

Task 3 Literature Review Book 8 Part 1: Mosquito Control Pesticides and Fish

Prepared for.

Suffolk County Department of Public Works
Suffolk County Department of Health Services
Suffolk County, New York

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LIST OF ABBREVIATIONS AND ACRONYMS

BPC Board of Pesticide Control

Bs Bacillus sphaericus
Bt Bacillus thuringiensis

Bti Bacillus thuringiensis var. israelensis

cfu colony forming units

DDT 1,1,1,-trichloro-2,2-bis(p-chlorophenyl)ethane

EC Emulsifiable Concentrate

EC₅₀ Effective concentration for 50% of organisms

EXTOXNET Extension Toxicology Network

LC₅₀ Lethal Concentration for 50 percent of organisms

LD Lethal Dose

LD₅₀ Lethal Dose for 50 percent of organisms

LOEC Lowest Observed Effect Level

MATC Maximum Acceptable Toxicant Concentration

mg/L milligrams per liter or parts per million

MMF Monomolecular Film

MSF Monomolecular Surface Films

ng/L nanograms per liter or parts per trillion NOEC No Observed Effect Concentration

NOEL No Observable Effect Level PAN Pesticide Action Network

PBO Piperonyl Butoxide

PIP Pesticide Information Profile

ppb Parts Per Billion ppm Parts Per Million

RED Reregistration Eligibility Decision
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

The Scoping process for the Suffolk County Vector Control and Wetlands Management Long-Term Plan and Generic Environmental Impact Statement, as well as comments received from the Citizens Advisory Committee, showed a need to discuss potential impacts from vector control pesticides on two subsets of aquatic organisms (fish and invertebrates), and to determine potential impacts on the food web as a whole. This report is intended to document research findings showing toxicity to fish associated with pesticides that are being considered for use by the Long-Term Plan. Other reports in Book 8 will address aquatic invertebrate and broader ecological issues.

This report accessed several databases to develop these data sets. To simplify characterizations of the results collected in them, some of these databases report the concentrations associated with impacts to organisms in qualitative terms – such as "slightly toxic," "very toxic," or "extremely toxic," or similarly-worded phrases. These are short-hand notions to allow for very simplified comparisons among different compounds. It must be understood that these compounds are all applied at different rates, often degrade in differing ways under specific conditions, and may partition and otherwise disperse in the environment entirely differently from each other. Therefore, it is unlikely that these compounds can be directly compared in terms of these shorthand descriptions, partially because these compounds are not intended to be applied in the same fashion, and so will not occur in the environment at the same concentrations. It must also be understood that the actual use of the pesticide will only have a toxic impact (as described) if it is found in the environment at the reported concentration, for the length of time that the particular test was staged.

The Pesticide Action Network (PAN) database was extensively relied on for this report. PAN explicitly describes its mission as the elimination of pesticide use. The authors of this report have not accessed the underlying research reported by PAN, and have assumed that some degree of scientific assessment of the methods and analyses that generated the reported results has occurred. It is assumed that PAN diligently sought out results that indicate the most severe impacts on organisms from use of the particular chemicals, in line with its stated goal, and that

the toxicities reported by PAN therefore constitute a worst case for potential impacts from these compounds. Impact assessments associated with later portions of the project may be compelled to further investigate any toxicities that are unique to PAN, and not generally reported in other databases.

Vector control pesticides can affect fresh water and marine fish by causing immediate acute toxicity on exposure. If these agents are persistent in the environment, they can cause chronic toxicity. Pesticides can also affect the organisms that fish consume, and so have an indirect impact on fish populations.

The potential toxicity of these agents on fish 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 LC₅₀, is calculated from acute toxicity tests. USEPA requires special labeling for outdoor use pesticides with an acute LC₅₀ of one part per million (1 ppm) or an EC₅₀, effective concentration, of 1 ppm for aquatic invertebrates. The EC₅₀ is that concentration that causes a 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]."

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 LC₅₀s, following USEPA protocols:

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

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, *Bacillus thuringiensis* variety *israelensis* (*Bti*), and monomolecular surface films (MSF). Very little information on *B. sphaericus* (*Bs*) was found, and so it was not specifically discussed. Adulticides were reviewed including naled, malathion, pyrethrin, permethrin, resmethrin, and sumithrin, and the synergist, piperonyl butoxide. The barrier treatment, garlic oil, was not researched, as it is generally found to be non-toxic to fish and invertebrates.

The following summarizes the reported results:

<u>Temephos</u> - Temephos is an organophosphate, classified by USEPA as slightly toxic. It breaks down rapidly in water and disappears in two days in oysters. The US Fish and Wildlife Service (USFWS) reported that the pesticide is moderately toxic to fish. It accumulates in fish tissues, but the effect is reversible. PAN found temephos to be slightly to moderately toxic to most fish tested. The exception was the mummichog (*Fundulus heteroclitus*), one of the most common fish of the estuarine marshes. PAN also reported that the temephos breakdown product, dimethyl phosphate, is slightly toxic.

<u>Methoprene</u> – USEPA removed the "do not use in fish-bearing waters" label restriction from all solid methoprene mosquito products in 2001. New York continues to prohibit the use of sustained release methoprene formulations to fish-bearing waters due to concerns over the teratogenicity (related to or causing malformations of an embryo or larva) of its breakdown products. Methoprene ranges from not acutely toxic to slightly toxic to moderately toxic, depending on the species tested.

<u>Bti</u> - Bacillus thuringiensis var. israelensis is a bacterium. USEPA reported no toxicity or pathogenicity to fresh water and salt water test organisms. EXTOXNET also concluded that Bti is practically nontoxic to fish.

Monomolecular Surface Films - MSFs are spread over the surface of a water body to change the surface tension and, thus, prevent larvae and pupae from breathing. Summary reports found that MSFs do not affect organisms that use gills to breathe and that oxygen continues to dissolve into the water, leaving fish unaffected. PAN found MSFs to range from not acutely toxic to slightly toxic. MSFs may impact non-target organisms that use the surface film, and some MSFs are registered for control of midges, an important food item for some fish.. While this is not strictly a toxic effect, it can still have an impact. There seems to be relatively little literature on this effect.

<u>Naled</u> - Naled is an organophosphate pesticide classified by EXTOXNET as highly toxic to moderately toxic to fish. PAN classified naled as moderately to very highly toxic to fish. The species with the greatest reported sensitivity to naled is the Western mosquitofish (*Gambusia affinis*), which is commonly stocked to consume mosquito larvae. Naled has a half-life of approximately two days in water, and degrades to dichlorvos. Ultraviolet light increases dichlorvos toxicity by five to 150 times. Dichlorvos does not significantly bioaccumulate in fish. It remains in solution, does not adsorb to sediments, and degrades primarily by hydrolysis, with a half-life of approximately four days in lakes and rivers.

Malathion - Malathion is a nonsystemic, wide-spectrum organophosphate neurotoxin that inhibits the action of the enzyme cholinesterase, required for the transmission of nerve impulses. Malathion has a wide range of 96-hour LC₅₀s in fish, ranging from slightly toxic for goldfish to very highly toxic in walleye, sheepshead minnow, threespine stickleback, inland silverside, and striped bass.

