Chapter Two

PESTICIDES

BACKGROUND

What Are Pesticides?

Pesticides are natural or synthetic agents that are used to kill unwanted plant or animal pests. While the term *pesticide* is now often associated with synthetic chemical compounds, it was not until relatively recently that synthetic pesticides came into use. Naturally occurring compounds or natural extracts have been used as pesticides since ancient times. The earliest pesticides were most likely salt, sulfurous rock, and extracts of tobacco, red pepper, and the like. It is rumored that the Napoleonic army used crushed chrysanthemums to control lice, with limited effectiveness. Petroleum oils, heavy metals, and arsenic were used liberally to control unwanted pests and weeds until the 1940s, when they were largely replaced for many uses by organic synthetic pesticides, the most famous of which is DDT.

Because the broad term *pesticide* encompasses a diverse collection of substances, an explanation of pesticide taxonomy and nomenclature is warranted. Pesticides can be classified either by target pest or by chemical identity.[1] Classification by target pest is perhaps the most familiar. For example, insecticides are pesticides that target insects, and herbicides target plants. There are many more examples (acaricides target ticks, nematocides target nematodes, etc.), but it is important for the purposes of this report to note that 11 of the 12 pesticides of concern identified by OSAGWI are insecticides and/or acaricides. The twelfth, DEET, is also directed against insects and ticks, but it is unique in that it is considered a repellent rather than an insecticide. To avoid confusion, the term pesticide is used in lieu of subclassification alternatives in this report.

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[1]Certainly there exist other bases for classification, for example, by formulation (emulsions, powders, etc.) or by mode of toxic action (cholinesterase inhibition, etc.). However, target pest and chemical identity are most often used—and are frequently a source of confusion.

Pesticides can also be organized by their chemical class. A pesticide class is a group of pesticidal compounds that share a common chemistry. For example, all pesticides in the class organophosphate (OP) are derivatives of phosphoric acid, and all pesticides in the class organochlorine are composed of carbon, hydrogen, and chlorine. There are also chemical subclasses of pesticides, but these are beyond the scope of this discussion. This report considers four chemical classes of insecticides, as well as the repellent DEET, which is more conveniently identified by its mode of use.

When discussing a pesticide, it is possible to refer to the pesticidal compound itself or to the pesticide product or formulation. The compound itself is also known as the active ingredient—the chemical responsible for killing the target pest. The formulation is the manner in which the active ingredient is delivered. Typical formulations include liquids, dusts, wettable powders, and emulsifiable concentrates. The pesticide formulation includes the active ingredient as well as other ingredients. These other ingredients may be inert, such as talcum powder, or they can act to enhance the pesticidal properties of the active ingredient. For example, some pesticide formulations include a synergist that enhances the toxic activity of the active ingredient. Other ingredients in many pesticide formulations are solvents. When considering the potential health effects of pesticides, it is important to consider the toxicity of the active ingredient as well as the other ingredients in the formulation. This is often a daunting task. Clinical reports of pesticide poisoning provide clues about the toxicity of the pesticide formulation or product, while controlled experiments involving laboratory animals may include the formulation or just the active ingredient alone.

Pesticide Regulation

The EPA regulates both active ingredients and pesticide formulations under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).[2] FIFRA gives the EPA the authority to regulate pesticides to ensure that their use does not have unreasonable adverse effects on humans and the environment. The registrant of a pesticide must submit specific data to the EPA to support the conclusion that the product meets this standard before the EPA will grant a registration that allows the pesticide to be marketed and sold. This can be a lengthy and expensive process. It includes approval of a pesticide label that provides information on the use and safety precautions related to the product. Under FIFRA, this label is legally binding. For example, it would be illegal to use a pesticide product in a food service establishment if the product is not specifically labeled for

[2]Despite its name, FIFRA governs all pesticides, not just those targeted against insects, fungi, and rodents.

that use. Following approval by the Armed Forces Pest Management Board (AFPMB), the U.S. military can procure pesticide products registered by the EPA and must follow the label instructions.

