Environmental Fate of Malathion

KayLynn Newhart
California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring Branch
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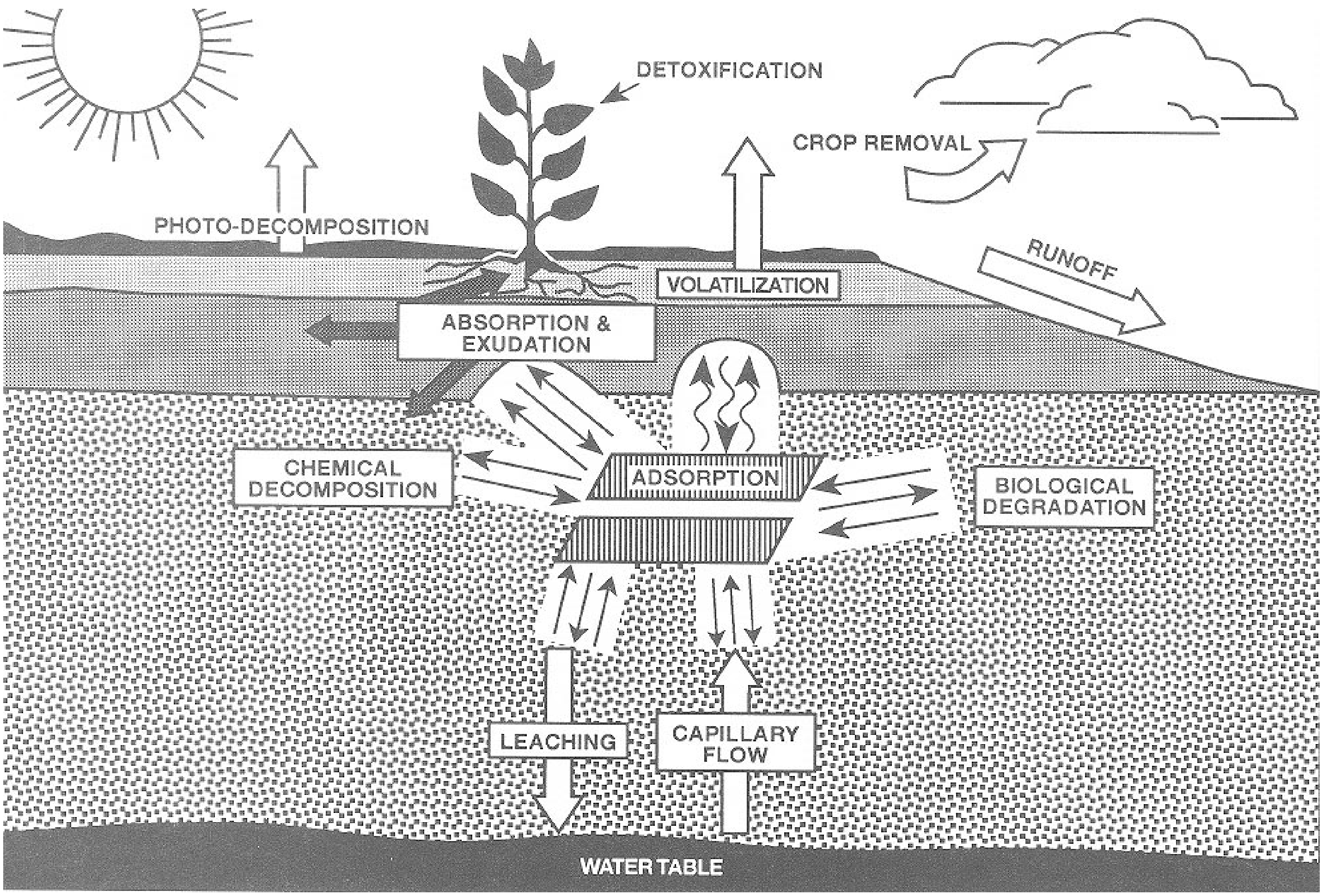


Petroff, Reeves, Diagram from: Factors affecting Pesticide Performance. Adjuvants and Surfactants. Montana State University. Montana Cooperative Extension Service.

Introduction

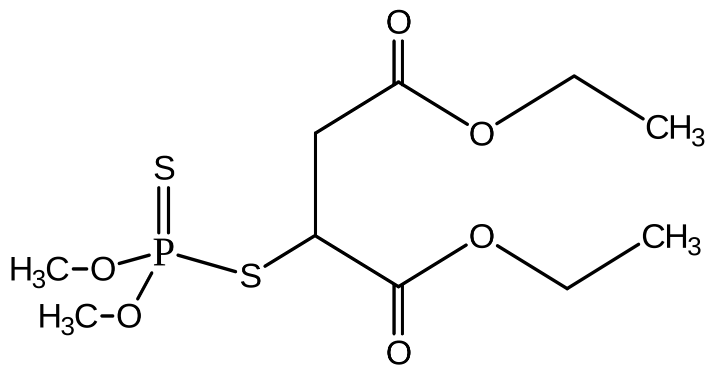
Malathion is an organophosphorus insecticide used in public health, residential, and agricultural settings as early as 1950. Over 100 food crops can be treated with malathion, and about half of total applications in the United States (U.S.) are on alfalfa, cotton, rice, sorghum, and wheat. Annual use of malathion is over 16.7 million lbs active ingredient (ai) per year of which approximately 12.5 million lbs ai is used on food crops alone (ATSDR, 2003). The following uses constitute 4.2 million lbs ai per year with application to stored commodities, empty storage facilities, home and garden, golf courses, mosquito abatement, ornamental nursery stock and turf, Christmas tree plantations, parks, cemeteries, garbage areas, irrigation systems, outdoor dwellings (domestic and commercial), intermittently flooded areas, sewage systems, pastures, and rangeland (ATSDR, 2003). Malathion has been used in three major regional eradication programs in the U.S., specifically Boll Weevil eradication on cotton (11.2 million lbs/year), Medfly control (800,000 lbs/year), and mosquito control (472,000 lbs/year). A non-FIFRA pharmaceutical use of malathion is as a pediculicide for head lice and ova (U.S.EPA, 2000). In 2004, the Department of Pesticide Regulation (DPR) reported that 492,307 pounds of malathion were used in California (California Department of Pesticide Regulation's Pesticide Use Database. 2004).

