., Lovelace Biomedical and Environmental Research Inst., Albuquerque, NM.	AD-A170 446/9/INW
SG SY	T	A	Toxicity and metabolism of colored smoke dyes	Henderson, R.F., Y.S. Cheng, J.S. Dutcher, T.C. Marshall and J.E. White. 1984. Studies on the Inhalation Toxicity of Dyes Present in Colored Smoke Munitions. Final Report for Phase I Studies. Generation and Characterization of Dye Aerosol. Department of Energy [DE], 1 Feb 84, 59p. AD-A142 491/0/INW. Prepared by Inhalation Toxicology Research Inst., Lovelace Biomedical and Environmental Research Inst., Albuquerque, NM.	AD-A142 491/0/INW
SG SY	T	A	Metabolism of dyes after inhalation by mice	Medinsky, M.A., Y-S Cheng, S.J. Kampcik, R.F. Henderson and J.S. Dutcher. 1986. Disposition and metabolism of ¹⁴ C-solvent yellow and solvent green aerosols after inhalation. Fundam Appl Toxicol. 7(1):170-178.	
SG SY	T	A	Toxicity to freshwater organisms	Paulson, R.L., D.J. Fisher and D.T. Burton. 1989. Comparative Toxicity of Solvent Yellow 33 (2-(2'-quinoliny)-1,3-indandione) and Solvent Green 3 (1,4-Di-p-toluidino-	

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				anthaquinone) Dyes to Freshwater Organisms. Chemosphere. 19(12):1959-1970.	
SG SY	T	A	Inhalation toxicity study	Sun, J.D., R.F. Henderson, T.C. Marshall, Y-S Cheng, J.S. Dutcher, J.A. Pickrell, J.L. Mauderly, F.F. Hahn, D.A. Banas, F.A. Seiler and C.H. Hobbs. 1987. The Inhalation Toxicity of Two Commercial Dyes: Solvent Yellow 33 and Solvent Green 3. Fundamental and Applied Toxicology, 8(3):358-371.	
SY	ET	A	Water quality criteria	Davidson, K.A. and P.S. Hovatter. 1987. Water Quality Criteria for Colored Smokes: Solvent Yellow 33, Final Report. Department of Energy [DE], Nov 87, 110p. Technical Report. ORNL-6383. DE88002682/INW. Prepared by Oak Ridge National Lab., TN.	DE88002682/INW
SY	T	A	Toxicity of Solvent Yellow in the Ames Test	Marrs, T.C., H.F. Colgrave, N.L. Cross, J.A.G. Edginton and B.C. Morris. 1988. Inhalation Toxicity of a Coloured Smoke and the Mutagenicity of Its Constituent Dyes, Solvent Yellow 33 (CI 47,000) and Disperse Orange 11 (CI 60,700) in the Ames Test. Jnl Haz Mat 17(3):269-285.	
TA	PT	C	Properties of TA	Anon. 1988. Terephthalic acid. Dangerous Properties of Industrial Materials Report. 8(4): 68-71.	
TA	P	A	Characterization of smoke from military smoke grenade	Anthony JS, CL Crouse, WT Muse, SA Thompson. Characterization of pyrotechnically disseminated terephthalic acid as released from the M8 smoke pot. Edgewood Research, Development, and Engineering Center, Aberdeen Proving Ground, MD.	
TA	T	A	Toxicity of TA to rats and mice	Hall IH, OT Wong, DJ Reynolds, R Simlot, JJ Chang. 1993. Terephthalic acid in Sprague-Dawley rats as a hypolipidemic agent. Arch Pharm. 326:5-13.	
TA	E	A	Biodegradation of TA	He X, Z Zhang, S MA. 1992. Study on biodegradability of terephthalic acid. China Journal of Environmental Science. 13(3):18-24.	
TA	T	C	Toxicity of TA	Hoshi A, R Yanai, K Kuretani. 1968. Toxicity of terephthalic acid. Chem Pharm Bull. 16(9):1655-1660.	
TA	T	A	Toxicity and biodegradation of TA	Kim M-N, B-Y Lee, I-M Lee, H-S Lee, J-S Yoon. 2001. Toxicity and biodegradation of products from polyester hydrolysis. Journal of Science and Health Part A: Toxic/Hazardous Substances and Environmental Engineering. A36(4):447-463.	
TA	E	A		Kleerebezem, R., Mortier, J., Hulshoff Pol, L.W. and Lettinga, G. 1997. Anaerobic pretreatment of petrochemical effluents: Terephthalic acid wastewater. 2. IAWQ International Conference on Pretreatment of Industrial Wastewaters, Athens (Greece), 16-18 Oct 1996.	
TA	E	A		Macarie, H., Noyola, A. and Guyot, J.P. 1992. Anaerobic treatment of a petrochemical wastewater from a terephthalic acid plant. Water Science and Technology. 25(7): 223-235.	

