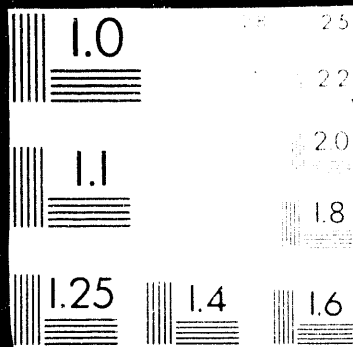


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ERDEC-CR-056

**ENVIRONMENTAL AND HEALTH EFFECTS REVIEW
FOR OBSCURANT GRAPHITE FLAKES**

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July 1993

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**U.S. ARMY
CHEMICAL
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Aberdeen Proving Ground, Maryland 21010-5423

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EXECUTIVE SUMMARY

Graphite flake obscurants represent a critical capability needed to defeat electromagnetic detection and targeting. However, the human and environmental health risks of such releases must be evaluated for system development tests and simulated battle field training.

The purpose of this environmental review is to provide a technical basis to establish the health and environmental effects of graphite flakes and to establish a basic resource for site-specific environmental assessments for training and test releases of graphite flakes. To accomplish this goal, existing health and ecosystem effects data were evaluated and compared with predicted levels of flake materiel in the field. Because fog oil provides visible obscuration and may be used in co-generation with graphite flakes, the potential health and environmental impacts of mixed releases of graphite flake and fog oil were also considered. The review identifies important gaps in the data base and provides a framework for structuring research needs.

Graphite flake dispersion and deposition for simulated mechanical and pyrotechnic releases were determined using a modified Gaussian atmospheric plume-dispersion model. Downrange air concentrations and surface mass loadings were estimated for single dissemination systems. Air concentrations and surface deposition decreased with downwind distance and with crosswind distance from the downwind vector at rates that were influenced by the atmospheric stability category. The potential for wind resuspension of graphite flakes is controlled by weathering processes and incorporation rates in soil. The most effective weathering processes on graphite flake are dew formation, precipitation, evaporation, and liquid-phase adhesion between deposited particles and surfaces.

The pathological and physiological response to graphite flake is similar to that of "nuisance dusts" and causes only transient pulmonary changes. Repeated exposure to very high concentrations (such as those near the source generator) may overwhelm the clearance mechanisms of the lung and result in pulmonary damage from the retained particles in unprotected individuals. However, these lesions either resolve with time or are of limited severity. Chemically, graphite flakes pose little risk to aquatic or terrestrial systems. Mechanical damage to plants and invertebrate and vertebrate organisms from the flakes is also minimal. Reduced visibility on public roadways is a possibility at some testing sites and may increase the risk of vehicular accidents.

Health effects of mixed aerosols of graphite and fog oil are similar to those produced by graphite flake alone. Environmental impacts of fog oil-coated graphite flakes are not well known.

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- In conducting research using animals, the investigators adhered to the "Guide for the Care and Use of Laboratory Animals" prepared by the Committee on Care and Use of Laboratory Animals of the Institute of Laboratory Animal Resources, National Research Council (NIH Publication No. 86-23, revised 1985).
- For the protection of human subjects, the investigators have adhered to policies of applicable Federal law 45 CFR 46.

Crystal J. Dwyer
PI Signature

11/16/92
Date

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PREFACE

The work described in this report was authorized under Contract No. 1FSL-2-4. This work was started in July 1991 and completed in May 1993.

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ENVIRONMENTAL AND HEALTH EFFECTS REVIEW FOR OBSCURANT GRAPHITE FLAKES

1.0 PURPOSE AND NEED

A variety of offensive and defensive systems and materials are employed on the battlefield. Warfare conditions and tactics require that land, sea, and air forces be trained with and have at their disposal the best defensive systems available. Among these systems, smokes and obscurants have long been employed to mask both troop and mechanized equipment movements. Smokes have been employed since the first world war to visually mask the movements of both ground and sea forces. The modern battlefield has become much more complex, with visual detection being augmented or replaced by a wide range of electromagnetic methods for detection and targeting. This has resulted in the need for specific types of electromagnetic obscurants, and thus, training and testing programs to assure tactical readiness. The testing and use of new generations of electromagnetic obscurants has been deemed essential by the Department of Defense.

The purpose of electromagnetic obscurants such as graphite flake is to provide the military with an additional level of protection beyond the visual and infrared spectrums, to spectral regions where classical white smokes (hexachloroethane, fog oil, red and white phosphorus) are ineffective. These flake materials are generally chemically inert and are less optically visible than classical white smokes. The electromagnetic category of obscurants represents a critical capability needed to enhance operations by denying the enemy information reflecting the location and movements of troops and equipment. Thus, it is necessary that these materials be employed in training under simulated battlefield conditions. This permits the development of hardware for generation and dissemination, and for the evaluation of the efficacy of specific systems during their development phases.

The objective of this effort is to provide a technical basis to establish the health and environmental effects of graphite flakes, and to establish a basic resource for environmental assessments for training and test releases of fibers. This review identifies important gaps in the data base and provides a framework for structuring research needs. Discussions are limited to graphite flake having physical dimensions measured in previous investigations. Although a brief review of potential impacts of combined graphite/fog oil releases is provided, a comprehensive review of the health and environmental effects of fog oils is beyond the scope of this study and is addressed in a separate report.

2.0 DESCRIPTION OF PROPOSED ACTION

Review of the use of graphite flake aerosols includes consideration of the material, dissemination, aerial transport, deposition, and potential health and environmental impacts. Health concerns center primarily around inhalation risk, and environmental concerns include potential terrestrial, aquatic, and marine impacts.

2.1 BACKGROUND

Graphite flake material must be disseminated and airborne to be effective as an electromagnetic obscurant. The efficacy of such aerosols under battlefield conditions depends on air concentrations, physical flake dimensions, and electrical properties.

Fakes are disseminated by mechanical methods to allow individual tactical units to defeat an opponent's electromagnetic tracking and targeting systems. Once dispersed, air concentrations are attenuated through plume dilution in the atmosphere and flake sedimentation and deposition to ground surfaces.

2.2 HISTORY

Naturally occurring and synthetic graphite materials have both commercial and military applications, with application depending on chemical composition and physical properties and characteristics of the bulk materials or individual platelets.

2.2.1 Commercial Applications

Graphite materials are inert and have refractory properties useful for a variety of commercial applications. They are used in manufacture of crucibles for melting nonferrous metals (refractory crucibles), pigment, foundry facings, recarbonizing steel, lubricants, electrodes, "lead" pencils, stove polish, matches and explosives, arc-lamp carbons, coating for cathode ray tubes, moderator in nuclear piles, filters in dry cells, and carbon brushes for electrical motors and equipment. Both synthetic and naturally occurring deposits of various grades are used as source materials.

2.2.2 Military Applications

Graphite flakes are used by the U.S. military as an obscurant.

2.3 PHYSICAL AND CHEMICAL NATURE OF GRAPHITE FLAKES

Graphite is a soft-scale form of carbon and can be natural or synthetic in origin. Commercial varieties can withstand temperatures up to 2820°C. Natural graphite is associated with quartz, iron oxide, mica, and granite impurities. Free silica content typically ranges from 1% to 25%. Synthetic graphite is formed by heating petroleum coke, a binder (usually coal tar pitch), and a petroleum-based oil to facilitate extrusion of the particles. The characteristics of synthetic graphite depend on the composition of the mixture components, the temperature and length of processing, and the degree orientation of the particles during extrusion.

Synthetic graphite is currently used by the U.S. military. Natural graphite has been considered in the past but is not currently expected to be used. Two synthetic graphite powders for which data exist are Micro-260 (manufactured by the Asbury Graphite Mills, Inc., Asbury, New Jersey), and KS-2 (manufactured by Dixon Ticonderoga Company, Lakehurst, New Jersey). These graphites are composed of particles of various sizes that are platelets (flakes). The chemical

composition of the bulk powders is predominantly carbon with trace impurities totaling < 1% by weight.

2.3.1 Physical Characteristics

During smoke generation, the powdered or pelletized graphite is ground and passed through a 45- μm screen; individual particles are typically much smaller than 45 μm . Graphite particles are rough platelets, or flakes. In general, the flakes have one physical dimension much smaller than the other two. Physical characteristics of the flakes were measured using scanning electron microscopy (Ligotke et al. 1989). The largest flake dimensions observed were < 20 μm , with most flakes smaller than 10 μm . Flake thickness, although variable, is typically between 0.1 and 1 μm . Figure 1 shows micrographs of both types of synthetic graphite flakes at a magnification of 3000x.

2.3.2 Chemical Characteristics

The graphite flake source material for smoke generators such as the prototype XM56 is chemically inert, insoluble in acids and alkalis, and has good refractory properties. The chemical composition of the bulk powder is predominantly carbon with trace impurities totaling < 1% by weight. The trace impurities include small quantities of silica, aluminum, iron, calcium, titanium, and magnesium.

2.4 MODE OF DISSEMINATION AND DISPERSION

Graphite flakes are disseminated to the environment from ground-based systems by the mechanical dispersion of bulk powders into the atmosphere. The powder is used directly or compressed into small pellets to improve handling and delivery to the air-ejector of smoke generators. Because the aerodynamic sizes of air-dispersed flakes are small, near-source surface deposition caused by particle settling is limited. Near-source deposition can be significant, however, if the air-ejector is oriented at or near parallel to the ground. The long-range downwind patterns resulting from dispersion and deposition depend on local meteorological conditions.

2.4.1 Mode of Dissemination

Graphite aerosols are disseminated as part of the obscuration reinforcing system (ORS) to provide large area cover. The material is not currently used in rapid obscuration systems (ROS) that provide short-term cover.

The graphite flake aerosols are mechanically generated using compressed-air systems. The system currently in use is the developmental XM56 smoke generator, a system that also allows simultaneous generation of fog oil obscurant. In the generator, source graphite is reduced in a grinder and de-agglomerated by fluid shear forces and particle-particle interactions in the expanding air flow of an air ejector. The generation rate is typically 4500 g/min (10 lb/min), and aerosol concentrations < 2 g/m³ are produced. The duration of the generation depends on the application, but is nominally 30 min (the time the generator can operate with one load of powder). Tests and training activities may involve generation periods longer or shorter than 30 min. It may also be expected that test sites will be used repeatedly, over periods of many years.

2.4.2 Aerodynamic Characteristics and Settling Velocity

The aerial dispersion of graphite flake aerosols to the environment, and their potential inhalability, are influenced by the aerodynamic characteristics of individual flakes. The aerodynamic characteristics of the flakes, in turn, are influenced by the physical shape, size, and density of the individual and agglomerated flakes suspended in air. The following information on

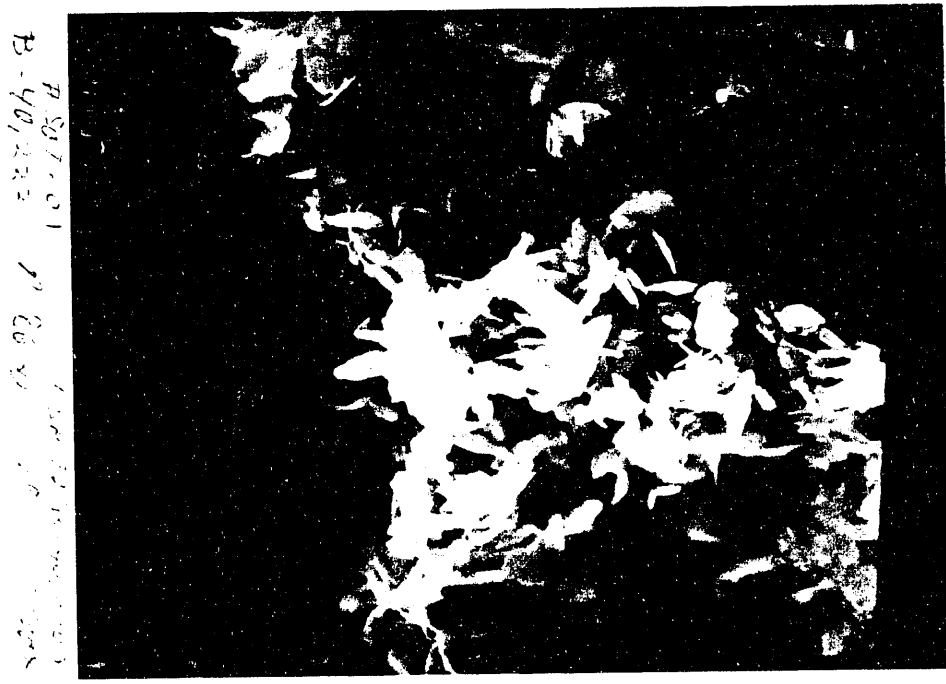


FIGURE 1 Scanning Electron Micrographs of Micro-260 (top photograph) and KS-2 (bottom photograph) Synthetic Graphite Samples at a Magnification of 3000x.

flake size distribution by equivalent aerodynamic size is sufficient for most environmental assessment requirements. A more detailed discussion of the aerodynamic characteristics and settling velocities of graphite flake aerosols is presented in Appendix A.