There are 38 basic producers of malathion and it is used in approximately 1,953 products worldwide (MeisterPro, 2003). Of those approximately 174 products are registered for use in the U.S. of which 36 products are currently registered for use in California (NPIRS, 2004). Malathion is formulated as an emulsifiable concentrate (EC), a dust (D), a wettable powder (WP), a pressurized liquid (PrL), and as ready-to-use liquids used for ultra-low-volume (ULV) application. Examples of common product names include Agrisect, Atrapa, Bonide, Prentox, Clean Crop malathion, Acme malathion, Black Leaf malathion spray, Eliminator, Fyfanon, and Gowan malathion dust.

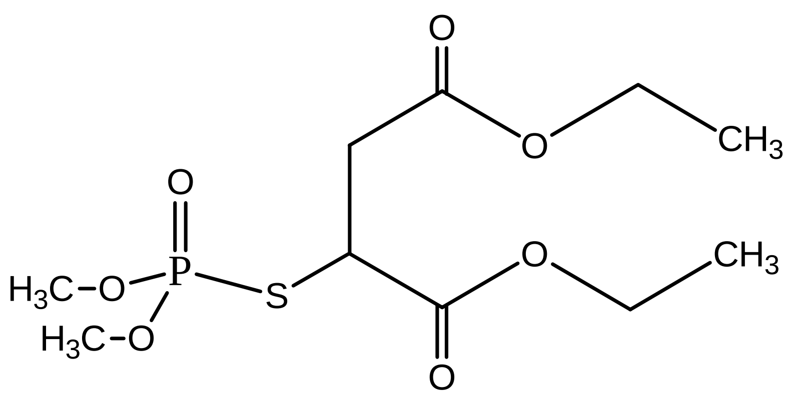
Malathion has a broad range of use with target pests in the orders dipterans, lepidoptera, hemiptera, coleoptera, and other orders. Malathion is a slightly toxic compound in EPA toxicity class III and labels for malathion products must carry the signal word "CAUTION".

Malaoxon is an oxygen analogue of malathion and it can be found either as an impurity in malathion product, or can be generated during the oxidation of malathion in air or soil. Malaoxon is the active cholinesterase inhibiting metabolite of malathion. Both malathion and malaoxon are detoxified by carboxyesterases to polar, water-soluble compounds that are excreted.

