Technically Speaking
Pesticides
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PESTICIDES

You have heard it. Pesticides are poisons. Pesticides can be converted to chemical warfare agents. The pesticides themselves can be used as chemical warfare agents. The same technology (e.g. crop dusters) for dispersing pesticides can be used to disperse chemical warfare agents.

These statements are a mixture of truths, exaggerations, or are mostly false. Let us take a look at these chemicals and what they can do.

What is a Pesticide?

A pesticide is an agent used to destroy pests. Pesticides include insecticides (destroys insects), herbicides (destroys plants), arachnicides (destroys spiders, mites, ticks), larvacides (destroys immature stages of insects such as grubs and caterpillars), fungicides (destroys fungus), rodenticides (kills mice, rats), molluscocides (destroys clams, snails, etc.) and fumigants. Sometimes insect repellents (such as DEET) and plant growth regulators are lumped in with discussions of pesticides. The agent is usually a chemical that destroys the unwanted pest, but the agent could also be a naturally occurring plant extract or bacteria that inflict a fatal disease on the targeted pest.

Much effort is spent developing new pesticides that are specific to the targeted pest but do not harm other life including humans. After the pesticide has accomplished its intended purpose, it should not persist in the environment. Some of the older pesticides developed decades ago have been since found to harm birds and other life, or were very poisonous to humans, and have been outlawed for use in the United States. Some may be produced or used in other countries for special use, such as use of DDT for control of mosquitoes where malaria is prevalent.

Pesticides may be applied to crops, to soils where crops are grown, buildings were crops are stored, ponds, forested areas, grasslands, applied topically to animals including humans, or put in cattle feed.

In lieu of pesticides, environmentally conscious people may advocate (1) control practices such as drainage of containers or ditches where mosquitoes may breed, (2) encouragement or addition of natural predators to control the unwanted pests, (3) crop rotation and (4) inclusion of "wild areas" within agriculture land. The wild areas provide a home for natural predators.

Pesticide Classifications

Pesticide formulations as used by the consumer contain one or more active ingredients plus various "inert" ingredients. The inert ingredients are there to give the formulation the desired physical characteristics so the pesticide can be easily and safely applied. Sometimes the formulations are mixed with fertilizers. Most formulations sold to the public are pellets, which are relatively dust free and release the active ingredient slowly. However some are applied as dusts or as aerosolized liquid droplets. Some are

fumigants and are released as vapors or gases. Some are poison bait and are used for rodents, birds, cockroaches, etc..

Pesticides are classified into either chemical classes or use classes according to the active ingredient. The U.S. Environmental Protection Agency recognizes 1000+ active ingredients and almost 90,000 different brand name formulations. Roughly 40 new active ingredients are approved each year. Some active ingredients have been withdrawn from use in the United States because of harm to people or the environment. A complete list is at http://www.epa.gov/pesticides/science/models_db.htm#databases The PEAC tool lists approximately 250 active ingredients including a few that have been withdrawn from use. The approximately 250 selected for display in the PEAC tool are or were either widely used or are relatively toxic.

Pesticide names (for active ingredients) are assigned by the International Organization for Standardization (England). The names assigned are unique and internationally recognized. The U.S. Environmental Protection Agency and California Department of Pesticide Regulation maintains a listing of brand name formulations.

Examples of Pesticide Use Classes

- Insecticides and arachnicides
- Herbicides
- Fungicides
- Molluscicides
- Avicides
- Rodenticides
- Growth hormones

Examples of Chemical Classes

- Carbamates
- Organophosphates
- Chlorinated hydrocarbons (Organochlorine pesticide)
- Bromated hydrocarbons
- Botanicals (natural pesticides derived from plants)
- Triazine and Triazoles
- Ureas
- Thiocarbamates
- Dithiocarbamates
- Dinitrophenols
- Substituted amides
- Bipyridilium pesticides
- Phenoxys
- Pyridines
- Inorganic

A more complete listing of classifications with specific pesticide examples may be found at the EXTOXNET website developed by several state cooperative extension offices and maintained by Oregon State University, at http://extoxnet.orst.edu/tibs/pestgrp.htm .

The U.S. Department of Transportation classifies pesticides by chemical classes. UN (United Nations) shipping numbers reflect this. However the UN numbers also take into account the "inert ingredients" because they affect whether the pesticide is shipped as a liquid or solid, and the flammability of the liquid. The following pesticide classes and corresponding UN#s are listed in the 2004 Emergency Response Guidebook:

Specific Listings

- Aluminum phosphide pesticide, UN# 3048
- Methyl parathion, liquid, UN#3018
- Methyl parathion, solid, UN#2783
- Parathion, UN#2783
- Parathion and compressed gas mixture, UN#1967
- Zinc phosphide, UN# 1714