Aerodynamic Characteristics: The airborne behavior of flakes can be generalized by considering the aerodynamic rather than the physical particle size. The aerodynamic diameter (D_a) of a flake is the diameter of a unit density sphere that settles at the same velocity as the flake. Classifying flakes by aerodynamic size also has the advantage that most considerations of the impact of flake aerosols on the environment (dispersion, deposition, and resuspension) and humans (inhalation) are influenced most strongly by aerodynamic size rather than physical shape.

For purposes of estimating atmospheric dispersion and potential inhalability, a typical field-generated graphite flake aerosol may be represented by an aerodynamic mass median diameter (AMMD) of 5 μm and a geometric standard deviation (GSD) of 2.5. This distribution was used to provide estimates of atmospheric dispersion and deposition (Appendix B), and in the discussion of the potential inhalation effectiveness of graphite flake aerosols. In considering potential inhalation effectiveness, roughly 34% of the mass of such an aerosol can be expected to consist of flakes with aerodynamic sizes smaller than 3.5 μm .

Settling and Deposition Velocities of Graphite Flakes: Knowledge of the rate at which airborne graphite flakes settle is necessary for estimating atmospheric dispersion and subsequent ground deposition of graphite flake aerosol plumes from the source of generation. Settling velocities (in still air) between about 0.004 and 1 cm/s correspond to flake sizes that make up about 90% of the mass of graphite flake aerosols. A settling velocity of 0.08 cm/s corresponds to a 5 μm AMMD that is typical of field-generated graphite flake aerosols.

The deposition velocity, the actual rate at which particles deposit to plant, soil, and other surfaces, exceeds the still-air settling velocity for particles < 30 μm (McMahon and Denison 1979; Sehmel 1980). For graphite flakes, deposition velocity may exceed settling velocity by a factor that ranges roughly between 2 and 10. The specific factor depends on particle and surface characteristics, atmospheric conditions, and nonsteady-state interactions of these parameters at the air-surface interface. For purposes of assessing the environmental dispersion and deposition of graphite flake aerosols, and in the absence of a specific relationship, deposition velocity was assumed to be 0.8 cm/s, a value greater than the settling velocity by a factor of 10.

2.4.3 Airborne Plume Dispersion

The dispersion of airborne graphite flakes from point of release, and their subsequent deposition to downwind areas are influenced by the aerodynamic characteristics of the released flakes and the local meteorological conditions, site geography, and surface terrain morphology. Thus the pattern and magnitude of aerial dispersion and deposition at a specific site will vary from test to test and will be different than that for other sites. General results of graphite flake plume dispersion calculations are presented here. A more detailed discussion of airborne graphite flake plume dispersion is presented in Appendix B.

Dispersion and deposition of graphite flake plumes were estimated for six test cases that included known source (smoke generator) characteristics, a range of expected atmospheric conditions, and estimated particle deposition velocity. The estimates were made for distances between 0.1 and 40 km (0.06 to 25 mi) downwind of the generator. As described in Appendix B, Cases 2 and 3 represent typical conditions, and may be considered baseline cases. Case 1 represents extremely unstable atmospheric conditions and resulted in the lowest air concentration and surface loading values. The moderately stable atmospheric conditions represented by Case 4 are very uncommon at most test sites; however, Case 4 was included to provide a worst-case

condition. Cases 1 through 5 were all selected to provide a range of atmospheric stability categories (ASC) and wind speeds (Appendix B, Table B.2). Because ASC C may be present for wind speeds between 2 and 5 m/s, it was included twice (Cases 2 and 5). ASC C was also selected for Case 6, which was included simply to demonstrate the scalar influence of increased time of generation on surface mass loading.

Airborne graphite flake concentrations were predicted to generally decrease from between 26 to 140 mg/m³ at downwind distances of 0.1 to 0.3 km, to < 0.001 to 0.01 mg/m³ at 40 km (graphical presentation of these results is shown in Appendix B). At comparable downwind distances, air concentration estimates for the test cases varied between 4 and 100 times depending on the ASC of each specific test case. Because lateral and vertical dispersion are very limited for ASC F, the maxima in air concentration at a elevation of 1 m may not occur within 0.1 km of the source, but rather between 0.1 and 0.3 km downwind. Crosswind profiles indicated progressively wider plumes for unstable atmospheric conditions (with ASC A being the extreme case).

Predicted graphite flake air concentrations exceed the 24-h average, secondary national ambient air quality standard (NAAQS) of 0.15 mg/m³ within downwind distances of 1.5 to 15 km from the source, depending on atmospheric conditions. Again, because of the intermittent nature and short duration of graphite flake generation under most testing and training scenarios, the 24-h averaging period, if applied to predicted graphite flake air concentration levels, would result in the reduction of the area in which concentrations may exceed the NAAQS to a distance within roughly 0.2 to 2 km of the generator for a single 30-min release (300 lb) from a single generator per day.

Predicted graphite flake surface deposition levels for Cases 1, 2, 3, 4, and 5 generally decreased from between 380 to 2100 mg/m² at a downwind distance of 0.1 to 0.3 km, to < 0.2 mg/m² at a distance of 40 km. As was the case for air concentration, surface deposition estimates for the test cases varied between 4 and 100 times at comparable downwind distances, and depended on the ASC of each specific test case. Surface deposition levels exceeding 1000 mg/m² were predicted within downwind distances of < 0.1 to 0.5 km of the source, with the specific distance varying with ASC. Surface deposition levels exceeding 1 mg/m² were predicted within 2 to 25 km of the source. Predicted surface deposition levels for Case 6 were greater than Case 2 by a factor of 10 (equal to the ratio of the smoke generation durations).

Downwind, centerline estimates of air concentration and surface loading should be used in predicting the impact of specific tests and training activities. The estimates should be applied to areas downwind of the test site and bounded by the range of expected wind directions. Unless the wind direction is constant, varying in direction by < 5% to 25% depending on ASC, the actual levels of aerosol mass concentration (C_m) and surface mass loading (ML) will be less than those predicted. This is because the actual centerline of the plume will tend to meander over the duration of the test, and no one location will be exposed to the highest concentrations throughout the duration of the test. Thus, C_m and ML estimates provided by the model will tend to be conservative. Crosswind estimates of C_m and ML will only be useful if wind direction does not vary.

Results of plume dispersion estimates apply to distances more than 0.1 km from the source. Deposition levels within 0.1 km of the source may be much greater than the predicted levels, and a visible "footprint" of concentrated graphite may be visible within about 0.1 km of the source if the plume is released horizontally or makes contact with the ground near the generator.

Plume dispersion results also only apply to the initial deposition of material. Although tests and training with graphite flake obscurants are expected to be limited to times when wind speeds are ≤ 4.5 m/s (10 mph) for logistical and tactical reasons, greater wind speeds occurring after release can cause redistribution of the material. This redistribution will only occur if high winds occur before the deposited material is incorporated in the soil column (i.e., through dew formation,

and rainfall). Thus consideration of the ultimate location of deposits of graphite flakes should consider, on a site by site basis, the frequency of high-velocity wind storms ($\gg 5$ m/s). Although redistribution of initial deposits by wind-induced resuspension will generally tend to further reduce surface mass loading levels in affected and downwind areas, the difficulty of predicting bulk material resuspension and redistribution processes hinders an accurate assessment. It is recommended that when the potential for resuspension is high (especially in dry areas with little vegetative cover), predicted downwind surface mass loading levels be assumed to potentially occur in adjacent areas downwind of typical wind storm directions. For example, if a surface loading rate resulting from the initial deposition from a test is predicted to be 1 mg/m^2 at a distance 10 km south of the source, and if wind storms are frequent from only the west, it would be reasonable to assume that resuspended material may ultimately deposit at similar surface concentrations over a distance of about 10 km to the east of the original location of deposition.

2.5 CONCERNS AND POTENTIAL IMPACTS

Concerns and potential impacts of the dispersion of graphite obscurant aerosols include direct health effects, environmental fate and effects, and secondary impacts.

2.5.1 Direct Health Effects of Graphite Flakes

The aerodynamic size of graphite flakes and their inert nature contribute to inhalability, long-term residence, and potential transmigration of the flakes in the human body. The health effects of graphite flakes are discussed in Section 4.2.

2.5.2 Environmental Fate and Effects

Graphite flakes will persist in the environment, although their toxicity is low. Primary areas of potential concern include resuspension (and downrange, offsite transport) and plant effects. The environmental fate and effects of graphite flakes are discussed in Sections 4.1, 4.3, and 4.4.

2.5.3 Secondary Impacts of Graphite Flake Use

No secondary impacts of graphite flake use are anticipated.

3.0 ENVIRONMENTAL TOXICITY LAWS AND REGULATIONS

This section discusses the regulatory requirements that are relevant to graphite flakes.

3.1 AIR QUALITY

No national emission standards for hazardous air pollutants (NESHAPS) exist or are proposed for graphite (40 CFR 61). The new Clean Air Act Amendments of 1990 do not identify graphite as a specifically regulated pollutant. However, the Clean Air Act regulations have set NAAQS for particulate matter less than 10 μm in diameter (PM-10) in 40 CFR 50. The 24-h air concentration standard for particulate matter is 150 $\mu\text{g}/\text{m}^3$ (24-h average concentration), and an annual geometric mean of 50 $\mu\text{g}/\text{m}^3$. States must have plans to maintain these standards. The severity of local regulations will largely depend on whether or not the State is in compliance with the Federal Standard. State regulations must be consulted to determine allowable rates of dissemination and compliance monitoring methods. The initial concentrations and dissipation of graphite flake aerosols are discussed in Section 2.4.3 and Appendix B, and can be used to estimate potential compliance with the NAAQS and local regulations.

Federal visibility assessments for certain scenic areas may impact on sources near such sites.

3.2 WATER QUALITY

No point discharge of pollutants to waters of the United States, as defined in the Clean Water Act, will occur due to the testing and demonstrating of the graphite flakes. Therefore, a national pollutant discharge elimination system (NPDES) permit will not be required (40 CFR 122). The final NPDES permit regulations for storm water (55 FR 47990, November 16, 1990) also do not appear to be applicable to the graphite flakes.

Because the flakes will be tested at a military installation having very large controlled land areas, it is not anticipated that the flakes will impact a community water supply system (40 CFR 141). Therefore, the Safe Drinking Water Act's National Primary Drinking Water Regulations may not be applicable for most sites and releases. Consideration by specific site is recommended. Underground injection of liquids will not occur; therefore, an underground injection control permit is not required.

3.3 HAZARDOUS SUBSTANCES AND WASTES

Carbon is neither a listed hazardous waste under the Resource Conservation and Recovery Act (RCRA) nor a hazardous substance under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

The U.S. Environmental Protection Agency (EPA) published on March 29, 1990, a toxicity characteristic leaching procedure (TCLP) final rule (55 FR 11798-11877). This rule replaced the extraction procedure toxicity test for use in determining whether a waste stream exhibits the toxicity characteristic, added 25 organic compounds to the list of toxic constituents, and set regulatory levels based on health-based concentration limits. Carbon is not a TCLP listed constituent.

Emergency Planning and Community Right to Know Act (1986) provisions are not applicable to carbon.

3.4 TRANSPORTATION

Graphite flake is not considered a flammable or combustible material under the Hazardous Materials Transportation Act (HMTA). Title C of the addresses Class A explosives. Class A explosives will be used in pyrotechnic devices for the dissemination of the flakes. Therefore, the transportation of the pyrotechnic devices are subject to the Class A explosives transportation regulations (49 CFR 173.53-173.87).

3.5 TOXIC SUBSTANCES

The Toxic Substances Control Act (TSCA) regulates the production, use, distribution, and disposal of chemical substances. This regulation is applicable to manufacturers and processors who must test certain substances to determine whether they present an unreasonable risk to health or the environment. The TSCA is not applicable in this situation and does not include carbon as a toxic substance.

3.6 STATE REGULATIONS

State regulations may differ from federal regulations. Therefore, state regulations should be consulted in locations where activities occur that involve graphite flakes.

4.0 ENVIRONMENTAL AND HUMAN HEALTH EFFECTS

Graphite flake aerosols are dispersed and become the source for exposures to the environment and humans. Transport by wind, deposition, and subsequent resuspension cause the dispersal of the graphite from the site of original release to the environment. Subsequent environmental and health effects include mammalian (including inhalation and dermal routes of exposure, and transmigration within the body), terrestrial, aquatic, and marine. Mitigation approaches to the source terms are not extensive compared to other materials (i.e., the white smokes and carbon fibers) because of the inert nature of graphite flakes. Other environmental impacts of the manufacture, use, and disposal of the material are likewise not anticipated to be severe.

4.1 NATURE OF SOURCE TERM

The source terms for exposure of the environment to graphite flakes released as aerosols include initial deposition from the obscurant plume and subsequent resuspension and re-deposition of the material. The source term is described in relation to 1) graphite aerosol release to the environment, and 2) potential inhalation of graphite aerosol by humans. Whether directly from the generation of graphite flake aerosols or via subsequent resuspension from surface and canopy deposits, airborne flakes may be inhaled by humans.

