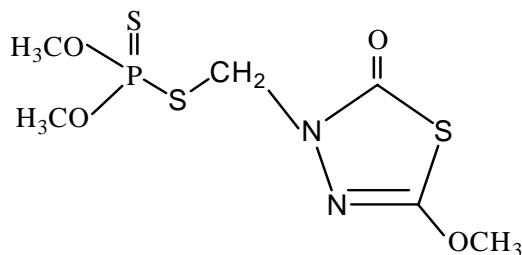


The Environmental Fate of Methidathion

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This document reviews all routes of environmental fate for methidathion under field conditions used in controlling a variety of insect pests. Methidathion is an organophosphate insecticide, chemical name: S-2, 3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-yl methyl O,O-dimethylphosphorodithioate.

TABLE 1. Physical Properties

Appearance:	colorless crystalline	b
Molecular Weight:	302.34	b
Solubility: Water	221 mg/L @ 22°C, pH 4.4	a
Melting Point:	39.5° C	b
Vapor Pressure:	3.37x10 ⁻⁶ mm Hg	a
Hydrolysis t _{1/2} :	37 days (pH 5)	f
	48 days (pH 7)	f
	13 days (pH 9)	f
Aquatic Photolysis t _{1/2} :	8.2 days	f
Aerobic Soil Metabolism t _{1/2} :	3.1, 11.3 days	a,f
Anaerobic Soil Metabolism t _{1/2} :	10 days	f
Soil Photolysis t _{1/2} :	1.54 days	a

Field Dissipation $t_{1/2}$:	5 - 30 days	a,f
Log Octanol-Water coefficient (log K_{ow}):	2.22	a
K_{oc}	400	b
Henry's Constant (K_H):	$1.66 \times 10^{-9} \text{ atm m}^3 \text{ g}^{-1} \text{ mol}^{-1}$	d
Vegetative $t_{1/2}$:	4.4 days	c

Acute Toxicities

Mallard LD ₅₀	23.6 mg/kg	e
Daphnia magna LC ₅₀ (48 hr)	7.2 ug/L	e
Mysid shrimp LC ₅₀ (96 hr)	0.7 ug/L	e
Rainbow Trout LC ₅₀ (96 hr)	10.5 ug/L	e
Bluegill Sunfish LC ₅₀ (96 hr)	17.2 ug/L	e
Honeybee LD ₅₀ (48 hr)	0.23 ug/bee	e

a DPR PestChem Database (Kollman and Segawa, 1995)

b Extoxnet

c L. Ross et al., 1997

d CIBA-GEIGY CORP 1987.

e DPR ecotox database (J. Shelgren, DPR Registration Branch)

f USEPA 1999b

GENERAL INFORMATION AND MODE OF ACTION

Methidathion is an active ingredient in the following products: Somonic, Somonil, Supracide, Suprathion, and Ultracide and is also formulated with many other pesticidal active ingredients. Formulations of the chemical include emulsifiable concentrate, wettable powder, and ultra low volume liquid. Currently, Supracide® is the only registered methidathion product in California (2002). Methidathion is highly toxic and classified as EPA toxicity class I (Danger). It is a Federally and California Restricted Use Pesticide. As such it can only be applied in California by a licensed pesticide applicator, or under the supervision of a licensed pesticide applicator. Methidathion is applied by fixed-wing aircraft, ground-boom sprayer, air-blast sprayer, low-pressure hand-wand, and by backpack sprayer.

Organophosphates (OP) such as methidathion share a common mechanism of toxicity: the inhibition of cholinesterase. Methidathion belongs to the OP sub-class of phosphorodithioates. In general, the oxygen analogs of phosphorodithioates (e.g., methidathion oxon, Figure 1) are much more potent cholinesterase inhibitors than the parent OPs, but are also more labile. The *in vivo* oxidation of phosphorodithioates to their more potent oxons is called activation.

Cholinesterase is an important enzyme needed for the proper functioning of the nervous systems of mammals, fish, invertebrates and insects. Cholinesterase catalyzes the breakdown of acetylcholine, a chemical produced in the body that is released by the nerves to activate muscle contractions. The inhibition of cholinesterase by OPs results in the accumulation of acetylcholine at the neuron/neuron and neuron/muscle junctions, causing rapid twitching of voluntary muscles and finally paralysis.

Methidathion is a non-systemic organophosphate insecticide registered for the control of a wide range of agricultural mite and insect pests in terrestrial food crops. Methidathion is used to protect plants from insects with sucking, chewing mouthparts such as scale, moths, and aphids.