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TA	T	C	Distribution, absorption, and excretion of TA in rats and rabbits	Moffitt AE Jr., JJ Clary, TR Lewis, MD Blanck, VB Perone. 1975. Absorption, distribution, and excretion of terephthalic acid and dimethyl terephthalate. American Industrial Hygiene Association Journal. 36(8):633-641.	
TA	T	C	Toxicity of TA smoke grenades to rats	Muse, W.T. Jr., J.S. Anthony, J.D. Bergmann, D.C. Burnett, C.L. Crouse, B.P. Gaviola and S.A. Thompson. 1997. Chemical and toxicological evaluation of pyrotechnically disseminated terephthalic acid smoke. Drug and Chemical Toxicology. 20(4):293-302.	
TA	T	A	Teratology study of TA in rats	Ryan BM, NS Hatoum, JD Jernigan. 1990. A segment II inhalation teratology study of terephthalic acid in rats. Toxicologist. 10(1):40.	
TA	T	A	Inhalation toxicity of TA to rats	Shi A, D Wang, X Wang, X Xu. 2000. Changes of pulmonary surfactant in the rat lung exposed to terephthalic acid. Wei Sheng Yan Jiu. 29(2):71-72.	
TA	TB	C	Uptake, metabolism, and accumulation of TA by chicken liver	Tremaine LM and AJ Quebbemann. 1985. The Renal Handling of Terephthalic Acid. Toxicol Appl Pharmacol. 77:165-174.	
TA	P	C		United States Environmental Protection Agency (USEPA). 1983. AP-42, Fifth Edition, Volume. Chapter 6: Organic Chemical Process Industry.	
TA	T	A	Toxicokinetics of TA in rats	Yao H, X Wang, D Wang, J Dai. 2001. Toxicokinetics of terephthalic acid. Wei Sheng Yan Jiu. 30(1):23-24.	
TA	T	A	Toxicity of TA to rat liver	Yao H, X Wang, X Xu, A Shi. 2002. Study on the injury of liver induced by terephthalic acid ethylene glycol and/or dowtherm A in rats. Wei Sheng Yan Jiu. 31(1):12-14.	
TA SR DR	T	A	Toxicity of colored smoke dyes	Brooks AL, FA Seiler, RL Hanson, RF Henderson. 1989. In vitro genotoxicity of dyes present in colored smoke munitions. Environ Mol Mutagen. 13(4):304-313.	
TD	T	A	Inhalation toxicity to rats	Bellmann, B., H. Muhle, O. Creutzenberg, S. Takenaka and W. Koch. 1987. Untersuchungen ueber den Einfluss nicht-toxischer Staee auf die Lungenreinigung und die Funktion der Alveolarmakrophagen. Schlussbericht. (Investigation of the influence of 'nuisance' dust inhalation on lung clearance and function of alveolar macrophages. Final report). TIB/A90-81062INW. Prepared for Bundesministerium fuer Forschung und Technologie, Bonn (Germany, F.R.) by Fraunhofer-Inst. fuer Toxikologie und Aerosolforschung, Hanover (Germany, F.R.).	TIB/A90-81062INW
TD	T	A	Toxicity profile	BIBRA Working Group. 1990. Titanium Dioxide. Toxicity Profile. The British Industrial Biological Research Association.	
TD	B	A	Bioaccumulation by mussels exposed to industrial effluent	Coulon, J., M. Truchet and R. Martoja. 1987. Chemical features of mussels (<i>Mutilus edulis</i>) in situ exposed to an effluent of the titanium dioxide industry. Ann Inst Oceanogr. 63(2):89-100.	
TD	E	A	Sediment contamination caused by deposition from industrial activities	da Silva, E.M., M.F.T. Navarro, A.F. Barros, M.F.V. Mota and C.B.A. Chastinet. 2000. Metals in the sediments of Jaua Lake (Camacari, Bahia, Brazil) following an episode of industrial contamination. Aquat Ecosyst Health Manage. 3(4):509-514.	

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TD	ET	A	Toxicity to rats of explosively disseminated TiO ₂ dust and by-products	Hilaski, R.J., J.D. Bergmann, J.C. Carpin, W.T. Muse, Jr. and S.A. Thomson. 1992. Acute Inhalation Toxicity Effects of Explosively Disseminated XM82 Grenade Titanium Dioxide. CRDEC-TR-363. Chemical Research, Development and Engineering Center, US Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.	
TD	PE	A	Literature review of titanium dioxide chemical properties, environmental exposure, effects, and regulations	U.S. Environmental Protection Agency. 1975. Literature Study of Selected Potential Environmental Contaminants, Titanium Dioxide. Final Report. ADL-C-77354, EPA-68-01-2688, EPA/560/2-75-001. Prepared by Arthur D. Little, Inc., Cambridge, MA for USEPA Office of Toxic Substances, Washington, D.C.	
TD	T	A	Inhalation and lung deposition in rats	Vincent, J.H. and K. Donaldson. 1990. A dosimetric approach for relating the biological response of the lung to the accumulation of inhaled mineral dust. Inst Occup Med. 47(5):302-307.	
TD	T	A	Inhalation and lung deposition in rats	Vincent, J.H., A.D. Jones, A.M. Johnston, C. McMillan, R.E. Bolton and H. Cowie. 1987. Accumulation of Inhaled Mineral Dust in the Lung and Associated Lymph Nodes: Implications for Exposure and Dose in Occupational Lung Disease. Ann Occup Hyg. 31(3):375-393.	
TD	PET	A	Environmental health criteria of titanium	WHO Working Group. 1982. Titanium. Environmental Health Criteria. PG-1-68.	
UG	E	C	Photodegradation of several anthraquinone dyes in soils	Adams, R.L., E.J. Weber and G.L. Baughman. 1994. Photolysis of smoke dyes on soils. Environ Toxicol Chem. 13(6):889-896.	
UG	E	N	Evaluation of soils and surface water at military ranges	Ampleman G, S Thiboutot, S Desilets, A Gagnon, A Marois. Evaluation of the soils contamination by explosives at CFB Hilliwack and CFAD Rocky Point. Defense Research Establishment Valcartier, Courcellette, Quebec.	
UG	B	C	Use of partition coefficient as indicator of bioaccumulation in fish	Anliker R, EA Clarke, P Moser. 1981. Use of the partition coefficient as an indicator of bioaccumulation tendency of dyestuffs in fish. Chemosphere. 10(3):263-274.	
UG	B	C	Estimated octanol-water coefficients and bioaccumulation potential	Anliker, R. and P. Moser. 1987. The limits of bioaccumulation of organic pigments in fish: Their relation to the partition coefficient and the solubility in water and octanol. Ecotox Env Safe 13:43-52.	
UG	B	C	Estimated octanol-water coefficients and bioaccumulation potential	Anliker, R., P. Moser and D. Poppinger. 1988. Bioaccumulation of dyestuffs and organic pigments in fish. Relationships to hydrophobicity and steric factors. Chemosphere 17(8):1631-1644.	
UG	P	N	Properties of military explosives	Anon. 1971. Engineering Design Handbook. Explosives Series. Properties of Explosives of Military Interest. US Army Material Command, Washington DC. Pamphlet No. AMCP 706-177.	
UG	E	C	Fate of dyes in aquatic systems	Baughman, G.L. and T.A. Perenich. 1988. Fate of dyes in aquatic systems. I. Solubility and partitioning of some hydrophobic dyes and related compounds. Environ Toxicol Chem. 7(3):183-200.	