As part of the registration process, the EPA differentiates between general-use and restricted-use pesticides (GUPs and RUPs), primarily on the basis of EPA toxicity class. GUPs can be sold to the public for unrestricted use, while RUPs can be sold to and used only by certified applicators.[3] The distinction between GUPs and RUPs can be somewhat confusing, because the classification can refer to either the active ingredient or the formulation. For example, the inclusion of some active ingredients makes any pesticide product an RUP, while in other cases, the distinction between GUP and RUP is made by pesticide formulation. Consider two pesticide products containing the same active ingredient but different formulations. If the EPA does not consider all products with this active ingredient to be RUPs, one of those products can be for general use and the other restricted, because their formulations might be considered to present different risks to humans or the environment.

Related to the distinction between GUP and RUP on a pesticide label is the EPA toxicity class. This classification is based on acute human toxicity, hazard to applicators, and ecological effects. The acute human toxicity is assessed via animal tests, and ecological effects include the potential for groundwater contamination. Each toxicity class is associated with a signal word, which must appear on the pesticide label. The toxicity classes are shown in Table 2.1.

PESTICIDE IDENTITY AND PROPERTIES

Tables in Chapters Four through Seven present the identity and chemical and physical properties of each pesticide of concern. This information is intended to enable cross-referencing regarding the chemical identity of the pesticides as well to provide data that may be useful in characterizing their environmental behavior and potential health effects. References for these tables include the

Table 2.1

EPA Pesticide Toxicity Classes

Toxicity Class	Toxicity Rating	Signal Word on Label
I	Highly toxic	DANGER-POISON
II	Moderately toxic	WARNING
III	Slightly toxic	CAUTION
IV	Practically non-toxic	CAUTION

[3]Or in some cases, applicators directly under their supervision.

Merck Index (10th ed., 1983), the EPA Integrated Risk Information Service (IRIS) database (http://www.epa.gov/iris), the EPA Pesticide Product Information System Databases (http://www.epa.gov/opppmsd1/PPISdata/index.html), the EXTOXNET database,[4] and pesticide labels graciously provided by the Entomological Sciences Division of the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM). Original references were obtained for verification. Occupational exposure values (standards and recommendations) were obtained from the American Conference of Governmental Industrial Hygienists (ACGIH, 1999);[5] reference doses and concentrations (RfD and RfC) were obtained from the IRIS database. In addition, Cheremisinoff and King (1994), Hornsby et al. (1996), and Kamrin (1997) provided references and directions to original sources.

The characteristics summarized in the physical and chemical properties tables for each pesticide of concern are described below.

Molecular Weight, Color, Form, and Odor. These entries are self-explanatory and are presented as the range of values reported in the referenced sources, where appropriate. The color, form, and odor of pesticides are generally restricted to the active ingredients and are given here because they may assist recall efforts of veterans being surveyed about their potential exposure to pesticides. It should be noted, however, that these values could be substantially different for pesticide formulations used during ODS/DS.[6]

Water Solubility. The water-solubility value is given for the active ingredient at room temperature, either 20°C or 25°C. Values are presented as milligrams of solute per liter of water (mg/L); in most cases, mg/L can also be reported as parts per million (ppm), even for very soluble compounds (Hornsby et al., 1996). Generally, the higher the value, the more readily the compound dissolves in water.

Partition Coefficient (K_{ow}). The octanol-water partition coefficient indicates how a chemical is distributed at equilibrium between organic (octanol) and aqueous (water) phases. This coefficient is primarily used in predicting the environmental fate of organic chemicals such as pesticides. The higher the coef-

[4]http://ace.ace.orst.edu/info/extoxnet. EXTOXNET is a cooperative effort of the University of California, Davis; Oregon State University; Michigan State University; Cornell University; and the University of Idaho. Primary files are maintained and archived at Oregon State University.

[5]This reference, published as a CD-ROM, includes the most recently published occupational exposure values from the ACGIH, the Occupational Safety and Health Administration (OSHA), and the National Institute for Occupational Safety and Health (NIOSH), and the carcinogenicity classifications given in this report.

[6]A separate, concurrent effort by RAND that surveyed some 2,000 PGWV addresses the formulations more specifically (Fricker et al., 2000).

ficient, the greater the propensity for the chemical to be partitioned to organic phases. This generally means that the chemical will tend to adhere to organic matter in the soil (e.g., organocolloids), but it may also indicate a tendency to accumulate in fat, although this behavior depends on other biological factors in the body. The partition coefficient is included in this report primarily because it is often used to estimate other chemical and physical properties.