4.1.1 Environmental Source Term (Deposition and Resuspension)

Graphite flake aerosols deposit to ground surfaces at rates that are influenced by atmospheric conditions and surface characteristics. The rates and magnitudes of flake deposition are discussed in Section 2.4.3 and in Appendix B. Estimates of surface mass loading for several typical atmospheric conditions range from 4 to 260 mg/m² at a distance of 1 km downwind of the source to < 0.01 to 0.2 mg/m² at a distance of 40 km downwind. Although the maximum surface deposit at 0.1 km or further downwind from the generator is estimated to be 2100 mg/m², the deposition of graphite flakes was still estimated to be < 10 mg/m² at all distances greater than about 7 km from the source, regardless of atmospheric stability category. Unless the average direction of wind is very steady, the actual deposition levels predicted above will be conservative as the airborne plume will tend to meander. Because of the uncertainty in wind speed, the area potentially impacted by graphite flake deposits should be determined as being bounded by the probable range of wind speeds. Often this may be $\pm 45^\circ$ from the expected mean wind vector. For example, if the mean wind direction is known to be from the northwest and directional variability is slight, the area potentially impacted by depositing graphite flakes might be considered to be encompassed by the directions east and south from the point of dissemination.

Flakes may be deposited to soil, vegetative, or water surfaces. After deposition the flakes may be incorporated into the surface, or may be resuspended by wind or mechanical disturbances (e.g., vehicular traffic and browsing animals). Incorporation may be augmented by dew formation, rainfall, or other mechanisms. Resuspension provides the potential for continued dispersal over a greater range than that of the initial deposition. Data concerning the resuspension of graphite flakes are not available; however, the potential for resuspension is greatest immediately after initial deposition and becomes small after the flakes are weathered and incorporated into the surface. Although specific rates are not known, the degree of resuspension from exposed surfaces and plant canopies could approach 100% before weathering, and flakes could be transported a few kilometers from the location of original deposition to ground surfaces, and longer distances from plant canopies (given that resuspension is most likely to occur during wind storms). After weathering has occurred, resuspension rates should be minimal.

4.1.2 Human Inhalation Source Term

The greatest risk to humans from graphite flakes is through inhalation. An inert chemical nature and an aerodynamic size distribution largely within the respirable size range suggests the potential for inspired flakes to deposit in all regions of the respiratory tract (including the aveolar regions).

The major determinant of inhalability of airborne particles is aerodynamic diameter (Miller et al. 1979). Airborne graphite flakes have aerodynamic diameters ranging from about 0.5 to 20 μm (settling velocities between 0.001 to 1.2 cm/s), and about one-half of the mass of a graphite flake aerosol consists of particles with aerodynamic sizes $< 3.5 \mu\text{m}$ (Section 2.4.2, and Appendix A). The American Conference of Governmental Industrial Hygienists (ACGIH) Air Sampling Procedures Committee (ACGIH 1985) described three aerosol mass fractions for inhalation studies. Based on an assumption of a spherical particle shape, between 70% and 100% of all graphite flakes are inspirable and between perhaps 30% and 70% are respirable (will penetrate to the aveolar region of the lung). Because only a small percentages of flakes have aerodynamic sizes greater than 10 μm , the actual mean inspirable fraction of flake aerosols may be greater than 90%. However, the quantity of particulate mass that is actually breathed and the fraction of inhaled aerosol that may deposit in the airways vary widely with individuals. Differences in health, age or breathing styles, and habits such as cigarette smoking affect inhalation and deposition of particles (Kleinerman et al. 1979). For a healthy person breathing through the mouth at 15 breaths per minute with a tidal volume of 1450 mL, deposition in the deep lung would be expected to be about 35%, 30%, 55%, and 10% for inhaled aerosols with aerodynamic diameters of 0.2, 1.0, 5.0, and 10.0 μm , respectively. Therefore about 30% to 50% of inhaled graphite particles having aerodynamic diameters less than or equal to the median diameter of obscurant aerosols will likely deposit in the alveolar region of the lung.

The influence of the platelet shape on inspirability and respirability should not considerably alter the deposition of graphite flakes within the respiratory tract. This is in part because the physical dimensions of the flakes are smaller than the critical diameters of passageways within the lungs (Timbrell 1982).

The aerodynamic size characteristics of graphite flake aerosols have been predicted based on measurements of full-scale graphite flake releases in a wind tunnel. Approximately one-third of the mass of a graphite flake aerosol may be expected to consist of particles with aerodynamic diameters $< 3.5 \mu\text{m}$ (Appendix A). Particles having aerodynamic diameters of 3.5 μm are thought to penetrate to the aveolar region of the human respiratory tract with an effectiveness of 50% (ACGIH 1985). Smaller particles penetrate with greater effectiveness, and larger particles penetrate with lesser effectiveness.

4.2 HUMAN HEALTH EFFECTS

Airborne flake material likely present the greatest risk to man through inhalation. The inert nature of the flakes and the potential for respiratory impact or transmigration within the body contribute to this risk.

4.2.1 Inhalation Toxicology

The pathology of graphite pneumoconiosis is similar to that of coal worker's pneumoconiosis (Gloyne et al. 1949; Lister and Wimborne 1972; Hanao 1983) and is characterized, in its simple form, by focal collection of dust-laden macrophages at the division of the respiratory bronchioles, reticulin deposits, and focal emphysema. A progressive form is also seen that moves from macular and nodular lesions to massive fibrosis with "graphite cyst," severe vascular sclerosis and cor pulmonae (Gaensler et al. 1966; Kleinerman et al. 1979). Over 600 cases

of pneumoconiosis have been reported in workers exposed to dusts containing natural or synthetic graphite (Hanao 1983).

The etiology of graphite pneumoconiosis is obscured, however, by the presence of fibrogenic constituents in the dusts inhaled by graphite workers. Both quartz and mica are common impurities associated with occupational exposures to natural graphite. Silica was implicated as the causative agent in mixed-dust pneumoconiosis in animal studies by Martin et al. (1972) and Schlipkoter and Hilscher (1972). These researchers demonstrated an induction of fibrotic lesions by inert dusts when quartz was added to the dust and administered by intraperitoneal injection or aerosol exposure. Graphite dusts causing pneumoconiosis in humans were found to contain from 2% to 25% free silica (Uragoda 1974; Gloyne et al. 1949; Dunner and Bagnall 1946). Acute exposure studies with rats have demonstrated that graphite without contaminating silica produced minimal, reversible pulmonary effects (Thomson et al. 1986 and 1987; Anderson et al. 1987). The effects included enzymatic and cytological alterations, and changes in pulmonary resistance, all of which were resolved within 14 days. Although the occupational exposure standard adopted by the ACGIH to protect against silica-induced fibrosis is 0.1 mg/m³ respirable quartz, more than 44% of employees exposed to synthetic graphite dust containing < 0.1 mg/m³ free silica exhibited pneumoconiosis (Okutani et al. 1964). Other researchers have reported massive fibrosis in workers exposed to quartz-free graphite atmospheres (Gaensler et al. 1966; Pendergrass et al. 1967a,b). More recently, epidemiological studies of miners in Britain showed that pulmonary damage was correlated to the mass concentration of respirable dusts if quartz content was < 7.5%. Subsequently, chronic inhalation studies with the nuisance dust, titanium dioxide, have shown that chronic exposures to high concentrations of dust particles overwhelm the lung clearance mechanisms, resulting in fibrotic lesions in response to the retained particles (Lee 1985). This mass loading effect was demonstrated for synthetic graphite dusts (silica content < 0.1 mg/m³) by Thomson et al. (1988).

Thus, graphite dust behaves biologically as a nuisance dust, producing little adverse effect when exposures are kept under control. The pulmonary response to nuisance dusts is characterized by accumulation of dust-laden macrophages in the alveoli, perivascular tissue, and bronchiolar region of the lung and the proliferation of Type II pneumocytes. No deposition of collagen fiber or alteration of stromal lung structure is observed. Exposures below 10 mg/m³ are unlikely to result in disease during the working lifetime of an individual. Because the presence of crystalline silica in graphite and graphite products appears to increase fibrogenic potential, occupational exposure standards are currently based on the silica content of the dust. The ACGIH (1986) has set the threshold limit value (TLV) at 10 mg/m³ total dust for natural and synthetic graphite exposure for graphite dusts containing < 1% free silica. This TLV is for a time-weighted average (TWA) exposure equivalent to an 8-h workday. For graphite dusts containing larger amounts of quartz, exposure must meet the appropriate TLV-TWA for silica to protect against respiratory fibrosis (i.e., 0.1 mg/m³ for respirable quartz). The ACGIH has issued a notice of intended change for the graphite exposure standards that will limit occupational exposure to all forms of graphite (except fibers) to 2 mg/m³ of the respirable fraction (ACGIH 1990).

For the dispersions of graphite flake plumes estimated in Section 2.4.3, air concentrations exceeding 10 mg/m³, the current TLV for graphite and other nuisance dusts, were predicted within downwind distances of 0.2 to 2.0 km of the source (the specific distance varied with ASC). Air concentrations exceeding 2 mg/m³, the proposed revised TLV, were predicted within 0.4 to 4 km of the source. While these comparisons may provide some guidance, it must be noted that the TLV of a material refers to the maximum limit recommended for 8-h days and 40-h work weeks in an industrial setting. This assumption is not well suited to most obscurant applications with the possible exception of the technicians operating smoke generators. A more appropriate exposure limit for the type of exposures (single or episodic) experienced in field applications of obscurants is the short-term exposure limit (STEL). However, no acute exposure limits have been determined for graphite. Generally, short-term exposures should not exceed 5 times the TLV-TWA (5 times

the TLV-TWA for graphite is 50 mg/m³). If the 2-mg/m³ TLV is applied, the potential STEL would be 10 mg/m³. To avoid pulmonary damage, the short-term exposure should be less than the STEL. To maintain a conservative approach to potential impacts associated with smoke tests, a STEL of 10 mg/m³ should be selected. Predicted air concentrations of graphite flakes exceed 50 mg/m³ (i.e., 5 times the 10 mg/m³ TLV) within downwind distances of 0.15 to 0.5 km of the source. If a STEL of 10 mg/m³ (5 times the proposed TLV of 2 mg/m³) is considered, safe levels of graphite flakes are exceeded within 0.2 to 2 km of the generator. It should be noted that, for rats, single exposures up to 500 mg/m³ of graphite flake caused only transient pulmonary damage (Thomson et al. 1986). However, repeated graphite exposures to lower airborne concentrations (100 mg/m³) of graphite flake apparently overwhelmed the clearance mechanisms and pulmonary lesions developed in response to the retained flakes (Thomson et al. 1988). Only relatively minor lesions develop from prolonged, repeated exposures (4 weeks and 13 weeks of exposure at 4 hours/day, 4 days/week) to graphite flakes or to mixed aerosols of graphite flake and fog oil (Aranyi et al. 1992). The lesions that failed to resolve during the 3-week or 6-week recovery periods were a mild inflammatory lesion characterized by increased total cells, increased percentage of neutrophils, and increased protein in lavage fluids, hyperplasia of lung epithelium, and a minor impairment of pulmonary function characterized by reduced respiratory system compliance and a decrease in static and dynamic lung volumes (Aranyi et al. 1992). No mortalities, clinical signs of toxicity, body weight changes, or reduction in pulmonary bactericidal activity were observed following the 4 or 13 weeks of exposure.

4.2.2 Transmigration of Flakes

Particles are removed from the deep lung by several processes including 1) phagocytosis by macrophages and transport to ciliated airways or lymphatics, 2) direct movement of the particle into the blood or lymphatics, and 3) dissolution in the fluid matrix of the lung and uptake by systemic blood (Phalen 1984). Clearance of the chemically inert graphite flakes from alveolar tissue is accomplished by the former two mechanisms. The majority of particles deposited in the lung are removed via the airway route. However, a small portion of the deposited mass that is removed from the lung enters the pulmonary lymphatics and is removed to the satellite lymph nodes in the mediastinum and at the hilus of the lung. The satellite lymph nodes filter out phagocytic cells and particles brought to them from the lung. If these nodes are laden with dust, some particles escape the filtration process. Although the lymph fluid is subject to successive filtrations, unfiltered dust may enter the thoracic lymph duct and be carried into the subclavian vein. Dissemination of coal dust throughout the body in this manner has been observed in coal miners (Kleinerman et al. 1979; LeFevre et al. 1982). Cells of the reticuloendothelial system in the spleen, bone marrow, and liver remove such particles from circulation producing focal pigmented deposits in these tissue (Kleinerman et al. 1979). Although impaired function in lymph nodes from transported particles is well established (Gross et al. 1973; Kleinerman et al. 1979), the impact of transported particles to other tissues is not fully evaluated, but, so far, has not been associated with any pathologic response (Kleinerman et al. 1979; LeFevre et al. 1982).

4.2.3 Dermal Pathologies

Deposits of graphite flakes (as with any particulate matter) in eyes, ears, and nasal passages may cause discomfort (ACGIH 1986). However, rabbit eye/skin irritation tests with graphite were negative (Manthei et al. 1980), and cutaneous toxicity studies in rabbits indicated that graphite has no effect via this route.