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UG	E	C	Environmental fate of colored smoke dyes	Baughman, G.L., E.J. Weber, R.L. Adams and M.S. Brewer. 1992. Fate of Colored Smoke Dyes. Supported by US Army Biomedical Research and Development Laboratory. Army Project No. 88PP8863.	
UG	T	N	Occupational exposure to explosives	Bodeau DT. 1993. Military energetic materials: Explosives and propellants. IN: Occupational Health: The Soldier and the Industrial Base. Textbook of Military Medicine. Part III. Preventative Medicine and the Environment, Volume 2. Deeter DP and JC Gaydos, Eds.	
UG	E	N	Literature review of fate and transport of explosives	Brannon JM and JC Pennington. Environmental fate and transport process descriptors for explosives. Army Engineer Waterways Experiment Station.	
UG	T	N	Toxicity of JA-2 solid propellant to rats	Brown LD, JD Justus, CR Wheeler, DW Korte. Acute oral toxicity of JA-2 solid propellant in Sprague-Dawley rats. Letterman Army Institute of Research, Presidio of San Francisco, CA.	
UG	E	A	Methods for assessing smokes, obscurants, and riot control agent effects on threatened and endangered species	Cassels,D.M., A.J. Krzysik and K.A. Reinbold. 2001. Methods for Field Studies of the Effects of Military Smokes, Obscurants, and Riot-Control Agents on Threatened and Endangered Species. Volume 3. Statistical Methods. - Final rept. ERDC/CERL-TR-01-59-VOL-3. ADA395028. Army Corps of Engineers. Construction Engineering Research Laboratory - Engineer Research and Development Center.	ADA395028
UG	E	N	Fate of explosives in soils from military sites	Checkai RT, MA Major, RO Nwanguma, JC Amos. Transport and fate of nitroaromatic and nitramine explosives in soils from open burning pen detonation areas. Edgewood Research, Development, and Engineering Center, Aberdeen Proving Grounds, MD.	
UG	E	A	Human health and environmental impacts of colored smokes/dyes	Cichowicz, J.J. and R.S. Wentzel. 1983. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 5. Dye/Colored Smokes. Department of Defense [DODXA], Jul 83, 110p. ARCSL-EA-83010. AD-A141 973/8/INW. Prepared by Chemical Research and Development Center, Aberdeen Proving Ground, MD.	AD-A141 973/8/INW
UG	ET	N	Residential exposure of emissions from firing range	Coakley SD and J Mobley. Residential exposure from inhalation of air emissions from firing of the M821 81mm high explosive cartridge. Army Center for Health Promotion and Preventative Medicine, Aberdeen Proving Ground, MD.	
UG	ET	N	Residential exposure of emissions from firing range	Coakley SD and R Chackleford. Residential exposure from inhalation of air emissions from firing of the M72A3 66mm heat rocket. Army Center for Health Promotion and Preventative Medicine, Aberdeen Proving Ground, MD.	

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UG	PETB	C	Literature review	Dacre, J.C., W.D. Burrows, C.W.R. Wade, A.F. Hegyeli, T.A. Miller and D.R. Cogley. 1979. Problem definition studies on potential environmental pollutants V. Physical, chemical, toxicological and biological properties of seven chemicals used in pyrotechnic compositions. Prepared by US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD for US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.	
UG	E	N	Analysis of airborne explosives combustion products	Einfield W, RA Rasmussen, CO Eckard, MB Johnson. Airborne gaseous and particulate products from large-scale bulk explosive detonations and propellant burns. Sandia National Labs, Albuquerque, NM.	
UG	T	N	Toxicity of explosives leachate to Daphnia	Haley MV, RT Checkai, CW Kurnas, RS Wentsel. Toxicity determination of explosives contaminated soil leachates to Daphnia magna using an adapted toxicity characteristics leaching procedure. Edgewood Research, Development, and Engineering Center, Aberdeen Proving Ground, MD.	
UG	PETB	C		HSDB. 2003. Hazardous Substances Databank. A Database of the National Library of Medicine's TOXNET System. Onlineat: http://toxnet.nlm.nih.gov . Accessed December 17, 2003.	
UG	E	N	Decomposition of nitroaromatics	Larson RA, PL Miller, TO Crowley. 1996. Borohydride photoreduction of nitroaromatic compounds related to military ordnance constituents. Environ Sci Technol. 30(4):1192-1197.	
UG	PET	A	Environmental fate of smoke combustion products	Leitner, P. 1986. Environmental Fate of Phosphates, Chlorides, and Organic Residuals from Combusted Military Smoke Materials: Final Report. Department of Energy [DE], 15 Jul 86, 20p. UCRL-15875. DE87006725/INW. Prepared by Dept. of Biology, Saint Mary's College, Moraga, CA.	DE87006725/INW
UG	T	N	Toxicity of JA-2 solid propellant to rabbits	LeTellier YC, CM Lewis. Acute oral toxicity of JA-2 solid propellant in rabbits. Letterman Army Institute of Research, Presidio of San Francisco, CA.	
UG	P	N	Physical and chemical characteristics of military explosives and propellants	Linder V. 1965. Explosives (Propellants). Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 8, pp. 659-719.	
UG	E	A	Combustion products of colored smokes	Loda, R.T. and T.P. Parr. 1984. Real-Time Fluorescence Analysis of the Controlled Incineration of Army Colored Smoke Compositions. Department of Defense [DODXA], Dec 84, 84p. Technical Report. NWC-TP-6559. AD-A152 479/2/INW. Prepared by Naval Weapons Center, China Lake, CA.	AD-A152 479/2/INW
UG	T	N	Toxicity of JA-2 solid propellant to mice	Morgan EW, DF Frost, CR Wheeler, DW Korte. Acute oral toxicity of JA-2 solid propellant in ICR mice. Letterman Army Institute of Research, Presidio of San Francisco, CA.	