<u>Pyrethrin</u> - Pyrethrins are natural insecticides produced by the chrysanthemum plant. Synthetic derivatives, called pyrethroids, have been developed. Both natural pyrethrins and pyrethroids are swiftly detoxified by insect enzymes, allowing recovery despite exposure to the pesticides. To delay the action of the enzyme so that a lethal dose is assured, organophosphates, carbamates, or synergists such as piperonyl butoxide (PBO) are added. Natural pyrethrin is classified as extremely toxic to aquatic life" by EXTOXNET. Species noted as being at risk include bluegill and lake trout. Natural pyrethrins are fat soluble, but they easily degrade when exposed to sunlight and so do not bioaccumulate.

<u>Permethrin</u> – Permethrin is a pyrethroid, and is considered very highly toxic by PAN to all fish species tested, except the common carp.

Resmethrin - Resmethrin, a pyrethroid, is classified by USEPA as a Restricted Use Pesticide for applications at or near aquatic sites because of potential fish toxicity. PAN classified the pesticide as very highly toxic to fish, with toxicities at or near 10 parts per billion.

<u>Sumithrin</u> - Sumithrin, also known as phenothrin, is classified by PAN as very highly toxic to fish. The Maine Board of Pesticide Control listed research showing that LC_{50} values for killifish were dependent on the isomer tested.

Piperonyl Butoxide – PAN classifies piperonyl butoxide as "moderately toxic" to fish.

It should be noted that although standard laboratory tests are useful for acute toxicity evaluations, they may not reflect field conditions where exposures range from minutes to weeks. Water collected from the field may contain other chemicals that could confound the effects of some of the pesticides tested and contribute to cumulative toxicity.

1. Introduction

1.1. USEPA Guidelines

Vector control pesticides generally affect fresh water and marine fish in two ways. There may be acute toxicity immediately on exposure or chronic toxicity for those agents that persist. Additionally, there may be impacts on the organisms that fish rely on for food. The potential toxicity of vector control agents on the aquatic environment, specifically to fish, is addressed as part of the registration process. As part of the USEPA pesticide 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 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) in the formulation. They include:

- 1. avian oral LC (with mallard or bobwhite quail),
- 2. avian dietary LC_{50} (mallards),
- 3. avian dietary LC_{50} (bobwhite quail),
- 4. fresh water fish LC_{50} (rainbow trout),
- 5. fresh water fish LC₅₀ (bluegill sunfish),
- 6. acute LC₅₀ fresh water 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, and 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.

the dermis and/or scarring)

Skin

Irritation

irritation at 72 hours

(no irritation or slight

erythema)

Although USEPA includes environmental hazards in its overall evaluation of pesticides, pesticides receive a general category rating by human toxicity characteristics. 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.

Study Category I Category II Category III Category IV > 500 thru 5000 mg/kg > 5000 mg/kgAcute Oral Up to and including 50 mg/kg > 50 thru 500 mg/kg Acute 2000 thru 5000 > 5000 mg/kg Up to and including 200 mg/kg > 200 thru 2000 mg/kg Dermal mg/kg > 0.5 thru 2 mg/liter Acute Up to and including 0.05 mg/liter > 0.05 thru 0.5 > 2 mg/liter Inhalation¹ mg/liter Corneal involvement Primary Corrosive (irreversible Corneal involvement or Minimal effects destruction of ocular tissue) or or other eye irritation clearing in less than Eye other eye irritation corneal involvement or irritation clearing in 8-21 days 24 hours Irritation clearing in 7 days or persisting for more than 21 days Primary Corrosive (tissue destruction into Severe irritation at 72 Moderate irritation at Mild or slight

Table 1 - USEPA Toxicity Categories

72 hours (moderate

erythema)

Table 2 - Signal word requirements associated with toxicity classes

hours (severe

erythema or edema)

Toxicity	Signal
Category	Word'
I	DANGER
II	WARNING
III	CAUTION
IV	CAUTION

USEPA has produced interpretations of the overall toxicity of the tested compounds. These shorthand descriptions are derives differently depending on the mode of exposure and kind of organism. Appendix A describes the classification process. USEPA (2003) requires the following labeling statement for outdoor use pesticides containing an active ingredient that for acute exposures causes a 50 percent mortality at a concentration of one part per million (ppm) ($LC_{50} = 1$ ppm) or for aquatic invertebrates (including estuarine species such as oyster and mysid shrimp) causes a non-lethal effect at a concentration of 1 ppm in 50 percent of the organisms (EC_{50}):

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

¹4-hr exposure

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 the following additional labeling statements, although the aquatic toxicity of the specific product may lead to more or less stringent statements.

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 washoff 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."

USEPA cites two extremes of aquatic toxicity between which all mosquito control products must use the labels described above. *Bacillus thuringiensis* (*Bt*) products, which are considered nontoxic 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."

1.2. Data Sources

The following 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

A summary of ecotoxicity data is presented for each pesticide and by taxonomic groups by 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."

It should be noted that, as an organization, PAN holds a particular viewpoint regarding pesticides. PAN states on its website that: "

Pesticides are hazardous to human health and the environment, undermine local and global food security and threaten agricultural biodiversity. Yet these pervasive chemicals are aggressively promoted by multinational corporations, government agencies, and other players in this more than \$35 billion a year industry. [PAN] works to replace pesticide use with ecologically sound and socially just alternatives."

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 3. 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 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 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 4 - Pesticide Information Available from EXTOXNET

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

1.2.3. Maine Board of Pesticide Control

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:

- Board of Pesticide Control;
- 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 fresh water invertebrates. It includes a large quantity of data for some compounds such as malathion, naled, resmethrin, *Bacillus thuringiensis* var. *israelensis*, methoprene, and temephos, and less data on others such as permethrin, phenothrin, *B. sphaericus (Bs)*, and monomolecular films (MMF). 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

Paul and Sinnott (2000) prepared graphic illustrations of the relative toxicity of commonly used vector control chemicals based on the "toxicity index." The Toxicity Index is derived by dividing the rate at which the pesticide is applied by the lowest recorded LC₅₀. The smaller the index, the less likely the risk of toxicity. Specific chemical toxicities are discussed below.

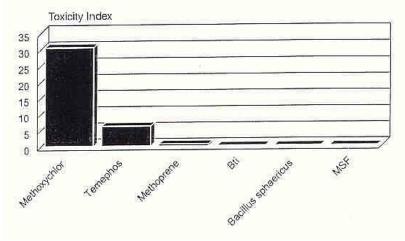


Figure 1 - Relative toxicity of larvicides to fish From Paul and Sinnott (2000)

Methoxychlor and temephos demonstrate the highest relative toxicity of the larvicides. Methoxychlor is not being considered for use in the Long-Term Plan.

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. When applied at 0.1 ppm directly to the water for use as a larvicide, it will not harm most non-target aquatic insects, and does not pose a significant threat to fish (Paul and Sinnott, 2000).

EXTOXNET cites a study that reports that temephos has the most adverse effect on rainbow trout with an $LD_{50} = 0.35$ mg/L and 3.49 mg/L for emulsifiable concentrate and technical grade compound of temephos, respectively (EXTOXNET, 1996a). Table 5 is the summary of data collected by the Maine BPC.