4.3 TERRESTRIAL EFFECTS

The determination of the impact of graphite flakes in terrestrial systems is required to understand the potential for damage to ecosystems.

4.3.1 Fate and Effects in Soils and Depuration

The fate of graphite flakes in soils over long time periods is not documented. Incorporation of graphite in surface soils could either increase or decrease permeability of the soil to infiltration depending on soil type.

4.3.2 Soil Invertebrates

Earthworms (*Eisenia foetida*) are key organisms in the soil community and are commonly used in bioassays to determine potential chemical effects. Studies of the toxicity of graphite flakes with earthworms indicated that the flakes are not toxic to soil invertebrates (Bowser et al. 1989). The authors tested graphite flakes at concentrations of 0%, 0.05%, 0.10%, 0.50%, and 1.00% graphite by weight incorporated into an artificial soil mixture. The worms were placed and left in the amended soil/flake mixture for 14 days. At the end of the exposure period, the worms were removed from the mixture, weighed, and examined to determine physical condition. The results of these experiments showed that the flakes produced no lethal effects at the concentrations tested. Sublethal effects were measured as weight changes and are listed in Table 1. In the table, uncertainty equals ± 1 standard deviation of 3 replicate samples. Although net weight increases appear less for earthworms exposed to graphite flakes, statistical evaluation using analysis of covariance techniques showed no significant differences ($p < 0.05$) between treatments (Bowser et al. 1989). The conclusions of the study indicated that graphite flakes were not toxic to earthworms at the concentrations tested.

No information is available on the specific effects of graphite flakes on the soil microbial community.

TABLE 1. Mean Weight Changes of Earthworms Exposed to Graphite Flakes in Soils (from Bowser et al. 1989)

Graphite Concentration	Mean Weight Body Weight (g) ^a		Net Weight Change (g)
	Beginning	Ending	
0.00 ^b	1.37 \pm 0.10	1.86 \pm 0.23	+ 0.49
0.05	1.32 \pm 0.05	1.71 \pm 0.01	+ 0.39
0.10	1.48 \pm 0.07	1.90 \pm 0.08	+ 0.42
0.55	1.34 \pm 0.13	1.71 \pm 0.10	+ 0.37
1.00	1.35 \pm 0.07	1.72 \pm 0.10	+ 0.37

^a Values are means \pm one standard deviation

^b Concentrations of graphite are by percent weight in soils

4.3.3 Terrestrial Plants

Knowledge of the fate and effects of graphite flakes on vegetation is necessary to evaluate the potential for adverse effects to ecosystem function, and more directly to determine the potential for uptake and translocation through the food chain. However, few studies have been undertaken to determine the toxicity of graphite flakes to plants.

One study conducted by Phillips and Wentzel (1990) to determine the potential toxicity of graphite flakes to terrestrial plants indicated no lethal or sublethal effects. The study was conducted using a modification of the Environmental Protection Agency's Environmental Effects Test Guidelines-Early Seedling Growth Toxicity Test (EPA 1982). Corn and cucumber plants were grown in soils amended with graphite flakes to concentrations of 0%, 0.05%, 0.10%, and 0.50% flakes by weight. In this study, measures of phytotoxicity were plant height and dry biomass as indicators of plant growth. Mean plant heights (± 1 standard deviation, N=30) are presented in Table 2.

TABLE 2. Mean Shoot Heights of Corn and Cucumber Plants After 14 Days Grown in Soil Amended with Graphite Flakes (from Phillips and Wentzel 1990)

Plant	Treatment Levels (Percentage Graphite in Soil, by Mass)			
	0.00%	0.05%	0.10%	0.50%
----- Plant Height (mm) ± 1 Standard Deviation (N=30) -----				
Corn	346.8 \pm 9.2	373.9 \pm 59.8	361.7 \pm 78.2	351.5 \pm 84.1
Cucumber: ^a	100.8 \pm 12.5	104.2 \pm 14.0	117.3 \pm 13.4	117.5 \pm 14.9
Cucumber:	97.4 \pm 8.8	98.3 \pm 10.7	97.0 \pm 10.9	93.9 \pm 27.6

^a The first of two studies done to evaluate the effects of graphite on shoot height in cucumber.

Using these results, a two-way analysis of variance (ANOVA) indicated no significant difference ($p < 0.05$) in shoot height of corn between control plants and corn plants grown in soils amended with graphite. However, the ANOVA of mean plant heights for the cucumber plants in the first study did indicate a significant difference ($p < 0.01$) between control and treated plants. Further evaluation showed a significant difference ($p < 0.01$) between the two lower concentrations (0.00% and 0.05%) and the two higher concentrations (0.10% and 0.50%), thus indicating that the addition of graphite flakes to soils significantly increased plant height. A second study to confirm this effect on cucumber plants showed no significant difference ($p < 0.05$) on mean plant height. In no case were differences in mean dry weights for either corn or cucumbers significantly different.

Although no adverse effects were noted in the study, Phillips and Wentzel (1990) did note an increase in the measured height of cucumbers grown in soils with graphite flake concentrations of 0.10% and 0.50% in one test. The increase may have resulted because the graphite flakes permitted better penetration of the soil by the young cucumber roots, or graphite flakes may have increased aeration of the soil or the water holding capacity of the soil to facilitate plant growth. They concluded that graphite flakes do not have an adverse effect on the vegetation when field-release concentrations are at or $< 0.50\%$ by weight in the soil.

4.3.4 Wildlife

Wildlife remaining within about 0.2 km to 4 km downwind of the test site (see Sections 4.1.2 and 4.2) during smoke-generating periods may inhale potentially harmful levels of graphite. This assumes that wild animals have about the same sensitivity to air pollutants as humans and receive (on a body-weight basis) equivalent doses in the environment. However, it has been shown that the volume of air breathed per minute per unit of body weight (i.e., the weight-specific

minute ventilation) varies greatly among mammals (Phalen 1984). Generally, the smaller the animal, the more air per minute per gram is inhaled. Compared to humans, rabbits ventilate 3 times and small rodents ventilate 8 to 13 times greater volumes of air on a per-body-weight basis (Phalen 1984). Larger animals such as deer and moose receive smaller doses than humans during inhalation exposures. Birds may be at even greater risk than represented in the human STEL because their respiratory rates are generally higher than mammals of comparable size. In addition, seasonal physiological changes, activities (e.g., flying), and breathing-zone differences (e.g., near the turbulent ground surface) further complicate the extrapolation of the human STEL to wild animals. Therefore, the STEL for humans should be viewed as relative estimates of the safe limits for wildlife in field situations.

Consumption of graphite flake while foraging is unlikely to cause any adverse effects to mammals or birds. Impact to wildlife from diminished food sources will probably be minimal because the area on which graphite flake deposits would be large enough to cause plant or invertebrate damage is relatively small to most foraging animals (Section 4.1.1).

4.4 FRESHWATER AND MARINE EFFECTS

Comparatively few studies have been conducted with graphite flakes compared to classical environmental pollutants. Available data concerning the aquatic effects of graphite flakes include 64-day microcosm tests and tests with single species of aquatic invertebrates.

4.4.1 Single-Species Toxicity Tests

The initial determination of the aquatic toxicity of graphite flakes was conducted using *Daphnia magna* in the 48-h acute toxicity test (Johnson and Landis 1988). One of the difficulties in measuring toxicity was the reliable dosing of the test organisms. Suspensions were prepared from flake material added to a diluent. Tests were conducted at 20°C with a 16- to 8-h light-dark cycle. The test media was autoclaved, aerated and hardened before addition of the test material.

The flake was toxic to the daphnids with a calculated EC₅₀ of 80.6 mg/L. Proton induced x-ray emission analysis on the flake indicated that contaminants such as iron were present in the material. These contaminants may have accounted for the observed toxicity.

One of the initial concerns in the evaluation of flake damage was the potential for mechanical damage occurring to the feeding and swimming appendages of the daphnids (Johnson et al. 1985; Johnson et al. 1986). To examine this possibility, suspensions of silica and titanium dioxide were tested in the same manner as the graphite flakes. Titanium dioxide and silica are inert materials that would simulate the possible mechanical damage without introducing chemical toxicity. At concentrations as high as 1000 mg/L neither material caused physical damage to the appendages of the daphnids. Grenade-released samples of titanium dioxide (i.e., titanium dioxide residues collected after detonating a grenade and then used for testing) also did not exhibit toxicity at 1000 mg/L (Appendix C [1]).

4.4.2 Fate in Aquatic Systems

No information available.

4.4.3 Microcosm Toxicity Test

Perhaps the most extensive study of the fate and effects of graphite in an aquatic system is the examination of graphite flake using the Standardized Aquatic Microcosm (SAM) by Landis et al. (1988, 1989). The 64-day SAM-protocol and its utility in ecotoxicological evaluation has been described by Taub (1989). Concentrations of graphite flake tested ranged from 0.01 to 10.0 mg/L.

Concentrations of higher than 100 mg/L were not used because determination of algal numbers and daphnid mobility could not be accurately conducted because of the opacity of the media. The authors reported that the microcosm exhibited a variety of effects due to the application of the graphite flake material. However, no supporting statistical analysis was supplied. The effects resembled some of the processes of cultural eutrophication and included reduced species diversity, elevated ammonia levels, and deviations in photosynthesis-respiration ratios from controls. Although it is difficult to imagine a pathway to incorporate inorganic carbon, the trace amounts of iron found in the flakes may have induced the effects seen in the microcosm at the highest concentration. A graphite flake material with lower amounts of impurities would likely have even less effect.

4.5 MITIGATION APPROACHES

Airborne graphite flakes are inhalable, and surface deposits can accumulate in terrestrial, aquatic, and marine systems as a result of research and development and performance testing. In some instances, mitigation approaches are recommended.

Mitigation approaches that involve reducing the amount of material disseminated during tests by reducing dispersion rates, the number of tests per site, altering the physical characteristics of the material, or the use of new (replacement) materials involve research and development and/or performance considerations and are beyond the scope of this review. Mitigation approaches are limited to activities that may reduce the impact of graphite flake aerosols as they are currently disseminated on health and the environment.

When possible, tests involving graphite obscurant aerosols should be performed in wind tunnels (such as the U.S. Army Breeze wind tunnel in Edgewood, Maryland) or in other facilities having particle filtration capabilities. The wind tunnel can be used to test full-scale systems, but is limited in its ability to test generation performance under extreme weather conditions (e.g., desert or arctic environments). Other wind tunnels are available to test reduced-scale dissemination systems for environmental deposition, resuspension, fate, and effects, and for bioavailability and toxicity to plants and animals.

4.5.1 Human Health

Because graphite flakes are largely inhalable and respirable, and because data suggest an occupational risk for workers after repeated or long-term exposure to dusts containing natural or synthetic graphite (Section 4.2.1), the inhalation of graphite flake aerosols should be limited. Respiratory protection should be provided to workers subjected to the airborne flakes greater than 10 mg/m³. Protective eyewear should also be provided to reduce potential for irritation.

4.5.2 Terrestrial Systems

In terrestrial systems, no *in situ* environmental mechanisms exist to attenuate graphite flake deposits. Graphite platelets do not have a physical structure (such as do fibers) that would limit incorporation into soils, and surface deposits are not expected to persist. In addition, because the bulk source of graphite flakes is finely divided powder, very heavy near-source deposits are less likely than for fiber aerosols. Mitigation efforts to limit resuspension may be performed in the vicinity of the disseminator using chemical fixation processes to provide a temporary reduction in resuspension until natural weathering processes act to fix the flakes to the surface. Examples of chemical fixatives (sprayed on contaminated surfaces) include polyvinyl alcohol/acetate, acrylates, and other similar environmentally acceptable alternatives.

For tests that are not dependent on plume dispersion characterization (e.g., mobile generator performance tests under temperature extremes), smoke deposition could be decreased by

elevating the plume. This can be accomplished by orienting the air ejector to a more vertical position. Alternatively, smoke down-wash could be decreased by ejecting the material at an angle to the mean wind direction (this may not be possible for moving units).

Airborne concentrations may exceed safe short-term limits for humans within several km of the source. Assuming these levels approximate harmful levels for other mammalian species and birds, generation should be avoided in areas where protected species or sensitive or concentrated populations (e.g., migrating birds, or calving herds) may be exposed to unsafe levels of graphite flakes. Special concern should be given to small animals which, because of their rapid metabolism, may inhale on a per gram-body weight basis far more contaminated air than is reflected in the STEL established for human health protection.

4.5.3 Freshwater and Marine Systems

No mitigation approaches are indicated based on the lack of observed toxicity of graphite flake to aquatic organisms. Use of graphite flakes should be restricted when it is known that recreationally or economically important fish species may be spawning in the area.

4.6 ENVIRONMENTAL IMPACTS OF RESEARCH AND DEVELOPMENT, MANUFACTURE, TRANSPORTATION, STORAGE, AND DISPOSAL

Safety issues are typically addressed in specific test plans and are not present in this review. Personnel safety is the responsibility of the test site range safety officer. The following will address the general aspects related to environmental impacts.

