DEGRADATION OF MALATHION IN THERMALLY GENERATED AEROSOLS[1]

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ABSTRACT. The degradation of malathion, undiluted and diluted with No. 2 fuel oil, in thermally generated aerosol clouds was examined at selected temperatures ranging from 121 to 566°C. Undiluted malathion residues decreased from 1.76 to 0.21 μg/ml over this range of temperatures. Malathion diluted with fuel oil decreased from 0.14 to 0.02 μg/ml as the temperature was increased 288 to 510°C.

Organophosphorus (OP) insecticides have been used in the pest management industry for decades. They accounted for approximately 30% of the registered synthetic insecticides and acaricides in the United States in 1975 (Matsumura 1975). Application techniques and equipment design have changed dramatically during this period for both row crops and the vector control industry. For vector control, thermo-fogging gave way to cold aerosol methods and is not routinely used in this country at present. This is not the case in other countries where thermofogging remains the primary application technique for vector control. For instance, in 1990, 95% of Lowndes Engineering (Valdosta, GA 31601) thermo-fog sales were to India and the Middle East (Lowndes Engineering, Inc., personal communication).

The pyrolysis involved in thermo-fogging may actually destroy the insecticide and release combustion by-products which may be more lethal than the original compound. The effects of these thermally generated products on both pest and non-target insects are largely unknown (Iyer and Parmar 1984).

Malathion [S-(1,2-dicarbethoxyethyl)-), O-dimethyldithiophosphate] is one of the OPs in widespread use in the disease vector control industry. Malathion is miscible with most organic solvents, hydrolyzes at pH ≤5 or ≥8, and decomposes at excessive temperatures (Iyer and Parmar 1984). Because of its low mammalian toxicity and its efficacy as a general insecticide, malathion is particularly useful in a variety of pest management situations. It has been studied in the laboratory extensively with respect to its pyrolytic breakdown. McPherson and Johnson (1956) investigated the thermal stability of malathion and concluded that heating in a test tube to about 132°C resulted in chemical degradation and production of SO_2. Ahling and Wiberger (1979) determined that destruction of malathion required a temperature >371°C. Infrared spectrum changes have also been reported when malathion was heated to 149°C in a furnace (Stojanovic et al. 1972). Malathion may have been converted to other carbonyl compounds at temperatures greater than 149°C (Stojanovic et al. 1972, Iyer and Parmar 1984). Stojanovic et al. (1972) reported changes in the infrared spectra of "thermo-shocked" malathion. Thermoshocking involves partial degradation of molecules by heating at temperatures much lower than that required for their complete destruction. In Stojanovic et al. (1972) the degradation temperature reported for malathion (149°C) was the lowest temperature at which a spectrum of the residue differed conspicuously from that of the untreated insecticide. Given the above laboratory findings, and since malathion is still used in thermo-fogging in some countries, this preliminary study investigated the degree of degradation in thermally generated aerosol clouds.

The thermal fogger utilized was a Leco 120D (Lowndes Engineering Co., Inc., Valdosta, GA 31601). A standard FMI laboratory pump (Fluid Metering, Inc., Oyster Bay, NY 11771) was connected directly to the Leco 120D heater and calibrated to deliver undiluted malathion (American Cyanamid, Wayne, NJ 07470) at 4 ounces per minute (4.3 = high label rate). Diluted malathion (5 fl oz per 5 gal of No. 2 fuel oil) was delivered at 12 fl oz per min. Heater temperatures at which air samples were collected were 121, 288, 343, 399, 454, 510 and 566°C. These temperatures were based on preliminary work indicating that 121°C was the lowest temperature at which a fog could be maintained with the Leco 120D. A temperature of 566°C was a safe upper limit at which the machine could be operated. Intermediate temperatures were based on a spread which was able to be maintained with the machine. Aerosol samples were also collected from a Leco HD cold aerosol generator. As a control, ambient air was sampled. Controls were treated in same manner as the test samples except for the inclusion of

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[1] The opinions and assertions contained herein are the private ones of the writers and are not to be construed as official or reflecting the views of the Navy Department or the Naval Service at large.

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Table 1. Residue samples for malathion (±SD) diluted with No. 2 fuel oil and undiluted malathion in thermal and cold generated aerosol clouds.

Dilution	Machine	Temp. (°C)	Malathion (mg/ml)
Undiluted	Leco 120D[1]	121	1.76 ± 0.31[2]
		288	1.46 ± 0.09
		343	1.06 ± 0.11
		399	0.49 ± 0.10
		510	0.34 ± 0.27
		566	0.21 ± 0.11
	Leco HD	39	1.10 ± 0.11
Diluted	Leco 120D[3]	288	0.14 ± 0.01
		343	0.01 ± 0
		510	0.02 ± 0.01
	Control	28	<0.001

[1] Flowrate = 4 fl oz/min.
[2] Detection limit = 0.001 mg/ml.
[3] Flowrate = 12 fl oz/min, 5 fl oz/gal of No. 2 fuel oil.

the malathion. Two samples were collected at each temperature setting.

Samples were collected with a Gilian Hi Flow Sampler Model HFS 513A (Gilian Instrument Corp., Princeton, NJ 08540). The air sampler was mounted on one end of a 152 × 2 cm dowel with 6.5 mm (1/4 in) flexible tubing extending to the opposite end of the dowel. The tubing was attached to a two-piece polystyrene cassette in which was placed a glass fiber paper (Gelman Type AE). The cassette was held to the dowel end by a standard alligator clip. Aerosol samples were collected for 30 sec in each of 2 replications.

Within 2 h after sampling, the filter was transferred to a clear 20 ml vial containing 15 ml of chromatography grade hexane (GC grade). Samples were then subjected to gas chromatograph analysis (Iyer and Parmar 1984) by Chemspec Internationale, Inc., Germantown, TN.

In general, both diluted and undiluted malathion residues (micrograms/milliliter) decreased over the range of temperatures examined. Malathion residues from the undiluted formulation at 121, 288, 343, 399, 510 and 566°C were 1.76, 1.46, 1.06, 0.49, 0.34 and 0.21 μg/ml, respectively (Table 1). Undiluted malathion residues from the cold aerosol Leco HD (39°F) was 1.1 μg/ml. It is clear that above 343°C malathion was significantly reduced by thermal decomposition. There were no other thermolysis products tested for in this GC analysis. These results show that malathion residues in dilute and undilute formulations decrease in thermal fogs as the temperatures at which they are generated, increase. Iyer and Parmar (1984) state that isomerization of malathion occurs on heating above approximately 150°C. These data, however, indicate that temperatures in excess of 343°C should not be utilized in generating thermo-fogs in order to prevent unnecessary decomposition of the active ingredient. This preliminary study on the degradation of malathion by heating in a standard mosquito control thermal fogger indicates that additional work should be undertaken to determine the efficacy of the malathion degradation products by standard bioassay tests.

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