Table 5 - Toxicity of Temephos to Fish by Maine BPC

Warm water fish LC ₅₀ (Median Lethal Concentration)	Cold water fish LC ₅₀
Bluegill Sunfish;	Rainbow trout:
96 hr $LC_{50} = 21,800$ ppb Technical Grade Active	96 hr LC ₅₀ = 3,490 ppb (TGAI) (1, 2)
Ingredient (TGAI*) (1, 2)	96 hr $LC_{50} = 580$ ppb (EC) (1)
96 hr LC ₅₀ = 1,140 ppb Emulsifiable concentrate 43%	160 ppb (EC) (2)
$(EC^{**})(1,2)$	Cut throat trout:
Fathead minnow:	1,279 ppb (2)
31,100 ppb (2)	Brook trout:
Channel catfish:	12,800 ppb (2)
10,000 ppb (2)	5,000 ppb (WP 50%) (2)
3,230 (EC 46%) (2)	Lake trout:
Largemouth bass:	3,650 ppb (2)
1,440 ppb (EC 46%) (2)	Coho salmon:
	350 ppb (EC 46%) (2)
	Atlantic salmon:
	21,000 ppb (2)
	(6,700 ppb (EC 46%) (2)

^{*} TGAI = Technical Grade Active Ingredient

Another study of the effects of temephos on bluegills (*Lepomis macrochirus*) was performed by Sanders *et. al.*, (1981). They found that 11 gram, 83 mm bluegills exposed to four to 40 µg/L of temephos (43% active ingredient) in a static water system accumulated the pesticide with no reported toxic endpoint.

PAN summarized a number of studies of the acute toxicity of temephos to fish that are summarized in Table 6. PAN also reported that the temephos breakdown product, dimethyl phosphate, is slightly toxic based on the results of a 96-hour LC₅₀ study of the fathead minnow, *Pimephales promelas*. The study found that the mean toxic dose was 18,000 μg/L.

^{**}EC = Emulsifiable Concentrate

⁽¹⁾ USEPA (1999)

⁽²⁾ TOXNET (2004a)

Number Common Name Scientific Name Average LC₅₀ Average Rating **Std Dev Studies** $LC_{50} (\mu g/L)$ 7,500 Moderately Toxic Japanese eel Anguilla japonica Killifish Aplocheilus lineatus 1,482 236.5 2 Moderately Toxic 2,000 Moderately Toxic Barb Barbus barbus plebejus 1 15,300 Slightly Toxic Carp, hawk fish Cirrhinus mrigala 1 Common, mirror, colored, carp Cyprinus carpio 33,500 1 Slightly Toxic Esox lucius 390 Highly Toxic Northern pike 1 40 Mummichog Fundulus heteroclitus 1 Very Highly Toxic Gambusia affinis 1,753 3,029 4 Moderately Toxic Western mosquitofish Eastern mosquitofish Gambusia holbrooki 39,500 1 Slightly Toxic Channel catfish Ictalurus punctatus 8,025 4,295 11 Moderately Toxic 12,266 Bluegill Lepomis macrochirus 11,612 11 Slightly Toxic 9 Largemouth bass Micropterus salmoides 5,289 3,779 Moderately Toxic Striped bass Morone saxatilis 1,000 2 Moderately Toxic Striped mullet 600 Mugil cephalus Highly Toxic Cutthroat trout Oncorhynchus clarki 1,814 1,165 5 Moderately Toxic 9 Moderately Toxic Oncorhynchus kisutch 1,604 952.8 Coho salmon, silver salmon Rainbow trout, donaldson trout Oncorhynchus mykiss 3,217 3,559 27 Moderately Toxic Pimephales promelas 56,067 31,066 3 Slightly Toxic Fathead minnow Slightly Toxic Poecilia reticulata 59,450 82,198 4 Guppy Atlantic salmon Salmo salar 24 Slightly Toxic 13,848 5,180 Brook trout Salvelinus fontinalis 14,960 10 Slightly Toxic 6,765 ake trout, siscowet Salvelinus namaycush 3,994 2,768 Moderately Toxic

Table 6 - Acute Aquatic Toxicity for Temephos to Fish by PAN

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. USEPA review of data submitted between 1993 and 1996 resulted in the removal of the "do not use in fish-bearing waters" label restriction from all solid methoprene mosquito products (USEPA, 2001a). However, New York State continues to prohibit the use of sustained release methoprene formulations to fish-bearing waters due to concerns over the teratogenicity (related to or causing malformations of an embryo or larva) of its breakdown products (Antunes-Kenyon and Kennedy, 2001).

The early life stages of the fathead minnow (*Pimephales promelas*) were subjected to various concentrations of methoprene by Ross *et al.* (1994). Newly spawned minnow eggs were exposed to concentrations ranging from 13 to 160 µg/L (S)-methoprene in a flow-through system. The

researchers found no significant reductions at p<0.05 for hatchability, fry survival, or total survival when compared to controls. However, concentrations greater than 84 μ g/L resulted in significant (p<0.05) reductions in length and weight. These results meant that the no observed effect concentration (NOEC) was 48 μ g/L and the lowest observed effect concentration (LOEC) was 84 μ g/L. The maximum acceptable toxicant concentration (MATC) (the geometric mean of the NOEC and LOEC) was 63.5 μ g/L. Table 7 shows the Maine BPC data.

Table 7 - Toxicity of Methoprene to Fish from Maine BPC

Warm water fish LC 50 (Median Lethal Concentration)	Cold water fish LC 50
Bluegill sunfish:	Rainbow trout:
96 hr LC 50 = 1,520 ppb (1)	96 hr LC 50 > 50,000 ppb (1)
96 hr TL 50 (median threshold limit) = 4,600 ppb (static) (2)	Juvenile Rainbow trout:
LC $50 > 370 \text{ ppb } (3)$	LC 50 = 106,000 ppb (2)
Channel catfish:	LC 50 = 760 ppb (3)
TL 50 > 100,000 ppb (static) (2)	LC 50 = 106,000 (2)
Fathead minnow:	Trout:
LEL (Lowest Effective Level) = 84 ppb (3)	TL 50 = 4,400 ppb (static) (2)
NOEL (No Observable Effect Level) = 48 ppb (3)	TL 50 = 106,000 ppb (static aerated) (2)
	Coho salmon:
	LC 50 = 86,000 ppb (2)

- 1) USEPA (1991)
- 2) Vershcueren, K. (1983)
- 3) Sandoz (1996)

According to PAN, methoprene was found to be not acutely toxic to the mummichog, a common Long Island wetland species, and slightly toxic to the fathead minnow, a species frequently used in bioassay toxicity tests (Table 8). It was moderately toxic to the bluegill, a species common to fresh water water bodies on Long Island.

Table 8 - Toxicity of Methoprene to Fish by PAN

Common Name	Scientific Name	Average LC ₅₀ (ug/L)	LC ₅₀ Std Dev	Number Studies	Average Species Rating
Mummichog	Fundulus heteroclitus	124,950		1	Not Acutely Toxic
Channel catfish	Ictalurus punctatus	100,000		3	Not Acutely Toxic
Bluegill	Lepomis macrochirus	9,638	10,473	6	Moderately Toxic
Coho salmon, silver salmon	Oncorhynchus kisutch	86,000		1	Slightly Toxic
Rainbow trout, donaldson trout	Oncorhynchus mykiss	44,361	44,673	9	Slightly Toxic
Fathead minnow	Pimephales promelas	10,000		5	Slightly Toxic
Australian blue-eye	Pseudomugil signifer	4,000		1	Moderately Toxic

In a test conducted by researchers at Southampton College in 2003 (Southampton College, 2004), the growth and survival of caged *Cyprinodon variegates* (sheepshead minnows) were

measured following exposure to a methoprene application. Growth and survival of the fish exposed to the pesticide were lower than those of fish in the control marshes. Methodological uncertainties, such as pesticide concentrations, however, make it impossible to identify the reasons for the differences. These results can be compared to those generated by the Long-Term Plan in the "Caged Fish Study," reported on as part of Task 12.