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
UG	E	A	Methods for assessing smokes, obscurants, and riot control agent effects on threatened and endangered species	Nam, S., M.E. Walsh, J. Day and K.A. Reinbold. 1999. Methods for Field Studies of the Effects of Military Smokes, Obscurants, and Riot-Control Agents on Threatened and Endangered Species. Volume 4. Chemical Analytical Methods. Department of Defense [DODXA], Jul 1999, 761p. CERL-TR-99/56. ADA368050INW. Prepared by U.S. Army Corps of Engineers - Construction Engineering Research Laboratory, Champaign, IL.	ADA368050INW
UG	PTB	C	Toxicity of military smokes and obscurants review	National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants. Volume 2. National Academy Press, Washington, D.C.	
UG	PTB	C	Toxicity of military smokes and obscurants review	National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants. Volume 3. National Academy Press, Washington, D.C.	
UG	E	N	Distribution and fate of munitions at training ranges	Pennington JC, TF Jenkins, G Ampleman, S Thiboutot, JM Brannon. Distribution and fate of energetics on DoD test and training ranges: Interim report 2. Army Engineer Waterways Experiment Station, Vicksburg, MS. Engineer Research and Development Center.	
UG	E	A	Methods for assessing smokes, obscurants, and riot control agent effects on threatened and endangered species	Sample, B.E., T.L. Ashwood, B.A. Carrico, L.A. Kszos and M.S. Nazerias. 1997. Methods for Field Studies of Effects of Military Smokes, Obscurants, and Riot-Control Agents on Threatened and Endangered Species. Volume 2: Methods for Assessing Ecological Risks. - Final rept. CERL-TR-97/140-VOL-2. AD-A333 828/2. Army Corps of Engineers - Construction Engineering Research Laboratory.	AD-A333 828/2
UG	ET	A	Environmental screening and ranking of smokes and obscurants; includes toxicity and mobility	Shinn, J.H., S.A. Martins, P.L. Cederwall and L.B. Gratt. 1985. Smokes and Obscurants: A Health and Environmental Effects Data Base Assessment. A First-Order, Environmental Screening and Ranking of Army Smokes and Obscurants. Phase 1. Department of Defense [DODXA], Mar 85, 121p. UCID-20931. AD-A185 377/9/INW. Prepared by Lawrence Livermore National Lab., CA. Environmental Sciences Div.	AD-A185 377/9/INW
UG	R	A	Overview of statutes and regulations related to smoke, obscurant, and riot-control agent use with respect to threatened and endangered species	Smith, T.S. 2004. Methods for Field Studies of Effects of Military Smokes, Obscurants, and Riot-control Agents on Threatened and Endangered Species. Volume 1. Background, Overview, Issues, and Recommendations. ERDC/CERL-TR-04-5. U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, Champaign, IL.	
UG	PT	C	Physical and chemical properties, toxicity and detoxification rates of military munitions	Stewart, C.E. and J.B. Sullivan, Jr. 1992. Military Munitions and Antipersonnel Agents. Hazardous Materials Toxicology, Clinical Principles of Environmental Health. Williams and Wilkins, Baltimore, Maryland.	
UG	E	N	Study of environmental quality effects of effluents at Badger Army Ammunition Plant	Stilwell JM, DC Cooper, MA Eischen, MC Matthews, BE Sherwood. 1976. Aquatic life field studies at Badger Army Ammunition Plant. NTIS. ADA-A033547.	