In 2001, a total of 93,055 pounds of methidathion were applied in California (DPR 2001 Pesticide Use Report). The highest uses were in stone fruits, citrus, artichokes, walnuts, almonds, and to a lesser extent olives.

ENVIRONMENTAL FATE

Chemical and physical properties of pesticides largely determine their occurrence, transport, and fate in the environment. These include aerobic and anaerobic metabolism half-lives, photolysis half-life, solubility, soil sorption coefficient (K_{oc}), vapor pressure, Henry's law constant, and hydrolysis half-life.

Air

Volatilization occurs when a chemical moves from a wet or dry surface into the atmosphere. The common processes by which chemicals enter the air are through drift during application, wind erosion of soil, or by post-application volatilization. The relative rates depend on a number of factors including: wind speed, terrain, temperature, soil,

concentration, vapor pressure and K_H . A low vapor pressure of 3.4×10^{-6} mm Hg indicates that methidathion is relatively non-volatile, and the low Henry's law constant of 1.66×10^{-9} atm $m^3 g \cdot mol^{-1}$ (Kollman and Segawa, 1995) suggests a relatively low potential for volatilization from water or moist soil.

However, Aston and Seiber (1997) measured residual methidathion and methidathion oxon in air during a study in the Sierra Nevada Mountains, east of the Central Valley. Among other chemicals methidathion and methidathion oxon were found at their highest concentration at Lindcove (elevation 475 ft) in air samples. Methidathion and the oxon were found in air at an average of 6600 pg/m^3 and 5200 pg/m^3 of air, respectively, during the in-summer use season.

Water

Methidathion is a moderately soluble pesticide with a water solubility of 221 mg/L. Consequently methidathion has the potential to run off into surface water depending on use conditions and environmental factors. Methidathion has been detected in California surface water as a result of rain runoff from wintertime dormant spray applications (e.g., Ganapathy et al., 1997; Nordmark et al. 1998; Ross et al., 1999).

Reported hydrolysis half-lives for methidathion are 37, 48, and 13 days at pH 5, 7 and 9, respectively (20°C) (USEPA, 1999b). The primary hydrolysis product was 2-methoxy-1, 3,4-thiadiazole-5 (4H)-one. The reported aqueous photolysis half-life of methidathion is 8.2 days (Table 1).

Soil

The relative tendency of a chemical to sorb to soil is described by Koc, the organic carbon-normalized soil sorption coefficient. In general, poorly soluble non-polar chemicals generally display a higher tendency to sorb to soil rather as opposed to remaining in the aqueous phase. Soils vary in organic carbon content, and as soil organic matter increases the fraction of pesticide sorbed also generally increases. Methidathion has a relatively low Koc value of 400 and thus has a relatively low affinity to sorb to soil particles. Consequently methidathion has potential to run off into surface water. In

contrast, methidathion has a low likelihood of leaching to ground water due to its relatively short soil half-life (Table 1); methidathion has not been detected in California ground water. Soil metabolism half-lives ranging from 1.5-8 days indicate that methidathion is not persistent in soil, as also shown indicated by reported field dissipation half-life of 5 days (Table 1). Microbial degradation appears to be the dominant route for methidathion degradation in laboratory soil degradation studies (USEPA, 1999b).

Vegetation

The main route of methidathion metabolism in plants is through hydrolysis to yield methidaoxon (Figure 1). Measured foliar dissipation half-lives range from 0.3 to 5 days (USEPA 1999b).

Bull (1968) assessed the metabolism of methidathion in cotton, alfalfa and bean plants. Plants were treated by foliar application, petiole injection and stem uptake. The only metabolite found in alfalfa and bean plants was methidathion oxon. It was found in low concentrations with a maximum of 1.3% of the application rate being detected one day after treatment

Apple trees were treated in a study by Eberle and Hormann (1971) to determine penetration of the compound into the fruit. Residues were found to be 0.5 ppm (5% of that applied), <0.02ppm and <0.01ppm at 1day, 4 weeks and 6 weeks, respectively, after application. This study concluded that plants readily absorb and degrade methidathion.

