Suffolk County Vector Control & Wetlands Management Long Term Plan & Environmental Impact Statement

Task 3 Literature Review
Book 8 Part 3: Mosquito Control Pesticides and Marine Invertebrates

Prepared for:

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May 2005

SUFFOLK COUNTY VECTOR CONTROL AND WETLANDS MANAGEMENT LONG - TERM PLAN AND ENVIRONMENTAL IMPACT STATEMENT

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LIST OF ABBREVIATIONS AND ACRONYMS

AI	Active Ingredient
BPC	Board of Pesticide Control
Bs	*Bacillus sphaericus*
Bt	*Bacillus thuringiensis*
Bti	*Bacillus thuringiensis israelensis*
cfu	colony forming units
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
EC	Emulsifiable Concentrate
EC_{50}	Effective concentration for 50% of organisms
EFC	Estimated Field Concentration
EXTOXNET	Extension Toxicology Network
ITU	International Toxicity Unit
IU	International Unit
LC_{50}	Lethal Concentration for 50 percent of organisms
LOEC	Lowest Observed Effect Concentration
MATC	Maximum Acceptable Toxicant Concentration
mg	milligram
mg/L	milligrams per liter or parts per million
MMF	Monomolecular Film
MSF	Monomolecular Surface Film
ng/L	Nanograms per liter or parts per trillion
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
PAN	Pesticide Action Network
PBO	Piperonyl Butoxide
PIP	Pesticide Information Profile
ppb	Parts Per Billion
ppm	Parts Per Million
RED	Reregistration Eligibility Document
TGAI	Technical Grade Active Ingredient
µg/L	micrograms per liter or parts per billion
USEPA	US Environmental Protection Agency
USFWS	US Fish and Wildlife Service
UV	Ultraviolet
WNV	West Nile Virus
WNVERAC	West Nile Virus Environmental Risk Advisory Committee

Executive Summary

Vector control pesticides can affect freshwater and marine invertebrates by causing immediate acute toxicity on exposure or by inducing chronic toxicity for agents that persist in the environment. Pesticides can also influence the organisms that invertebrates rely on for food. The potential toxicity of these agents on aquatic invertebrates is addressed during the US Environmental Protection Agency (USEPA) registration process. The Lethal Concentration of the agent at which 50 percent of the organisms die, the LC_{50}, is calculated from acute toxicity tests. USEPA requires special labeling for outdoor use pesticides with an acute LC_{50} of one part per million (ppm) or an EC_{50} of 1 ppm for aquatic invertebrates. The EC_{50} is that concentration that causes a non-lethal effect in 50 percent of the organisms. These pesticides must state "This pesticide is toxic to [fish] [fish and aquatic invertebrates] [oysters/shrimp] or [fish, aquatic invertebrates, oysters and shrimp]."

The Pesticide Action Network (PAN) summarizes ecotoxicology data from the USEPA database for aquatic and terrestrial life, and from peer-reviewed literature and data files provided by various US and international government agencies. PAN lists the acute toxicities of pesticides according to their LC_{50}s:

- very highly toxic (<100 µg/L),
- highly toxic (100-1,000 µg/L)
- moderately toxic (100-1,000 µg/L)
- slightly toxic (10,000-100,000 µg/L)
- not acutely toxic (>100,000 µg/L).

The Extension Toxicology Network (EXTOXNET) is a university consortium that issues a Pesticide Information Profile (PIP) based on extensive research by the government, universities, and manufacturers. The PIPs contain information on the ecological effects and environmental fate of common pesticides.

Four larvicides were reviewed including temephos, methoprene, and *Bacillus thuringiensis* variety *israelensis* (*Bti*), and monomolecular surface films (MSFs). Adulticides were reviewed including naled, malathion, pyrethrin, permethrin, resmethrin, sumithrin, methoxychlor, and the synergist, piperonyl butoxide (PBO).

Temephos - Temephos is an organophosphate classified by USEPA as slightly toxic. It breaks down rapidly in water and disappears in two days in oysters. According to the PIP produced by EXTOXNET, the pesticide is highly to very highly toxic to aquatic organisms. The US Fish and Wildlife Service (USFWS) reported that the pesticide affects a wide range of crustaceans, insects, and mollusks. PAN classifies temephos as ranging from not acutely toxic to highly toxic, depending upon the type of invertebrate being tested.

Methoprene - The USEPA Reregistration Eligibility Document (RED) for methoprene concluded that

> "sensitive life stages of non-target organisms, *i.e.*, nymph and larvae, and non-target aquatic organisms that are highly related to mosquitoes, *i.e.*, dragonfly, are not affected by methoprene up to 1,000 ppb."

Methoprene degrades rapidly in sunlight, both in water and on inert surfaces. According to the USEPA RED Fact Sheet, methoprene, when applied according to the manufacturer's instructions, should be detected in the environment in the range of four ppb (based on both laboratory and field measurements).

Estuarine invertebrate life-cycle toxicity research by USEPA demonstrated minimal chronic risk. USEPA therefore found that neither chronic nor acute exposures to methoprene would be toxic to non-target species. A study by the Massachusetts Pesticide Bureau of the State Department of Food and Agriculture concluded that methoprene is toxic to insects of the order Diptera (true flies including houseflies, mosquitoes, midges, and gnats). It found that methoprene is toxic to insects from 12 other orders, including Hemiptera (six-legged insects and those with numerous legs), Lepidoptera (butterflies and moths), and Coleoptera (beetles and weevils). Mosquitoes and midges showed the greatest susceptibility. However, its conclusion was that methoprene would have little effect on most non-target insects including mosquito predators because environmental concentrations following applications are significantly lower than the acute toxicity concentrations. PAN classified methoprene as ranging from slightly toxic to very highly toxic, depending on the type of invertebrate tested.

Bti - *Bti* is a bacterium. USEPA found some strains of Bti could kill other, non-target dipterans; USEPA also found that other kinds of *Bacillus thuringiensis* (but not the *israelensis* variation) reduced the number of lepidoptera the year of spray, and in the following year. Even when impacts to particular populations were detected, overall arthropod species abundance was unaffected. Particular species where numbers were reduced by *Bti* use recovered soon after applications stopped. Overall, *Bti* toxicity and infectivity risks to non-target invertebrates, when applied at label use rates, were called minimal to nonexistent.

Monomolecular Surface Films - MSFs are spread over the surface of a waterbody to change the surface tension and thus prevent mosquito larvae and pupae from breathing. Summary reports found that MSF does not affect organisms that use gills to breathe and that oxygen continues to dissolve into the water, leaving fish and other aquatic organisms unaffected. PAN classified MSF as moderately toxic to zooplankton.

Naled - Naled is an organophosphate pesticide classified by EXTOXNET very highly toxic to aquatic invertebrate species. USEPA includes dichlorvos, the naled degradation product, in toxicity class I - highly toxic, because it may cause cancer and there is only a small margin of safety for other effects. According to EXTOXNET, ultraviolet (UV) light increases dichlorvos toxicity to aquatic life by 5 to 150 times. PAN classified naled from moderately toxic to very highly toxic, depending on the type of invertebrate tested.

Malathion - Malathion is an organophosphate ranked as slightly toxic by USEPA. According to EXTOXNET, malathion is highly toxic to aquatic invertebrates with EC_{50} values from 1 µg/L to 1 mg/L. PAN classified malathion as slightly toxic to very highly toxic, depending on the type of invertebrate tested. In particular, some freshwater insects and crustaceans demonstrated sensitivity to malathion in the range of one part per billion to 10 parts per billion (ppb). Some estuarine species also were impacted at these concentrations; while others were not affected at all (oysters had an EC_{50} greater than 1,000,000 ppb).

Pyrethrins - Pyrethrins are natural insecticides produced by the chrysanthemum plant. Synthetic derivatives, called pyrethroids, are more effective. Pyrethrins are contact poisons that penetrate insect nervous systems, rendering them unable to move or fly. They are swiftly detoxified by insect enzymes, which enables them to recover. To delay the action of the enzyme so that a lethal effect occurs, organophosphates, carbamates, or synergists such as PBO are added. Natural pyrethrin is classified as extremely toxic to aquatic life by EXTOXNET. PAN classified pyrethrin as very highly toxic to insects and zooplankton.

Permethrin - Permethrin is a pyrethroid rated moderately to practically non-toxic by USEPA. PAN classified permethrin as slightly toxic to very highly toxic, depending on the type of invertebrate tested. Some crustaceans had LC_{50} values as low as 0.02 ppb to 2.2 ppb.

Resmethrin - Resmethrin, a pyrethroid, is rated slightly toxic to practically non-toxic by USEPA. It is usually applied with the synergist PBO to increase its toxic effects. PAN classified resmethrin as ranging from slightly toxic to very highly toxic.

PAN also classified PBO as "moderately toxic" to most invertebrates.

Sumithrin - Sumithrin, also known as phenothrin, is slightly to practically non-toxic to freshwater crustaceans. However, it was found to be significantly more toxic to the marine shrimp, *Americamysis bahia* where its LC_{50} was 0.03 µg/L.

Methoxychlor – Methoxychlor is classified by EXTOXNET as very highly toxic to aquatic invertebrates. PAN classified methoxychlor as moderately toxic to very highly toxic, depending on the type of invertebrate tested.