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
UG	E	N	Guide for explosives contamination characterization	Thiboutot S, G Ampleman, AD Hewitt. Guide for characterization of sites contaminated with energetic materials. Engineering Research and Development Center, Hanover, NH. Cold Regions Research and Engineering Lab.	
UG	E	A	Increased K levels in groundwater and plants associated with smoke munitions landfill	Vroblesky, D.A., T.M. Yanosky and F.R. Siegel. 1992. Increased Concentrations of Potassium in Heartwood of Trees in Response to Groundwater Contamination. EGWSEI. 19(2):71-74.	
UG	E	A	Fate of anthraquinone based dyes in sediment	Yen C-P C et al. 1991. Fate of commercial disperse dyes in sediments. Environ Toxicol Chem. 10(8):1009-1018.	
V	ET	A	Water quality criteria	Davidson, K.A., P.S. Hovatter and R.H. Ross. 1988. Water Quality Criteria for Colored Smokes: 1,4-Diamino-2,3-Dihydroanthraquinone: Final Report. Department of Energy [DE], Jan 88, 70p. ORNL-6410. DE88004328/INW. Prepared by Oak Ridge National Lab., TN.	DE88004328/INW
V R	T	N	Toxicological evaluation of Disperse Violet 1 impurified with Disperse Red 15 for use in cosmetic products	SCCNFP. 2002. Opinion of the Scientific Committee on Cosmetic Products and Non-Food Products Intended for Consumers. Concerning: Disperse Violet 1 Impurified with Disperse Red 15. SCCNFP 19th Plenary Meeting, Feb. 27, 2002.	
WP	T	C	Toxicological profile	ATSDR. 1997. Toxicological Profile for Wjite . Prepared for Agency of Toxic Substances and Disease Registry.	
WP	E	A	Evaluation of long-term hazards of disposed WP munitions	Berglind, R. and C. Henriksson. 2000. Kvarlaemnad roekammuniton med vit Fosfor(P4). Miljoerisker ur ett Langtidsperspektiv (Left Obscurant Ammunition Focusing on White (P4) Environmental Effects in a Long-Term Perspective). Technical report. September 2000. FOA-R-00-01569-222-SE. PB2002-100659. Foersvarets Forskningsanstalt, Umea (Sweden). Avedelningen foer NBC Skydd.	PB2002-100659
WP	BT	N	Assimilation of elemental from seawater	Dyer WJ, DF Hiltz, RG Ackman, J Hingley and GL Fletcher. In vivo assimilation by cod muscle and liver tissue of elemental from polluted sea water. Jnl Fish Res Board of Can 27(6):1131-1139.	
WP	EB	N	Analysis of duck gizzards from munitions site	Johnston, J.J., D.A. Goldade, D.J. Kohler and J.L. Cummings. 2000. Determination of white residues in ducks: an atomic emission detection/compound-independent calibration-based method of generating residue data for risk assessment and environmental monitoring. Environ Sci Technol. 34(9):1856-1861.	
WP	E	A	Fate and transport of WP in a salt marsh	Lawson, D.E., L.E. Hunter, S.R. Bigl, B.M. Nadeau and P.B. Weyrick. 1996. Physical System Dynamics and White Fate and Transport, 1994, Eagle River Flats, Fort Richardson, Alaska. Technical report. August 1996. CRREL-96-9. AD-A317 624/5. Cold Regions Research and Engineering Lab., Hanover, NH.	AD-A317 624/5
WP	T	N	Aquatic survey	Manuel KS, ES Bender, JG Pearson. 1976. Results of Aquatic Surveys at Pine Bluff Arsenal, Arkansas, September 1973-October 1974. NTIS ADA-024 382.	

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
WP	PE	N	Atmospheric behavior of WP smoke	Milham, M.E., D.H. Anderson and R.H. Frickel. 1982. Infrared Optical Properties of Derived Smoke. Appl Opt. 21(14):2501-2507.	
WP	B	N	Transfer of wp from hen to egg	Nam S.I., D.L. MacMillan and B.D. Roebuck. 1996. Translocation of white from hen (<i>Gallicus domesticus</i>) to eggs. Environ Tox Chem 15(9):1564-1569.	
WP	B	N	Uptake and loss in kestrels	Nam, S.I., B.D. Roebuck and M.E. Walsh. 1994. Uptake and loss of white in American kestrels. Environ Tox Chem 13(4):637-641.	
WP	ET	N	Toxicity and fate of WP combustion products	Payne, M.P., R.O. Shillaker and A.J. Wilson. 1993. Phosphoric acid, pentoxide, oxychloride, pentachloride, pentasulphide. HSE Toxicity Review. V 30.	
WP	T	C	Particle-size dependency of toxicity	Roebuck, B.D., S.I. Nam, D.L. MacMillan, K.J. Baumgartner and M.E. Walsh. 1998. Toxicology of white (P4) to ducks and risk for their predators: effects of particle size. Environ Tox Chem 17(3):511-518.	
WP	ET	C	WP transfer from prey to predator	Roebuck, B.D., M.E. Walsh, C.H. Racine, L. Reitsma, B. Steele, S.I. Nam. 1994. Predation of ducks poisoned by white : exposure and risk to predators. Environ Toxicol Chem. 13(10):1613-1618.	
WP	E	N	Environmental fate literature review	Spangord R.J., R. Rewick, T.W. Chou, R. Wilson and R.T. Podoll. 1987. Environmental Fate of White Felt and Red Butyl Rubber Military Screening Smokes. DAMD17-82-C-2320. AD-176922. Prepared by SRI International, Menlo Park, CA, for US Army Medical Research and Development Command, Frederick, MD.	
WP	ET	C	Effects of ingestion by waterfowl and transport to predators	Sparling, D.W. and N.E. Federoff. 1997. Secondary poisoning of kestrels by white . Ecotoxicology. 6(4):239-247.	
WP	T	N	Toxicity studies in waterfowl	Sparling, D.W., R. Grove, E. Hill, M. Gustafson and L. Comerchi. 1994. Toxicological studies of white in waterfowl. Interagency Expanded Site Investigation: Evaluation of White Contamination and Potential Treatability at Eagle River Flats, Alaska. FY93 Final Report, p. 133-151. (C.H. Racine and D. Cate, Eds.) Prepared by Cold Regions Research and Engineering Lab., Hanover, NH for U.S. Army Directorate of Public Works, Garrison, AK.	
WP	T	C	Toxicity testing on mallards	Sparling, D.W., S. Vann and R.A. Grove. 1998. Blood changes in mallards exposed to white . Environ Toxicol Chem. 17(12):2521-2529.	
WP	T	C	Effects of WP on mallard reproduction	Vann, S.L., D.W. Sparling, M.A. Ottinger. 2000. Effects of white on mallard reproduction. Environ Toxicol Chem. 19(10):2525-2531.	
WP	T	C	Comparative toxicity of WP to several duck speceis	Steele, B.B., L.R. Reitsma, C.H. Racine, S.L. Burson, R. Stuart, R. Theberge. 1997. Different susceptibilities to white poisoning among five species of ducks. Environ Toxicol Chem. 16(11):2275-2282.	
WP	T	N	Plant response to smoke exposure	Tolle, D.A., M.F. Arthur, K.M. Duke and J. Chesson. 1990. Ecological effects evaluation of two smoke-producing compounds using terrestrial microcosms. ASTM SPEC	