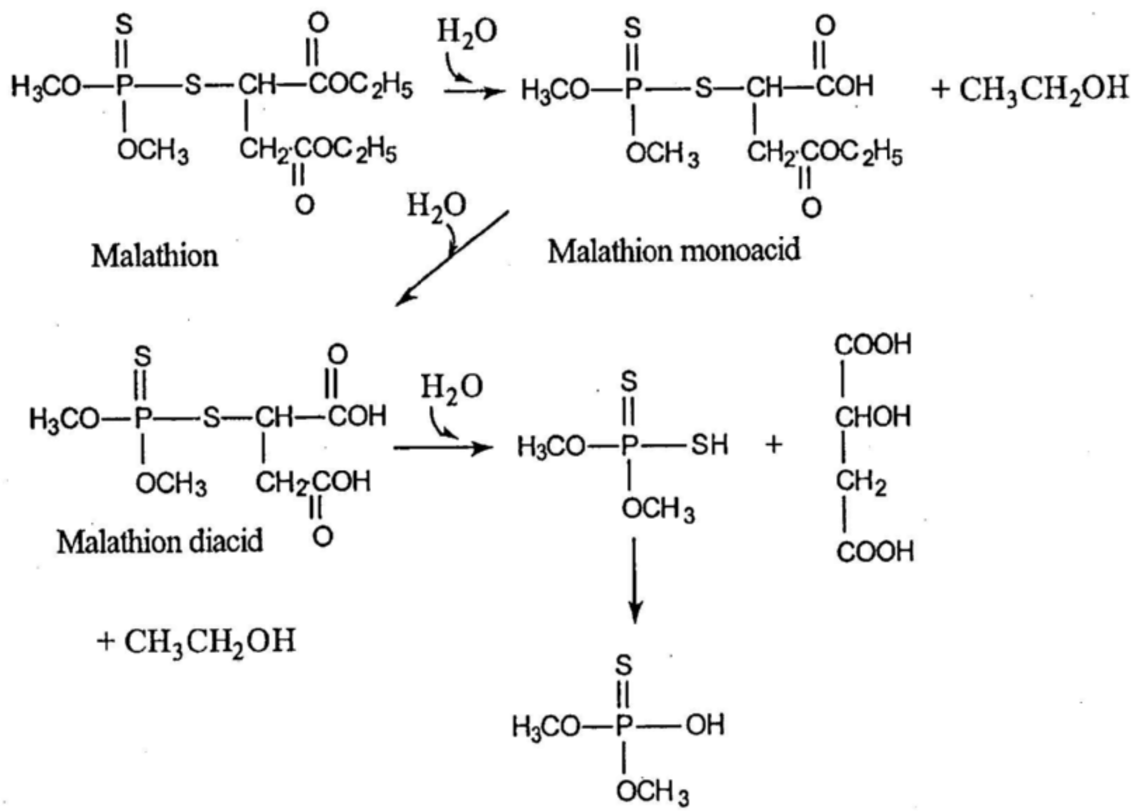
Chemical Structure of Malathion



Chemical Structure of Malaoxon



Degradation Pathway of Malathion



Physical Characteristics of Malathion

Composition: Diethyl (dimethoxythiophosphorylthio)succinate Properties: Clear to amber liquid with a mercaptan odor. Henry's Law Constant: $4.89X10^{-9}$ atm/m^3 mol Specific Gravity: 1.23 at 25°C Melting Point: 2.85°C Molecular Weight: 330.36 Water Solubility: 130 mg/L Partition Coefficient: 2.7482 Adsorption Coefficient: 1,800 Vapor Pressure: $3.38X10^{-6}$mm Hg at 30°C Miscible in most organic solvents; limited solubility in aliphatic hydrocarbon.

Environmental Fate

Air

Malathion and malaoxon can be transported in air by drift from applications to non-target sites. Movement in air can also occur due to volatilization, fog, and wind. Residues in small droplets produced by ultra low volume (ULV) aerial applications have been shown to drift for long distances, causing adverse effects in surrounding waterways (Lenoir, 1999). Concentrations of malathion have been measured at levels high enough to cause mortality for non-target invertebrates as far as 200 meters from the application site (USEPA, 2000). There are currently no aerial buffers on malathion labels to mitigate potential for offsite movement (ATSDR, 2003).

In 1990, the California Department of Food and Agriculture monitored air samples for malathion and malaoxon during Mexican fruit fly eradication in San Diego County (Turner et al. 1991). An area-designated habitat of an endangered species (Least Bell's Vireo) just outside of the southeastern boundary of the treatment area was monitored for malathion deposition during applications. Concentrations detected were 16.97 $\mu g/ft^2$ during the first application and 24.02 $\mu g/ft^2$ during the last application. The study concluded that drift was the likely cause of these detections.

The California Department of Food and Agriculture monitored malathion and malaoxon during the eradication of Mediterranean fruit flies in Southern California in 1990 (Segawa et al. 1991). Several sites were "flagged" to be intentionally avoided by aircraft applying malathion bait spray. The concentration at these sites ranged from 1.0 $\mu g/m^2$ to 101 $\mu g/m^2$. The study concluded that 92% of the total of malathion applied was accounted for on the ground surface of the targeted spray areas. The 8% of malathion unaccounted for either degraded before hitting the ground, volatilized before sample collection, or drifted outside of the target area.

Environmental sampling was conducted in Ventura County, California during the Mediterranean Fruit Fly Eradication Program from 1994-1995 (Sanders, 1994). Deposition of malathion averaged 8.21 mg/m^2. Malaoxon was not detected in 25 percent of the samples with the highest malaoxon concentration at 0.07 mg/m^2. Malathion air concentration averaged 0.004 ug/m^3 during the pre-spray interval and then was elevated to 0.067 ug/m^3 during application. Air concentrations remained elevated measuring 0.049 ug/m^3 during the 24 hours immediately following application and at 0.042 ug/m^3 for the interval 24-48 hours after application. Malaoxon was detected at an average concentration of 0.010 ug/m^3 during both the first postspray and second postspray sampling intervals. The highest concentration in air was 0.176 ug/m^3.

The Florida Department of Environmental Protection (FDEP, 1998) conducted a drift study assessing the biological effect of malathion following ULV applications made for Mediterranean Fruit Fly eradication. Biological assessment was conducted for five lakes in Umatilla, Florida in the shallow (littoral zone) areas of each lake. The macroinvertebrate community measured in the lakes consisted of a number of water mites (*Ephemeroptera, Acariformes, Hydrodroma),* caddisflies (*Trichoptera),* mayflies (*Ephemeroptera*), midges (*Polypeilum halterale*), freshwater worms (*Oligochaete*), and flatworms (*Turbellarians*). Samples collected post application showed a reduction or total absence of *Turbellarians* and of O*ligochaetes* in lake sediments as well as other organisms. In four lakes there were declines of total numbers of organisms and diversity index declines in three lakes. Malathion water column concentrations ranged from 0.3 to 4.5 ug/l. Recommendations from the results of the study supported preserving a 100 foot buffer around waterbodies when malathion was applied by air. It was also suggested while malathion can effect organisms in the water column, that monitoring for measurable effects to sediment dwelling organisms should also be done when using malathion for future Medfly eradication.

Volatilization of malathion was also reported in a study conducted in agricultural conditions in the Bologna province, Italy (Ferari et al., 2003). Air concentrations of malathion were monitored 2-3 weeks after pesticide applications to a bare, silty-textured soil. The authors estimated malathion volatilization at 1.3 mg/m^2 during the day and 0.9 mg/m^2 during the night. The study concluded that for pesticides with vapor pressures between 5×10^{-3} and 5×10^{-2} volatilization can represent up to 22.6% of the total fate in the environment. Consequently, volatilization may result in significant exposures in air and may impact the air quality of the area surrounding the agricultural field.