Laboratory vs. *in situ* testing – Research suggests that although standard laboratory tests are useful for acute toxicity evaluations, they may not reflect field conditions where exposures range from minutes to weeks. Some experimental data suggests that if tests were conducted using water collected from the field, toxic concentrations might be found to be substantially lower for some organisms.

1. Introduction

1.1. USEPA Guidelines

Vector control pesticides can affect freshwater and marine invertebrates in several ways. There may be acute toxicity immediately on exposure or chronic toxicity for those agents that persist; and there may be impacts on the organisms that fish rely on for food. The potential toxicity of these agents on the aquatic environment, specifically to fish, is addressed as part of the registration process. As part of the USEPA pesticides labeling requirements, an Environmental Hazards Statement must be included to address transport, use, storage, or spill of the product to water, soil, and air, and for impacts to beneficial insects, plants, and wildlife. Generally, USEPA uses information from seven types of acute toxicity studies that are performed on the technical grade of the active ingredient(s) (TGAI) in the formulation. They include:

1. avian oral LC_{50} (with mallard or bobwhite quail),
2. avian dietary LC_{50} (mallards),
3. avian dietary LC_{50} (bobwhite quail),
4. freshwater fish LC_{50} (rainbow trout),
5. freshwater fish LC_{50} (bluegill sunfish),
6. acute LC_{50} freshwater invertebrates (*Daphnia magna* or water flea),
7. honeybee contact LC_{50}.

USEPA may also use data on a chemical's "potential to contaminate groundwater or surface water, to drift, to adversely affect non-target plants and bees." Bioassays are conducted for the toxicity testing required by USEPA. Standard USEPA organisms are utilized such as the fathead minnow, *Pimephales promelas*. Review of all data is conducted by the Environmental Fate and Effects Division of USEPA. The work may be further subjected to other scientific peer reviewers.

Although USEPA includes environmental hazards in its overall evaluation of pesticides, pesticides receive a general category rating by human toxicity characteristics, according to Table 1-1. USEPA requires that a Signal Word be attached to containers of pesticides based on the most severe toxicity category assigned to the five acute toxicity studies (Table 1-2).

Table 1-1 - USEPA Toxicity Categories

Study	Category I	Category II	Category III	Category IV
Acute Oral	Up to and including 50 mg/kg	> 50 thru 500 mg/kg	> 500 thru 5000 mg/kg	> 5000 mg/kg
Acute Dermal	Up to and including 200 mg/kg	> 200 thru 2000 mg/kg	> 2000 thru 5000 mg/kg	> 5000 mg/kg
Acute Inhalation[1]	Up to and including 0.05 mg/liter	> 0.05 thru 0.5 mg/liter	> 0.5 thru 2 mg/liter	> 2 mg/liter
Primary Eye Irritation	Corrosive (irreversible destruction of ocular tissue) or corneal involvement or irritation persisting for more than 21 days	Corneal involvement or other eye irritation clearing in 8-21 days	Corneal involvement or other eye irritation clearing in 7 days or less	Minimal effects clearing in less than 24 hours
Primary Skin Irritation	Corrosive (tissue destruction into the dermis and/or scarring)	Severe irritation at 72 hours (severe erythema or edema)	Moderate irritation at 72 hours (moderate erythema)	Mild or slight irritation at 72 hours (no irritation or slight erythema)

[1] 4-hr exposure

Table 1-2 - Signal word requirements associated with toxicity classes

Toxicity Category	Signal Word'
I	DANGER
II	WARNING
III	CAUTION
IV	None Required

USEPA (2003) requires the following labeling statement for outdoor use pesticides that contain an active ingredient (AI) that for acute exposures causes a LC_{50} of 1 ppm or that for aquatic invertebrates (including estuarine species such as oyster and mysid shrimp) causes a EC_{50} of 1 ppm:

> "This pesticide is toxic to [fish] [fish and aquatic invertebrates] [oysters/shrimp] or [fish, aquatic invertebrates, oysters and shrimp]."

If use of the pesticide may result in fatality to birds, fish, or mammals, USEPA (2003) requires the following statement:

> "This pesticide is extremely toxic to [birds], [mammals], [fish], or [birds and mammals and fish]."

USEPA labeling requirements for mosquito control pesticide products may require one or both of the following additional labeling statements, although the aquatic toxicity of the specific product may lead to more or less stringent statements. USEPA cites two extremes of aquatic toxicity between which all mosquito control products must use the labels described below. *Bacillus thuringiensis (Bt)* products, which are considered non-toxic to aquatic organisms, would not require any statement. However, some pyrethroids are "highly toxic to aquatic organisms and may require stronger precautions than those listed below, tailored to the specific products, in order to prevent water contamination."

Larvicides - "Aquatic organisms may be killed in waters where this pesticide is used. Consult with the State agency with primary responsibility for regulating pesticides before applying to public waters to determine if a permit is needed."

Adulticides - "Do not apply over water, except where mosquitoes are emerging or swarming, or to treat vegetation where mosquitoes may rest. Drift and wash off from vegetation may be hazardous to aquatic organisms [and wildlife] in or adjacent to treated areas. Do not contaminate water when disposing of equipment wash waters or rinsate. Before making the first mosquito control application in a season, consult with the State agency with primary responsibility for regulating pesticides to determine if permits are required."

1.2. Data Sources

The following three summary databases have been generally relied upon for this report: PAN, EXTOXNET, and "Human Health and Environmental Relative Risks of West Nile Virus (WNV) Mosquito Control Products," a document by the State of Maine's Board of Pesticide Control (BPC). Each is described below.

1.2.1. Pesticide Action Network (PAN)

A summary of ecotoxicity data is presented for each pesticide and by taxonomic groups by the PAN (Orme and Kegley, 2004). PAN collects information on the toxicology of pesticides to aquatic organisms primarily from USEPA's ECOTOX (ECOTOXicology) database. According to the ECOTOX website,

> "It provides single chemical toxicity information for aquatic and terrestrial life. Peer-reviewed literature is the primary source of information encoded in the database. Pertinent information on the species, chemical, test methods, and results presented by the author(s) are abstracted and entered into the database.

> Another source of test results is independently compiled data files provided by various United States and International government agencies."

PAN assigns an Average Group Toxicity that is the acute toxicity of a particular chemical to groups of organisms (amphibians, fishes, zooplankton, etc.). The average acute toxicity assigned by PAN is based on the LC_{50} according to guidelines established by Kamrin (1997) and listed in Table 1-3 below. PAN also provides a Toxicity Range for the organism groups from the most sensitive to the least sensitive members of the group, including outlier species. An outlier species is one where the LC_{50} value for a particular chemical/species combination was more than two standard deviations from the average value. PAN also includes Average Species LC_{50}, which was calculated by excluding outliers.

Table 1-3 – PAN Average Group Toxicity

Toxicity Category	LC_{50} (µg/L)
Very highly toxic	<100
Highly toxic	100-1,000
Moderately toxic	1,000-10,000
Slightly toxic	10,000-100,000
Not acutely toxic	>100,000

1.2.2. Extension Toxicology Network (EXTOXNET)

Additional data is presented from EXTOXNET, which is a cooperative effort of 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. A PIP is available for each pesticide that includes the information in Table 1-4, below. Each PIP is extensively referenced using research by government agencies and university research laboratories. Original research by manufacturers submitted during the registration process is also referenced.

Table 1-4 - Pesticide Information Available from EXTOXNET

• Trade and Other Names • Regulatory Status • Chemical Class • Introduction • Formulation • Toxicological Effects • Physical Properties • Exposure Guidelines • Basic Manufacturer	• Ecological Effects o Effects on birds o Effects on aquatic organisms o Effects on other organisms • Environmental Fate o Breakdown in soil and groundwater o Breakdown in water o Breakdown in vegetation

1.2.3. Maine Board of Pesticide Control (BPC)

Another source of summary information is the Maine BPC publication "Human Health and Environmental Relative Risks of WNV Mosquito Control Products" (Hicks, 2001). The BPC is part of Maine Department of Agriculture. A subcommittee of the BPC, the West Nile Virus Environmental Risk Advisory Committee (WNVERAC), prepared the toxicity reviews and risk assessments. The members of the subcommittee were:

- BPC;
- Maine Forest Service;
- Maine Department of Environmental Protection;
- National Marine Fisheries Services;
- Maine Atlantic Salmon Commission;
- Maine Department of Marine Resources;
- University of Maine Cooperative Extension Pest Management Office;
- Maine Department of Inland Fisheries and Wildlife.

The report organizes toxicity data for aquatic species into warm water fish, cold-water fish, estuarine and marine species, and freshwater invertebrates. It includes a large quantity of data for some compounds such as malathion, naled, resmethrin, *Bti*, methoprene, and temephos, and less data on others such as permethrin, phenothrin, *Bacillus sphaericus (Bs)*, and monomolecular films (MMFs). Data from the Maine BPC is included in this report for each of the pesticides in tabular form, derived from "Human Health and Environmental Relative Risks of WNV Mosquito Control Products, Appendix IV, Toxicity Review" (http://www.state.me.us/agriculture/pesticides/wnv/ appendix4.htm).