Agent	Category	Status	Notes	Citation	NTIS Order Number/ Media Code
				TECH PUBL, ASTM, Philadelphia, PA. No. 1091, pp. 127-142.	
WP	B	N	Accumulation in rats administered WP	Truhaut, R., J.R. Claude and J.M. Warnet. 1971. Study of the incorporation of 3-H-9-10 palmitic acid in the triglycerides and lipoproteins of rats poisoned by white . CR Hebd Seances Acad. 272(18):2400-2403.	
WP	E	N	Characterization of smoke effects on vegetation, soils, and microbes	Van Voris P, MW Ligothke, KM McFadden, SMW Li, BL Thomas. 1987. Evaluate and Characterize Mechanisms Controlling Transport, Fate, and Effects of Army Smokes in and Aerosol Wind Tunnel: Transport, Formations, Fate and Terrestrial Ecological Effects of Red Butyl Rubber and White Obscurant Smokes: Final Report. NTIS, Springfield, VA.	
WP	P	N	Analytical method for determining white phosphorous levels in sediment	Walsh, M.E. and S. Taylor. 1993. Analytical methods for white residues in munitions-contaminated sediments. Anal Chim Acta. 282(1):55-61.	
WP	E	N	Loss of wp from sediment	Walsh, M.E., C.M. Collins and C.H. Racine. 1996. Persistence of white (P4) particles in salt marsh sediments. Environ Tox Chem 15(6):846-855.	
WP	E	N	Remediation methods for WP contamination	Walsh, M.R., M.E. Walsh and C.M. Collins. 1999. Remediation methods for white contamination in a coastal salt marsh. Environ Conserv. 26(2):112-124.	
WP	E	N	Environmental impacts of WP smoke	Yon, R.L. 1984. Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants. Volume 2. Red, White, and Plasticized White . ARCSL-EA-83004. Chemical Systems Laboratory, Chemical Research and Development Center, US Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Edgewood, MD.	

Table 2. Physical and chemical properties of selected smokes and obscurants.

Constituent	Appearance	CAS Number	Molecular Weight (g)	Melting Point Deg C	Boiling Point Deg C	Vapor Pressure @20 Deg C mm Hg	Henry's Law Constant (H) atm m ³ /mole	Water Solubility mg/L	BCF L/kg	Log K _{ow}	Log K _{oc}
Fog Oil Smoke	clear and bright	na	na	-40	327	< 0.1		negligible			
Hexachloroethane Smoke	colorless crystals	67-72-1	236.74	185	186	0.4	2.2E-2 - 2.8E-3	7.7	307.5	3.34 - 4.14	4.3
White Phosphorus Smoke	white crystalline solid, darkens from exposure to light	7723-14-0	123.88	44.1	280	0.025	2.1E-3 - 1.4E-3	3	3.162	3.08	3.05
Colored Smokes											
Vat Yellow 4	viscous orange liquid	128-66-5	332	385	548.94	8.34E-12	8.31E-12	0.00264	1991	6.28	4.9095
1,4-diaminoanthraquinone	colored liquid or powder; often purple	128-95-0	238	268	448.73	2.00E-10	4.79E-10	0.33	5.88	3	1.9286
Benzanthrone	pale yellow needles	82-05-3	230.27	170	403.17	2.21E-07	6.61E-08	0.24	145.8	4.81	4.09
Solvent Yellow 33	bright greenish yellow powder	8003-22-3	273.29	241	449.23	9.88E-09	6.12E-14	0.169	41.4	4.1	3.58
Solvent Green 3	black powder	128-80-3	418.5	218	598.47	7.05E-13	1.47E-16	6.98E-06	45.79	8.69 - 9.3	5.5968
Solvent Red 1	reddish brown solid	1229-55-6	278.31	183	430.05	6.29E-09	1.07E-10	0.00033	10	5.59 - 7.5	4.4251
Disperse Red 9	red powder and chunks	82-38-2	237.26	171	396.88	1.90E-11	2.4E-9 - 2.9E-8	0.119	negligible	3.99 - 4.10	3.5441
Disperse Red 11	reddish	2872-48-2	268	242	472.38	1.95E-09	2.35E-17	0.482	14.29	3.5	1.79
1,4-Diamino-2,3-Dihydroanthraquinone	violet	81-63-0	242.28	349.84	411.93	1.30E-07	3.98E-17	insoluble	3.162	0.54	2.4572
Brass Flakes											
Copper (approx 70%)		7440-50-8	63.55	1083	2595	4.29E-09	0.0245	4.21E+05	3.16	-0.57	1.155
Zinc (approx 30%)		7440-66-6	65.37	419.5	908	3.87E-05	0.0245	3.44E+05	3.16	-0.47	1.155
(o-Chlorobenzol) malononitrile (CS)	white crystalline solid	2698-41-1	188.62	95	310	3.40E-05	1.00E-08	51.9	30	2.76	3.2374
Dibenz (b,f) - 1,4-oxazepine (CR)	pale yellow crystalline solid	257-07-8	195.22	95.92	95.92	0.000129	8.88E-06	limited	97.76	3.49	4.5755
Titanium Dioxide	white powder	13463-67-7	79.9	1843	2500-3500	2.45E+03	4.89E-02	insoluble	10.38	2.23	1.3755
Polyethylene Glycol (PEG)	viscous colorless liquid	25322-68-3	150.18	-65	na	0.859	1.31E-07	1.00E+06	na	-1.2	na
Graphite Flakes	copper colored paste	7782-42-5	na	na	260	na	na	insoluble	na	na	na

Notes:

Physical-chemical properties taken from Hazardous Substances Data Base (HSDB) and EPI v.3.0 (EPA chemical estimation software)

Table 3. Combustion products and reactions of white phosphorous.