2.3. Bacillus thuringiensis var. israelensis

Bacillus thuringiensis var. israelensis is classified by the 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 its Reregistration Eligibility Decision (RED) for *Bti*, USEPA (1998a) reported on the potential impacts to non-target fresh water and marine fish. During fresh water testing no toxicity or pathogenicity was evident in the bluegill or the rainbow trout. For estuarine and marine animal studies, USEPA found that *B. thuringiensis* did not demonstrate toxicity or pathogenicity to sheepshead minnows (Table 9).

Table 9 - Toxicity of Bti to Fish from Maine BPC

Warm water fish LC 50 (Median Lethal Concentration)	Cold water fish LC 50	Estuarine and Marine Toxicity
Bluegill Sunfish:		Sheepshead minnow:
		$NOEL > 2 \times 10^{10} \text{ cfu/g food}$
8.9×10^9 to 1.6×10^{10} colony forming	$> 8.7 \times 10^9 \text{ to} > 1.4 \times 10^{10} \text{ cfu/l}$	$LC_{50} > 7.2 \times 10^9 \text{ cfu/g food}$
	Oral LC ₅₀ $> 5.3 \times 10^9$ to 1.7 x 10^{10}	Oral LC ₅₀ > 2 x 10^{10} cfu/g
Oral LC ₅₀ $> 4.3 \times 10^9$ to 1.3 x 10 ¹⁰	cfu/gram food	
cfu/gram food		

USEPA (1998a)

At label rates, therefore, *Bti* toxicity and infectivity risks to non-target fresh water fish and estuarine and marine animals are minimal to nonexistent. However, USEPA discussed concerns about 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 implemented new 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.

Milam *et al.* (2000) exposed *Gambussia affinis*, the mosquitofish to *Bti* with no acute mortality up to 1 mg/L. Merritt and Wipfli (1999) exposed trout to *Bti* for 24 hours and reported LC₅₀s of 1,500 to 2,000 ppm, depending on the species.

EXTOXNET (1996b) concluded that *Bti* is practically nontoxic to fish. The conclusion was based on:

- rainbow trout and bluegill 96-hour exposures at 560 and 1,000 mg/L, resulting in no adverse effects
- American eel exposures to concentrations 1,000 to 2,000 times expected ambient exposures with no negative impacts
- field observations of brook trout, common white suckers, and smallmouth bass one month after exposure showing no adverse effects.

2.4. Monomolecular Surface Films (MSFs)

MSFs are alcohols comprised of the chemical poly (oxy-1, 2-ethanediyl), alpha-isooctadecylomega-hydroxy. They are spread over the surface of a water body 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 the siphons/tubes, 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 in the water, leaving fish and other aquatic organisms unaffected. The conclusion was that "MSF is not very toxic to aquatic life" and that isostearyl alcohol does not bioaccumulate. They estimated that MSFs degrade within two to ten days.

For MSFs, the USEPA (2000) lists a mean LC₅₀ of 290,000 parts per billion (ppb) for bluegill sunfish and 98,000 ppb for rainbow trout. PAN cited an additional study that reported an LC₅₀ of 300,000 ppb for sheepshead minnows. Based on these tests, PAN assigned MSFs a rating of not acutely toxic for minnows and bluegills and slightly toxic for trout.

3. Adulticides

Paul and Sinnott (2000) prepared graphic illustrations of the relative toxicity of commonly used vector control chemicals based on a toxicity index, which is derived by dividing the rate at which the pesticide is applied by the lowest recorded LC₅₀. The smaller the index, the less likely is the risk of toxicity. Specific chemical toxicities are discussed below.

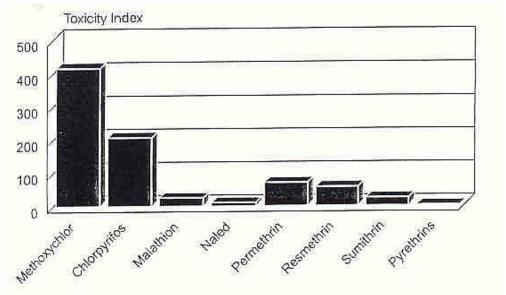


Figure 2 - Relative toxicity of adulticides to fish From Paul and Sinnott (2000)

Methoxychlor and chlorpyrifos have the highest relative toxicity, followed by permethrin and resmethrin. Methoxychlor is not being considered as an adulticide under the Long-Term Plan.

3.1. Naled

Naled is a broad-spectrum organophosphate pesticide in USEPA category I. EXTOXNET (1996b) found naled to be highly to moderately toxic to fish. Reported 96-hour LC₅₀ values were 0.127 mg/L in cutthroat trout, 0.195 mg/L in rainbow trout, and 0.087 mg/L in lake trout. Higher LC₅₀s included 3.3 mg/L in fathead minnow, 2.2 mg/L in bluegill sunfish, and 1.9 mg/L in largemouth bass (Johnson and Finley, 1980). The reported LC₅₀ for goldfish is 2 to 4 mg/L (Kidd and James, 1991). Toxicity values from EXTOXNET, USEPA, and USFWS are found in Table 10. PAN also collected toxicity values for naled (Table 11), classifying it as moderately to

very highly toxic to fish. The species with the greatest reported sensitivity to naled is the Western mosquitofish (*Gambusia affinis*), which is commonly stocked to consume mosquito larvae. Naled was also found to be very highly toxic to lake trout.

Naled rapidly degrades in water, with a reported half-life of about two days (US Public Health Service, 1995). Naled degrades to dichlorvos. USEPA places dichlorvos in toxicity class I - highly toxic, because it may cause cancer and there is only a small margin of safety for other effects (USEPA, 1998b). According to EXTOXNET (1996b):

"Ultraviolet (UV) light makes dichlorvos 5 to 150 times more toxic to aquatic life (US Public Health Service, 1995)...The LC_{50} (96-hour) for dichlorvos is 11.6 mg/L in fathead minnow, 0.9 mg/L in bluegill, 5.3 mg/L in mosquito fish...3.7 mg/L in mummichogs, and 1.8 mg/L in American eels. The LC_{50} (24-hour) for dichlorvos in bluegill sunfish is 1.0 mg/L (USEPA, 1988). Dichlorvos does not significantly bioaccumulate in fish (Howard, 1991)...In water, dichlorvos remains in solution and does not adsorb to sediments. It degrades primarily by hydrolysis, with a half-life of approximately 4 days in lakes and rivers."