2. Larvicides

2.1. Temephos

Temephos is an organophosphate. Products that contain temephos are classified as slightly toxic (USEPA toxicity class III) and must carry the Signal Word WARNING. The EXTOXNET PIP (EXTOXNET, 1996a) indicates that temephos breaks down rapidly in water. For example, one study found temephos sprayed in a Florida mangrove swamp was detectable two hours but not four hours after application. In simulated tide pools, temephos persisted for up to four days and in oysters for two days after application.

When applied at 0.1 ppm directly to the water for use as a larvicide, Paul and Sinnott (2000) stated that it would not harm most non-target aquatic insects. However, the EXTOXNET PIP (EXTOXNET, 1996a) refers to the emulsifiable concentrate (EC) and wettable powder of temephos as highly to very highly toxic to aquatic organisms. The PIP also states that some freshwater aquatic invertebrates such as amphipods are “very highly susceptible” to temephos, as are some marine invertebrates such as mysids. Abate 4E (46% EC) is referred to as “very highly toxic” to saltwater species such as the pink shrimp (LC_{50} = 5 ppb) and the Eastern oyster (LC_{50} = 19 ppb). Similar information is shown in Table 2-1 from re-registration information collected for USEPA.

In its synopsis of the non-target effects of temephos, the USFWS reported it has an effect on a wide range of crustaceans, insects, and mollusks (USFWS, 1998). The USFWS also reported sub-lethal effects for some crustaceans and mollusks.

Table 2-1 - Toxicity of Temephos to Invertebrates by Maine BPC

Estuarine and Marine Toxicity
Eastern oyster: 96 hr EC 50 = 220 ppb (TGAI*) (1) 96 hr EC 50 = 170 ppb (EC**) (1) **Pink shrimp**: 48hr EC 50 = 5.3 ppb (EC) (1) ***Gammarus lacustris****:* 80 ppb (2)

* TGAI = Technical Grade Active Ingredient **EC = Emulsifiable Concentrate
1) USEPA (1999)
2) TOXNET (2004a)

PAN summarized the acute toxicity of temephos to invertebrate taxonomic groups. Its results are shown in Table 2-2 below. The pesticide is considered highly toxic to some crustaceans and insects, and to zooplankton.

Table 2-2 - Toxicity of Temephos to Aquatic Organism Groups from PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Moderately Toxic	Moderate Toxicity
Annelids	Moderately Toxic	Moderate Toxicity
Crustaceans	Highly Toxic	Moderate to Very High Toxicity
Fish	Slightly Toxic	Slight to Very High Toxicity
Insects	Highly Toxic	Moderate to Very High Toxicity
Molluscs	Not Acutely Toxic	Not Acutely Toxic to Slightly Toxic
Zooplankton	Highly Toxic	Highly Toxic

The acute aquatic toxicity of temephos as determined for a number of invertebrates is summarized in Table 2-3.

Table 2-3 - Acute Aquatic Toxicity for Temephos for Various Invertebrate Groups by PAN

Common Name	Scientific Name	Average LC_{50} (µg/L)	LC_{50} Std Dev	Number Studies	Average Species Rating	Outlier Results
Annelida						
Polychaete	*Nereis glandicincta*	1,500		1	Moderately Toxic	
Crustaceans						
Fish louse	*Argulus*	24		1	Very Highly Toxic	
Shrimp	*Caridina denticulata*	320		1	Highly Toxic	
Sand shrimp	*Metapenaeus monoceros*	45		1	Very Highly Toxic	
Korean or Oriental shrimp	*Palaemon macrodactylus*	1,374	1,126	2	Moderately Toxic	
Kuruma shrimp	*Penaeus japonicus*	1		1	Very Highly Toxic	
Jumbo tiger prawn	*Penaeus monodon*	45		1	Very Highly Toxic	
Fiddler crab	*Uca pugnax*	9,120		1	Moderately Toxic	Outlier
Molluscs						
Horn shell	*Cerithidea cingulata*	58,000		1	Slightly Toxic	
Salt marsh snail	*Melampus bidentatus*	293,000		2	Not Acutely Toxic	
Zooplankton						
Copepod subclass	*Copepoda*	130		1	Highly Toxic	
Scud	*Gammarus lacustris*	491.7	376	7	Highly Toxic	
Copepod	*Mesocyclops hyalinus*	210	14.1	3	Highly Toxic	

2.2. Methoprene

Methoprene is a slightly to practically nontoxic compound in USEPA toxicity class IV. Labels for containers of products containing methoprene must carry the Signal Word CAUTION. Acute, short-term, and subchronic-effects studies were conducted on non-target immature and adult arthropods (Crustacea and Insecta, including shrimp, damselfly, beetle, and tadpole) for the USEPA RED for methoprene. The research found 24- and 48-hour LC_{50} values over 900 ppb (USEPA, 2001a). The RED also makes the statement

> "Acute, short-term and subchronic effects studies on non-target immature and adult arthropods [Crustacea and Insecta, including shrimp, damselfly, beetle, tadpole] demonstrates 24- and 48-hour LC_{50} values >900 ppb…sensitive life stages of non-target organisms, *i.e.*, nymph and larvae, and non-target aquatic organisms that are highly related to mosquitoes, *i.e.*, dragonfly, are not affected by methoprene up to 1000 ppb."

USEPA concerns over the estuarine invertebrate toxicity were alleviated by studies that followed the original methoprene USEPA (1991). Estuarine invertebrate life-cycle toxicity research in 1996 with mysid shrimp demonstrated minimal chronic risk (USEPA, 2001a).

PAN assigned crustaceans a highly toxic Average Acute Toxicity and Acute Toxicity Range for methoprene based on the studies incorporated in their review (Table 2-4). PAN classified methoprene as very highly toxic to insects.

Table 2-4 - Summary of Acute Toxicity by Organism Group for Methoprene by PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Crustaceans	Highly Toxic	Highly Toxic
Fish	Slightly Toxic	Not Acutely Toxic to Moderate Toxicity
Insects	Very Highly Toxic	Very Highly Toxic
Molluscs	Slightly Toxic	Slight Toxicity
Zooplankton	Moderately Toxic	Moderate to Very High Toxicity

The Maine BPC summarized reported values for the toxicity of methoprene to invertebrates for a variety of life stages (Hicks, 2001). Table 2-5 includes LC_{50} and EC_{50} values as well as Maximum Allowable/Acceptable Toxicant Concentration (MATC). The data suggest that some crustaceans are not particularly sensitive to methoprene (*eg.* gammarids and mud crabs) whereas other crustaceans are (*eg.* mysids and daphnids).

Table 2-5 - Toxicity of Methoprene to Invertebrates by Maine BPC

Estuarine and Marine Toxicity	Freshwater Invertebrates
Mud crab: gametes in @ 1,300 ppb (1) **Adult grass shrimp**: Slightly toxic (3) not acutely toxic (2) **Juvenile grass shrimp and larval mud-crabs**: Very highly toxic (3) not acutely toxic (2) ***Gammarus aequicauda:*** 96 hr LC_{50} = 2,150 ppb (_) (3, 4) 96 hr LC_{50} = 1,950 ppb (_) (3, 4) **Mysid Shrimp**: 96 hr LC_{50} = 110 ppb (4) 28 day MATC = > 98 ppb (4) **Oyster (larvae)**: 48 hr LC_{50} = 247 ppb (4) **Oyster shell deposition**: 96 hr = 1,400 ppb (4)	**Daphnia**: 48 hr EC_{50} 89 ppb (3) 42 day MATC 27 - 51 ppb (3) 48 hr EC_{50} = 360 ppb (4) 42 day MATC 51 ppb (4)

(1) USEPA (1991)
(2) Wellmark (2001)
(3) Vershcueren (1983)
(4) Sandoz (1996)

In an earlier study that supports the USEPA conclusions, Brown *et al*. (1996) tested selected pesticides for their acute toxicity to the estuarine shrimp *Leander tenuicornis*. They found that methoprene was the least toxic of the tested compounds, with a median LC_{50} of 14.32 ppm (approximately 2,000 times greater than the estimated field concentration [EFC] for a 15-cm-deep pool).

A review of the impacts of methoprene on non-target aquatic organisms was conducted by Antunes-Kenyon and Kennedy (2001) for the Massachusetts Pesticide Bureau of the State Department of Food and Agriculture. They concluded that methoprene is toxic to those insects that are members of the order Diptera (true flies including houseflies, mosquitoes, midges, and gnats). The authors also suggest that methoprene is toxic to a range of insects from 12 other orders, including Hemiptera (six-legged insects and those with numerous legs), Lepidoptera (butterflies and moths), and Coleoptera (beetles and weevils). In all cases reviewed by the researchers, mosquitoes and midges showed the greatest susceptibility to methoprene. Short-term toxicity studies reviewed in the study indicated that methoprene is not likely to impact most non-target insects, including mosquito predators. This result, which is seemingly at odds with the finding that methoprene is toxic at certain concentrations to many species of interest, is accounted for because environmental concentrations following applications are significantly lower than the toxicity concentrations for most aquatic non-target insects. Antunes-Kenyon and Kennedy (2001) based their conclusions in part on the results of a study that utilized the double isomer formulation, (R,S)-methoprene, rather than the more commonly used single isomer formulation of the pesticide, (S)-methoprene. However, Celestial and McKenney (1994) found that larvae of the estuarine mud crab, *Rhithropanopeus harrisii*, were more sensitive to the single isomer formulation of the pesticide, (S)-methoprene, than to the double isomer formulation, (R,S)-methoprene (see below). However, the LC_{50} values for some of the mosquito predators are two orders of magnitude higher than that for mosquitoes, which suggests that the pesticide may be effective against mosquitoes without impacting other organisms.