Soil Sorption Coefficient (K_{oc}). This coefficient is sometimes called an adsorption coefficient. The distinction between adsorption and absorption is that the latter requires the movement of a chemical across a barrier such as tissue or a cell membrane. The soil sorption coefficient more accurately measures the chemical's propensity to "attach," or adsorb, to soil particles. The term *soil sorption coefficient* is used to avoid confusion. The utility of this measurement is that it assists in predicting whether a pesticide will remain dissolved in solution or will become adsorbed to soil particles after its application (or following a spill). If a pesticide is adsorbed to soil particles, it may be less available for biodegradation or for runoff or leaching. This assessment could be useful in estimating the potential for pesticide exposure. Generally, K_{oc} values below 500 indicate little or no adsorption of the pesticide to soil (indicating a high possibility of runoff or leaching).

Vapor Pressure. This value is given in millimeters of mercury (mm Hg), the unit of measure most often used. To convert to millipascals (mPa), one divides this value in mm Hg by 7.52×10^{-6} (Hornsby et al., 1996). Vapor pressure is a measure of the tendency of a pesticide to volatilize, a phase change that can affect estimations of exposure. Generally, the lower the vapor pressure, the lower the volatilization tendency of the chemical. Vapor pressure values are given for active ingredients of pesticides in this report.

EPA Toxicity Classification. The EPA toxicity classifications presented in this report were discussed above (Table 2.1).

ACGIH Threshold Limit Values–Time-Weighted Average (TLV–TWA). These values are developed by ACGIH as guidelines to assist in the control of health hazards and are not legal standards. TLVs refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.[7] TLV–TWA represents these concentrations as the time-weighted average

[7]This definition is provided by ACGIH (1999), which explains that, "Because of wide variation in individual susceptibility . . . a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness. . . . Individuals may also be hypersusceptible or otherwise unusually responsive to some

concentration for a conventional eight-hour workday and a 40-hour workweek. Substances listed with the designation "skin" refer to the potential significant contribution to overall exposure by the cutaneous route. TLVs are based on available information from industrial experience and from experimental animal and human studies, and, when possible, from a combination of the three.

NIOSH Recommended Exposure Limits (REL–TWA, REL–STEL, and IDLH). These values are recommended by the National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention (CDC). Acting under the authority of the Occupational Safety and Health Act (OSHAct) of 1970 (29 USC Chapter 15) and the Federal Mine Safety and Health Act of 1977 (30 USC Chapter 22), NIOSH develops recommended exposure limits (REL) for hazardous substances or conditions in the workplace. The REL–TWA values are time-weighted average airborne concentrations for up to a 10-hour workday during a 40-hour workweek. Short-term exposure limits (REL–STEL) are 15-minute TWA exposures that should not be exceeded at any time during the workday. For most substances with a TLV–TWA, there is currently not enough toxicological information available to warrant a STEL, as evidenced by the limited availability of STELs reported here. IDLH values are concentrations that are immediately dangerous to life or health.

OSHA Permissible Exposure Limits (PEL–TWA). These regulatory limits are established by the Occupational Safety and Health Administration (OSHA) and have the force of law in occupational environments where OSHAct is applicable. PELs are also time-weighted averages and assume exposures of eight hours a day for a 40-hour workweek. PELs are based on human and animal studies, allowing for scientific uncertainty.

EPA Oral Reference Doses (RfD) and Inhalation Reference Concentrations (RfC). The RfD and RfC can be used to estimate a level of environmental exposure at or below which no adverse effect is expected to occur. The RfD or RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure that is likely to be without appreciable risk of deleterious effects to humans, including sensitive subgroups, over a lifetime. These values are based on lifetime exposure.[8]

Carcinogenicity. Carcinogenicity classifications are provided as reported by the ACGIH, the EPA, and the International Agency for Research on Cancer (IARC). These classifications are summarized in Table 2.2. They are generally

industrial chemicals because of genetic factors, age, personal habits (e.g., smoking, alcohol, or other drugs), medication, or previous exposures."