4.6.1 Environmental Impacts of Research and Development

Environmental impacts of graphite flake use should be minimal based on available data and commercial and military uses. The environmental dissemination of flake material results in two levels of contamination. The first is the relatively large area of soil or water surface on which dispersed flakes are deposited. Including worst-case conditions, surface deposits are estimated to be $< 10 \text{ mg/m}^2$ at distances greater than 0.7 to 7 km from the source, depending on atmospheric stability category. At these levels, terrestrial, aquatic, and marine risks from flake resuspension are minimal. The second level, which is applicable to terrestrial applications where release is from stationary sources, where higher accumulations of flakes occur around generators or point sources (0.7 to 70 g/m^2), physical removal or in-place fixation is recommended.

Personnel protection is recommended for individuals within the airborne flake clouds and in situations where resuspension of deposited flakes is potentially possible. At a minimum this should include use of full-face particle masks for respiratory protections and prevention of eye irritation. Respiratory exposure to airborne graphite flake may also be harmful to other vertebrate species, particularly small mammals and birds. The population stability of species with critically low populations (endangered species) can be affected by a small increase in mortality, therefore generation of flake material and the potential for significant resuspension of the flakes should be avoided in areas (or at times) where such species are present. Also, populations of animals may be impacted by respiratory exposures to airborne graphite flake when they are concentrated within a small area. Dispersion of graphite flakes should be avoided in areas or at times when migrant species are congregating in high-risk exposure areas.

4.6.2 Manufacture and Transportation

Graphite flake is not listed as hazardous material under regulations of the HMTA in 49 CFR 171-179.

A portion of the HMTA regulations addresses explosives where transport of Class 1.1-1.2 explosives is subject to regulations in 49 CFR 173.50-173.63.

4.6.3 Storage

Storage of graphite for future use is not subject to regulation under RCRA because unused graphite flake is not considered hazardous waste.

4.6.4 Disposal

Graphite is not hazardous waste under RCRA. Thus, disposal of these flakes can be conducted according to nonhazardous waste disposal methods of the particular installation.

5.0 CONCLUSIONS

Evaluations of the environmental and toxicological impacts of the dispersion of graphite flake aerosols to the environment have been reviewed and are summarized in this section. Where insufficient data exist to provide summary conclusions, or where the addition of data would serve useful purpose in expanding the environmental assessment of graphite flake aerosols, such data needs are identified.

5.1 ENVIRONMENTAL AND TOXICOLOGICAL IMPACTS

The impacts of graphite flake aerosols are discussed for dissemination and deposition, environmental toxicity, human health risk, terrestrial impacts, and freshwater and marine impacts.

5.1.1 Environmental Dissemination and Deposition

Potential impacts from the dissemination of graphite flakes depend on air concentrations in the case of human inhalation or dermal exposure, or the mass loading of ground, vegetative, and aquatic surfaces in the case of environmental impacts. Graphite flakes are dispersed by mechanically producing flake aerosols at a steady rate for periods of minutes to a few hours. Dispersion and deposition of flakes is dependent on the aerodynamic behavior of the flakes in air. The aerodynamic size of individual flakes in the aerosols range primarily between 0.5 and 20 μm , with the flakes having settling velocities between 0.001 and 1.2 cm/s. The mean aerodynamic size is about 3.5 μm , having a settling velocity of 0.04 cm/s.

Downrange air concentrations and surface deposits may be measured during and after tests, or may be predicted using simple or complex dispersion and deposition models. While models will predict average concentrations, field sampling will reveal maxima and minima influenced by site- and test-specific atmospheric and surface conditions. A Gaussian atmospheric plume dispersion model that was modified to also predict deposition was used to estimate air concentrations and surface mass loadings downrange of single dissemination systems. Estimates of air concentrations for several typical atmospheric conditions ranged from 26 to 140 mg/m^3 at distances of 0.1 to 0.3 km downwind from the source, to < 0.001 to 0.01 mg/m^3 at 40 km. Only under the "worst case" atmospheric conditions expected during typical operations was the concentration 0.1 to 0.3 km downwind of the source estimated to exceed 110 mg/m^3 . Even for this case, however, concentrations decreased to < 10 mg/m^3 at distances greater than about 2 km from the source. Air concentrations also decreased with increasing crosswind distance from the downwind vector from the source at rates that were influenced by ASC.

Estimates of surface mass loading for several typical atmospheric conditions ranged from 380 to 2100 mg/m^2 at distances of 0.1 to 0.3 km downwind of the source, to < 0.2 mg/m^2 at 40 km. The deposition of graphite flakes was estimated to be < 1 mg/m^2 at distances greater than about 2 to 25 km from the source, depending on atmospheric stability category. Surface deposits also decreased with increasing crosswind distance from the downwind vector from the source at rates that were influenced by the ASC. Large percentages of deposited graphite flakes may be resuspended in the event of a wind storm (approaching 100% depending on surface type) before weathering occurs or before flakes are incorporated into the surface. The most probable effective weathering processes will be dew formation and evaporation and precipitation.

5.1.2 Material Toxicity

Graphite flakes typically used for obscuration contain very low levels of silica, thus reducing the risk of graphite pneumoconiosis in workers and terrestrial wildlife exposed to the flake. Chemically, the flakes pose little or no risk to the environment. Mechanical damage to plants and vertebrate and invertebrate organisms from exposure to graphite flakes is also minimal.

5.1.3 Human Health Risk

A large portion of the mass of a graphite flake aerosol consists of particles that will likely deposit in the deep lung. In the lung, graphite flakes behave as a “nuisance” dust causing only transient histological and physiological changes. However, high concentrations of dust can overwhelm the clearance mechanisms of the respiratory tract resulting in pulmonary damage from the retained particles and impaired function of the lymph nodes from transported graphite particles. Concentrations that may pose a risk of lung damage from graphite flakes can occur during generation (or resuspension) within 2 km of the source. Repeated exposure to elevated concentrations appear more hazardous than single exposures to higher concentrations of the particles. Yet only minor impacts to respiratory structure and function occur following repeated exposures to $\geq 100 \text{ mg/m}^3$ graphite flake (alone or co-generated with fog oil) at frequencies and for durations much greater than those encountered during typical production prove-out tests. A minor risk of physico-mechanical damage to unprotected skin and eyes also exists.

5.1.4 Terrestrial Impacts

No information is available concerning potential short- or long-term effects on the soil microbial community from exposure to flakes deposited to and incorporated in soils. Likewise, little information is available on the deposition and retention of graphite flakes on soil or plant surfaces or on the effects of graphite to terrestrial plants and animals.

Graphite flakes have not been shown to be toxic to either soil invertebrates or plants (Bowser et al. 1989; Phillips and Wentzel 1990). The deposition and incorporation of graphite flakes on soils may actually enhance plant growth through aeration of soils and enhancement of water infiltration. This type of effect would be expected to be short term in nature and attenuate as the graphite flake material became incorporated into the soils. On the other hand, a high concentration of particles on the soil surface might form a crust and also might change the albedo of that area (Black and Mack 1986). In arid areas, formation of a crust could adversely affect water infiltration. Concentrations of ground-deposited flakes beneath the plant canopy could also influence the energy budget, and thus the water budget, for that individual plant. Under those conditions, plants growing in areas with limited water supplies may be adversely effected over the short term by such changes in growth conditions. No information is available to support a conclusion for either of these impact scenarios. Because of differences in the weight-specific minute volume and structure of the respiratory system, birds may inhale much higher doses of flakes (Phalen 1984) than those considered for human health assessment. However, the response of wild birds to graphite flake is undocumented.

5.1.5 Freshwater and Marine Impacts

In general, graphite flake and related materials show little or no acute toxicity in the systems studied to date. At concentrations below 100 mg/L, only the graphite flake (Micro 260) exhibited a toxic effect. Often, effects at concentrations above 100 mg/L were not observed because the opacity of the material made scoring of the toxicity test difficult. In the larger microcosm system, the principal effects were in the alteration of community metabolism. The increase in respiration and in waste product production is indicative of nutrient addition. Micro-260 is known to contain trace amounts of iron, an essential nutrient. The persistence of the carbon materials, in addition with trace amounts of contaminants may cause long-term effects. Monitoring of the training sites and disposal areas may be warranted. However, compared to materials such as fuel oil particulate matter or brass dust, carbon flakes pose less hazard to aquatic ecosystems.

5.2 DATA NEEDS

The existing set of data related to the environmental fate and toxicological effects of graphite flake aerosols is not complete. Suggested research tasks are identified here where additional information would aid the environmental assessment of the military use of the material.

5.2.1 Aerodynamic Behavior of Flakes

The aerodynamic behavior of many types of materials having platelet-shaped primary particles have been determined (Davies 1979). Data available for graphite flakes are not sufficient to allow determination of dynamic shape factors. Tests to determine this parameter would increase the understanding of the aerodynamic characteristics of airborne flakes.

5.2.2 Graphite Flake Deposition, Resuspension, Fate, and Depuration

Graphite flakes generated singly (in the absence of fog oil) will resuspend from surfaces at varying rates that depend on surface characteristics and the presence or absence of weathering processes. Resuspended flakes will provide a secondary source of the material to potentially effect health and the environment. Measurements of flake resuspension and weathering rates should be made to characterize this secondary source aerosol, to aid predictions of dose to plants, soils and water, and to determine the effectiveness of natural weathering processes to reduce resuspension rates.

Data are needed to define rates of deposition to and depuration from plant, soil, and water surfaces. Deposition rates and surface retention effectiveness should be studied. Information is needed concerning the potential for flakes to adhere to and persist on soil and vegetation surfaces. Fate and effects studies are also recommended to determine the impact of the range of field mass loadings on soils, plants, and microorganisms.

5.2.3 Bioavailability and Toxicity of Graphite Flakes

The persistence of the carbon materials and trace amounts of associated contaminants may have long term effects in aquatic ecosystems. Monitoring of the training sites and disposal areas may be warranted. However, graphite flakes pose less hazard to aquatic ecosystems compared to materials such as fuel oil particulate matter or brass dust.

The health risk of environmental releases of graphite flakes to avian wildlife is unknown. It is important to determine potential adverse effects in birds because they are often more sensitive to airborne pollutants than mammals, have high public visibility and are used as bioindicators of ecosystem health. Mammalian inhalation data cannot be applied to avian species because of fundamental differences in their respiratory systems, respiratory physiology such as weight specific minute ventilation, and immune response. Also, many areas where field testing occurs are potential habitats of protected species and access to contaminated airstreams is difficult to control. Therefore, information on the hazardous short-term levels of airborne graphite flake in birds is needed to evaluate the safety of environmental releases of graphite flake to wild bird populations.

No information is available on some of the protected wildlife species encountered in areas used for extreme climate testing. Tests using surrogate species for protected species during sensitive life stages (e.g., the desert tortoise during periods of the reproductive cycle) are needed to fully assess the impact of large airborne concentrations or surface deposits of obscurant smokes on wild animals. The impact of graphite flake generation and resuspension on insects, key components of the terrestrial system, is unknown. The survival, fecundity, life-stage susceptibility of at least 1 key pollinator and 2 or 3 species of beneficial predators, scavengers, or species with with soil-dwelling larval stages should be assessed.

5.2.4 Mitigation Approaches

When possible, research and development and performance tests involving graphite obscurant aerosols should be performed in wind tunnels (such as the U.S. Army Breeze wind tunnel in Edgewood, Maryland) or in other facilities having particle filtration capabilities. The wind tunnel can be used to test full-scale systems and reduce the amount of field work that would otherwise be necessary. Other wind tunnels are available to test reduced-scale dissemination systems for environmental deposition, resuspension, fate, and effects, and for bioavailability and toxicity to animals.

In addition to measurements of the effectiveness of natural weathering processes to fix graphite particles to surfaces (and prevent resuspension), the use of artificial methods to provide temporary or permanent reductions in flake resuspension should be tested.

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APPENDIX A

AERODYNAMIC CHARACTERISTICS AND SETTLING VELOCITIES OF GRAPHITE FLAKES

The shape and density of airborne particles affect their aerodynamic characteristics. Because graphite flakes are not spherical, aerodynamic drag and gravitational settling are not simple to determine theoretically. While measurements may be made of non-spherical particles to determine dynamic shape parameters, another approach is to measure the aerodynamic size of the particles using devices that classify airborne particles by their inertia. Because knowledge of the aerodynamic size of graphite flakes is sufficient for most environmental assessment requirements, consideration of dynamic shape factor of graphite flakes is limited to a brief discussion at the end of this appendix.

Aerodynamic Characteristics: The aerodynamic behavior of flakes can be generalized by considering aerodynamic particle size rather than physical particle size. The aerodynamic diameter (D_a) of a flake is the diameter of a unit density sphere that settles with the same velocity as the flake. The aerodynamic diameter of graphite flake aerosols may be measured directly, without the need to measure dynamic shape parameters or to consider the orientation of flakes as they settle. Examples of instruments for measuring the aerodynamic size of flakes include inertial particle spectrometers, cyclones, cascade impactors, and certain optical instruments. Classifying flakes by aerodynamic size also has the advantage that most considerations of the impact of flake aerosols on the environment (dispersion, deposition, and resuspension) and man (inhalation) are influenced most strongly by aerodynamic size rather than physical shape.