Property	Phosphorus Trioxide	Phosphorus Pentaoxide	Ortho-phosphorus acid	Ortho-phosphoric acid	Phosphine
Molecular Formula	P_4O_6	P_4O_{10}	$H_3P_4O_3$	H_3PO_4	PH_3
Molecular Weight	219.89	283.89	82	98	34
Color	White	White	Yellow	Colorless	Colorless
Physical state	Solid	Solid	Solid	Liquid or Solid	Gas
Melting Point	23.8°C	340°C	73.6°C	42.35°C	-133.5°C
Boiling Point	173.8°C (in nitrogen)	Sublimes @ 360°C	Decomposes @ 200°C	Decomposes @ 213°C	-87.4°C (autoignites @ 37.7°C)
Density, g/cm ³	2.135 @ 21°C	2.39	1.651 @ 21.2°C	1.834 @ 15°C	1.529 g/L
Solubility:					
Water	Decomposes to $H_3P_4O_3$ 20°C	Decomposes to $H_3P_4O_3$ 20°C	694 g/mL @ 40°C	548 g/100 in cold water	0.398 g/L @ 17°C
Organic solvent(s)	Soluble in CO ₂ , chloroform ether	Insoluble in acetone	Soluble in ethanol	Soluble in ethanol	Soluble in Ethanol, ether
Partition coefficients					
Log K _{ow}	No data	No data	No data	No data	No data
Log K _{oc}	No data	No data	No data	No data	No data
Vapor Pressure	No data	No data	No data	No data	760 mm @ -87.4°C
Henry's Law constant at 20°C	No data	No data	No data	No data	0.09 atm·m ³ /mol
Combustion Reactions of White Phosphorus					
$P_4 + 3O_2$	$\Rightarrow P_4^{3+}O_6$	(phosphorus trioxide)			
$P_4 + 5O_2$	$\Rightarrow P_4^{5+}O_{10}$	(phosphorus pentaoxide)			
$P_4O_{10} + 6H_2O$	$\Rightarrow 4H_3P^{+5}O_4$	(orthophosphoric acid)			
$P_4O_{10} + 2H_2O$	$\Rightarrow 4HP^{+5}O_3$	(metaphosphoric acid)			
$P_4O_{10} + 4H_2O$	$\Rightarrow 2H_4P_2^{+5}O_7$	(pyrophosphoric acid)			
$P_4O_6 + 2H_2O$	$\Rightarrow 4HP^{+3}O_2$	(metaphosphorous acid)			
$P_4O_6 + 6H_2O$	$\Rightarrow 4H_3P^{+3}O_3$	(orthophosphorus acid)			
$P_4 + 8H_2O$	$\Rightarrow 4H_3P^{+3}O_2 + 2H_2$	(hypophosphorus acid)			
$4H_3PO_3$	$\Rightarrow 4H_3P^{+5}O_4 + P^{-3}H_3$	(phosphine by disproportionation)			
$3H_3PO_4$	$\Rightarrow 4H_5P_3^{+5}O_{10} + 2H_2O$	(triphosphoric acid)			

Table 4. Major components of M18 colored-smoke grenades and 40-mm colored-smoke cartridges (weight/percent).

Component	Yellow				Red				Green				Violet
	M18		40 mm		M18		40 mm		M18		40 mm		M18
	old	new	old	new	old	new	old	new	old	new	old	new	old
Vat yellow 4	14.0		17.0						4.0		6.0		
Solvent yellow 33		42.0		42.0						12.6		12.5	
Disperse red 9					40.0		44.0						8.4
Solvent red 1						34.2		38.0					
Disperse red 11						6.8		7.0					
Solvent green 3									28.0	29.4	27.3	29.5	
Benzthron	24.5								8.0		11.0		
1,4-Diamino-2,3-dihydroanthraquinone													33.6
Sulfur	8.5												9.0
Sodium bicarbonate	33.0												24.0
Potassium chlorate	20.0	24.1	28.5	28.4	26.0	17.7	27.9	21.5	27.0	25.0	28.5	28.5	25.0
Magnesium carbonate		17.5		10.3		9.6		4.0		15.5		10.5	
Terephthalic acid						14.0		8.0					
Sugar		16.4		19.3		17.7		21.5		17.5		19.0	
Polyvinyl alcohol				2.0				2.0				2.0	
Stearic acid				0.5		0.5		0.5				0.5	

Adapted from:

National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants, Volume 3. National Academy Press.

Table 5. Major combustion products of the new colored-smoke M18 grenades.