Fish and Invertebrates

Even though methidathion has relatively low persistence in the environment, the expected dissipation rate on wildlife food items is slow enough that birds and mammals may be exposed to concentrations exceeding chronic levels of concern for several weeks. (U.S. EPA 1999a) Studies showed there is a potential it will accumulate in fish tissues. Levels of residue in bluegill fish, after one month of exposure to low concentrations (0.05 ug/L) in water, were 1.0 ug/kg in the edible tissue, 3.9 ug/kg in non-edible tissue, and 2.4 ug/kg in whole fish (Exttoxnet 2002).

California Department of Fish and Game identified methidathion toxicity thresholds for freshwater and saltwater organisms. *Ceriodaphnia dubia* is found to be the

most acutely sensitive (mean 96-h LC₅₀ 2.2 ug/L) freshwater species, and *Mysidopsis bahia* is found to be the most acutely sensitive (mean 96-h LC₅₀ 0.7 ug/L) saltwater species (Menconi and Siepmann, 1996).

Methidathion concentrations may exceed levels of concern for both acute and chronic effects to fish, mammals, birds and aquatic invertebrates. (U.S. EPA 1999a)

ENVIRONMENTAL MONITORING

The Department of Pesticide Regulation, along with many other state and private agencies, sample for methidathion in surface water. Methidathion is considered important to California's dormant-spray water quality/aquatic toxicity concerns. It has had substantial use as a dormant spray pesticide throughout the 1990's and has been detected in surface water in several studies.

Methidathion has been detected chronically in the Sacramento-San Joaquin River system; concentrations have been as high as 15.1 ug/L, although more typical detections range from 0.07 to 2.45 ug/L (Menconi and Siepmann, 1996). Bioassays were used to determine potential biological effects of pesticide-contaminated water collected during a dormant spray study conducted by U.S. Geological Survey and California Regional Water Quality Control Board (Kuivila and Foe, 1994). Seven day *C. dubia* mortality was observed on February 12, 13, and 14, 1993. *C. dubia* was found to have an LC₅₀ for methidathion of 8.3 ppb.

In 1992 and 1993 the Department of Pesticide Regulation began frequent sampling of the San Joaquin River to characterize water quality, identify toxicity sources, and determine mass loading of insecticides during high use seasons (i.e. winter dormant sprays and spring/summer applications) (Ross et al. 1999). Methidathion was detected in 16 of 78 samples collected during a Langrangian study and in 6 of 30 samples collected during a temporal survey. Langrangian study concentrations ranged from 0.07 to 12.4 ug/L, and 0.07 to 0.33 ug/L during the temporal survey (Ross et al. 1999).

In the summers of 1991 and 1992, methidathion was detected in one of 112 samples (0.9%), at 0.11 ppb. The low detection is probably due to the fact that even though 66,793 lbs were applied in the three counties within the watershed, methidathion is a dormant season (December-March) insecticide (Ross et al. 1999).

During a 1994 storm event, along with other organophosphates, methidathion concentrations ranging up to 0.104 ppb were detected in the Sacramento River Basin (Domagalski, 1994). The highest concentration occurred at peak discharge, and lower concentrations were measured at the decline of discharge.

In 1998, Dow AgroSciences, monitored surface water at three locations on the lower reach of Orestimba Creek, Stanislaus County, California. Mass loading into the main-stem San Joaquin River for the year long study of methidathion was estimated at 0.08% of the 163.1 lbs applied to fields draining into the creek (Poletika and Robb, 1998)

SUMMARY

Methidathion is a pesticide that kills mites and insects. It is effective by disrupting the nervous system and causing paralysis. It is applied mainly during the dormant season. High uses are for food crops including, stone fruits, citrus, artichokes, walnuts and almonds.

Methidathion is relatively non-volatile. Furthermore the low Henry's Law constant of $1.66 \times 10^{-9} \text{ atm m}^3 \text{ g} \cdot \text{mol}^{-1}$ indicates that it volatilizes slowly from water.

Methidathion is relatively soluble and has a moderately low Koc of 400. These properties indicate that methidathion is relatively mobile in soil, and has the potential to move off-site after application in surface water runoff. However leaching appears unlikely due to its relatively short soil half-life, and methidathion has not been detected in California ground water. Methidathion has a hydrolysis half-life of 48 days at pH 7 (20°C), and photodegradation may be an important dissipation route with a reported half-life of 8.2 days. Soil metabolism half-lives of 3-11 days and field dissipation half-lives of 5-30 days indicate that methidathion is unlikely to persist in soil.

Methidathion has been detected frequently in the Sacramento-San Joaquin River system; concentrations have been as high as 15.1 ug/L, although more typical detections ranged from 0.07 to 2.45 ug/L.