The aerodynamic size distribution of graphite flake aerosols were measured in reduced-scale and full-scale experiments. M. W. Ligojke, PNL Earth Sciences Division, conducted reduced-scale measurements of two synthetic graphites (unpublished). These measurements were conducted in a wind tunnel. The average aerodynamic mass median diameter (AMMD) of Micro-260 graphite aerosols was about 2.5 μm , with a geometric standard deviation (GSD) of about 2.4. The AMMD and GSD of KS-2 graphite aerosols were 3.5 μm and 2.1, respectively. These results were based on cascade impactor measurements using glass fiber substrate and correcting measured quantities for internal sampler losses. Subsequently, full-scale tests of an XM56 smoke generator using only graphite flakes (no fog oil), were performed in the U.S. Army Breeze wind tunnel at Aberdeen Proving Ground, Maryland. Cascade impactor measurements conducted by Ligojke (unpublished) resulted in an average AMMD of 5.6 μm , with a GSD of 2.6. Approximately 80% of the aerosol mass consisted of flakes having aerodynamic diameters between 1.7 and 1.9 μm .

The reduced-scale tests were performed at concentrations less than those expected in the field, and thus coagulation was limited and measured aerodynamic particle sizes may have been less than those expected in the field. The aerosols produced during the full-scale tests were constrained in a (albeit large) wind tunnel and may have been influenced by coagulation to a greater extent than aerosols produced in the field. For these reasons, an aerodynamic size distribution having an AMMD of 5 μm and a GSD of 2.5 was selected for the current assessment, to represent field-generated aerosols. This distribution was used to provide estimates of atmospheric dispersion, and deposition (Appendix B), and potential inhalation effectiveness of graphite flake aerosols. In considering potential inhalation effectiveness, roughly 34% of the mass of the aerosol may be expected to consist of flakes with aerodynamic sizes smaller than 3.5 μm .

Settling and Surface Deposition Velocities of Graphite Flakes: The rate at which individual particles settle is necessary information for determining the atmospheric dispersion of graphite flake aerosol plumes from their source of generation. The settling velocity V_s of graphite flakes may be calculated directly from the measured aerodynamic size distribution as

$$V_s = (\rho_0 g D_a^2) / (18\eta) \quad (A.1)$$

where ρ_0 is unit density (1 g/cm³), g is the acceleration of gravity (981 cm/s²), D_a is the aerodynamic diameter of a graphite flake, and η is the viscosity of air (1.79 x 10⁻⁴ g/[cm-s] at standard temperature and pressure [STP]). Settling velocities (in still air) corresponding to the range of aerodynamic particle sizes present in graphite aerosols are shown in Table A.1. The median settling velocity of a graphite flake aerosol having an AMMD of 5 μ m and GSD of 2.5 is estimated to be 0.08 cm/s. Settling velocities of individual graphite flakes within the aerosol are estimated to range between < 0.004 cm/s to more than 1 cm/s.

The actual rate at which particles deposit to plant, soil, and other surfaces exceeds the still-air settling velocity for particles < 30 μ m (after McMahon and Denison 1979; Sehmel 1980). For particles having aerodynamic sizes between 1 and 10 μ m, the deposition velocity, V_d , exceeds V_s by a factor that ranges roughly between 2 and 10. The specific factor depends on particle and surface characteristics, atmospheric conditions, and nonsteady-state interactions of these parameters at the air-surface interface. Wind speed also influences V_d ; while $V_d \sim V_s$ at slow wind speeds, V_d will be greater than V_s at wind speeds anticipated in the field during the production of graphite flake aerosols. Although no comparable data is available for graphite flakes, the V_d of brass flake aerosols has been shown to increase by a factor of about 4 as canopy-height wind speed was increased from 1 to 5 m/s (Cataldo et al. 1990). At higher wind speeds (wind storms), the relationship between V_d and V_s is less clear because of complex air-surface interactions and resuspension of deposited flakes. For purposes of assessing the environmental dispersion and deposition of graphite flake aerosols, and in the absence of a specific relationship, V_d is assumed to be greater than V_s by a factor of about 10, and to be equal to 0.8 cm/s. A V_d of 0.8 cm/s may be conservative by a factor of 1 to 5. In Appendix B, this V_d was used for cases involving wind speeds of 2 and 5 m/s; although actual deposition rates are anticipated to vary with wind speed, no such data are available for graphite flake aerosols.

Dynamic Shape Factor of Flakes: Volume and dynamic shape factors may be determined for non-spherical particles. The volume shape factor, α_v , relates the volume of a platelet to the average projected area diameter, D_p , measured with the platelet resting on its plane of maximum stability. The dynamic shape factor, χ , is the ratio of the drag of a specific nonspherical particle to a spherical particle of the same material having the same volume and at the same settling velocity (as if the original nonspherical particle was melted to form a spherical droplet). A dynamic shape correction factor may be determined and applied to relate the aerodynamic behavior of such nonspherical particles to equivalent spheres. The dynamic shape factor χ is defined as

$$\chi = F_D / (3\pi\eta V D_e) \quad (A.2)$$

where F_D is the drag force, η the viscosity, V the velocity, and D_e the diameter of the equivalent volume sphere (Hinds 1982). D_e is diameter of a sphere having the same volume as the platelet. Using Stoke's law, the terminal settling velocity for irregular particles is

$$V_s = (\rho_p g D_e^2) / (18\eta\chi) \quad (A.3)$$

where ρ_p is the density of the particle, and g is the acceleration of gravity (Hinds 1982). Flakes will settle more slowly than their equivalent volume spheres.

Although typical values of both α_v and χ are available for many irregularly shaped mineral particles, only α_v is available for graphite. Davies (1979) listed the volume and dynamic shape factors for a selected number of minerals and other materials. Table A.2 shows some of this information. While it is likely that the form of graphite named "flake graphite" is similar to that considered in this review, it is possible that plumbago could also be similar to current sources. In the absence of measured dynamic shape factors for either flake graphite or plumbago, it is not possible to determine a direct comparison of the aerodynamic size of a flake and D_p , however, based on the volume shape factor it can be seen that flake graphite is an intermediate case between most minerals and mica.

TABLE A.1 Settling Velocities of Graphite Flakes Suspended in Air Based on Aerodynamic Diameter

Aerodynamic Particle Size (μm)	0.5	1.0	2.0	3.5	5.0	10	20
Settling Velocity (cm/s)	0.0010	0.0035	0.013	0.039	0.078	0.305	1.21

TABLE A.2 Volume and Dynamic Shape Factors and Parameters for Selected Minerals (after Davies 1979)

Dust	Density (g/cm^3)	Volume Shape Factor (α_v)	D_g/D_p	Dynamic Shape Factor (χ)	D_g/D_p
Anthracite coal	1.5	0.16	0.67	1.37	0.70
Bituminous coal	1.4	0.23-0.25	0.76	1.05-1.11	0.87-0.90
Quartz	2.65	0.21	0.87	1.36	1.51
Diamond	3.35	0.35	0.87	1.1	1.08-1.34
Glass	2.6				0.92
Talc	2.6	0.16	0.68	2.04	0.73-0.77
Asbestos (ground)	2.5				0.93-1.32
Sand	2.5	0.26	0.79	1.57	1.00
Limestone		0.16	0.67		
Plumbago		0.16	0.67		
Gypsum		0.13	0.63		
Flake graphite		0.023	0.35		
Mica		0.003	0.18		

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APPENDIX B

ESTIMATED AERIAL DISPERSION AND DEPOSITION OF GRAPHITE FLAKES IN THE ENVIRONMENT

The dispersion of airborne graphite flakes from point of release, and their subsequent deposition to downwind areas are influenced by the aerodynamic characteristics of the released flakes, including both individual flakes and agglomerated flakes (produced by incomplete aerosolization of the source powder), and by the local meteorological conditions, site geography, and surface terrain morphology. In addition, the retention effectiveness of flakes by the surfaces they first deposit to, and the subsequent resuspension rates from these surfaces are influenced by surface conditions, the interaction of flake plumes with the environment, the fluctuating state of meteorological conditions, and the irregular nature of site terrain. Thus the pattern and magnitude of aerial dispersion and deposition at a specific site will vary from test to test and will be different than that for other sites. The dissemination system will also influence plume dispersion and deposition via operational parameters that include flake generation rate, duration of operations, degree of separation of primary particles, and the initial graphite flake plume height.

Estimates of the dispersion, air concentration, and deposition of graphite flakes are necessary to evaluate the potential impact of tests and training activities on the environment. General predictions of the pattern of graphite flake plume dispersion and deposition for an ideal site were made using a Gaussian plume dispersion model (e.g., Wark and Warner 1976) that was modified to include source depletion and the gravitational settling and removal of suspended graphite flakes. The Gaussian model was selected because it is the most basic and most commonly used dispersion model and for reasons summarized by Hanna et al. (1982):

- 1) It produces results that agree with experimental data as well as any model.
- 2) It is fairly easy to perform mathematical operations on the equation.
- 3) It is appealing conceptually.
- 4) It is consistent with the random nature of turbulence.
- 5) It is a solution to the Fickian diffusion equation for constants K (eddy diffusion) and u (wind speed).
- 6) Other so-called theoretical formulas contain large amounts of empiricism in their final stages.

There are two primary differences between the predictions based on the Gaussian model and the pattern of deposition likely to be seen in the field. First, while model results indicate gradual changes in air concentration and surface deposition with increasing downwind distance from the source, survey of an actual field site will reveal areas of flake deposition maxima and minima. Second, the model assumes a wind vector that is constant in direction and time whereas the deposition of flakes in the field will reflect the fluctuating nature of both the mean wind vector and flake resuspension rates. Greater than normal deposition may also potentially occur immediately downwind of the generator, and may potentially be enhanced by wind eddies formed in the lee of the smoke generator. These differences between model predictions and field conditions will affect both local and long-range transport from point of release. For the transport of graphite flakes from specific sites under well defined conditions, and after an analysis of the benefit of potentially improved plume dispersion estimates, more sophisticated models or models prepared for specific sites can be applied on a case-by-case basis. One example of such a model is the Industrial Source Complex Dispersion Model (Wackter and Foster 1986). Another example is the Real-Time Volume Source Dispersion Model (Bjorklund 1990), which is currently widely-accepted and is used by staff at the Meteorology Division, Dugway Proving Grounds, Utah.

The modified Gaussian plume dispersion model provides an estimate of the concentration of graphite flakes in air at locations downwind of the point of release as defined by coordinates x , y , and z , where x is the downwind coordinate, y is the crosswind coordinate, and z is the vertical coordinate. In the equation, Q_p is the mass rate of flake generation, in g/s, u is the magnitude of

$$C_{(x,y,z,H)} = Q_p [Q_x/Q_p] [2\pi u \sigma_y \sigma_z]^{-1} \exp[-0.5 \{ (y/\sigma_y)^2 + [(z-(H-V_s(x/u)))/\sigma_z]^2 \}] \quad (B.1)$$

the mean wind, in m/s, H is the height of the plume at the point of release, V_s is the settling velocity of flakes in the plume, in cm/s, and σ_y and σ_z are the standard deviations of plume dispersion in the y and z coordinates, respectively, expressed in meters. The leading term in Equation B.1, Q_x/Q_p , is a source-depletion term that is included to account for the reduction in the total airborne mass of a smoke plume as deposition occurs between the site of dissemination and a given downwind distance. Q_x/Q_p is determined numerically (Briggs et al. 1973; Hanna et al. 1982). The model assigns values to the crosswind and vertical standard deviations of plume dispersion as functions of the ASC which is in turn influenced by wind speed and insolation level. Plume reflection from the top of a mixing layer is not considered in the model.

To provide estimates of the rate of flake deposition to ground surfaces per unit of surface area, w in g/(m²-s), Equation B.1 was converted using the relationship:

$$w_{(x,y,0,H)} = V_d C_{(x,y,0,H)} \quad (B.2)$$

In Equation B.2, V_d is the deposition velocity of graphite flakes, a parameter that is generally greater than V_s for small particles. Using Equation B.2, estimates of the deposition of graphite flakes to ground surfaces, ML , in g/m², were determined by multiplying w by the duration of flake dissemination, Δt , in seconds.

$$ML_{(x,y,0,H)} = w_{(x,y,0,H)} \Delta t = C_{(x,y,0,H)} V_d \Delta t \quad (B.3)$$

Dispersion and deposition of graphite flake plumes were estimated for 6 test cases that included known source (smoke generator) characteristics, a range of expected atmospheric conditions, and estimated particle deposition velocity. A description of each test case is shown in Table B.1. Cases 2 and 3 represent typical conditions, and may be considered baseline cases. Case 1 represents extremely unstable atmospheric conditions during which tactical release of obscurant smoke may be least effective because of rapid plume dispersion. Case 4 represents atmospheric conditions (ASC F) that are not common at most sites, but was included because it represents a worst-case condition. Cases 1 through 5 were selected to provide a range of ASC and wind speeds. Because ASC C may be present for wind speeds between 2 and 5 m/s, it was included twice (Cases 2 and 5). ASC C was also selected for Case 6 which was included simply to demonstrate the scalar influence of increased time of generation on surface mass loading. The model parameters included the following: generation rate, Q_p ; height of initial release, H ; mean wind speed, u ; ASC; mean flake settling velocity, V_s ; mean deposition velocity, V_d ; and duration of generation, Δt . Results were determined as average air concentration downwind of the source and at an elevation of 1 m, C_m , and surface mass loading, ML .