Table 10 - Toxicity of Naled to Fish from Maine BPC

Warm water fish LC ₅₀ (Median Lethal Concentration)	Cold water fish LC ₅₀	Estuarine and Marine Toxicity
Bluegill sunfish:	Rainbow trout:	Sheepshead minnow:
96 hr $LC_{50} = 2,200 \text{ ppb } (1)$	96 hr $LC_{50} = 160 - 345$ ppb $(1, 3, 4)$	$LC_{50} = 1,200 \text{ ppb } (1)$
Large mouth bass:	Cutthroat trout:	
96 hr LC ₅₀ = 1,900 ppb (1)	$LC_{50} = 127 \text{ ppb } (1, 3)$	
Fathead Minnow:	Lake trout:	
$LC_{50} = 3,300 \text{ ppb } (1)$	$LC_{50} = 87 \text{ ppb } (1, 3)$	
$LC_{50} = 4,200 \text{ ppb } (2)$	$LC_{50} = 113 \text{ ppb } (2)$	
Channel catfish:		
$LC_{50} = 710 \text{ ppb } (1)$		
Large mouth bass:		
$LC_{50} = 1,900 \text{ ppb } (1,3)$		
Goldfish:		
2,000 to 4,000 ppb (3)		
Early life stage fathead minnow:		
NOEC (No Observable Effect Level) =		
6.9 ppb		
MATC (Maximum Allowable Toxicant		
Concentration) = 10 ppb		
LOEC (Lowest Observed Effect		
Concentration) = 15 ppb (1)		

- (1) USEPA (1997)
- (2) USFWS (1993)
- (3) EXTOXNET (1996b)
- (4) TOXNET (2004b)

Zacco platypus

Moderately Toxic

Common Name Scientific Name Avg Species LC_{50} Number Outlier Avg LC₅₀ (ug/L) **Std Dev Studies Species Rating** Result? Sheepshead minnow Cyprinodon variegatus 1.200 Moderately Toxic Western mosquitofish Gambusia affinis 3.40 0.10 Very Highly Toxic Channel catfish Ictalurus punctatus 873.3 231.0 Highly Toxic 470.0 30.0 Spot Leiostomus xanthurus Highly Toxic 1,301 Bluegill Lepomis macrochirus 1,478 Moderately Toxic Largemouth bass Micropterus salmoides 1.900 Moderately Toxic Striped bass Morone saxatilis 500.0 2 Highly Toxic White mullet Mugil curema 550.0 50.0 Highly Toxic Golden shiner Notemigonus 6,300 200.0 Moderately Toxic Outlier crvsoleucas Cutthroat trout Oncorhynchus clarki 134.0 9.90 3 Highly Toxic Rainbow trout, donaldson Oncorhynchus mykiss 243.7 188.3 19 Highly Toxic trout Medaka, high-eyes Oryzias latipes 3,000 Moderately Toxic 424.3 Fathead minnow Pimephales promelas 3,600 Moderately Toxic Atlantic salmon Salmo salar 165.0 Highly Toxic Lake trout, siscowet Salvelinus namaycush 95.7 12.3 3 Very Highly Toxic

5,200

Table 11 - Toxicity of Naled to Fish by PAN

3.2. Malathion

Oikawa

Malathion is a nonsystemic, wide-spectrum organophosphate insecticide. Malathion is a slightly toxic compound in USEPA toxicity class III. Labels for products containing it must carry the Signal Word CAUTION. It was developed in the 1950's and so is one of the earliest organophosphate insecticides. Malathion is a neurotoxin that affects the nervous system by inhibiting the action of the enzyme cholinesterase, which is required for the transmission of nerve impulses. Malathion is used for the control of sucking and chewing insects on fruits and vegetables, and for mosquitoes and flies. Malathion may also be found in formulations with many other pesticides (EXTOXNET, 1996c)

Malathion has a wide range of 96-hour LC₅₀s in fish (Table 12). Its toxicity is classified by EXTOXNET (1996c) as very highly toxic in the walleye (LC₅₀ = 0.06 mg/L), highly toxic in brown trout (LC₅₀ = 0.1 mg/L) and the cutthroat trout (LC₅₀ = 0.28 mg/L), moderately toxic in fathead minnows (LC₅₀ = 8.6 mg/L), and slightly toxic in goldfish (LC₅₀ = 10.7 mg/L).

PAN collected many studies on the impact of malathion to fish. Table 13, modified from PAN information, lists primarily studies that examined the impact of malathion on fish species found on Long Island, although these species are not necessarily native. Malathion was classified as slightly toxic by PAN to two of the species, eastern mosquitofish and fathead minnows. Malathion was classified as moderately toxic to killifish, carp, northern puffer, and white perch. However, some studies also found that malathion should be classified as highly toxic to killifish or carp. Malathion was classified as highly toxic to the American eel, the mummichog, the western mosquitofish, spot, sunfish, pumpkinseed, bluegill, Atlantic silverside, largemouth bass, mullet, trout, yellow perch, and Eastern mudminnow. Five species were more sensitive, with malathion being classified as very highly toxic:

- sheepshead minnow
- threespine stickleback
- inland silverside
- striped bass
- walleye

According to studies summarized in the Environmental Fate and Exposure section of the Hazardous Substances Database (TOXNET 2004c), malathion is degraded in the atmosphere by reaction with hydroxyl radicals and light with a half life of approximately five hours. Malathion reportedly biodegrades rapidly with 80 to 95 percent biodegradation detected over 10 days. Complete degradation of malathion by biological and physical means is reported to occur after 25 days in estuarine water (Walker, 1976, as cited in TOXNET, 2004c). The same study reported ninety-nine percent of malathion degraded after 18 days. Walker also reported complete degradation in estuarine sediments after three days, considerably more rapidly than in water.

Table 12 - Toxicity of Malathion to Fish from the Maine BPC

Warm water fish	Cold water fish	Estuarine and Marine Toxicity
Bluegill sunfish:	Rainbow trout:	Marine fish:
96 hr LC ₅₀ = 20,000 - 103,000 ppb (1, 2)	96 hr LC ₅₀ = 200,000 ppb (1)	Flow through 48 hr LC ₅₀ = 150 to 330 ppb (4)
96 hr LC ₅₀ , EC formulation = 10 ppb (1)	96 hr LC_{50} = EC formulation 30 ppb	Sheepshead minnow:
96 hr LC ₅₀ 's 20 ppb, 30 ppb, 110 ppb (2)	(1)	Flow through 96 hr LC ₅₀ = 33 ppb (4)
24 hr LC ₅₀ 's = 170 ppb (3), 20 ppb (2)	$96 \text{ hr LC}_{50} = 4 \text{ ppb soap lake strain } (4,$	
Green sunfish:	6) - 200 ppb strains not specified (6, 2)	
96 hr $LC_{50} = 175 \text{ ppb } (2)$	24 hr $LC_{50} = 100 \text{ ppb } (4, 2)$	Eastern mudminnow:
Redear sunfish:	96 hr LC ₅₀ = 68 ppb (2)	96 hr LC ₅₀ = 240 ppb (2)
96 hr $LC_{50} = 62 \text{ ppb } (2)$	Brown trout:	14 day $LC_{50} = 0.140 \text{ ppb } (2)$
Pumkinseed	96 hr $LC_{50} = 100$ ppb (5, 4, 2)	Banded Killifish:
96 hr $LC_{50} = 480 \text{ ppb } (2)$	Cut throat trout:	96 hr LC ₅₀ = 240 ppb (2)
Largemouth bass:	96 hr $LC_{50} = 280 \text{ ppb } (2)$	Mummichog
96 hr LC ₅₀ = 285 ppb, 50 ppb (2)	Lake trout:	96 hr $LC_{50} = 250$ ppb (2)
Striped bass (could be estuarine):	96 hr $LC_{50} = 76 \text{ ppb } (2)$	96 hr $LC_{50} = 240 \text{ ppb } (2)$
96 hr $LC_{50} = 39$ ppb, 14 ppb (2), 60 ppb	Coho salmon:	American eel:
(4)	96 hr $LC_{50} = 170 \text{ ppb } (2)$	96 hr $LC_{50} = 480 \text{ ppb } (2)$
Yellow perch:	96 hr $LC_{50} = 101 \text{ ppb } (2)$	Eel:
96 hr $L\hat{C}_{50} = 263 \text{ ppb } (2)$	Chinook salmon:	96 hr LC_{50} = 82 ppb (2)
White perch:	$96 \text{ hr LC}_{50} = 23 \text{ ppb } (2)$	
96 hr $LC_{50} = 1,100 \text{ ppb } (2)$		
Walleye:		
96 hr LC_{50} = 60 ppb (5), 64 ppb (4)		
Gold fish:		
96 hr $LC_{50} = 10,700$ ppb (2)		
Carp		
96 hr $LC_{50} = 6,590$ ppb (2)		
96 hr $LC_{50} = 1,900 \text{ ppb } (2)$		
Black bullhead:		
96 hr LC_{50} = 12,900 ppb (2)		
Channel catfish:		
96 hr $LC_{50} = 8,970$ ppb (2)		
Tilapia mossambica		
48 hr $LC_{50} = 367 \text{ ppb } (2)$		
Guppies		
96 hr $LC_{50} = 1,200 \text{ ppb } (2)$		
Fathead minnow		
96 hr $LC_{50} = 8,650$ ppb (2)		
Gasterostrus aculeatus (three spine		
stickleback (3)		
24 hr $LC_{50} = 76.9 \text{ ppb } (2)$		