Methidathion is highly acutely toxic to aquatic organisms. LC_{50} for methidathion are 10.5 ug/L in rainbow trout and 17.2 ug/L in bluegill sunfish (DPR 2002).

While extensive persistence appears unlikely, dissipation rates are slow enough that birds and mammals may be exposed to concentrations exceeding levels of concern for several weeks.

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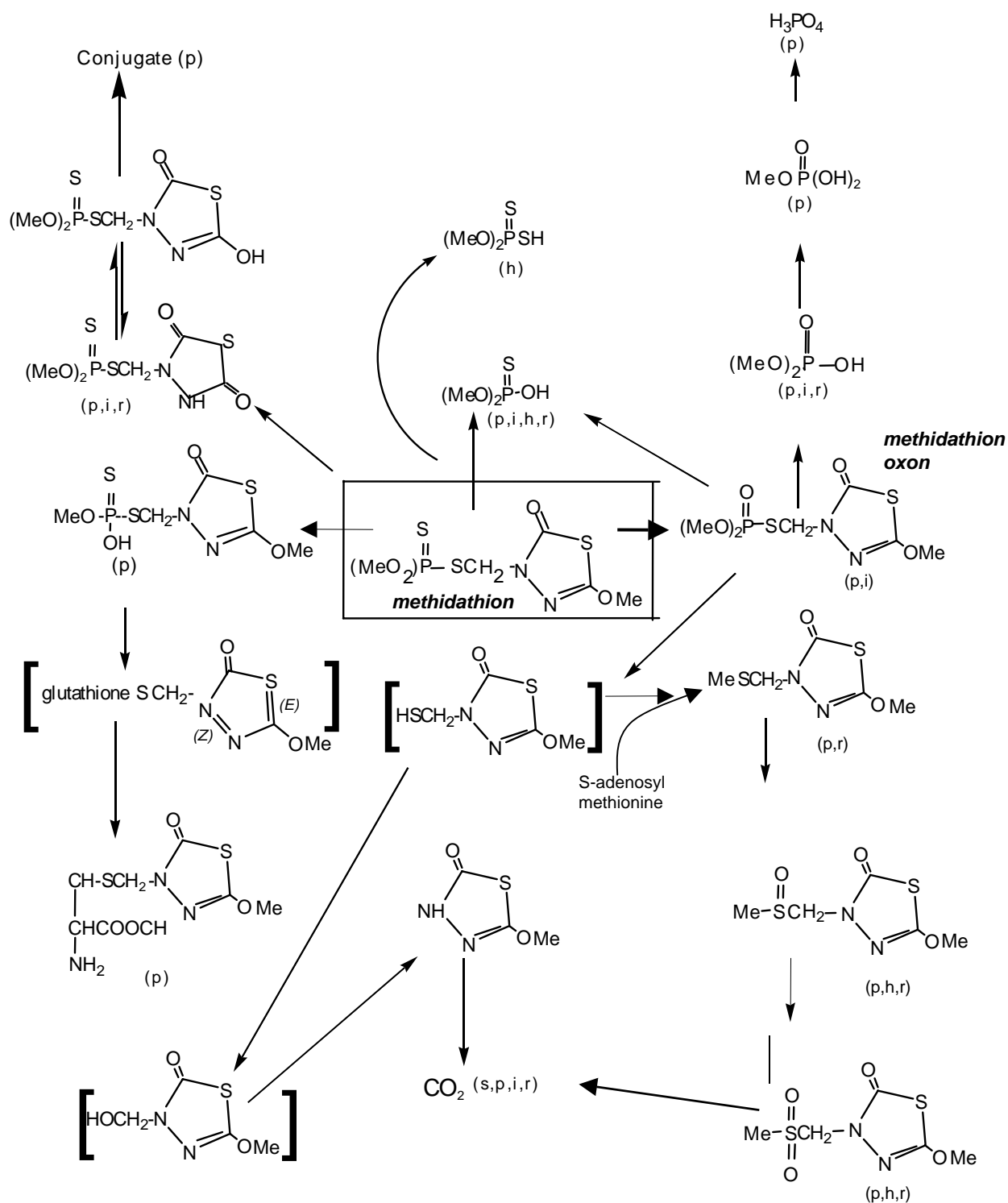


Figure 1. Proposed routes of methidathion metabolism. p= plants, i = insects, h=human, r=rats. After Royal Society of Chemistry, 1999.