To provide general air concentration and surface deposition levels for the six test cases, values for Pasquill-type ASC were determined based on information in Table B.2 (Gifford 1976; Hanna et al. 1982). Plume dispersion parameters σ_y and σ_z were calculated based on the open-country formulas recommended by Briggs (1973) and shown in Table B.3.

TABLE B.1 Test Cases for Estimating Graphite Flake Plume Dispersion in the Atmosphere and Deposition to Ground Surfaces

Case	Parameter	Q _p (g/s)	Height (m)	Velocity (m/s)	ASC	V _d (cm/s)	Δt (min)
1	ASC	76	5	2	A	0.8	30
2	ASC	76	5	2	C	0.8	30
3	ASC	76	5	5	D	0.8	30
4	ASC	76	5	2	F	0.8	30
5	u	76	5	5	C	0.8	30
6	Δt	76	5	2	C	0.8	300

TABLE B.2 Meteorological Conditions Defining Pasquill Turbulence Types (after Gifford 1976; Hanna et al. 1982)

Surface Wind Speed, m/s	Daytime Insolation			Nighttime Conditions	
	Strong	Moderate	Slight	Thin Overcast or > 4/8 Low Cloud	≤ 3/8 Cloud
<2	A	A-B	B		
2	A-B	B	C	E	F
4	B	B-C	C	D	E
6	C	C-D	D	D	D
>6	C	D	D	D	D

Atmospheric conditions: A) extremely unstable, B) moderately unstable, C) slightly unstable, D) neutral, E) slightly stable, and F) moderately stable.

TABLE B.3 Formulas for Determining σ_y and σ_z for Atmospheric Plume Dispersion Estimates for 0.1 to 10 km (from Briggs 1973)

Pasquill ASC	σ_y (m)	σ_z (m)
<u>Open-Country Conditions</u>		
A	$0.22x(1+0.0001x)^{-1/2}$	0.20x
B	$0.16x(1+0.0001x)^{-1/2}$	0.12x
C	$0.11x(1+0.0001x)^{-1/2}$	$0.08x(1+0.0002x)^{-1/2}$
D	$0.08x(1+0.0001x)^{-1/2}$	$0.06x(1+0.0015x)^{-1/2}$
E	$0.06x(1+0.0001x)^{-1/2}$	$0.03x(1+0.0003x)^{-1}$
F	$0.04x(1+0.0001x)^{-1/2}$	$0.016x(1+0.0003x)^{-1}$
<u>Urban Conditions</u>		
A-B	$0.32x(1+0.0004x)^{-1/2}$	$0.24x(1+0.001x)^{1/2}$
C	$0.22x(1+0.0004x)^{-1/2}$	0.20x
D	$0.16x(1+0.0004x)^{-1/2}$	$0.14x(1+0.0003x)^{-1/2}$
E-F	$0.11x(1+0.0004x)^{-1/2}$	$0.08x(1+0.00015x)^{-1/2}$

For the plume dispersion test cases, Q_p was assumed to be 76 g/s (10 lb/min), the nominal dissemination rate of the XM56 obscurant generator. Height was estimated to be 5 m, a value that includes the minimal plume rise anticipated during optimum conditions for generating a near-ground obscurant cloud. Plume-rise should be considered, and a modified H determined, for specific tests if graphite flakes are to be generated under other conditions. Wind speed was assumed to range between 2 and 5 m/s (2 and 11 mph). ASC was determined (Table B.2), and six test cases were selected that spanned the range of expected conditions. In general, ASC A and B may provide poor obscuration, but good mixing, and ASC D may provide good obscuration. ASC E and F are less common. Mass concentration and surface mass loading estimates for ASC B and E were not determined, but may be obtained by application of the model or graphically by simply interpolating between ASC A and C, and D and F, respectively. V_s and V_d for graphite flakes were estimated to be 0.08 and 0.8 cm/s, respectively, as described in Appendix A. Finally, a Δt of 30 min was selected for most cases, based on operational characteristics of the XM56. This duration is expected to be greatly exceeded at some installations over periods of days or years because of testing or training activities. One test case (Case 6) was determined for a duration of 300 min, or ten times the typical duration of generation, to demonstrate the scalar influence of time on deposition. For multiple generators located in close proximity, C_m will be a scalar value of the C_m predicted for a single generator times the number of actual generators used for a given test or training activity. Multiple generators well-spaced will result in C_m that is dependent on the spacing of the generators as well as downwind distance.

The influences of values of Q_p and u on air concentration, and Q_p , u , V_d , and Δt on surface deposition that differ from the six test cases may be estimated by scaling specific values to values determined for the test case having the same ASC. This is possible because the exponential function of Equations B.1 and B.2 is close to unity for the ranges of the parameters. For example, if graphite flakes are dispersed at a rate Q_p' that differs from the nominal rate, air concentration and surface deposition estimates may be determined by directly scaling the results by the ratio of Q_p' to Q_p (e.g., $C_m' = C_m[Q_p'/Q_p]$, and $ML' = ML[Q_p'/Q_p]$). Other relationships include: $C_m' = C_m(u/u')$; $ML' = ML(u/u')$; $ML' = ML(V_d'/V_d)$; and $ML' = ML(\Delta t'/\Delta t)$. The influence of alternate values of H (5 m was selected for the test cases) cannot be scaled, but are limited for moderate changes in H (about 2 to 20 m).

Results of estimated graphite flake plume dispersion and deposition are shown for selected test cases in Figures B.1 and B.2 and for all test cases in Tables B.4 and B.5. The parameters used for each test case are listed in the left side of each worksheet in the tables. Estimates were made for downwind distances between 0.1 and 40 km (0.06 to 25 mi), and for crosswind locations 1 km downwind of the source. The graphite flake aerosol concentration, C_m and C_m^* , was estimated for each location at an elevation of 1 m using Equation B.1. In the Tables, C_m is the concentration estimate made assuming no surface reflection, and C_m^* is the estimate made assuming 100% surface reflection. Because the actual reflection coefficient is not known for graphite flakes, C_m^* should be considered as the most conservative result. (The difference between C_m and C_m^* is a factor of 2 except very close to the generator). Consequently, results for each test case were plotted (Figures B.1 and B.2) using C_m^* results.

Airborne graphite flake concentrations for Cases 1, 2, 3, and 4 (shown in Figure B.1) generally decreased from between 26 to 140 mg/m³ at downwind distances of 0.1 to 0.3 km, to < 0.001 to 0.2 mg/m³ at 40 km. At comparable downwind distances, air concentration estimates for the test cases varied between 4 and 100 times depending on ASC. Because lateral and vertical dispersion is very limited for ASC F, the maxima in air concentration at an elevation of 1 m may not occur within 0.1 km of the source. Crosswind profiles (Tables B.4 and B.5) indicated progressively wider plumes for unstable atmospheric conditions, with ASC A being the extreme case. Air concentrations exceeding 10 mg/m³ (the current TLV for synthetic graphite dust) were predicted within downwind distances of 0.2 to 2 km of the source, with the specific distance

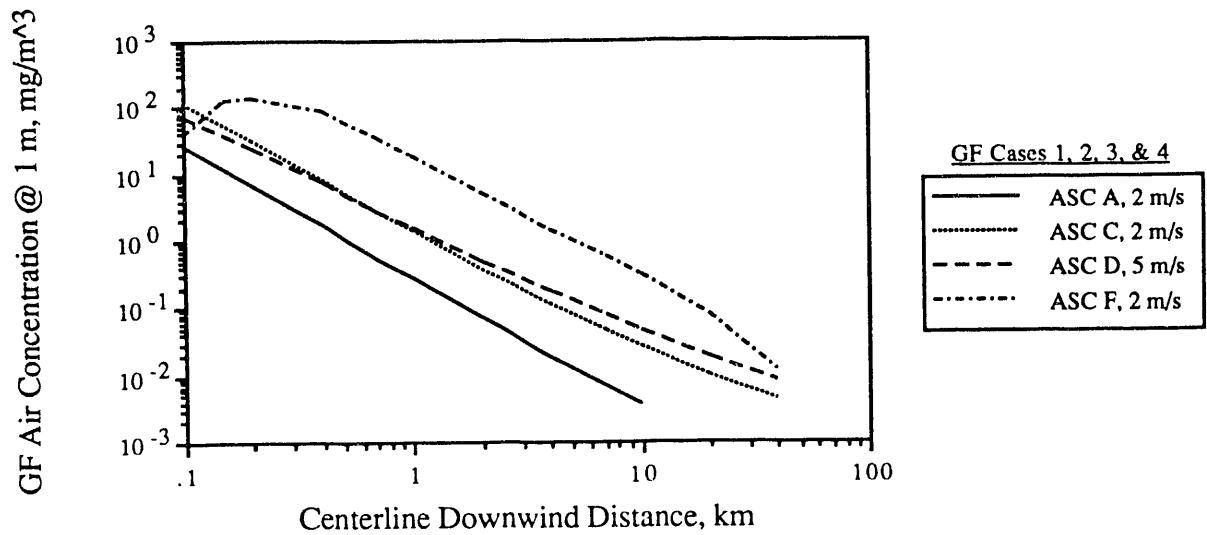


FIGURE B.1 Estimated Atmospheric Dispersion of Graphite Flake Plumes. Concentrations were determined using a modified Gaussian plume dispersion model and an elevation of 1 m. For clarity only Cases 1 through 4 are shown. The air concentration for Case 5 was within the range shown, that for Case 6 was identical to Case 2.

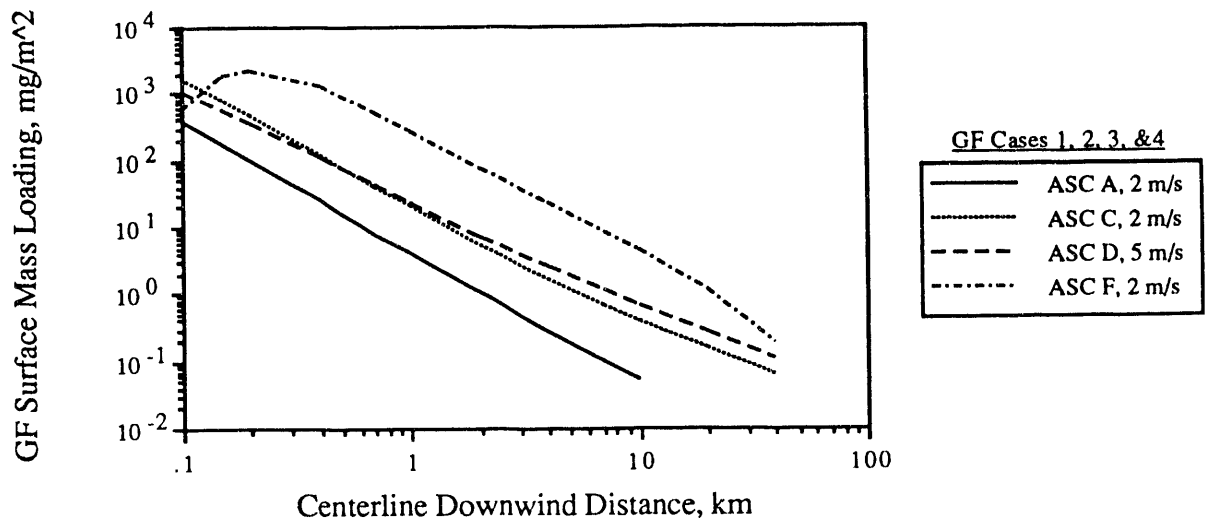


FIGURE B.2 Estimated Graphite Flake Deposit Pattern. Mass loading was determined using a modified Gaussian plume dispersion model (at ground level). For clarity only Cases 1 through 4 are shown. The mass loading for Case 5 was within the range shown, that for Case 6 was greater than Case 2 by a factor of 10.