Celestial and McKenney (1994) tested the influence of methoprene on the larval development and survival of the estuarine mud crab, *Rhithropanopeus harrisii*. They found that crab larvae exposed continuously to 1,000 µg/L of methoprene did not survive past zoeal stage I. In addition, continuous exposure to 100 µg/L of methoprene increased crab larval mortality, through all stages, except for zoeal stage II. Development duration also increased through all zoeal stages. Mud crab larvae were more sensitive to the pesticide than the grass shrimp, *Palaemonetes pugio*. According to the USEPA RED Fact Sheet, methoprene should not reach 100 ppb in environmental concentrations, when applied according to the manufacturer's instructions, but actually should be more in the range of four ppb (based on both laboratory and field measurements). USEPA therefore determined that methoprene concentrations should not prove to be toxic to aquatic non-target species, either in terms of acute or chronic exposure.

Bircher and Ruber (1988) studied the toxicity of methoprene to salt marsh copepods and described it as a relatively safe form of mosquito control. They did find evidence of some damage to the early life stages of the copepod, where methoprene concentrations exceeded 100 ppb. As was the case for other reports, the effects from methoprene, if any, were found to be transient.

Methoprene degrades rapidly in sunlight, both in water and on inert surfaces. Within three days of application, 90 percent will degrade via photolysis and microbial metabolism; without microbial metabolism, photolysis will degrade 80 percent in 13 days (USEPA, 2001). Overall, methoprene has a half-life ranging from 30 hours to 14 days, depending on environmental conditions. Higher temperatures and salinity lead to higher degradation rates (Glare and O'Callaghan 1999). The effects of methoprene last up to a week, but it reaches undetectable levels in ponds within 48 hours of application (Madder, 1980 and Schaefer and Dupras, 1973).

Numerous studies have examined the impact of methoprene on food chains and the ecology of entire groups of organisms. These reports are examined in a separate report on the impact of vector control pesticides and marsh management on food chains.

2.3. Bacillus thuringiensis var. israelensis (Bti)

Bti is a bacterium, and therefore is referred to as a "biopesticide" or microbial pesticide by USEPA. Biopesticides require similar labeling as chemical pesticides (USEPA, 2003). The label must show the number of viable units (spores, cells, colony forming units [cfu], etc.) per unit weight or volume of the product. The strain variety must be shown as well as the percent AI for each order of insects affected. The potency must be included in International Units (IU) per milligram (mg) of product. USEPA (2003) stated that ingredient statements for lepidopteran (moths and butterflies) active *Bt* products reflect the equivalence of 500,000 IU per mg of product equal to 100% AI. Percent AI is calculated on the product potency compared to the 100% AI assumption of 500,000 IU/mg. Thus, a 16,000 IU/mg product would be 3.2 percent. It is classified by USEPA as toxicity class III – "slightly toxic." Products containing *Bti* must carry the Signal Word CAUTION because of its potential to irritate eyes and skin.

In the RED for *Bti*, USEPA (1998) reported on the potential impacts to non-target terrestrial and aquatic invertebrates. USEPA cited a reduction in the number of adult and larval lepidoptera the year of spray and some reduction extending into the following year due to reduction of larvae the previous year. The agency reported, however, that *Bti* does not affect overall arthropod abundance, including beetles, sucking insects such as aphids, leafhoppers, or cicadas and spiders. Low-level mortality to terrestrial insect predators and parasites was noted by USEPA only in a laboratory study at doses higher than the recommended label use rates. Effects on predators and parasites of insects appeared to be indirect, resulting from reductions in target organism population decline. Other than target insects and their parasites and predators, USEPA identified few other species that are affected. The RED also stated that species that demonstrated an affect during extended exposure to the pesticide recovered soon after pesticide use stopped.

The RED reported that *Bti* has no appreciable effect on aquatic invertebrates. Field studies found no adverse affect on the abundance or composition of benthic organisms, or on the immature or adult stages of mayflies, caddisflies, dragonflies, damselflies, beetles, midges, and dobsonflies. Decreases in *Daphnia* was attributed to factors other than *Bti* toxicity. USEPA reports that the risk of *Bti* to daphnids and other aquatic invertebrates applied at label use rates is minimal to nonexistent because the environmental concentration is less than that at which effects were observed in laboratory settings.

USEPA concluded that, overall, *Bti* toxicity and infectivity risks to non-target invertebrates when applied at label use rates is minimal to nonexistent. However, USEPA expressed concerns over contaminants produced as a byproduct of the manufacturing process. During the fermentation process, other exotoxins can be produced by the *Bacillus* bacteria. Following the RED, USEPA required manufacturers to implement controls over the fermentation process to make it more predictable and lessen the conditions that could give rise to exotoxin formation. In addition, *Bti* products must undergo a 10-day *Daphnia magna* bioassay to certify the manufacturing process. A summary of the toxicity test results for freshwater, estuarine, and marine organisms from the RED is shown in Table 2-6.

Table 2-6 - Toxicity of *Bti* to Invertebrates by Maine BPC

Estuarine and Marine Toxicity	Freshwater Invertebrates
Grass shrimp: No Observable Effect Level NOEL* > 2 x 10^{10} cfu/g food (1) NOEL > 4.2 x 10^{10} cfu/g food (1) Copepod: NOEL = 50 mg/kg (sediment) (1)	Daphnia: 21 Day (EC 50) Median Effective Concentration = 5,000 - 50,000 ppb = µg/L (1)

*NOEL = No Observed Effect Level
(1) USEPA (1998)

Merritt and Wipfli (1999) exposed a variety of non-target organisms to *Bti* over a three-year period. They reported "no negative impacts" on the following invertebrate predators:

- Plecoptera (stoneflies)
- Odonata (dragonflies and damselflies)

- Megaloptera (alderflies, dobsonflies, snake flies)
- Trichoptera (caddice flies)
- Diptera (housefly, mosquitoes, midges, and gnats)
- Trichoptera (caddice flies)
- Ephemeroptera (mayflies)

Predators often consumed more *Bti*-contaminated (dead) black fly larvae than live larvae, with no adverse effects. In fact, the study found that detritivores (mainly mayflies) consumed large amounts of *Bti*-contaminated black fly larvae. Furthermore, these mayflies gained body mass faster and developed over a shorter time than control organisms. Merritt and Wipfli identified some Dipteran species that were sensitive to doses of *Bti*, but at concentrations 100 times normal field application rates.

Brown *et al.* (1996) tested selected pesticides for their acute toxicity to the estuarine shrimp *Leander tenuicornis* and found that *Bti* had an LC_{50} of 60 x 10^6 International Toxicity Units (ITU), approximately 200 times the EFC for a 15-cm-deep pool.

Roberts (1995) conducted a study of the impact of *Bti* on salt marsh crustaceans that are predators of mosquito larvae. Roberts worked with *Gammarus duebeni* and *Palaemonetes varians*, both predators of mosquito larvae. The researcher found no adverse effects when the gammarids and palaemonids were exposed to *Bti*, and to mosquito larvae killed by *Bti*. Fecal pellets collected from the exposed test animals and placed in clean seawater were toxic to mosquito larvae the following day. However, these fecal pellets failed to kill mosquitoes after six days in seawater.

Numerous studies examined the potential impact of *Bti* on ecosystems and food chains. These reports are examined in a separate report on the impact of vector control pesticides and marsh management on food chains.

2.4. Monomolecular Surface Films (MSFs)

MSFs are alcohols comprised of the chemical poly (oxy-1, 2-ethanediyl), alpha-isooctadecyl-omega-hydroxy. They are spread over the surface of a waterbody to change the surface tension and thus prevent larvae and pupae from extending their tubes through to the air to breathe.

Deprived of air through these siphons, the mosquito larvae and pupae die within 24 to 72 hours. Paul and Sinnott (2000) found that MSFs do not affect organisms that use gills to breathe. Additionally, they found that atmospheric oxygen continues to dissolve into the water, leaving fish and other aquatic organisms unaffected. They found that MSFs are not very toxic to aquatic life and that isostearyl alcohol does not accumulate in the environment. They estimated that MSFs degrade within two to ten days.

USEPA (2000) reported a mean LC_{50} of 1,900 ppb for daphnids.

PAN includes MSFs in its evaluation of nontarget pesticide impacts (Orme and Kegley, 2004). It classified MSFs as moderately toxic to zooplankton, a finding based on one study of mysid shrimp that resulted in an LC_{50} of 9,000 µg/L.