Smoke	Combustion Products	Reference
Yellow	2-(2'-quinolyl)-1,3-indandione (QID); 2,3-benzacridine-1,4-dione; 2,3-benzacridine-9-one; an isomer of 2,3-benzacridine-1,4-dione; an isomer of QID. 5-10% insoluble residue	NRC, 1999; Buchanan and Ma, 1988
Green	1,4-di- <i>p</i> -toluidino-9,10anthraquinone (PTA); QID; 1- <i>p</i> -toluidinoanthraquinone and isomer of QID (approx. 3%). 3.4% insoluble residue	NRC, 1999; Buchanan and Ma, 1988
Red	α -methoxybenzenazo- β -naphthol (MBN) (unaffected major dye component); 1,4-diamino-2-methoxyanthraquinone (DMA) (unaffected major dye component); 2-methoxyaniline and 2-naphthol. 3.7 - 4.5% insoluble residue	NRC, 1999; Buchanan and Ma, 1988

Sources:

National Research Council, Subcommittee on Military Smokes and Obscurants. 1999. Toxicity of Military Smokes and Obscurants, Volume 3. National Academy Press.

Buchanan, MV and CY Ma. 1988. Chemical characterization and toxicologic evaluation of airborne mixtures. Chemical characterization of colored signal smokes. Final Report. ORNL/TM-1195.

AD A209 379. Oak Ridge National Laboratory, Oak Ridge, TN.

Table 6. Composition of grenade particulates by weight percent following combustion.

Constituent	Red Smoke Grenade	Violet Smoke Grenade	Yellow Smoke Grenade	Green Smoke Grenade
a-methoxybenzenazo-P-naphthol (MBN)	35			
methyl substituted DMA		3		
dimethyl substituted DMA		1		
1,4-diamino-2-methoxyanthraquinone (DMA)	7	55		
1,4-bis(methylamino)anthraquinone		4		
l-(2-hydroxyethylamino)-4-(methylamino)-anthraquinone (HEMA)		4		
1,4-bis(hydroxyethylamino)anthraquinone		ND		
1-aminoanthraquinone		1		
Aminoanthraquinone	ND			
Aminomethoxyanthraquinone		1		
1,4-diamino-anthraquinone		2		
1-amino-4-methylaminoanthraquinone		3		
2-methoxyaniline	4			
N-acetylmethoxyaniline	<0.1			
N-formylmethoxyaniline	ND			
2-naphthol	1			
Naphtho-(1,2-d)oxazole	4			
C ₁ Naphtho-(1,2-d)oxazole	0.5			
Aminonaphthol	0.1			
Methoxyphenylnaphthol	2			
2-(2'-quinolynyl)-1,3-inandione (QID)			71	27
10H-2,3-benzacridine-9-one			3	
2,3-benzacridine-1,4-dione			0.5	
Isomer of 2,3-benzacridine-1,4-dione			0.9	
Isomer of QID			0.3	0.3
1,4-di-p-toluidinoanthraquinone (PTA)				58
1-p-toluidino-4-hydroxyanthraquinone (THA)				0.8
1-p-toluidinoanthraquinone (TA)				0.2
Insoluble residue	3.7	3.4	9.9	3.4

(From Buchanan and Ma 1988.)

Table 7. Summary of adequacy of information available for ecological risk assessment.

Constituent	Environmental Fate and Transport			Bioaccumulation and Trophic Transfer		Toxicity (Ingestion Studies)						
	Air	Aquatic	Terrestrial	Aquatic	Terrestrial	Aquatic Invertebrates	Fish	Soil Fauna	Plants	Birds	Mammals	Reptiles and Amphibians
Fog Oil Smoke	Excellent	Adequate	Adequate	Adequate	Inadequate	Inadequate	No Data	Adequate	Adequate	Adequate	Inadequate	No Data
Hexachloroethane (HC) Smoke	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Inadequate	Inadequate	Adequate	Adequate	Adequate	No Data
White Phosphorous (WP) Smoke	Excellent	Excellent	Excellent	Excellent	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	No Data
Colored Smokes	Inadequate	Adequate	Inadequate	Inadequate	No Data	Inadequate	No Data	No Data	No Data	No Data	No Data	No Data
Brass Flakes	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	No Data
Graphite Flakes	Adequate	No Data	No Data	No Data	No Data	No Data	No Data	Inadequate	No Data	No Data	No Data	No Data
Titanium Dioxide	Inadequate	Inadequate	Inadequate	Inadequate	No Data	Adequate	Inadequate	No Data	No Data	No Data	No Data	No Data
Polyethylene Glycol (PEG)	Adequate	Inadequate	Inadequate	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
(o-Chlorbenzol)malononitrile (CS)	Adequate	Inadequate	Inadequate	No Data	No Data	Inadequate	Inadequate	No Data	No Data	No Data	No Data	No Data
Dibenz(bf)-14-oxazepine (CR)	Adequate	Inadequate	Inadequate	Inadequate	Inadequate	Inadequate	Inadequate	No Data	No Data	No Data	No Data	No Data
Terephthalic Acid	Adequate	Adequate	Adequate	Inadequate	Inadequate	No Data	No Data	No Data	No Data	No Data	Inadequate	No Data

Key to Table:

No data

Inadequate - some data are available but inadequate for modeling

Adequate - data are adequate for modeling but only limited data from one to three studies are available

Excellent - high quality data are available from four or more laboratory and/or field studies

Notes: 1 - one study on dermal absorption in salamanders is available and is adequate for deriving a TRV

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14. ABSTRACT <p>As with many anthropogenic substances, there is concern about the potential impacts on ecosystems and their component species resulting from military training and testing exercises using chemical agents, obscurants, and other smokes. The purpose of this report is to provide a review and summary of literature and other reports on the fate and environmental effects of military smokes, obscurants, and other comparably used compounds.</p> <p>Specifically, the focus is on species of high interest. Species of high interest include those species considered to be threatened and endangered as defined in the Endangered Species Act, and species found on United States Army and other military installations where smokes, obscurants, and riot control agents are used for military training and testing purposes.</p> <p>This report provides a literature review of topics where literature is sufficient and an annotated bibliography for instances where the literature search revealed either a paucity of citations or largely inaccessible primary literature.</p>					
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