Table 1. Pesticide classes and UN Shipping Numbers

Pesticide Class	Solid, toxic	Liquid, toxic	Liquid, toxic, flammable	Liquid, flammable, toxic
Arsenical pesticide	2759	2994	2993	2760
Benzoic derivative pesticide	2769	3004	3003	2770
Bipyridilium pesticide	2781	3016	3015	2782
Carbamate pesticide	2757	2992	2991	2758
Copper based pesticide	2775	3010	3009	2776
Coumarin derivative pesticide	3027	3026	3025	3024
Dithiocarbamate pesticide	2771	3006	3005	2772
Organochlorine pesticide	2761	2996	2995	2762
Organophosphorus pesticide	2783	3018	3017	2784
Organotin pesticide	2786	3020	3019	2787
Pesticide, n.o.s.	2588	2902	2903	3021
Phenoxyacetic acid derivative pesticide	3345	3348	3347	3346
Phenoxy pesticide	2765	3000	2999	2766
Phenyl urea pesticide	2767	3002	3001	2768
Phthalimide derivative pesticide	2773	3008	3007	2774
Pyrethroid pesticide	3349	3352	3351	3350
Thiocarbamate pesticide	2771	3006	3005	2772
Triazine pesticide	2763	2998	2997	2764

There are also generic listings for insecticide gases.

- Insecticide gas, n.o.s., UN# 1968
- Insecticide gas, toxic, flammable, n.o.s., UN#3355
- Insecticide gas, toxic, n.o.s., UN#1967
- Insecticide gas, flammable, n.o.s., UN#1954 or UN#3354

The words "toxic" and "poisonous" are synonymous in the 2004 Emergency Response Guidebook, and n.o.s. means "not otherwise specified". However, "Liquid, toxic", "Liquid, toxic, flammable" and "Liquid, flammable, toxic" have different meanings as defined by DOT:

- Liquid, flammable, toxic: flash point less than 23°C [23°C = 73.4°F]
- Liquid, toxic, flammable: flash point between 23°C and 61°C
- Liquid, toxic: flash point over 61°C [141.8°F]

Parathion and methyl parathion also fall into the general classification of organophosphorous pesticides.

How Toxic are Pesticides to Humans?

It depends upon the particular pesticide. Some are highly toxic and some are practically nontoxic. Some may be acutely toxic but display no long-lasting effects if and when the person recovers. Exposure to other pesticides may increase the risk of cancer or motor impairment later in life.

The U.S. National Library of Medicine maintains a data base on toxicity of chemicals including pesticides. To access this, go to http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB, and enter the pesticide name or its CAS number.

Acute toxicity is measured in terms of exposure of the chemical to a test animal, usually a rat. The dosage (mg of chemical per kilogram of body weight) which kills 50% of the test animals is called LD_{50} . Exposure may be by ingestion, skin contact (a patch containing the chemical is attached to the animal), or by inhalation. LC_{50} is the concentration of chemical in the air that kills 50% of the animals over a specified time period, usually 1 or 4 hours. The inference is made that the animal toxicity data can be transferred to humans. Pregnant females and the very young are often more susceptible.

Table 2. Toxicity data for seven of the more toxic pesticides:

Pesticide	Pesticide Chem Class	Ingestion, LD_{50}, mg/kg body wt.	Dermal, LD_{50}, mg/kg body wt.	Inhalation, LC_{50}, mg/m^3
Aldrin	Organochlorine	39 to 45 (rat); human child death at 8 mg/kg	90 to 150	
Dieldrin	Organochlorine	65 (human); 38 (rat)	120 to 215	
Endrin	Organochlorine	7.5 to 18	12 to 60	
Lindane	Organochlorine	76 to 190 rat; human 120	50 to 1000	
Paraquat	Bipyridilium	35 (human); 110 to 150 (rat)	80 to 325	
Parathion	Organophosphorus	2 to 30	6.8 to 50	84 (4 hours)
Phorate	Organophosphorus	1.8 to 3.7	2.5 to 6.2	30 (1 hour)

Aldrin, Dieldrin, Endrin, and Parathion are now banned in U.S.
Aldrin, and Dieldrin may cause cancer (from animal studies)
Paraquat, parathion may also be possible cancer agents.

Data on lethal toxicity are difficult to come by, especially with inhalation studies using test animals so there are some blanks in the above table. Sometimes there are toxicity

information from different tests and different research groups so data is reported as a range, e.g. oral 2 to 30 mg/kg for parathion.

Can Pesticides Be Used As Chemical Warfare Agents?

Another question can be asked: Can pesticides be converted to chemical warfare agents?

Most pesticides exhibit little or no toxicity. Only a very few are classified by the U.S. Environmental Protection Agency as "Highly Toxic". The "Highly Toxic" pesticides are either now banned from use in the United States or are classified as "Restricted Use", that is they may be obtained and used only by certified operators. However, old stockpiles may exist, and pesticides banned in the United States might be used in other countries.

There are many other toxic industrial chemicals in wide use (e.g. concentrated sulfuric acid, anhydrous ammonia, hydrogen chloride, etc.), which are highly toxic if inhaled but are not normally thought of as chemical warfare agents. Chlorine, a widely used industrial chemical, has been used as a chemical warfare agent during World War I.

The main reason that pesticides are linked to chemical warfare agents is that some pesticides and some chemical warfare agents kill by inhibiting the enzyme cholinesterase. This enzyme is found in all animal life, including humans and insects. The enzyme is important in functioning of the nervous system.