3. Adulticides

3.1. Naled

Naled is an organophosphate pesticide that is included in toxicity Class I by USEPA. EXTOXNET (1996b) classifies naled as very highly toxic to aquatic invertebrate species. It cited studies by Johnson and Finley (1980), who reported 96-hour LC_{50} values of 0.4 µg/L in *Daphnia*, 8 µg/L in stoneflies, and 18 µg/L in scuds and sideswimmers. Naled is rapidly broken down in water, with a reported half-life of about two days (TOXNET, 2004a). It is practically nonpersistent in the environment according to one study, with a reported field half-life of less than one day (Wauchope *et al.*, 1992). It degrades quickly in sunlight to dichlorvos (Gallo and Lawryck, 1991; Kidd and James, 1991). Naled is not highly soluble in water and does not bind strongly to soils (Wauchope *et al.*, 1992). It is rapidly broken down if wet and it is moderately volatile (TOXNET, 2004a). Most naled reaching the soil is degraded by microorganisms. Therefore, it is not considered to be a potential groundwater contaminant. Plants that take up naled reductively eliminate bromine from naled to form dichlorvos, which may evaporate or be further metabolized (Kidd and James, 1991).

USEPA placed dichlorvos, the naled degradation product, in toxicity class I (highly toxic) because it may cause cancer. UV light increases dichlorvos toxicity to aquatic life five to 150 fold (EXTOXNET, 1996b). Grass shrimp are more sensitive to dichlorvos than the sand shrimp, hermit crab, and mummichog. An LC_{50} (96-hour) for dichlorvos was reported to be four µg/L in sand shrimp (EXTOXNET, 1996b).

Table 3-1 - Toxicity of Naled to Invertebrates by Maine BPC

Estuarine and Marine Toxicity	Freshwater Invertebrates
Sheepshead minnow: LC_{50} = 1,200 ppb (1) **Shrimp**: LC_{50} = 9.3 - 92 ppb (1) LC_{50} = 8.8 ppb **Oyster**: LC_{50} = 170 - 190 ppb (1)	***Daphnia* spp**: LC_{50} = 0.3 - 0.4 ppb (1) LC_{50} = 0.3 ppb (2) ***Simocephalus serrulates***: LC_{50} = 1.1 ppb (1) **Stonefly**: LC_{50} = 8 ppb (1, 3) **Scud**: LC_{50} = 18 ppb (1, 3) **Side swimmers**: LC_{50} = 18 ppb (3) **Freshwater Invertebrates**: LC_{50} = ppb (2)

(1) USEPA (1997)
(2) USFWS (1993)
(3) EXTOXNET (1996b)

PAN included naled in its evaluation of nontarget pesticide impacts (Orme and Kegley, 2004). It rated naled as moderately toxic to crustaceans, highly toxic to insects and very highly toxic to zooplankton (see Table 3-2, below).

Table 3-2 - Summary of Acute Toxicity by Organism Group for Naled from PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Moderately Toxic	Slight to Moderate Toxicity
Crustaceans	Moderately Toxic	Moderate to Very High Toxicity
Fish	Moderately Toxic	Moderate to Very High Toxicity
Insects	Highly Toxic	High to Very High Toxicity
Zooplankton	Very Highly Toxic	High to Very High Toxicity

3.2. Malathion

Malathion was developed in 1950 as one of the earliest organophosphate insecticides. It is ranked as a slightly toxic compound in USEPA toxicity class III. It is used to control sucking and chewing insects including mosquitoes and flies. Malathion can be found in formulations with many other pesticides. According to EXTOXNET (1996c), malathion is highly toxic to aquatic invertebrates. Aquatic invertebrate sensitivity varies, however, with EC_{50} values from one µg/L (ppb) to one mg/L (ppm) (Menzie, 1980).

PAN includes malathion in its evaluation of nontarget pesticide impacts (Orme and Kegley, 2004). It rates malathion as moderately toxic to crustaceans, highly toxic to insects and the benthic community, very highly toxic to zooplankton, and slightly toxic to annelids, echinoderms, mollusks, nematodes and flatworms (see Table 3-3, below). However, the acute toxicity range is much greater than other pesticides, from slight toxicity to very high toxicity for several organism groups. For example, the average species LC_{50} for cyclopoid copepods is one µg/L, but is 52,500 µg/L for rotifers.

Table 3-3 - Summary of Acute Toxicity by Organism Group for Naled from PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Highly Toxic	Moderate to Very High Toxicity
Annelida	Slightly Toxic	Slight to Moderate Toxicity
Crustaceans	Moderately Toxic	Slight to Very High Toxicity
Echinoderms	Slightly Toxic	Slight Toxicity
Fish	Moderately Toxic	Slight to Very High Toxicity
Insects	Highly Toxic	Moderate to Very High Toxicity
Marine Benthic Community	Highly Toxic	Highly Toxic
Mollusks	Slightly Toxic	Not Acutely Toxic to Very High Toxicity
Nematodes and Flatworms	Slightly Toxic	Slight to Moderate Toxicity
Zooplankton	Moderately Toxic	Slight to Very High Toxicity

The Maine BPC (2004) reported on studies conducted to determine the toxicity of malathion to invertebrates. Freshwater insects and crustaceans demonstrated a smaller sensitivity range to malathion, with LC_{50} values from just below one ppb to 10 ppb and higher (Table 3-4). Estuarine test organisms had a broader range of toxicity from an LC_{50} of one ppb for *Gammarus lacustris* to 1,000 ppb for blue crabs and an EC_{50} greater than 1,000,000 for oysters (Table 3-4).

Table 3-4 - Toxicity of Malathion to Invertebrates by Maine BPC

Estuarine and Marine Toxicity	Freshwater Invertebrates
Oyster:	***Daphnia**:*
EC_{50} > 1,000,000 ppb (1)	96 hr LC_{50} = 1,000 ppb (1)
Shrimp:	24 hr LC_{50} = 0.9 ppb (2, 4)
EC_{50} > 2,600 - 3,100 ppb (1)	48 hr LC_{50} = 1.8 ppb (2, 3)
LC_{50}'s Range from 0.76 to 81.5 ppb water and grass shrimp (2)	48 hr EC_{50} = 2.2 ppb (EC) (3)
LC_{50}'s Range from 2.2 to 280 ppb in shrimp (3)	48 hr EC_{50} = 1 ppb (3)
Gammarus lacustris:	1 wk LC_{50} = 3 ppb (2)
96 hr LC_{50} = 1 ppb (4)	21 D LOEC* = 0.1 ppb; NOEC** 0.06 ppb (3)
Sand shrimp:	**Daphnids**:
96 hr LC_{50} = 33 ppb (4)	48 hr LC_{50} = 0.69 ppb (3)
Grass shrimp:	**Scud**:
96 hr LC_{50} = 82 ppb (4)	48 hr LC_{50} = 1.8 ppb (3)
Hermit Crab:	96 hr LC_{50} = 0.5 ppb (3)
LC_{50} = 83 ppb (2, 4)	96 hr LC_{50} = 0.76 ppb (4)
Blue Crab:	**Crayfish**:
LC_{50} > 1000 ppb	96 hr LC_{50} = 180 ppb (3, 4)
Macrobrachium lamarrei:	**Glass shrimp**
48 hr LC_{50} = 1,870 ppb (4)	96 hr LC_{50} = 12 ppb (3)
	96 hr LC_{50} = 90 ppb (4)
	Seed shrimp:
	49 hr LC_{50} = 47 ppb (3)
	Stone fly:
	96 hr LC_{50} = 10 ppb (4)
	96 hr LC_{50} = 1.1 ppb (4)
	96 hr LC_{50} = 2.8 ppb (4)
	96 hr LC_{50} = 0.96 ppb (4)
	Damsel fly:
	96 hr LC_{50} = 10 ppb (4)
	Caddis fly:
	96 hr LC_{50} = 5 ppb (4)
	Snipe fly:
	96 hr LC_{50} = 385 ppb (4)

*LOEC = Lowest Observed Effect Concentration
**NOEC = No Observed Effect Concentration

(1) USEPA (1988a)
(2) Vershcueren, K. (1983)
(3) USEPA (2001b)
(4) TOXNET (2004b)

3.3. Pyrethrins and Pyrethroids

Pyrethrins are natural insecticides produced by certain species of the chrysanthemum plant. Synthetic derivatives of the chrysanthemumic acids have also been developed as insecticides. These are called pyrethroids and tend to be more effective than pyrethrins (EXTOXNET, 1996d). Pyrethrins and pyrethroids are contact poisons that quickly penetrate the nervous system of insects, rendering them unable to move or fly away after just a few minutes. Pyrethrins and pyrethroids, however, are swiftly detoxified by enzymes in the insect enabling some pests to recover (EXTOXNET, 1996d). To delay the action of the enzyme so that a lethal dose is assured, organophosphates, carbamates, or synergists, such as PBO, are sometimes added to the pesticide formulation.

3.3.1. Pyrethrin

Pyrethrin is classified as extremely toxic to aquatic life by EXTOXNET (1996e). Toxicity increases with higher water temperatures and acidity. Pyrethrins are highly fat soluble, but they are rapidly metabolized, and so do not accumulate in the body (EXTOXNET, 1996e). Pyrethrins are not persistent and breakdown rapidly when exposed to sunlight (Paul and Sinnott, 2000). PAN includes results of toxicity tests completed for pyrethrin II (Table 3-5) and classified it as very highly toxic to insects and zooplankton. That classification is based on the results of three tests with the stonefly (*Pteronarcys californicus*) that resulted in an average acute toxicity of 5.8 µg/L.