[8]http://www.epa.gov/iris/limits.htm.

Table 2.2

Carcinogenicity Classifications

Agency/Categories	Classification
ACGIH	
A1	Confirmed human carcinogen
A2	Suspected human carcinogen
A3	Confirmed animal carcinogen with unknown relevance to humans
A4	Not classifiable as a human carcinogen
A5	Not suspected as a human carcinogen[a]
EPA – 1986[b]	
A	Human carcinogen
B	Probable human carcinogen
B1 subgroup	Limited evidence from epidemiological studies
B2 subgroup	Sufficient evidence from animal studies; inadequate or no evidence from epidemiological studies
C	Possible human carcinogen
D	Not classifiable as to human carcinogenicity
E	Evidence of non-carcinogenicity for humans
EPA – 1996	
K	Known human carcinogen
L	Likely to produce cancer in humans
CBD	Cannot be determined
NL	Not likely to be carcinogenic in humans
IARC	
1	Carcinogenic to humans
2A	Probably carcinogenic to humans
2B	Possibly carcinogenic to humans
3	Unclassifiable as to carcinogenicity in humans
4	Probably not carcinogenic to humans

[a]The categories A4 and A5 can be confusing. The basic difference is that A4 substances cause concern that they could be carcinogenic for humans but cannot be assessed conclusively because of a lack of data; A5 substances are not suspected to be human carcinogens, based on human epidemiologic studies, or because the evidence suggesting a lack of carcinogenicity in experimental animals is supported by mechanistic data.

[b]As found in the 1986 *Risk Assessment Guidelines* (EPA/600/8-87/045). New guidelines for carcinogen risk assessment were proposed in 1996 (1996 *Proposed Guidelines for Carcinogen Risk Assessment*, Federal Register: 61[79]:17960-18011). These new guidelines were proposed due to advances in toxicological science. One significant limitation of the old guidelines is that a compound was considered carcinogenic if there was evidence of carcinogenicity from one exposure pathway, even in the absence of such evidence from other pathways. None of the pesticides of concern have been classified under the 1996 system; the old classifications are presented here for future comparisons.

based on the availability and weight of evidence of carcinogenicity from properly designed animal and human studies.

PESTICIDE USE IN ODS/DS

In every war and military conflict, combat effectiveness has been significantly reduced by disease, and a large number of diseases can be directly linked to disease-carrying organisms such as arthropods and rodents.[9] Not only can these organisms transmit disease, their bites can result in distracting and demoralizing conditions and can cause serious secondary infections and allergic reactions. For these reasons, pest control is of significant military importance, affecting not only troop morale and welfare but also overall unit combat effectiveness and strength.

During ODS/DS, insects and rodents were of particular concern as potential disease vectors. The primary focus for pest management was on ground troops.[10] With roughly one-half million personnel deployed to the region in a very short time, under widely varying living, working, and threat conditions, this logistical challenge was large.

Pests of concern in the Persian Gulf region included arthropods such as sand flies, "filth flies," black flies, mosquitoes, cockroaches, lice, ticks, scorpions, spiders, and centipedes. These vermin are capable of transmitting major diseases such as viral encephalitis, malaria, sand fly fever, and leishmaniasis, as well as being an extreme nuisance because of their overabundance.[11] Rodents such as rats, mice, and voles were also of concern as disease vectors and contaminants of food supplies.

During ODS/DS, military authorities recommended various pesticides to control a variety of pests. The pesticides recommended for use by U.S. forces were listed by the AFPMB and approved for use by the EPA. Table 2.3 lists the pesticides used or potentially used by U.S. military units during ODS/DS. As detailed in Chapter One, OSAGWI has identified 12 pesticides that it considers to be of particular concern either because of toxicity or expected exposure; these pesticides are identified in bold type in Table 2.3.

More than 35 types of pesticides and pesticide products were used by military personnel during ODS/DS. None of the pesticides used was unique to the military; all are, or were at the time, legally available for civilian uses in the United States or other countries. When the provided quantities of pest-control products ran very low, purchases were made from the local economy in Saudi Arabia. For example, insecticide bait containing the active ingredient azamethiphos was reportedly purchased in Saudi Arabia and used by U.S. units. This

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[9]*Personal Protective Techniques Against Insects and Other Arthropods of Military Significance*, U.S. Army Technical Information Memorandum No. 36, Armed Forces Pest Management Board.