Other studies have also indicated transport of malathion over large distances. In California, LeNoir et al. (1999) reported that malathion applied in lower elevations of California volatilize under high temperatures in summer and was transported to higher elevations of the Sierra Nevada mountain range. The authors measured high volume air, dry deposition, and surface water samples in the Central Valley and at various elevations in Sequoia National Park. Malathion and other pesticides were measured in high volume air, dry deposition, and surface water samples collected a various elevations in Sequoia National Park to determine atmospheric transport of pesticides. Detailed pesticide use was collected in Fresno and Tulare counties immediately downwind of the park's entrance. Although malathion usage was not significant at any time, it has widespread home, garden and mosquito abatement uses. Malathion use ranged from zero kg a.i. up to 2,280 kg a.i./month from January through December 1995 in Fresno County. Tulare County use ranged from 2 kg a.i. up to 4,456 kg a.i./month for the same time period. At Kaweah Reservoir at 200 m air samples resulted in two detections of 0.29 and 0.40 ng/m^3 in May and June. At Ash Mountain air samples collected at 533 m had a single detection of malathion on May 30 of 0.15 ng/m^3. In surface water samples collected at elevations from 118 m up to 3,322 m malathion was detected in six locations ranging from 64.97 ng/L up to 83.0 ng/L.

In a study of the Chesapeake Bay on the east coast malathion was present in 30% of air samples and 50% of rain samples collected in Spring and Summer 1995 with maximum wet deposition flux measurement for malathion at 1.8 ug/m^2 –d (Harman-Fetcho et al., 2000). On the east coast of central Florida, malathion was found to drift on to shoreline beaches and surface water near coastal marshes due to ULV applications for mosquito control (Clark et al.1993). In addition, a study conducted in the Florida Keys (Hennessey et al., 1992) found aerial thermal fog drifted 750 m into protected no-spray zones of endangered species habitat.

<u>Water</u>

Degradation of malathion in water is pH dependant and degrades quickly in water with pH > 7.0. Malathion does not accumulate in sediment but can be present in sediment following application.

Hydrolysis is the main route of degradation in alkaline aerobic conditions. The half-life range of malathion is 0.2 weeks at pH 8.0 compared to 21 weeks at pH 6.0. Metabolites resulting from hydrolysis include malaoxon, malathion alpha and beta monoacid, diethyl fumarate, diethyl thiomalate, O,O-dimethylphosphorodithioic acid, diethylthiomalate, and O,O-dimethylphosphorothionic acid.

Biodegradation also plays a role when pH <7.0 and the rate of hydrolysis is slow relative to the rate of biodegradation. Breakdown constituents of biodegration include beta monocaboxylic acid dicarboxylic acid, and diethyl thiomalate. Malathion is not persistant under anaerobic conditions. However, malaoxon has higher solubility and the potential for runoff is greater.

Detections of Malathion and Malaoxon in Water

Aerial application of malathion bait mixture to eradicate the Mediterranean fruit fly in California prompted a study of the levels of malathion and malaoxon in water. Segawa, et al., (1990) found an average of 49.4 ug/L malathion in freshwater ponds and 9.38 ug/L in swimming pools sampled immediately after application. The average level of malaoxon was 0.80 ug/L in the ponds and 16.5 ug/L in the swimming pools. In addition water runoff was sampled from two rivers, two runoff channels, and a marsh in areas where drainage could be impacted by malathion applications. Concentrations exceeded 3.54 ug/L malathion (24-hour exposure) on three of eight sampling dates. The authors concluded that the most likely occurrence of an environmental impact from high concentrations of malathion would be from winter applications when rainfall is the heaviest.

Water samples were also taken in subsequent Mediterranean fruit fly eradication spraying. In 1994, during a six-week period in Riverside, California (Ando et al. 1994) monitored malathion and malaoxon detections in water throughout the application period. Concentrations of malathion in rain runoff to storm drains were measured as high as 583 ug/L. Additionally, malathion and malaoxon were analyzed in water samples obtained during the 1994-1995 Mediterranean Fruit Fly Eradication Program in Ventura County in samples following applications malathion concentrations averaged 44.2 ug/L (ranging from 39.1 to 50.3 ug/L) and malaoxon concentration averaged 0.05 ug/L. In rain runoff samples the highest malathion concentration of 787.1 ug/L occurred 3 days following application in Calleguas Creek. The highest malaoxon concentration was 160.2 ug/L at the same location 12 days following application. Malathion and malaoxon were also detected at Calleguas Creek, a freshwater channel that enters Mugu Lagoon is located within Naval Weapons Station, Point Mugu in Southern Ventura County. It provides one of the largest undeveloped coastal wetlands and contains protected riparian areas and has important recreation uses as well. Detections of malathion were reported at 11.1 ug/L and 2.62 ug/L. The study results showed that concentrations were potentially toxic to aquatic life, although no fish kills were reported.

Storm water runoff from urban areas was found to have higher levels of malathion than agricultural settings in a study conducted by USGS as part of the National Water Quality Assessment Program in the Tuolumne River Basin in Modesto, California (Kratzer, 1998). Stormwater runoff samples from agricultural and urban areas were analyzed for pesticides during a February 8-10 storm event for agricultural areas and for urban sites February 13-14 in 1995.

Malathion detections ranged from 0.038 mg/L up to 0.068 mg/L from five storm drains in Modesto, California. In agricultural runoff samples malathion was detected 10 times at less than 0.005 and up to .096 ug/L at two other urban runoff sites. All of the urban runoff samples exceeded the National Academy of Engineering guidelines for chronic criteria for the protection of freshwater aquatic life for malathion (0.1-0.008 mg/L). Less degradation from soil occurs where malathion lands on urban hard surfaces, resulting in more material moving off targeted application areas in rain runoff (USGS, 2000).