- (1) USEPA (1988a)
- (2) TOXNET (2004c)
- (3) Vershcueren, K. (1983)
- (4) USEPA (2001b)
- (5) Extoxnet (1996c)
- (6) Mayer and Ellersieck (1986)

Table 13 - Toxicity of Malathion to Fish by PAN

Common Name	Scientific Name	Avg Species LC ₅₀ (ug/L)	LC ₅₀ Std Dev	Number Studies	Avg Species Rating
American eel	Anguilla rostrata	291.2	264.7	5	Highly Toxic
Killifish	Aplocheilus lineatus	1,062	87.5	2	Moderately Toxic
Sheepshead minnow	Cyprinodon variegatus	46.3	9.57	3	Very Highly Toxic
Common, mirror, colored, carp	Cyprinus carpio	5,921	5,038	41	Moderately Toxic
Carp	Cyprinus carpio carpio	138.0		1	Highly Toxic
Carp	Cyprinus carpio communis	4,500	İ	1	Moderately Toxic
Banded killifish	Fundulus diaphanus	303.3	57.9		Highly Toxic
Mummichog	Fundulus heteroclitus	146.1	149.8	9	Highly Toxic
Striped killifish	Fundulus majalis	260.0	14.1	3	Highly Toxic
Western mosquitofish	Gambusia affinis	385.9	355.8	8	Highly Toxic
Eastern mosquitofish	Gambusia holbrooki	12,780		1	Slightly Toxic
Minnow and Carp	Garra gotyla gotyla	3,500			Moderately Toxic
Threespine stickleback	Gasterosteus aculeatus	85.8	8.96	8	Very Highly Toxic
Silver carp	Hypophthalmichthys molitrix	1,500		1	Moderately Toxic
Spot	Leiostomus xanthurus	440.0	155.6	3	Highly Toxic
Green sunfish	Lepomis cyanellus	306.0	191.2	9	Highly Toxic
Pumpkinseed	Lepomis gibbosus	666.7	185.7	3	Highly Toxic
Bluegill	Lepomis macrochirus	156.2	137.6	37	Highly Toxic
Redear sunfish	Lepomis microlophus	116.0	54.0	4	Highly Toxic
Cyprinid	Leucaspius delineatus	9,625	1,985	2	Moderately Toxic
Inland silverside	Menidia beryllina	0.16	0.09	3	Very Highly Toxic
Atlantic silverside	Menidia menidia	251.7	89.6	3	Highly Toxic
Largemouth bass	Micropterus salmoides	302.9	55.9	8	Highly Toxic
White perch	Morone americana	1,700	432.0	3	Moderately Toxic
Striped bass	Morone saxatilis	85.5	107.4	17	Very Highly Toxic
Striped mullet	Mugil cephalus	686.7	193.3	3	Highly Toxic
White mullet	Mugil curema	760.0	190.0	2	Highly Toxic
Killifish	Nothobranchius guentheri	6,900		1	Moderately Toxic
Rainbow trout, Donaldson rout	Oncorhynchus mykiss	118.8	71.2	47	Highly Toxic
Yellow perch	Perca flavescens	317.8	94.8	4	Highly Toxic
Fathead minnow	Pimephales promelas	15,938	5,880	24	Slightly Toxic
Brown trout	Salmo trutta	132.5	40.5	4	Highly Toxic
Brook trout	Salvelinus fontinalis	140.0	15.8	4	Highly Toxic
Lake trout, siscowet	Salvelinus namaycush	114.4	40.3	5	Highly Toxic
Northern puffer	Sphoeroides maculatus	6,083	2,348		Moderately Toxic
Walleye	Stizostedion vitreum vitreum	79.3	21.7	3	Very Highly Toxic
Eastern mudminnow	Umbra pygmaea	190.0	50.0	2	Highly Toxic

3.3. Pyrethrins and Pyrethroids

Pyrethrins are natural insecticides produced by certain species of the chrysanthemum plant. Synthetic derivatives of the chrysanthemumic acids have been developed as insecticides. These are called pyrethroids and tend to be more effective than natural pyrethrins (EXTOXNET, 1996e). EXTOXNET explains the action of natural pyrethrins as contact poisons that quickly penetrate the nervous system of insects, rendering them unable to move or fly away after just a few minutes. Natural pyrethrins, however, are swiftly detoxified by enzymes in the insect enabling some pests to recover (EXTOXNET, 1996e). 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 pyrethrins.

3.3.1. Pyrethrin

Pyrethrin is classified as "extremely toxic" to aquatic life by EXTOXNET. Species noted as being at risk include bluegill and lake trout. Toxicity increases with higher water temperatures and acidity. Natural pyrethrins are highly fat soluble, but they easily degrade 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).

3.3.2. Permethrin

Permethrin is a synthetic pyrethroid. It is a moderately to practically non-toxic pesticide in USEPA toxicity class II or III, depending on the formulation. Formulations are placed in class II due to their potential to cause eye and skin irritation. Products containing permethrin must bear the Signal Word WARNING or CAUTION, depending on the toxicity of the particular formulation. As a group, synthetic pyrethroids were toxic to all estuarine species tested. Permethrin, being fat-soluble, can bioconcentrate. The bioconcentration factor in bluefish is 715 and for catfish it is 703. EXTOXNET classifies it as having a low to moderate potential to bioaccumulate. Table 14 lists the toxicity information collected by the Maine BPC.