[10]Indigenous pests were not considered a significant threat to personnel remaining on naval vessels. It was expected that their exposure was no different from that of personnel afloat in any other part of the world; therefore, no special studies of that group have been performed.

[11]See note 9 above.

Table 2.3

Pesticides Used or Potentially Used During ODS/DS

Active Ingredient Product	Synonyms, Trade Names	Target Pests
Allethrin	d-trans-Allethrin	Insects
Aluminum phosphide	Phostoxin, Fumitoxin, AlP	Stored product pests
Amidinohydrazone	Combat	Insects
Azamethiphos	Snip Flykiller, Alfacron	Flies
Bacillus thurengiensis	Teknar	Mosquito larvae
Bendiocarb	Ficam W	Roaches, fleas, ticks, mosquitoes, other arthropods
Boric acid	Whitmire (PT 240) Perma-dust	Insects
Brodifacoum	Talon G	Rodents
Bromadiolone	Maki	Rodents
Carbaryl	Sevin	Ants, fleas, other insects
Chlorophacinone	Rozol	Rodents
Chlorpyrifos	Dursban	Mosquitoes, other insects, ticks, mites
Cypermethrin	Demon	Insects
Deltamethrin		Insects
Diazinon		Insects
Dichlorvos	DDVP,	Insects
Diethyl-*m*-toluamide	DEET, 3M Insect/Arthropod and Cutter Insect Repellents	Sand flies, other insects, ticks
Diphacinone	P.C.Q., Rodent Cake, Di-Blox	Rodents
Ethyl hexanediol		Insects
Lindane		Lice
Malathion		Insects
Methomyl	Flytek	Flies
Pentachlorophenol		Fungi
Permethrin	Permanone	Insects
Pet flea and tick collars	Amitraz, carbaryl, chlorpyrifos, methoprene, permethrin, phosmet, propoxur, tetrachorvinphos	Insects, ticks
***d*-phenothrin**		Insects
Pindone		Rodents
Propoxur	Baygon	Flies, roaches, other insects
Pyrethrum/pyrethrins	Pyrenone	Mosquitoes, flies
Resmethrin		Insects
Sulfur	Chigg-Away	Chiggers (mites)
Valone		
Warfarin	O-R-500, Rodex, Final, Erase	Rodents

Source: Provided by OSAGWI.

product, manufactured by Ciba Geigy, is not available in the United States.[12] Local firms provided pest control services in selected areas, and around some industrial camps they applied pyrethroid insecticides and malathion on

[12]CDR T. Wayne Gale, presentation at the 137th Armed Forces Pest Management Board Meeting, July 18, 1991. CMAT Control #1997269-0000-014.

portable latrines. The actual total usage of pesticides by U.S. forces during ODS/DS is unknown, but estimates for pesticides acquired within the military supply system have been made from records indicating the amounts sent to the Gulf region minus the amounts returned (see Fricker et al., 2000). Total usage does not include any pesticides in the possession of units at the outset of ODS/DS or pesticides acquired outside the military supply system. Thus, it does not include any pesticides acquired from the local economy or any that personnel obtained on their own—factors that could lead to underestimates of pesticide use. There is anecdotal information that some troops obtained pest-control products such as citronella candles from private sources. And some service members brought or had mailed to them unauthorized pesticides such as pet flea and tick collars that were designed to protect pets. During ODS/DS, a popular actor who visited the area advised the viewing audience of a television show to send these pet collars to U.S. service personnel.[13] Other practices could have led to overestimates of pesticide use. These practices include units keeping pesticides received during ODS/DS and returning them to their units' supply stocks rather than the supply system, and giving pesticides to coalition partners. Both practices would result in overestimations of pesticide use when the "supplies in minus supplies out" method of estimating is employed.

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[13]CAPT Herbert T. Bolton, "Pesticide Use by U.S. Forces During Operations Desert Shield and Desert Storm," AFPMB Testimony to the National Institutes of Health Technology Assessment Workshop on the Persian Gulf Experience and Health, April 27, 1994.