Groundwater

Malathion is moderately to highly mobile in soil and has been detected in groundwater in one well in California (0.32 ug/L), two wells in Mississippi (0.03-0.053 ug/L), and nine wells in Virginia (range 0.007-6.17 ug/L). Generally, degradation occurs rapidly and groundwater contamination has not been found to be widespread. EFED concluded that there is potential for movement of malathion to groundwater especially in soils with low organic matter and high sand content. Also, since the normal site of application of malathion is to foliage, application to foliage is potentially a factor that mitigates movement to ground water. In California, pesticides have been determined to move to ground water as a result of non-point source applications of soil-applied pesticides (Schuette et al., 2005). Application to foliage allows for exposure of residues to degradation from processes such as photolysis, resulting in a reduced potential for significant movement to ground water.

Surface Water

DPR has been collecting data for pesticide sampling in a Surface Water Database (http://www.cdpr.ca.gov/docs/sw/surfdata.htm). The database contains 7,000 sampling records for malathion sampled between August 1990-June 2005. Of those samples, 306 contained malathion at concentrations ranging from .005 ug/L to 6.0 ug/L.

Malathion was also reported in samples collected for the NAWQA program conducted by USGS. That study provides a nationwide study of pesticides in surface and ground water. Table 1 contains a summary of malathion detections in samples USGS collected during the study for 1992 to 1996. These results indicated that urban streams had the most detections (19.57 % of 327 total samples) followed by large streams and rivers (8.16% of 245 total samples). The highest concentrations were found in urban streams with 17.13% of samples greater than 0.1 ug/L and 7.03 greater than 0.05 ug/L. The least amount of detections were in major aquifers, shallow groundwater agricultural areas and no detections in shallow groundwater urban areas. This implies that urban use of malathion could be a major contributor to off-site movement of malathion to adjacent urban waterways.

Table 1. Malathion detections in ground and surface water from USGS-NAWQA program (1992-1996).

Sites Sampled	Total Samples	% Samples Malathion Detected	% Samples >=0.01 ug/L	% Samples >=0.05 ug/L
Surface Water				
1,058	5,196	7.45	5.51	1.81
Agricultural Stream Sites				
40	1,000	5.60	3.70	0.50
Urban Streams				
11	327	19.57	17.13	7.03
Integrator Sites (large streams and rivers)				
14	245	8.16	6.12	1.22
MajorAquifers				
933	not reported	0.43	0.11	ND
Shallow Groundwater-Agricultural Areas				
924	924	0.32	0.11	0.11
Shallow Groundwater Urban Areas				
924	301	ND	ND	ND

Terrestrial Fate

The primary route of malathion degradation in soil is through aerobic soil metabolism. The half-life of malathion in soil was reported to be 3 days in alkaline soil and 7 days in acidic soil. Biodegradation by microorganisms is an important fate process in soil. This is especially true when pH<7.0. Malathion mono and dicarboxylic acids, malaoxon, ethyl hydrogen fumarate, diethyl thiosuccinate, and CO_2 are degradates that have been identified in laboratory and field studies. The major metabolite in soil is malathion beta monoacid and has a reported half-life of 4-6 days (Paschal et al., 1976).

A study of malathion persistence in water, sand, soil, and plant matrices showed that malathion degrades to malaoxon less quickly in soils with greater amounts of organic matter affecting pesticide fixation in soils (Neal et al. 1993). The study supported this because since more rapid degradation occurred in sandy soil lacking an organic fraction. It was found for soil that the time it took for reduction to 50% of the initial concentration was less than 12 hours. The sand matrix showed this reduction to be 20% in less than 12 hours. Pashal and Neville (1976) suggested that malaoxon persistence was more likely in loamy soil. The rate of hydrolysis was reported at 50-90% in 24 hours.

Effects on Aquatic Species

Aquatic organisms are affected at environmental concentrations less than 100 ug/L. Concentrations at these levels have been routinely detected at presently recommended application rates in adjacent tributaries and retention ponds near urban areas. USGS data indicated higher levels of malathion and more detections in urban streams than were monitored in rural and agricultural areas (USGS NAWQUA, 2000). In 96-hour toxicity studies, the LC_{50} values for fish ranged from 4-11,700 ug/L and 0.5-3,000 ug/L for aquatic invertebrates. Malathion detections have been more common and at higher levels in urban surface water areas. Risks to aquatic species become greater when repeated applications occur, resulting in continual exposure to peak concentrations. Malathion has a high potential to drift from ultra-low volume (ULV) applications and impact aquatic habitat. Toxicity to fish species (Table 2) varies from very highly toxic (<0.1 ug/l) to practically non-toxic (>100 ug/l).

Table 2. Relative toxicities to various fish and species exposed to malathion.