Table 14 - Toxicity of Permethrin to Fish from Maine BPC

Warm water fish	Cold water fish
Bluegill sunfish:	Atlantic salmon:
96 hr LC 50 = 4.9 ppb (1), 1.8 ppb (2, 3), 0.9 ppb (4)	96 hr LC 50 = 1.5 ppb (1, 4), 1.8 ppb (2), 2.2 ppb (4)
Fathead minnow:	Coho salmon:
96 hr LC 50 = 16,000 ppb (3), 2.0 ppb (4)	96 hr LC 50 = 17 ppb (4)
Sheepshead minnow:	Rainbow trout:
96 hr LC 50 = 7.8 ppb (4)	24 hr LC 50 = 12.5 ppb (2)
Carp:	48 hr LC 50 = 5.4 ppb (2)
96 hr LC 50 = 15 ppb (4)	96 hr LC 50 = 0.62 ppb to 314 ppb (depending on size) (4)
Channel catfish:	Brook trout:
96 hr LC 50 = 5.4 ppb (4)	96 hr LC 50 = 2.3 ppb, 3.2 ppb, 3.2 ppb, 5.2 ppb static (3)
Mosquito fish:	
96 hr LC 50 = 15 ppb (4)	
Large mouth bass:	
96 hr LC 50 = 8.5 ppb (4)	
Himedaker:	
48 hr LC 50 = 60 ppb (4)	
Atlantic silverside:	
96 hr LC 50 = 2.2 ppb (4)	
Striped mullet:	
96 hr LC 50 = 5.5 ppb (4)	

- (1) USFW (1992)
- (2) EXTOXNET (1996d)
- (3) TOXNET (2004d)
- (4) Aventis (2001)

Table 15 lists PAN toxicity summaries. With the exception of the common carp, permethrin is considered very highly toxic by PAN to all listed species.

Table 15 - Toxicity of Permethrin to Fish - PAN Summary of Local and Related Fish

Common Name	Scientific Name	Avg LC ₅₀ (ug/L)	LC ₅₀ Std Dev	Number Studies	Avg Species Rating
Sheepshead minnow	Cyprinodon variegatus	87.0	110.2		Very Highly Toxic
Common, mirror, colored, carp	Cyprinus carpio	114.9	221.5	19	Highly Toxic
Northern pike	Esox lucius	10.0	3.94	6	Very Highly Toxic
Western mosquitofish	Gambusia affinis	19.7	27.7	9	Very Highly Toxic
Bluegill	Lepomis macrochirus	8.21	4.54	31	Very Highly Toxic
Inland silverside	Menidia beryllina	27.5	-	1	Very Highly Toxic
Bass	Micropterus	8.50	-	1	Very Highly Toxic
Largemouth bass	Micropterus salmoides	8.50	-	1	Very Highly Toxic
Striped mullet	Mugil cephalus	5.50	-	1	Very Highly Toxic
Rainbow trout, donaldson trout	Oncorhynchus mykiss	23.7	60.6	50	Very Highly Toxic
Fathead minnow	Pimephales promelas	21.0	17.1	26	Very Highly Toxic
Atlantic salmon	Salmo salar	6.75	5.25	2	Very Highly Toxic
Brook trout	Salvelinus fontinalis	3.66	1.06	8	Very Highly Toxic

Milam *et al.* (2000) tested the response of *Gambusia affinis* (mosquitofish) to permethrin (Biomist®). The researchers found that when used alone, it was 130 times more toxic to G. *affinis* than when mixed with mineral oil per the manufacturer's label instructions.

3.3.3. Resmethrin

Resmethrin is a synthetic pyrethroid widely used to control flying and crawling insects in homes, greenhouses, indoor landscapes, mushroom houses, industrial sites, to control stored product insects, and for mosquito control. It is also used for fabric protection, pet sprays, and shampoos, and it is applied to horses or in horse stables. Resmethrin is classified as a slightly toxic to practically non-toxic compound in USEPA toxicity class III (EXTOXNET, 2004e). Insecticides containing resmethrin must, therefore, be labeled with the Signal Word "Caution." Resmethrin is classified by the USEPA as a Restricted Use Pesticide for applications at or near aquatic sites because of potential fish toxicity. PAN classified the pesticide as very highly toxic for the 84 studies cited on the toxicity of resmethrin to fish (Table 16). The studies referenced in the PAN database and those cited in the summary by the Maine BPC (Table 17) report toxicities in the single digit parts per billion.

Table 16 - Toxicity of Resmethrin to Fish from PAN

Common Name	Scientific Name	Avg LC ₅₀ (ug/L)	LC ₅₀ Std Dev	Number Studies	Avg Species Rating	Outlier Result?
White sucker	Catostomus commersoni	2.79	0.46	2	Very Highly Toxic	
Sheepshead minnow	Cyprinodon variegatus	11.0	-	1	Very Highly Toxic	
Western mosquitofish	Gambusia affinis	6.09	0.85	2	Very Highly Toxic	
Channel catfish	Ictalurus punctatus	21.6	9.25	9	Very Highly Toxic	Outlier
Bluegill	Lepomis macrochirus	2.87	1.79	17	Very Highly Toxic	
Largemouth bass	Micropterus salmoides	0.83	0.17	2	Very Highly Toxic	
Coho salmon, silver salmon	Oncorhynchus kisutch	1.22	0.60	5	Very Highly Toxic	
Rainbow trout, donaldson trout	Oncorhynchus mykiss	1.90	1.15	18	Very Highly Toxic	
Yellow perch	Perca flavescens	1.44	0.92	4	Very Highly Toxic	
Fathead minnow	Pimephales promelas	5.56	2.56	7	Very Highly Toxic	
Brown trout	Salmo trutta	1.19	0.30	4	Very Highly Toxic	
Brook trout	Salvelinus fontinalis	4.09	1.86	9	Very Highly Toxic	
Lake trout, siscowet	Salvelinus namaycush	1.40	0.39	4	Very Highly Toxic	

Table 17 - Toxicity of Resmethrin to Fish from the Maine BPC

Warm water fish	Cold water fish	Estuarine & Marine Toxicity
Bluegill sunfish:	Rainbow trout:	Sheepshead minnow:
96 hr LC 50 = 0.75 - 2.6 ppb (1)	96 hr LC 50 = 0.28 -2.4 ppb (1)	8.8 ppb (1)
96 hr LC $50 = 2.62$ ppb (static) $(2, 3)$	96 hr LC 50 = 3.14 ppb (4)	Killifish (mummichog):
96 hr LC $50 = 0.75$ ppb (flow) (2)	Steelhead trout:	48 hr LC 50 = 300 ppb (3)
96 hr LC 50 = 1.7 ppb (3)	96 hr LC $50 = 0.45$ ppb (static) $(2, 3)$	
96 hr LC 50 = 7.2 ppb (4)	96 hr LC 50 = 0.275 ppb (flow) (2)	
Yellow perch:	Lake trout:	
96 hr LC $50 = 0.236$ ppb (static) $(2, 3)$	96 hr LC 50 = 1.7 ppb (3)	
96 hr LC 50 = 0.513 ppb (flow) (2)	Coho salmon:	
Fathead minnow:	96 hr LC 50 = 1.8 ppb (3)	
96 hr LC 50 = 3 ppb (3, 4)	96 hr LC $50 = >150$ ppb (static) $(2, 3)$	
Channel catfish:	96 hr LC 50 = > 0.277 ppb (flow) (2)	
96 hr LC 50 = 16.6 ppb (3)		
96 hr LC 50 = 15 ppb (4)		
Carp:		
48 hr LC 50 = 44 ppb static (3)		
96 hr LC 50 = 3.95 ppb (4)		
Yellow perch:		
96 hr LC 50 = 2.36 ppb (4)		
Green sunfish:		
96 hr LC 50 = 4.40 ppb (4)		
Sheepshead minnow:		
96 hr LC 50 = 11 ppb (4)		

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

In a test conducted by researchers at Southampton College in 2003 (Southampton College, 2004), the growth and survival of caged *Cyprinodon variegates* (sheepshead minnow) were measured following exposure to a Scourge® (resmethrin) application. Growth of the fish exposed to the pesticide was lower than fish studied in control marshes. Methodological uncertainties make the reasons for the difference impossible to determine. In particular, the pesticide exposure was not measured, nor was dissolved oxygen. In addition, there were substantial differences between the treated and "control" areas that could have influenced the results. These results can be compared to those generated by the Long-Term Plan in the "Caged Fish Study," reported on as part of Task 12.