Table 3-5 - Summary of Acute Toxicity by Organism Group for Pyrethrin II by PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Moderately Toxic	Slight to Moderate Toxicity
Insects	Very Highly Toxic	Very Highly Toxic
Zooplankton	Very Highly Toxic	Very Highly Toxic

3.3.2. Permethrin

Permethrin is a pyrethroid, found to be a moderately to practically non-toxic pesticide in USEPA toxicity class II or III, depending on the formulation. Formulations are placed in class II if they have the potential to cause eye and skin irritation. Products containing permethrin must bear the Signal Word WARNING or CAUTION, depending on the formulation.

PAN summarizes the acute toxicity of permethrin by organism group (Table 3-6). PAN lists permethrin as very highly toxic to crustaceans citing, among others, three studies on the fiddler crab (*Uca pugilator*) that report an average species LC_{50} of 4.21 µg/L (Table 3-7). Other studies reported by PAN were completed on the Eastern oyster, *Crassostrea virginica*, adults, spat, and larvae. Less-than-two-hour-old larvae exposed for 48 hours to 1,000 µg/L of permethrin exhibited abnormal growth. Oyster spat exposed for 96 hours to 40.7 µg/L of permethrin were reportedly immobilized. The feeding behavior of the blue mussel, *Mytilus edulis*, was affected after a seven-day exposure to 400 µg/L of permethrin. Studies on the affects of permethrin exposure to zooplankton were variable (Table 3-8); PAN summarized the data by classifying permethrin as very highly toxic to marine zooplankton, but less so for freshwater zooplankton. Permethrin was classified as slightly toxic to freshwater oligochaete worms with an average species LC_{50} of 83,933 µg/L, based on three studies.

Table 3-6 - Summary of Acute Toxicity by Organism Group for Permethrin by PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Annelida	Slightly Toxic	Slight Toxicity
Crustaceans	Very Highly Toxic	Very Highly Toxic
Fish	Highly Toxic	Moderate to Very High Toxicity
Insects	Moderately Toxic	Slight to Very High Toxicity
Mollusks	Slightly Toxic	Not Acutely Toxic to High Toxicity
Nematodes and Flatworms	Slightly Toxic	Slight Toxicity
Phytoplankton	Slightly Toxic	Slight Toxicity
Zooplankton	Moderately Toxic	Slight to Very High Toxicity

Table 3-7 - Summary of Acute Aquatic Toxicity of Crustaceans to Permethrin by PAN

Common Name	Scientific Name	Avg LC_{50} (ug/L)	LC_{50} Std Dev	Number Studies	Avg Species Rating	Outlier Result?
Ostracod	*Cypria*	5.00		1	Very Highly Toxic	
Crayfish	*Orconectes*	3.00		1	Very Highly Toxic	
Crayfish	*Orconectes immunis*	0.60	0.60	2	Very Highly Toxic	
Northern pink shrimp	*Penaeus duorarum*	0.31	0.13	4	Very Highly Toxic	
Crayfish	*Procambarus blandingii*	210.0		1	Highly Toxic	Outlier
Red swamp crayfish	*Procambarus clarkii*	0.69	0.29	18	Very Highly Toxic	
Fiddler crab	*Uca pugilator*	4.21	2.40	3	Very Highly Toxic	

Table 3-8 - Summary of Acute Aquatic Toxicity of Permethrin to Zooplankton by PAN

Common Name	Scientific Name	Avg LC_{50} (ug/L)	LC_{50} Std Dev	Number Studies	Avg Species Rating	Outlier Result?
Water flea	*Alonella*	4.00	-	1	Very Highly Toxic	
Opossum shrimp	*Americamysis bahia*	0.06	0.03	4	Very Highly Toxic	
Water flea	*Daphnia carinata*	28,375	12,007	4	Slightly Toxic	
Water flea	*Daphnia magna*	7.89	7.40	19	Very Highly Toxic	
Water flea	*Daphnia pulex*	7,754	14,520	11	Moderately Toxic	
Calanoid copepod	*Diaptomus*	7.00	-	1	Very Highly Toxic	
Cyclopoid copepod	*Eucyclops*	5.00	-	1	Very Highly Toxic	
Scud	*Gammarus pseudolimnaeus*	0.29	0.08	4	Very Highly Toxic	
Water flea	*Moina macrocopa*	30,875	13,078	4	Slightly Toxic	Outlier
Water flea	*Scapholeberis kingi*	13.0	-	1	Very Highly Toxic	
Calanoid copepod	*Spicodiaptomus chilospinus*	5.50	0.50	2	Very Highly Toxic	

The Maine BPC summarized results for a number of invertebrate species (Table 3-9). The LC_{50} for both freshwater and estuarine crustacean species tested ranged from 0.02 ppb to 2.2 ppb. The molluscan species tested were far less sensitive to permethrin, with LC_{50} values several orders of magnitude greater than that of crustaceans. The freshwater Mayfly nymph was two orders of magnitude less sensitive to the pesticide than the crustaceans tested.

Table 3-9 - Toxicity of Permethrin to Invertebrates by Maine BPC

Estuarine and Marine Toxicity	Freshwater Invertebrates
Shrimp: 96 hr LC_{50} = 0.02 ppb to 1.2 ppb (1) **Fiddler crab**: 96 hr LC_{50} = 2.2 ppb (1) **Crayfish**: 96 hr LC_{50} = 0.21 ppb (1) **Lobster**: 96 hr LC_{50} = 0.73 ppb (1) **Oyster**: 96 hr LC_{50} > 4,800 ppb (1) **Oyster larval (pacific):** 96 hr LC_{50} > 4,800 ppb (1) **Oyster larval (eastern):** 96 hr LC_{50} > 1,000 ppb (1)	***Daphnia***: LC_{50} = 0.039 ppb (2) 48 hr LC_{50} = 0.6 ppb (1) **Mayfly nymph**: LC_{50} = 100 ppb (2) **Crayfish**: LC_{50} = 0.21 ppb (2)

(1) Aventis (2001)
(2) USFWS (1992)

3.3.3. Resmethrin

Resmethrin, a pyrethroid, is slightly toxic to practically non-toxic, ranked by the USEPA in toxicity class III. Paul and Sinnott (2000) described it as a “broad spectrum pesticide,” because it kills both target and nontarget insects. The insecticide is usually applied with the synergist PBO to increase its toxic effects (see section 3.5 for more on PBO).

PAN includes resmethrin in its evaluation of nontarget pesticide impacts (Orme and Kegley, 2004). It classified resmethrin as moderately toxic to crustaceans, highly toxic to insects and the benthic community, very highly toxic to zooplankton, and slightly toxic to annelids, echinoderms, mollusks, nematodes and flatworms.

The Maine BPC (2004) reported on studies conducted to determine the toxicity of resmethrin to invertebrates. Shrimp toxicity was 1.3 ppb whereas oyster toxicity was reported as 1,790 ppb. Daphnids were sensitive to resmethrin at levels similar to marine shrimp, though the results of one test showed far less sensitivity.

Table 3-10 - Toxicity of Resmethrin to Invertebrates by Maine BPC

Estuarine and Marine Toxicity	Freshwater Invertebrates
Shrimp: 1.25 ppb (1) 1.3 ppb (2) **Oyster**: 1,790 ppb (1)	***Daphnia****:* LC_{50} = 2.4 ppb (4) 48 hr LC_{50} = 3.7 ppb (2) ***Daphnia pulex***: 3 hr LC_{50} = 15,000 ppb static (3) **Swamp crawfish**: 0.0082 ppb (4)

(1) USEPA (1988b)
(2) Aventis (2001)
(3) TOXNET (2004c)
(4) EXTOXNET (1996e)

3.3.4. Sumithrin (Phenothrin)

Sumithrin is also known as phenothrin, or as its trade name, Anvil®. According to research cited in PAN, freshwater water fleas (*Daphnia magna*) less than 24 hours old became immobile when exposed over 48 hours to a concentration of 300,000 µg/L sumithrin. Sumithrin was reportedly significantly more toxic to the marine shrimp, *Americamysis bahia*. The LC_{50} for less than 24-hour old opossum shrimp when exposed over 96 hours to sumithrin was 0.03 µg/L.

The Maine BPC cited research that demonstrated that LC_{50} values for *Daphnia pulex* exposed to sumithrin were 50,000 ppb, which was independent of the isomer tested (Table 3-11). *Daphnia magna* were less sensitive, with a reported LC_{50} value of 300,000 ppb.