Species	**Toxicity LC50 (96-hour) (ug/L)**
Walleye (*Stizostedion vitreum*)	0.06
Brown trout (*Salmo trutta*)	0.1
Cutthroat trout (*Salmo clarki*)	0.28
Rainbow trout (*Oncorhynchus mykiss*)	4.0
Fathead minnow (*Pimephales promelas*)	8.6
Sheepshead minnow (*Cyprinodon variegatus*)	33.0
Western Mosquitofish (*Gambusia affinis*)	50.0
Goldfish (*Carassius auratus*)	10.7
Bluegill sunfish (*Lepomis macrochirus*)	20.0
Largemouth bass (*Micropterus salminoides*)	250
Channel catfish (*Ictalurus punctatus*)	7,620
Coho salmon (*Oncorhynchus kisutch*)	170
Striped bass (*Marone saxatilis*)	60.0

U.S. EPA defines a Risk Quotient (RQ) as the ratio of the estimated environmental concentration of a chemical to a toxicity test effect level for a given species. To estimate potential ecological risk, EPA integrates the results of exposure and ecotoxicity using the quotient method. Risk quotients (RQs) are calculated by dividing exposure estimates by ecotoxicity values, both acute and chronic, for various wildlife species. RQs are then compared to levels of concern (LOCs). Generally, the higher the RQ, the greater the potential risk. Risk characterization provides further information on the likelihood of adverse effect occurring by considering the fate of the chemical in the environment, communities and species potentially at risk, their spatial and temporal distributions, and the nature of the effects observed in studies (U.S.EPA, 1999).

The U.S. EPA RQ acute criteria for malathion of aquatic invertebrates ranges from 8.2-226 ug/L. The chronic RQ ranges from 33-931 ug/L for invertebrates and is 0.04-1.0 ug/L for fish. The acute RQ for fish species ranges from 0.3-7.4 ug/L.

The Bureau of Sport Fisheries and Wildlife in 1969 observed synergism in bluegill and rainbow trout when malathion was mixed with Baytex, EPN, parathion, perthane, and carbaryl. Additive effects were also noted from combinations with DDT and toxaphene. Chronic effects on growth of Flagfish (*Jordanella floridae*) have been observed from mixtures of endrin and malathion (Hermanutz et al. 1985).

A number of growth anomalies have also been observed when fish were exposed to malathion and malaoxon. Although malathion caused no mortality of *Clarias gariepinus* (African catfish) embryos at 5.0 mg/L, the LOEC value of 10 mg/L was found for Zebra fish (*D. rerio)*. There was also no effect on hatching of *C. gariepinus* observed up to the highest concentraion of malathion tested, but the hatching of *D. rerio* was inhibited at 3.0 mg/L. Reduced survival of *C. gariepinus* larvae was observed at 20.0 mg/L and for *D. rerio* larvae the value of 43 mg/L caused reduced survival. The study results also included observations of abnormal body axis development in *C. gariepinus*, and pericardial edema in *D. rerio* exposed to 1.25 mg/L and 3.0 mg/L malathion (Nguyen et al., 2001). *Oncorhynchus mykiss* (rainbow trout) exposed to concentrations up to 40 ug/L caused significant changes in swimming behaviors due to inhibition of cholinesterase (Beauvais et al. 2000).

There have been reports of gill malfunctions and respiratory distress in bluegills as an early symptom of malathion exposure due to the loss of adhesion between epithelial cells and the underlying pillar cell system, resulting in the collapse of the lamellae structural integrity (Richmonds et al., 1989).

In other studies, an LOEC value of 1.0 mg/L was obtained in the 32-day Early Life Stage test with *D. rerio*. When killifish (*Fundulus heteroclitus*) were exposed to malathion for 55 days at a concentration of 10 mg/L, abnormal axis formation in the embryos was observed at this concentration (Crawford et al. 1985).

The California Department of Fish and Game (DFG) conducted a hazard assessment of the insecticide malathion to aquatic organisms in the Sacramento and San Joaquin rivers in 1998. The most acutely sensitive freshwater species was found to be the stonefly (*Isoperia sp*.) with a Genus Mean Acute Value (GMAV) of 0.69 ug/L malathion. The most acutely sensitive saltwater species was the mysid (*Mysidopsis bahia*) with a GMAV of 5.20 ug/L. The lowest Maximum Acceptable toxicant Concentration (MATC) for bluegill (*Lepomis macrochirus*) was 5.16 ug/L. The Final Chronic Values (FAV) for malathion were found to be 0.86 ug/L for freshwater and the interim saltwater FAV was 0.67 ug/L. DFG found that freshwater organisms should not be affected if the one hour concentration of malathion does not exceed the Criterion Maximum Concentration (CMC) of 0.43 ug/L. The CMC level of malathion was exceeded seven times in the Sacramento Valley rice growing areas from April 1990 to June 1996. In the San Joaquin River system the maximum concentration of malathion was 0.28 ug/L in 1992.

The United States Fish and Wildlife Service (USFWS. 1969) concluded that malathion is classified as highly to very highly toxic to aquatic early life stages of non-target insects (Table 3).

Table 3. Toxicity to Aquatic Larvae of Terrestrial Insects.

Species	LC50 (ppb)
Stonefly (*Claasenia sabulosa*)	2.8
Stonefly (*Pteronarcella badia*)	1.1
Stonefly (*Isoperla sp.*)	0.69
Damselfly (*Lestes congener*)	10.0
Caddisfly (*Hydropsyche sp.*)	5.0
Caddisfly (*Limnephalus sp.*)	1.3
Snipefly (*Atherix variegata*)	385

USFWS results for acute toxicity to freshwater and marine and estuarine invertebrates are included in Table 4.

Table 4. Acute toxicity (LC50) values for freshwater and marine (estaurine) invertebrates.