3.3.4. Sumithrin (Phenothrin)

Sumithrin is also known as phenothrin. Its Trade name is Anvil[®]. PAN summarized studies that exposed fish to sumthrin (Table 18). Sumithrin is classified by PAN as very highly toxic to the listed species.

Table 18 - Toxicity of Sumithrin to Fish - PAN Summary of Local and Related Fish

Common Name	Scientific Name	Avg LC ₅₀ (ug/L)	LC ₅₀ Std Dev	Number Studies	Avg Species Rating
Bluegill	Lepomis macrochirus	16.9	1.10	2	Very Highly Toxic
Inland silverside	Menidia beryllina	66.2	27.9	2	Very Highly Toxic
Rainbow trout, donaldson trout	Oncorhynchus mykiss	9.05	7.65	2	Very Highly Toxic

The Maine BPC cited research that demonstrated that LC₅₀ values for killifish were dependent on the isomer tested (Table 19). Warmwater fish (bluegills) and coolwater fish (trout) were similarly sensitive to sumithrin (18 ppb and 17 ppb respectively).

Table 19- Toxicity of Sumithrin to Fish from Maine BPC

Bluegill sunfish:	Rainbow trout:	Killifish (mummichog):
96 hr LC ₅₀ = 18 ppb $(1, 2)$	96 hr $LC_{50} = 17$ ppb $(1, 2)$	48 hr $LC_{50} = 10,000$ ppb (- trans) (2)
Goldfish:		48 hr $LC_{50} = 10,000$ ppb (- cis) (2)
48 hr $LC_{50} = 0.25 - 0.5$ ppb (2)		48 hr $LC_{50} = 120 \text{ ppb (+ trans) (2)}$
		48 hr $LC_{50} = 170 \text{ ppb } (+ \text{ cis}) (2)$
		48 hr $LC_{50} = 200$ ppb (racemic mix) (2)

⁽¹⁾ Tomlin (1994)

3.4. Piperonyl butoxide

PAN classifies the synergist piperonyl butoxide as moderately toxic (Table 20).

Table 20 - Toxicity of Piperonyl Butoxide to Fish - PAN Summary of Local and Related Fish

Common Name	Scientific Name	Avg LC ₅₀ (ug/L)			Avg Species Rating
Sheepshead minnow	Cyprinodon variegatus	1,974	1,966	2	Moderately Toxic
Bluegill	Lepomis macrochirus	4,581	3,694	6	Moderately Toxic
Rainbow trout, donaldson trout	Oncorhynchus mykiss	3,901	3,191	10	Moderately Toxic

⁽²⁾ TOXNET (2004f)

4. Effect of In-Situ versus Laboratory Testing

Milam *et. al.* (2000) conducted a test of seven vector control chemicals including Dursban®, malathion, Permanone®, Abate®, Scourge®, *Bti*, and Biomist®. The authors suggest that *in situ* testing may generate different results than standard laboratory toxicity testing. They tested the response of *G. affinis* to concentrations of Abate® (Temephos) in both laboratory water and ditch receiving water. The LC₅₀ value for the fish in the receiving water (0.014 mg/L) was lower than in the laboratory water (0.039 mg/L). Control organisms showed no adverse effects to ditch receiving water. They concluded that the ditch water, in and of itself, was not the cause of the increased sensitivity. However, it seems possible that other factors in the environment enhanced the pesticide impact.

In another test, they found that Biomist® used alone was 130 times more toxic to *G. affinis* than when mixed with mineral oil per the manufacturer's label instructions. This suggests that the choice of diluents for pesticides may affect toxicity of particular pesticides to fish.

Experimental results are shown in Table 21, below.

Table 21 - LC₅₀ values for fish from acute 24- and 48-h toxicity tests

Chemical	Pesticide	Organism	24-hr LC ₅₀	48-hr LC ₅₀
Permethrin	Biomist w/oil	Gambusia affinis		25,119 mg/L
	Biomist	Gambusia affinis	193.1 mg/L	1
		Pimephales promelas		33.9 mg/L
		Pimephales promelas		>75 mg/L
	Permanone	Gambusia affinis		0.0027 mg/L
Chloropyrifos	Durban	Gambusia affinis	0.11 mg/L	1
		Gambusia affinis		0.45 mg/L
		Anopheles quadrimaculatus		1.0 μ/L
Temephos	Abate	Gambusia affinis		0.039 mg/L
		Gambusia affinis		0.014 mg/L*
Malathion	Malathion	Gambusia affinis		1.23 mg/L

From Milam et. al. (2000) * Tests conducted with ditch receiving water.

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APPENDIX A How OPP Uses Ecotoxicity Data

How OPP Uses Ecotoxicity Data

After reviewing an individual toxicity or ecological effects study for a pesticide, EPA scientists develop a **data evaluation record** (DER) for the study. A DER summarizes the toxicity to certain species groups that are expected to be exposed to the pesticide. The templates for these DERs can be accessed at <a href="http://www.epa.gov/pesticides/regulating/studyprofiletemplates/studyprofiletem

The conclusions from all the individual ecotoxicity DERs are then integrated and summarized in a stressor-response profile, the final product of the ecological effects characterization. The profile presents the suite of effects for various animals and plants and an interpretation of available incidents information and monitoring data. The Agency compares the stressor-response profile with potential exposure levels to determine the risk of exposure-related effects.

In developing its ecological effects characterization, EPA uses either a five-step or a three-step scale of toxicity categories to classify pesticides based on toxicity data:

Ecotoxicity Categories for Terrestrial and Aquatic Organisms Avian

Acute Oral		Dietary	
Concentration (mg/kg)	Toxicity Category	Concentration (ppm)	Toxicity Category
<10	very highly toxic	<50	very highly toxic
10-50	highly toxic	50-500	highly toxic
51-500	moderately toxic	501-1000	moderately toxic
501-2000	slightly toxic	1001-5000	slightly toxic
>2000	practically nontoxic	>5000	practically nontoxic

Aquatic Organisms: Acute

Concentration (ppm)	Toxicity Category
<0.1	very highly toxic
0.1 - 1	highly toxic
>1 - 10	moderately toxic
>10 - 100	slightly toxic
>100	practically nontoxic

Wild Mammals: Acute Oral

Concentration (mg/kg)	Toxicity Category
<10	very highly toxic
10 - 50	highly toxic
51 - 500	moderately toxic
501 - 2000	slightly toxic
>2000	practically nontoxic

Non-Target Insects: Acute Toxicity

Concentration (ug/bee)	Toxicity Category
<2	highly toxic
2 - 11	moderately toxic
>11	practically nontoxic

APPENDIX B

About the Pesticide Action Network Database

About the Pesticide Action Network 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 <u>here</u>.

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 <u>Value-Added Features</u>), 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 <u>here</u>.

California Pesticide Use Reporting Data

We obtain the California PUR data directly from the Department 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 <u>here</u>. 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 <u>Pesticide Tutorial</u> 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