Table 3-11 - Toxicity of Sumithrin to Invertebrates by Maine BPC

Daphnia magna: 96 hr LC_{50} >300,000 ppb (1) ***Daphnia pulex***: 48 hr LC_{50} = 50,000 ppb (- trans) (2) 48 hr LC_{50} = 50,000 ppb (- cis) (2) 48 hr LC_{50} = 50,000 ppb (+ trans) (2) 48 hr LC_{50} = 50,000 ppb (+ cis) (2) 48 hr LC_{50} = 50,000 ppb (racemic mix) (2)

(1) USEPA (1987)
(2) TOXNET (2004d)

3.4. Methoxychlor

Methoxychlor is listed as practically nontoxic, in USEPA toxicity class IV. Methoxychlor is similar in structure to DDT. Unlike DDT, it has relatively low toxicity and relatively short persistence in biological systems. However, EXTOXNET classifies methoxychlor as very highly toxic to fish and aquatic invertebrates. Johnson and Finley (1980) reported 96- or 48-hour LC_{50} values for methoxychlor of less than 0.1 mg/L for *Daphnia*, scuds, sideswimmers, and stoneflies. Maximum bioconcentration estimates were reported for mussels, at 12,000, and snails, at 8,570 (Trabalka and Garten, 1982). Practically no metabolism of the pesticide was seen in *Daphnia* or in mayflies (Johnson and Finley, 1980).

PAN classifies methoxychlor as very highly toxic to crustaceans, insects, and zooplankton, highly toxic to annelid worms, and moderately to highly toxic to Pacific coast snails, clams, and oysters (Table 3-12).

Table 3-12 - Summary of Acute Toxicity by Organism Group for Methoxychlor by PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Highly Toxic	Highly Toxic
Annelida	Highly Toxic	Highly Toxic
Crustaceans	Very Highly Toxic	Very Highly Toxic
Fish	Highly Toxic	Moderate to Very High Toxicity
Insects	Very Highly Toxic	Very Highly Toxic
Molluscs	Moderately Toxic	Moderate to High Toxicity
Phytoplankton	Moderately Toxic	Slight to High Toxicity
Zooplankton	Very Highly Toxic	Very Highly Toxic

Table 3-13 - Summary of Acute Toxicity of Zooplankton to Methoxychlor by PAN

Common Name	Scientific Name	Avg LC_{50} (μg/L)	LC_{50} Std Dev	Number Studies	Avg Species Rating	Outlier Group?
Water flea	*Daphnia magna*	408.6	669.7	13	Highly Toxic	Outlier
Scud	*Gammarus fasciatus*	3.47	1.84	7	Very Highly Toxic	
Scud	*Gammarus lacustris*	1.58	0.95	6	Very Highly Toxic	
Scud	*Gammarus pseudolimnaeus*	2.77	2.52	16	Very Highly Toxic	
Grass shrimp, freshwater prawn	*Palaemonetes kadiakensis*	14.0	15.6	8	Very Highly Toxic	
Marsh grass shrimp	*Palaemonetes vulgaris*	14.7	1.89	3	Very Highly Toxic	

Table 3-14 - Summary of Acute Toxicity of Crustacea to Methoxychlor by PAN

Common Name	Scientific Name	Avg LC_{50} (µg/L)	LC_{50} Std Dev	Number Studies	Avg Species Rating	Outlier Group?
Aquatic sowbug	*Asellus aquaticus*	1.33	0.47	3	Very Highly Toxic	
Aquatic sowbug	*Asellus brevicaudus*	54.2	39.0	5	Very Highly Toxic	
Dungeness or edible crab	*Cancer magister*	204.2	359.9	10	Highly Toxic	Outlier
Bay shrimp, Sand shrimp	*Crangon septemspinosa*	6.00	2.16	3	Very Highly Toxic	
Crayfish	*Orconectes nais*	1.34	1.03	5	Very Highly Toxic	
Crayfish	*Orconectes virilis*	4.60	2.45	2	Very Highly Toxic	
Longwrist hermit crab	*Pagurus longicarpus*	7.67	0.94	3	Very Highly Toxic	
Korean or Oriental shrimp	*Palaemon macrodactylus*	3.61	3.16	2	Very Highly Toxic	
Spot shrimp	*Pandalus platyceros*	25.0		1	Very Highly Toxic	
Northern pink shrimp	*Penaeus duorarum*	2.03	1.04	3	Very Highly Toxic	

3.5. Piperonyl butoxide (PBO)

PAN summarized the acute toxicity of the synergist PBO by organism group Table 3-15. PBO is moderately toxic to most invertebrates, although it is classified as very highly toxic for crustaceans. That classification, however, is based on one test with the northern pink shrimp (*Penaeus duorarum*), where the average species LC_{50} was 1.25 µg/L. The other three crustacean studies referenced found LC_{50}s of 1,600 to 8,004 µg/L (Orme and Kegley, 2004).

Table 3-15 - Summary of Acute Toxicity by Organism Group for PBO by PAN

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Highly Toxic	Moderate to High Toxicity
Annelida	Moderately Toxic	Moderate Toxicity
Crustaceans	Moderately Toxic	Moderate to Very High Toxicity
Fish	Moderately Toxic	Moderate Toxicity
Insects	Moderately Toxic	Moderate Toxicity
Zooplankton	Moderately Toxic	Moderate to High Toxicity

PAN reported that larvae of the Eastern oyster, *Crassostrea virginica*, were immobilized when exposed to an average concentration of 4,100 µg/L PBO for 48 hours. Oyster spat exposed to the synergist for 96 hours became immobilized at an average concentration of 230 µg/L. Hard clam (*Mercenaria mercenaria*) larvae were immobilized when exposed to an average concentration of 330 µg/L for 48 hours. PAN classified PBO as moderately toxic to the oligochaete worm, *Lumbriculus variegates*, based on one study where the LC_{50} was 3,540 µg/L.

Five of the six studies found PBO to be moderately toxic to crustaceans; the exception was Northern pink shrimp, which was more sensitive (Table 3-16). PBO was reportedly moderately to highly toxic to smaller crustaceans found in the zooplankton (Table 3-17).

Table 3-16 - Summary of Acute Toxicity of Crustacea to PBO by PAN

Common Name	Scientific Name	Avg LC_{50} (ug/L)	LC_{50} Std Dev	Number Studies	Avg Species Rating
Aquatic sowbug	*Asellus brevicaudus*	8,004	5,651	3	Moderately Toxic
Shrimp	*Palaemon paucidens*	3,500		1	Moderately Toxic
Northern pink shrimp	*Penaeus duorarum*	1.25		1	Very Highly Toxic
Kuruma shrimp	*Penaeus japonicus*	1,600		1	Moderately Toxic

Table 3-17 - Summary of Acute Toxicity of Zooplankton to PBO by PAN

Common Name	Scientific Name	Avg LC_{50} (ug/L)	LC_{50} Std Dev	Number Studies	Avg Species Rating
Water flea	*Ceriodaphnia dubia*	665.0	335.0	2	Highly Toxic
Water flea	*Daphnia magna*	2,830		1	Moderately Toxic
Water flea	*Daphnia pulex*	1,620		1	Moderately Toxic
Scud	*Hyalella azteca*	530.0		1	Highly Toxic

4. Laboratory versus In Situ Pesticide Toxicity Testing

Milam *et al.* (2000) suggested that although standard laboratory tests of 24 to 96 hour duration (bioassays) are useful for acute toxicity evaluations, they "seldom reflect field conditions where exposure may range from a few minutes to several weeks." The authors found acute effects for larval mosquitoes (*Anopheles quadrimaculatus*) did not occur except at concentrations above those where effects were measured for non-target species (Table 4-1). Specifically, up to 31.4 µg/L of pesticide was needed to kill the mosquitoes, but substantial mortality for non-target organisms occurred at concentrations as low as 2.7µ/L, although the same pesticides were generally not tested for mosquitoes and non-target organisms.

This study does raise the issue that *in situ* testing may generate different results than standard laboratory toxicity testing. One reason for this could be that water collected from treated ditches and stagnant areas following a storm event might contain other chemicals (including non-vector control pesticides) that could confound the effects of some of the products tested. These other chemicals could be contributors to cumulative toxicity.

Although the cumulative toxic effects referred to by Milan *et al.* (2000) may be real, most toxicity research is conducted under controlled laboratory conditions specifically to isolate the effects of individual chemicals. It is, however, important to remember there is a potential for cumulative toxicity, and that this can have real-world impacts, although such data are generally unavailable.

Table 4-1 - LC_{50} values for invertebrates and mosquitoes from acute 24- and 48-h toxicity tests

Chemical	Pesticide	Organism	24-hr LC_{50}	48-hr LC_{50}
Permethrin	Biomist w/oil	*Ceriodaphnia dubia*	--	38.1 mg/L
		Daphnia pulex	--	1.20 mg/L
		Daphnia pulex	--	16.32 mg/L
	Biomist	*Daphnia pulex*	>1.0 mg/L	--
	Permanone	*Ceriodaphnia dubia*	--	0.60 µg/L
		Anopheles quadrimaculatus	--	1.0µ/L
Resmethrin	Scourge	*Ceriodaphnia dubia*	--	0.85
		Anopheles quadrimaculatus	--	1.0 µ/L
Microbial	B.t.i. granule	*Daphnia magna*	626.6 mg/L	--
		Daphnia pulex	--	0.34 mg/L
	B.t.i. liquid	*Daphnia pulex*	--	3.90 µg/L
		Anopheles quadrimaculatus	--	7.6 µg/L
Chloropyrifos	Durban	*Anopheles quadrimaculatus*	--	1.0µ/L
Temephos	Abate	*Anopheles quadrimaculatus*	--	31.4 µg/L
Malathion	Malathion	*Anopheles quadrimaculatus*	--	1.0 µg/L

From Milam *et. al.* (2000)

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APPENDIX A: ABOUT THE PESTICIDE ACTION NETWORK PESTICIDE DATABASE

ABOUT THE PESTICIDE ACTION NETWORK PESTICIDE DATABASE

(From the PAN website, www.pesticideinfo.org)

Overview

The PAN Pesticide Database brings together a diverse array of information on pesticides from many different sources, providing human toxicity (chronic and acute), ecotoxicity and regulatory information for about 6,400 pesticide active ingredients and their transformation products, as well as adjuvants and solvents used in pesticide products.