Species	EC50 or LC50 (ppb)
Water flea (*Daphnia pulex*)	1.8 (48 hr EC50)
Scud (*Gammarus lacustris*)	1.8 (48 hr LC50)
Scud (*Gammarus fasciatus*)	0.5 (96 hr LC50)
Daphnid (*Simocephalus serrulatus*)	0.69 (48 hr LC50)
Crayfish (*Orconectes nais*)	180 (96 hr LC50)
Glass shrimp (*Palaemonetes kadiakensis*)	12.0 (96 hr LC50)
Seed shrimp (*Cypridopsis vidua*)	47 (49 hr LC50)
Water flea (*Daphnia magna*)	1.0 (48 hr EC50)
Sowbug (*Asellus brevicaudus*)	3,000 (96 hr LC50)
Mysid (*Mysidopsis bahia*)	2.2 (96 hr LC50)
Pink shrimp (*Penaeus duorarum*)	280 (48 hr LC50)
Eastern oyster (*Crassostrea virginica*)	2,960 (96 hr EC50)
Blue crab (*Callinectes sapidus*)	1,000 (48 hr LC50)

Biota Effects of Malathion

Amphibians

Bullfrogs (*Rana catesbeiana*) were exposed to malathion in water in a 28-day static renewal test (Fordham et al., 2000). Survival was decreased at the level of 2,500 ug/L and higher. Development of tadpoles was significantly delayed by malathion exposure as well. The study suggests that malathion may decrease thyroid function in tadpoles. Equilibrium posture was also found to be impaired in tadpoles from all of the treatment groups (500 to 3,000 ug/L). This can be detrimental to survivability due to predation loss and decreased feeding. Based on the study results it appears unlikely that overt mortality would occur since the exposure was higher than what is documented in wetlands and streams currently.

In another study (Taylor et al.1999), adult male Woodhouse's toads (*Bufo woodhousi*) died at a higher rate and developed disease when exposed externally to either a high or low sublethal dose (0.011 or 0.0011 mg malathion/gram toad). The study concluded that Woodhouse's toads exposed to field grade malathion were more susceptible to disease.

Notochordal effects and bent spines were observed in *Xenopus* (frogs) as well as a general retardation in growth and development and vascular abnormalities (Snawder and Chambers, 1989, 1990, 1993).

Avian

Malathion is potentially hazardous to avian species at application rates above 2.5 lbs ai/acre (U.S.EPA. 2000). Many malathion labels list application rates greater than 6.25 lbs ai/acre. Concerns exist regarding long term exposure to repeated high residues and subsequent chronic effects on reproduction of exposure to nests and juvenile birds. Sublethal effects to birds from acetylcholinesterase inhibition may include reduced nesting behavior, disorientation, and loss of motor coordination leading to reduced ability to cope with the daily stresses of survival under natural conditions. There have been observations of abnormal feathering and beak deformation in birds exposed to malathion and malaoxon. U.S.EPA concluded as part of a revised risk assessment of malathion that chronic exposure to birds is of concern because consecutive applications at peak use rates are not restricted. While malathion is non-persistant in the environment, repeated exposures can occur up to 14 days that subject birds to repeat doses. This is of greater concern when birds are nesting. Risk quotients (RQ) for dietary risk to avian species exposed to malathion are 0.001-0.72 mg/kg (acute) and 0.01-18.1 mg/kg (chronic).

The reported acute oral LD_{50} values for various bird species are: mallards, 1,485 mg/kg; pheasants, 167 mg/kg; blackbirds and starlings, over 100 mg/kg; and chickens, 525 mg/kg. The 5- to 8-day dietary LC_{50} is greater than 3,000 ppm in Japanese quail, mallard, and northern bobwhite quail, and is at 2,639 ppm in ring-necked pheasants. About 90% of malathion is thought to be metabolized and excreted in urine 24 hours after birds ingest it.

In a study in Ohio, (Giles et al.1970), a 20-acre watershed was treated with malathion radio-isotope tagged with sulfur 35. The application rate was 2 lbs a.i./acre with 4 successive malathion treatments. Birds showed adverse reaction up to 48 hours post application. Lack of birds singing was observed for 2 days. By day 4 singing intensity was the same as the control area. The study suggests sublethal insecticidal effects possibly due to reduction in food source or bird emigration from treated areas. Raiodioactivity was detected in collected bird's whole organ tissues. Insectivorous birds had high radioactivity on their feathers.

Enhanced toxicity effects in birds have been observed when propicoanzole, vincloxolin, and clomitrimazole are used with malathion (Martin et al. 1995). In addition, Japanese quail, red-legged partridge, and pigeons showed increased toxicity to malathion when exposed at the same time to the fungicide prochloraz (Riviere et al.1985).

Mammals and Reptiles

Sublethal effects occur to mammals and reptiles due to their susceptibility to the inhibition of acetylcholinestease. U.S.EPA has concluded that small mammals are at risk when exposed to the highest application rates of malathion (U.S. EPA. 2000). The exposure RQs for small mammals are 0.10-3.65 ug/L for acute and 0.005-3.0 ug/L chronic effects. In the Ohio study, white footed mice (*Peromyscus leucopus novaboracensis*) population was reduced by 45% in the treated area, based on pre and post application trapping counts. The chipmunk population was reduced 30-55% in a forested area treated with 2 lbs a.i./acre per acre of malathion. The study concluded that these reductions were due to sublethal productivity and survival effects (Giles et al.1970).

Plants

Malathion has not been shown to cause serious hazards to terrestrial plants or aquatic algae. However, studies support that malathion is taken up and stored in plant tissues (U.S.EPA. 2000). The half-life of malathion on plant surfaced ranges from <0.3-8.7 days. In the Ohio study mentioned earlier (Giles et al.1970), radioactivity was high in the tissues of plants sampled in the treated areas due to active uptake of the malathion. Metabolites of malathion were detected in new stem and leaf growth up to one-year post application.