TABLE B.4 Graphite Flake Dispersion and Deposition Estimates Using a Modified Gaussian Plume Model for Cases 1, 2, and 3

Case:	No. 1	x (km)	y (km)	Sig. y	Sig. z	Qx/Qp	Cm (mg/m ³)	Cm* (mg/m ³)	ML (mg/m ²)
Qp (g/s) =	76	0.1	0	22	20	0.98	1.3 e+01	2.6 e+01	3.8 e+02
u (m/s) =	2	0.2	0	44	40	0.97	3.3 e+00	6.7 e+00	9.6 e+01
ASC =	A	0.4	0	86	80	0.96	8.4 e-01	1.7 e+00	2.4 e+01
H (m) =	5	0.7	0	149	140	0.95	2.7 e-01	5.5 e-01	7.9 e+00
Δt (min) =	30	1	0	210	200	0.94	1.4 e-01	2.7 e-01	3.9 e+00
z (m) =	1	2	0	402	400	0.93	3.5 e-02	7.0 e-02	1.0 e+00
Vs (cm/s) =	0.08	4	0	744	800	0.92	9.4 e-03	1.9 e-02	2.7 e-01
Vd (cm/s) =	0.8	7	0	1181	1400	0.92	3.4 e-03	6.7 e-03	9.7 e-02
Src-Depl:	yes	10	0	1556	2000	0.92	1.8 e-03	3.6 e-03	5.2 e-02
Iterations =	100	20	0	2540	N D				
Type =	rural	40	0	3935	N D				
Cm (0% reflection)		1	0.1	210	200	0.94	1.2 e-01	2.4 e-01	3.5 e+00
Cm* (100% reflection)		1	0.2	210	200	0.94	8.6 e-02	1.7 e-01	2.5 e+00
ML (surface loading)		1	0.4	210	200	0.94	2.2 e-02	4.4 e-02	6.3 e-01

Case:	No. 2	x (km)	y (km)	Sig. y	Sig. z	Qx/Qp	Cm (mg/m ³)	Cm* (mg/m ³)	ML (mg/m ²)
Qp (g/s) =	76	0.1	0	11	8	0.98	6.0 e+01	1.1 e+02	1.6 e+03
u (m/s) =	2	0.2	0	22	16	0.95	1.6 e+01	3.2 e+01	4.6 e+02
ASC =	C	0.4	0	43	31	0.93	4.2 e+00	8.3 e+00	1.2 e+02
H (m) =	5	0.7	0	74	52	0.90	1.4 e+00	2.8 e+00	4.0 e+01
Δt (min) =	30	1	0	105	73	0.89	7.0 e-01	1.4 e+00	2.0 e+01
z (m) =	1	2	0	201	135	0.86	1.9 e-01	3.8 e-01	5.5 e+00
Vs (cm/s) =	0.08	4	0	372	239	0.83	5.7 e-02	1.1 e-01	1.6 e+00
Vd (cm/s) =	0.8	7	0	591	361	0.81	2.3 e-02	4.6 e-02	6.6 e-01
Src-Depl:	yes	10	0	778	462	0.79	1.3 e-02	2.7 e-02	3.8 e-01
Iterations =	100	20	0	1270	716	0.77	5.1 e-03	1.0 e-02	1.5 e-01
Type =	rural	40	0	1968	1067	0.73	2.1 e-03	4.2 e-03	6.1 e-02
Cm (0% reflection)		1	0.1	105	73	0.89	4.5 e-01	8.9 e-01	1.3 e+01
Cm* (100% reflection)		1	0.2	105	73	0.89	1.1 e-01	2.3 e-01	3.3 e+00
ML (surface loading)		1	0.4	105	73	0.89	4.9 e-04	9.7 e-04	1.4 e-02

Case:	No. 3	x (km)	y (km)	Sig. y	Sig. z	Qx/Qp	Cm (mg/m ³)	Cm* (mg/m ³)	ML (mg/m ²)
Qp (g/s) =	76	0.1	0	8	6	0.99	4.2 e+01	7.2 e+01	1.0 e+03
u (m/s) =	5	0.2	0	16	11	0.98	1.3 e+01	2.5 e+01	3.6 e+02
ASC =	D	0.4	0	31	19	0.96	3.8 e+00	7.6 e+00	1.1 e+02
H (m) =	5	0.7	0	54	29	0.95	1.4 e+00	2.8 e+00	4.1 e+01
Δt (min) =	30	1	0	76	38	0.94	7.8 e-01	1.6 e+00	2.2 e+01
z (m) =	1	2	0	146	60	0.91	2.5 e-01	5.0 e-01	7.2 e+00
Vs (cm/s) =	0.08	4	0	270	91	0.88	8.7 e-02	1.7 e-01	2.5 e+00
Vd (cm/s) =	0.8	7	0	430	124	0.85	3.9 e-02	7.7 e-02	1.1 e+00
Src-Depl:	yes	10	0	566	150	0.83	2.4 e-02	4.7 e-02	6.8 e-01
Iterations =	100	20	0	924	216	0.78	9.5 e-03	1.9 e-02	2.7 e-01
Type =	rural	40	0	1431	307	0.72	3.9 e-03	7.9 e-03	1.1 e-01
Cm (0% reflection)		1	0.1	76	38	0.94	3.3 e-01	6.6 e-01	9.5 e+00
Cm* (100% reflection)		1	0.2	76	38	0.94	2.5 e-02	5.0 e-02	7.2 e-01
ML (surface loading)		1	0.4	76	38	0.94	8.3 e-07	1.7 e-06	2.4 e-05

* Continuous generation, source-depleting, tilting plume, 0.1 km ≤ x ≤ 40 km.

TABLE B.5 Graphite Flake Dispersion and Deposition Estimates Using a Modified Gaussian Plume Model for Cases 4, 5, and 6

Case:	No. 4	x (km)	y (km)	Sig. y	Sig. z	Qx/Op	Cm (mg/m ³)	Cm* (mg/m ³)	ML (mg/m ²)
Qp (g/s) =	76	0.1	0	4	2	1.00	3.8 e+01	3.9 e+01	5.6 e+02
u (m/s) =	2	0.2	0	8	3	0.99	1.1 e+02	1.4 e+02	2.1 e+03
ASC =	F	0.4	0	16	6	0.92	4.9 e+01	8.6 e+01	1.2 e+03
H (m) =	5	0.7	0	27	9	0.83	1.8 e+01	3.5 e+01	5.0 e+02
Δt (min) =	30	1	0	38	12	0.76	9.4 e+00	1.8 e+01	2.6 e+02
z (m) =	1	2	0	73	20	0.63	2.6 e+00	5.1 e+00	7.4 e+01
Vs (cm/s) =	0.08	4	0	135	29	0.49	7.5 e-01	1.5 e+00	2.2 e+01
Vd (cm/s) =	0.8	7	0	215	36	0.37	2.9 e-01	5.7 e-01	8.2 e+00
Srcce-Depl:	yes	10	0	283	40	0.29	1.5 e-01	3.1 e-01	4.4 e+00
Iterations =	100	20	0	462	46	0.14	3.9 e-02	7.8 e-02	1.1 e+00
Type =	rural	40	0	716	49	0.04	6.1 e-03	1.2 e-02	1.8 e-01
Cm (0% reflection)		1	0.1	38	12	0.76	3.0 e-01	5.9 e-01	8.5 e+00
Cm* (100% reflection)		1	0.2	38	12	0.76	1.0 e-05	2.0 e-05	2.8 e-04
ML (surface loading)		1	0.4	38	12	0.76	1.2 e-23	2.4 e-23	3.4 e-22

Case:	No. 5	x (km)	y (km)	Sig. y	Sig. z	Qx/Op	Cm (mg/m ³)	Cm* (mg/m ³)	ML (mg/m ²)
Qp (g/s) =	76	0.1	0	11	8	0.99	2.4 e+01	4.5 e+01	6.5 e+02
u (m/s) =	5	0.2	0	22	16	0.98	6.7 e+00	1.3 e+01	1.9 e+02
ASC =	C	0.4	0	43	31	0.97	1.8 e+00	3.5 e+00	5.0 e+01
H (m) =	5	0.7	0	74	52	0.96	5.9 e-01	1.2 e+00	1.7 e+01
Δt (min) =	30	1	0	105	73	0.95	3.0 e-01	6.0 e-01	8.7 e+00
z (m) =	1	2	0	201	135	0.94	8.4 e-02	1.7 e-01	2.4 e+00
Vs (cm/s) =	0.08	4	0	372	239	0.93	2.5 e-02	5.1 e-02	7.3 e-01
Vd (cm/s) =	0.8	7	0	591	361	0.92	1.0 e-02	2.1 e-02	3.0 e-01
Srcce-Depl:	yes	10	0	778	462	0.91	6.1 e-03	1.2 e-02	1.8 e-01
Iterations =	100	20	0	1270	716	0.90	2.4 e-03	4.8 e-03	6.9 e-02
Type =	rural	40	0	1968	1067	0.88	1.0 e-03	2.0 e-03	2.9 e-02
Cm (0% reflection)		1	0.1	105	73	0.95	1.9 e-01	3.8 e-01	5.5 e+00
Cm* (100% reflection)		1	0.2	105	73	0.95	4.9 e-02	9.8 e-02	1.4 e+00
ML (surface loading)		1	0.4	105	73	0.95	2.1 e-04	4.2 e-04	6.0 e-03

Case:	No. 6	x (km)	y (km)	Sig. y	Sig. z	Qx/Op	Cm (mg/m ³)	Cm* (mg/m ³)	ML (mg/m ²)
Qp (g/s) =	76	0.1	0	11	8	0.98	6.0 e+01	1.1 e+02	1.6 e+04
u (m/s) =	2	0.2	0	22	16	0.95	1.6 e+01	3.2 e+01	4.6 e+03
ASC =	C	0.4	0	43	31	0.93	4.2 e+00	8.3 e+00	1.2 e+03
H (m) =	5	0.7	0	74	52	0.90	1.4 e+00	2.8 e+00	4.0 e+02
Δt (min) =	300	1	0	105	73	0.89	7.0 e-01	1.4 e+00	2.0 e+02
z (m) =	1	2	0	201	135	0.86	1.9 e-01	3.8 e-01	5.5 e+01
Vs (cm/s) =	0.08	4	0	372	239	0.83	5.7 e-02	1.1 e-01	1.6 e+01
Vd (cm/s) =	0.8	7	0	591	361	0.81	2.3 e-02	4.6 e-02	6.6 e+00
Srcce-Depl:	yes	10	0	778	462	0.79	1.3 e-02	2.7 e-02	3.8 e+00
Iterations =	100	20	0	1270	716	0.77	5.1 e-03	1.0 e-02	1.5 e+00
Type =	rural	40	0	1968	1067	0.73	2.1 e-03	4.2 e-03	6.1 e-01
Cm (0% reflection)		1	0.1	105	73	0.89	4.5 e-01	8.9 e-01	1.3 e+02
Cm* (100% reflection)		1	0.2	105	73	0.89	1.1 e-01	2.3 e-01	3.3 e+01
ML (surface loading)		1	0.4	105	73	0.89	4.9 e-04	9.7 e-04	1.4 e-01

* Continuous generation, source-depleting, tilting plume, 0.1 km ≤ x ≤ 40 km.

varying with ASC. Air concentrations exceeding 2 mg/m^3 (the proposed future TLV for natural and synthetic graphite dust) were predicted within 0.4 to 4 km of the source.

Predicted graphite flake surface deposition levels for Cases 1, 2, 3, and 4 (shown in Figure B.2) generally decreased from between 3.8×10^2 to $2.1 \times 10^3 \text{ mg/m}^2$ at a downwind distance of about 0.1 km, to $< 0.2 \text{ mg/m}^2$ at a distance of 40 km (Figure B.2). As was the case for concentration, surface deposition estimates for the test cases varied between 4 and 100 times at comparable downwind distances, and depended on ASC. The maxima in surface deposition for ASC F may not occur within 0.1 km of the source. Surface deposition levels exceeding 1000 mg/m^2 were predicted within downwind distances of < 0.1 to 0.5 km of the source, with the specific distance varying with ASC. Surface deposition levels exceeding 1 mg/m^2 were predicted within 2 to 25 km of the source.

Cases 5 and 6 were not plotted but air concentration and surface loading estimates are listed in Table B.5. Estimates of air concentration and surface loading for Case 5 are within the ranges shown for Cases 1, 2, 3, and 4 in Figures B.1 and B.2. Estimates of air concentration for Case 6 are identical to those for Case 2. Estimates of surface loading for Case 6 are greater than those of Case 2 by a factor of 10.

Downwind, centerline estimates of air concentration and surface loading should be used in predicting the impact of specific tests and training activities. The estimates should be applied to areas downwind of the test site and bounded by the range of expected wind directions. Unless the wind direction is constant, varying in direction by < 5 to 25% depending on ASC, the actual levels of C_m and ML will be less than those predicted. This is because the actual centerline of the plume will tend to meander over the duration of the test, and no one location will be exposed to the highest concentrations throughout the duration of the test. Thus, C_m and ML estimates provided by the model will tend to be conservative. The crosswind estimates of C_m and ML (Tables B.4 and B.5) will only be useful if wind direction does not vary.

APPENDIX B REFERENCES

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- Hanna, S. R., G. A. Briggs, and R. P. Hosker, Jr. 1982. Handbook on Atmospheric Diffusion. DOE/TIC-11223 (DE82002045), Office of Health and Environmental Research, Office of Energy Research, U.S. Department of Energy. National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia.
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APPENDIX C

SUPPLEMENTAL REFERENCES

Appendix C is a companion document of this report. Request for the appendix may be addressed to the Contract Officer's Representative (COR) as listed in Box 11 of the Report Documentation page.

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