The chemical warfare agents which inhibit cholinesterase include the nerve agents Sarin, VX, Soman, and Tabun. Pesticides that inhibit cholinesterase fall under the general class of organophosphorus pesticides and to a lesser extent the carbamate pesticides.
The nerve agent sarin was originally developed in Germany prior to World War II as a pesticide for killing aphids.

Symptoms of cholinesterase inhibition are as follows:

- Mild Poisoning: Tiredness, weakness, dizziness, nausea, and blurred vision. Symptoms appear usually within 4 to 24 hours of exposure in the case of pesticides, sooner in the case of toxic nerve agents.

- Moderate Poisoning: Headache, sweating, tearing, drooling, vomiting, tunnel vision, and twitching. Symptoms appear usually within 4 to 24 hours of exposure in the case of pesticides, sooner in the case of nerve agents.

- Severe Poisoning (a single large dose or repeated smaller dosages): Abdominal cramps, involuntary urination and/or defecation, muscular tremors, staggering gait, pinpoint pupils, hypotension (drop in blood pressure), slow heartbeat, difficulty breathing, possible convulsions, possible coma, and possible death. Symptoms can appear within seconds (by inhalation) or minutes (skin contact) in the case of lethal doses of nerve agents.

There are a couple of important differences between nerve agents and pesticides that make it difficult for pesticides to be used as chemical warfare agents. The main difference is that the nerve agents are much more powerful, and can kill by inhalation or by absorption through the skin. It is much more difficult for a person to kill himself by inhalation of a pesticide or by applying the pesticide to the skin. There have been deaths by ingestion of toxic pesticides.

The dosages of nerve agents required a 70 kg (154 lb) man [from Lane's Chem-Bio Handbook] are listed below:

Table 3. Calculated Lethal Dose of Nerve Agents for a 70 kg Person

Nerve Agent	Dermal LD_{50} , mg liquid on skin	Inhalation LCt_{50} , mg-min/m^3
Tabun (GA)	1000	400
Sarin (GB)	1700	100
Soman (GD)	350	50
VX	10	10

Table 4. Calculated Lethal Dose of Selected Pesticides for a 70 kg Person [from EXTOXNET website], based on rat LD_{50} studies.

Pesticide	Dermal LD_{50} , mg liquid or solid on skin (dermal patch)	Inhalation LCt_{50} , mg-min/m^3
Isofenphos	10290	31200 to 34500
Parathion	476 to 3500	20160
Phorate	175 to 434	14400
Phosmet	221200 to 324800	16560
Carbofuran	>70000	10320 to 12720

At first glance, it appears that parathion and phorate are as toxic as the nerve gases based on dermal absorption. The nerve agents (tabun, sarin, etc.) are absorbed rapidly through the skin whereas the pesticides are more slowly absorbed. A dermal patch with the chemical underneath the patch was attached to the test animal for days to allow time for absorption. Realistically, a person can shower and wash off the pesticides. Nevertheless, skin contact with many pesticides must be avoided.

Phorate is one of the most toxic organophosphorus pesticides still in use in the United States. Deaths have occurred due to skin absorption [case history studies at http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~mpj1wV:1]. Repeated exposure can result in the person developing increased susceptibility. Relative to other pesticides it is more rapidly absorbed through the skin. China is a major exporter of this and other toxic pesticides [see http://www.shiji-pesticide.com/].

Pesticides which display cholinesterase activity have very low vapor pressures. They must be dispersed as a dust or dissolved in a liquid and dispersed as an aerosol. Because relatively large amounts are required to kill, they are less attractive as a chemical warfare agent. Nevertheless, exposure to even small amounts of some of the more toxic pesticides can result in headaches, nausea, and possibly other incapacitating symptoms.

Cholinesterase inhibition was the subject of the June 2003 AristaTek Newsletter article, at /Newsletter/03%2006%20June/NERVE%20AGENTS,%20PESTICIDES,%20AND%20CHOLINESTERASE%20INHIBITION.htm.

Can pesticides be converted to nerve agents? Not easily, although some may be convertible to more toxic substances. The government HSDB website gives details on the raw ingredients required to manufacture various pesticides. The raw ingredients for some pesticides are quite toxic.

Personal Protective Equipment

Information on Personal Protective Equipment for the more toxic pesticides is in the NIOSH Pocket Guide, the 2004 Emergency Response Guidebook, and in the HSDB website at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB . Generally, positive pressure fully protective suits fitted with self-contained breathing apparatus (SCBA) are required for ambient concentrations above "Immediately Dangerous to Life and Health" (IDLH). A full-face piece respirator fitted with a P100 filter and organic cartridge may be used for many pesticides if the ambient concentration is below IDLH. There are variations on this depending upon the chemical. Air-Supplied systems are also permitted under certain situations. For some pesticides, positive pressure "escape hoods" with an air-purifying respirator are permitted at concentrations above IDLH up to some maximum level.

Additional Websites for Pesticide Listings

Contact Artistatek by E-mail or phone.