Non-target Beneficial Insects

Malathion as a foliar residue is highly toxic to honeybees for as much as 48 hours post application. Malathion's average half-life ranges from 1-10 days on foliage. This latent residue is suspected to cause acute losses in other beneficial insect populations (U.S.EPA, 2000).

Gary et al. (1984) reported significant mortality to honeybees in apiaries to malathion bait used to treat mosquitos. The application rate was 175.4 ml malathion technical and 701.8 ml Staley's Protein Bait/hectare applied weekly in the San Francisco Bay area. The bodies of dead bee were collected daily at the hives entrance and pollen samples were collected. Bee death was determined due to malathion contaminated pollen (2.06 mg/L) and body residue levels of 0.9-5.3 mg/L on the bees themselves.

In addition to killing the targeted pests, a range in mortality has been observed for non-target insects and spiders. In tests conducted in Pleasanton and Woodside, California, mortality of dipterids, Lepidoptera larvae, spiders, cynipoidea, hemiptera, and pscoptera were observed in a treated area with malathion bait spray (Dahlsten.1985).

During the California Medfly Eradication Program, (Oshima et al. 1982) observed that non-targeted lacewings and dipterids were attracted to the malathion bait and killed.

Lastly, in a study conducted in 1999 on the effects of ULV pyrethrin, malathion, and permethrin on nontarget inverterates and mosquitofish, only a drop in nontarget invertebrates at the time of initial application of malathion was reported (Jensen et al. 1999). Post treatment sampling of studied macroinvertebrates midges (*Chironomidae*), damselfly and dragonfly nymphs (*Odonata*), mayfly nymphs, water boatmen, snails, backswimmers (*Notonectidae*), and beetles showed recovery after 24-hours and actual increases in population from 1-3 days post-application. Mosquito fish (*Gambusia*) were not affected.

Reported Adverse Environmental Events

Numerous incidents have been reported concerning mortality and illness to fish and wildlife in the U.S. due to malathion. Information was compiled on incidents by the U.S.EPA including freshwater, marine and estuarine events (U.S.EPA. 2000). Numerous fish kills attributed to malathion have occurred in small streams and ponds with slow flow rates when toxic levels are reached. Incidences of fish kills have occurred as a result of use in large watershed areas where heavy rainfall contributed to runoff to aquatic habitat areas.

Application Methods and Drift in Relation to Environmental Effects

Ultra low volume (ULV) applications are normally used when applications are made in mosquito abatement or with boll weevil eradication. These applications produce smaller than normal droplets that can travel over long distances. More than half of the malathion applied in the U.S. is applied by ULV methods. A demonstration (Penn State University.1993) assessed ULV applications such as those used in the Boll Weevil Eradication Program. The study utilized Spraying Systems stainless steel 8002 Flat Fan spray tips, pointed straight down, flying 5 feet above the crop canopy. Applications were 1 lb a.i./acre of 95% malathion, and 17 runs were made under different meteorological conditions. Maximum depositions were 21, 12, 2.8, and 0.7% of the expected maximum at 100, 200, 300, and 1000 meters downwind. The highest amount of drift at 1 kilometer occurred in stable atmospheric conditions. Higher drift occurred at shorter distances during unstable windy conditions. Averages of deposition showed 9.4% at 100 meters and 0.08% at 1000 meters. EECs were then calculated with the deposition rates for varying depths of water based on expected drift using a 6 inch to 6 foot depth range for a one acre pond. Varying the drift parameters was done with PRZM and EXAMS modeling.

Levels of concern for fish are exceeded at 100 and 200 meters with maximum drift values (Table 5). Risk quotients were based on fish LC_{50} for bluegill (20 ppb) and *Daphnia magna* LC_{50} (1.0 ppb).

Table 5. Maximum downwind drift aquatic EECs and rish quotients based on Penn State drift study 1993.

	100 m (21% deposition)			200 m (12% deposition)			300 m (2.8% deposition)		
water depth (inches)	EEC	RQ (fish)	RQ (daphnid)	EEC	RQ (fish)	RQ (daphnid)	EEC	RQ (fish)	RQ (daphnid)
6	154	7.7	154	88	4.4	88	20.5	1.0	20.5
72	25.6	1.28	25.6	7.3	0.37	7.3	1.7	0.1	1.7

Ground and airblast applications are commonly used in agriculture. When buffer zones are used with ground application less drift to off-site aquatic areas is thought to occur. However, drift and runoff remain the common causes of off-site deposition of malathion especially in aquatic situations. Adult mosquito control (adulticiding) is commonly done by aerial and fogging applications. Thermal aerosols or fogs create droplet sizes <20μm that can travel in air currents and dissipate mostly in air.

Conclusions

Malathion is considered lower in toxicity and less persistent (1 to 25 days in soil) than other organophosphorus pesticides. Therefore, extensive use of malathion has occurred in the past 45 years in the U.S. It has been widely used in government eradication programs for mosquitoes, bollworm, and fruitflies. In water, malathion has a half-life of approximately one week and is more stable in acidic aquatic conditions. Malathion is soluble in water and can be highly mobile in soil although the low persistence and application to foliage provide for a relatively low risk to contaminate groundwater. However, a few detections of malathion have been reported in groundwater in various locations in the U.S. Malathion is thought not to bioconcentrate in aquatic species but can be acutely toxic to many species. Malathion is highly toxic to larval stages of amphibians and to aquatic invertebrates.Adverse effects have been reported regarding mortality and illness to fish and wildlife. Malathion is slightly to moderately toxic to birds and slightly toxic to mammals. More studies are needed to determine chronic effects and exposure to malathion degradates and impurities.

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