This database of active ingredients has been integrated with the U.S. EPA product databases, which provide information on formulated products (the form of the pesticide that growers and consumers purchase for use) containing the active ingredients. The information is most complete for pesticides registered for use in the United States.

References to data sources can be found by clicking on the underlined term describing the data or by going to the **Pesticide Tutorial** from the sidebar menu of this page or from the home page.

Accuracy of the data

To ensure that our data are accurate and have been peer reviewed by scientists, we do not use anecdotal evidence of any sort in the PAN web site. All of our information is backed up by rigorous scientific studies and most of the data are taken from official sources of weight-of-the-evidence-type evaluations when they are available. When official lists do not exist, we have presented a variety of original data sources that refer to the peer-reviewed scientific literature. The specifics are highlighted below for each toxicity type.

Techniques Used to Ensure Data Accuracy

Most of the toxicity information comes directly from official sources such as the U.S. Environmental Protection Agency (U.S. EPA), World Health Organization (WHO), National Toxicology Program (NTP), National Institutes of Health (NIH), International Agency for Research on Cancer (IARC), the European Union (EU), and the State of California.

The fact that most of the data are available in electronic form nearly eliminates the possibility of data entry errors, so if our official data sources are correct, the PAN data are too. Interestingly, what we have found is that these official lists themselves have a number of errors. The fact that we are comparing multiple lists allows us to find and correct errors in identifying numbers, chemical classifications and use types. Because of this extensive cross-comparison between data sets, errors and inconsistencies are quickly found and corrected.

Validation and Review

For validation and review, the Beta version of every release of the database is sent to about 200 individuals with a request for feedback and criticism. We typically receive about 50 formal reviews back from chemists, toxicologists, biologists, geologists, activists, and regulators, and modify the database based on their suggestions.

In short, we believe our data set of summary pesticide information to be the best one available on the Internet. Where we've interpreted the original information to create summaries or comparisons, we have clearly documented our methods so the technique is transparent and the user can judge for him/herself the validity of the approach.

Carcinogenicity

We utilize five different sources of carcinogenicity data: The International Agency for Research on Cancer, the U.S. National Toxicology Program, California's Proposition 65 list, the U.S. EPA Toxics Release Inventory list, and the U.S. EPA Office of Pesticide Programs List of Chemicals Evaluated for Carcinogenic Potential. The ratings presented are taken directly from the source list and all are based on weight-of-the-evidence evaluations. Cancer data are current as of October 3, 2002. More detail about cancer listings can be found here.

Acute Toxicity

We utilize up to four different sources of acute toxicity data: The World Health Organization's Hazard Rankings, the U.S. National Toxicology Program acute toxicity data, U.S. EPA ratings (Category I-IV) of technical grade pure active ingredients (where a consensus rating exists) and

Material Safety Data sheets. Acute toxicity data are current as of October 3, 2002. More detail about acute toxicity data can be found here.

Reproductive and Developmental Toxicity

Information on reproductive and developmental toxicants is obtained from two sources, the State of California's Proposition 65 list of chemicals and the U.S. EPA Toxics Release Inventory (TRI) list. Again, because the data are entered electronically, our list is as correct as the source lists. Reproductive and developmental toxicity data are current as of October 3, 2002. More detail about the Proposition 65 list can be found here and about the U.S. EPA TRI list here.

Endocrine Disruption

It is more difficult to find an "official" list of endocrine disrupting chemicals, since the U.S. EPA has not yet created such a list, although the screening of chemicals to determine the endocrine-disrupting abilities of a large number of chemicals is in progress. Our endocrine disruptor list was taken from a variety of sources summarizing endocrine disrupting effects of chemicals. All of these summary lists are based on research in the scientific literature where endocrine disrupting effects have been observed for humans or animals. Endocrine disruption data are current as of October 3, 2002. More detail about the endocrine disruptors can be found here.

The European Union recently released (July 2001) a comprehensive list of possible endocrine disruptors, complete with references to over 900 original peer-reviewed journal articles. We plan to include this list sometime in 2002 or early 2003.

Neurotoxic Cholinesterase Inhibitors

The list of cholinesterase inhibitors started with California Department of Pesticide Regulation and U.S. EPA lists; however, these documents only include pesticides registered for use in the U.S. There are many organophosphorus pesticides used in developing countries which we designated as cholinesterase inhibitors based on chemical structure. Because the mechanism of action of the organophosphates and phosphorothioates has been determined, a particular chemical structure can be reliably associated with the toxic effects associated with cholinesterase inhibition.

The carbamate pesticides were more difficult, since a slight change in chemical structure renders them inactive as cholinesterase inhibitors. For these, Materials Safety Data Sheets (MSDSs) were used to designate a pesticide as a cholinesterase inhibitor. Cholinesterase inhibitor data are current as of October 3, 2002. More detail about cholinesterase inhibitors here.

Regulatory Status

The regulatory status of a particular chemical (active or cancelled) for the U.S. was taken directly from U.S. EPA's Pesticide Product Information System (PPIS) product data and California Department of Pesticide Regulation's list of active ingredients. U.S. EPA product information data are current as of September 26, 2002. Our information on Prior Informed Consent (PIC) and Persistent Organic Pollutant chemicals is from the United Nations Environment Programme (UNEP) web sites and is current as of September 26, 2002. Information on active ingredients registered for use in countries around the world was obtained from the appropriate government authority. The currency of each of these data sets is provided in the references section of each country page. More detail about regulatory information here.

Ecotoxicity

All Ecotoxicity information is taken from the U.S. EPA AQUIRE database. We have simplified the data somewhat by summarizing some information (see below in Value-Added Features), but the original data are available for the user to evaluate as well. The ecotoxicity data are current as of September 26, 2002. More details about ecotoxicity can be found here.

California Pesticide Use Reporting Data

We obtain the California PUR data directly from the Deparment of Pesticide Regulation and do a number of data processing steps to clean up the data and summarize the information by all combinations of crop, chemical, and location. Our methodology for processing the data is described in detail here. The California PUR data are current as of October 3, 2002. We anticipate the 2001 data to be released before the end of 2002.

Value-Added Features

Two additional features of the database are a result of our own work, rather than simply bringing existing lists together. These are the Ecotoxicity Summaries and the Parent Chemical/Related chemical groupings.

Ecotoxicity Summaries

The Ecotoxicity Summaries provide a narrative ranking of toxicity by both organism group and by species. For example, a look at the Chemical Information page for Diazinon shows the following summary information by organism group:

Organism Group	Average Acute Toxicity	Acute Toxicity Range
Amphibians	Slightly Toxic	Moderately to Slightly Toxic
Annelida	Moderately Toxic	Moderately Toxic
Crustaceans	Highly Toxic	Very Highly to Moderately Toxic
Fishes	Moderately Toxic	Very Highly to Slightly Toxic
Aquatic Insects	Highly Toxic	Very Highly to Moderately Toxic
Molluscs	Moderately Toxic	Very Highly to Slightly Toxic
Zooplankton	Highly Toxic	Very Highly to Moderately Toxic

By giving both the range and the average rating, a summary view is provided with no loss of the extreme ends of the data set. The original data are also just one click away, where the user can view each individual study. Summaries are also provided by species. Details on how the summaries were created can be found here.

Parent/Related Chemical Groupings

The Parent/Related Chemical groupings provide the user with information about related chemicals. Many compounds in the database are chemically similar to each other; however, typically only one of a group of similar compounds has been evaluated for its toxicological properties. We call this compound the "parent." In many (but not all) cases, other related chemicals will have similar toxicological effects and/or similar chemical reactivity. We wanted to formally group similar compounds to make it possible for the user to:

- Know which compounds are chemically similar
- View the toxicological properties of the parent compound when evaluating a related compound

The Chemical Classification (organophosphorus compounds, urea compounds, etc.) is one way of broadly categorizing chemicals. By creating Parent/Related Chemical rollup categories, we have taken this classification scheme to a finer level of detail. Details about how Parent/Related Chemical groups were assigned can be found here.

Definitions and References

All data sources are fully referenced, and an enterprising user will be able to very quickly obtain the original data sets. The Pesticide Tutorial overview page provides an index to the different data sets, also accessible by clicking on any of the underlined terms on the data pages. The reference documents define the terms, cite the data sources, and discuss the accuracy, currency, and comprehensiveness of each source. There are also links to the original data source, if the data are on the web.