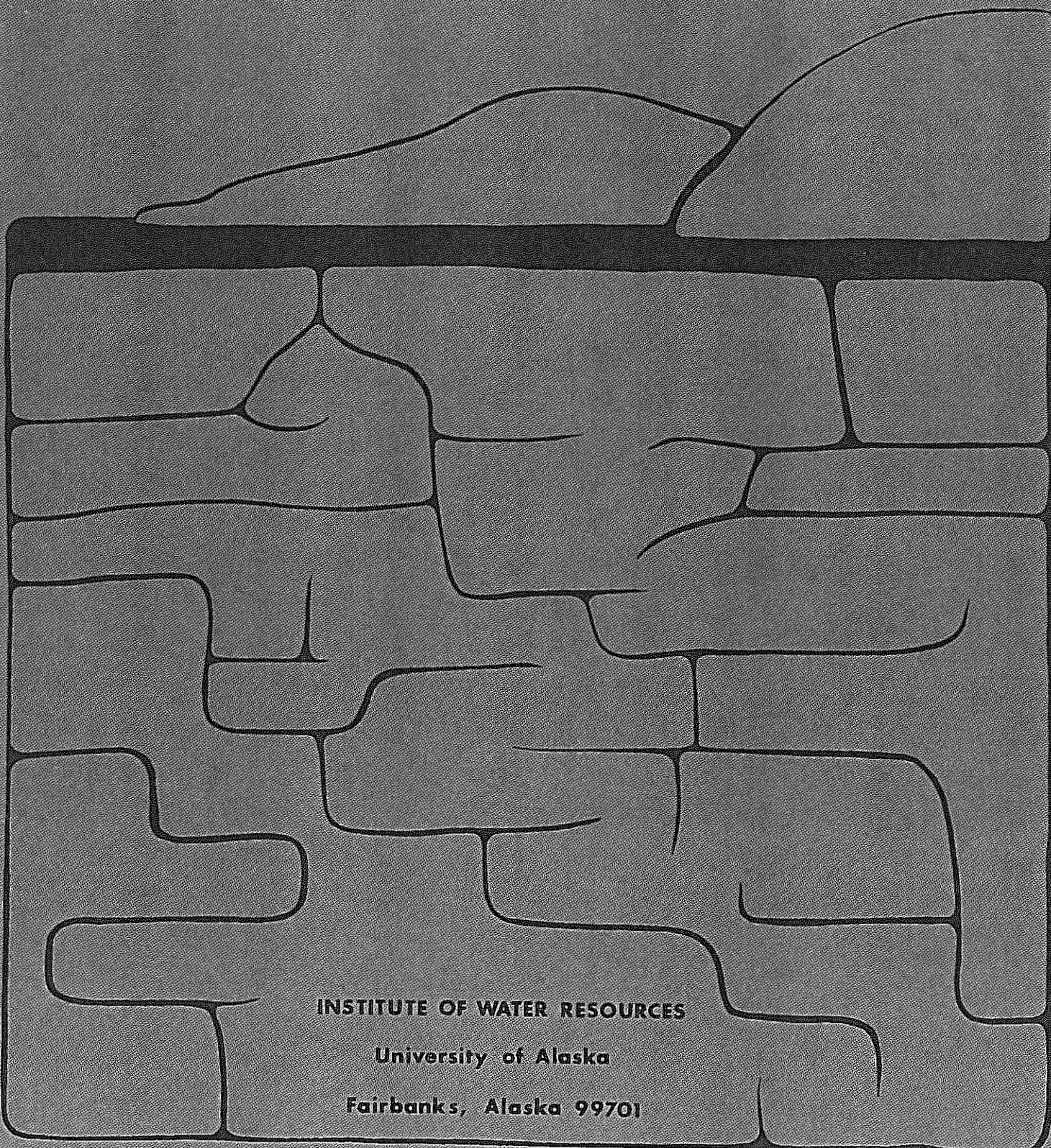


PHOTOCHEMICAL DEGRADATION
OF MALATHION



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Photochemical degradation of malation
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Completion Report
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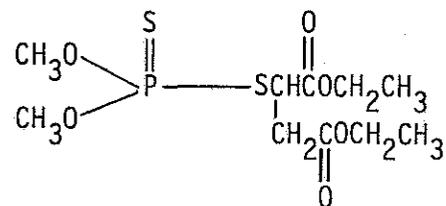
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INTRODUCTION

This is the final completion report for a two-year project which began 1 November 1975. The original completion date was extended to 30 September 1977 to allow collection of samples and data through the summer of 1977.

Malathion is a thiophosphate insecticide, 0,0-dimethyl-S-(1,2-dicarbethoxyethyl) phosphorodithioate:



It is less toxic than DDT and decomposes over a much shorter period of time. With the suspension of DDT in pest control programs in 1965, use of malathion has been increasingly widespread in Alaska's interior.

In spite of its low toxicity to animals, malathion is poisonous at some level. Lethal doses for domestic sheep and cattle are 150 mg/kg and 200 mg/kg of body weight, respectively. The fatal dose of malathion for a 70 kg man has been estimated to be 60 g, with some clinical exceptions (McKee and Wolfe, 1963; Hayes, 1964). Dietary levels (ppm) producing minimal or no effect after continuous feeding for 90 days to 2 years to rats and dogs have been reported as 100-1000 and 100, respectively (Lehman, 1965). On the other hand, malathion has been identified by gas chromatography in extracts of water associated with several fish kills (Garrison, Keith, and Alford, 1972).

In a study of malathion persistence in the soil near Fairbanks, Alaska, during the summer of 1967, half of the sampling sites showed the presence of malathion and its oxidation product, malaoxon, prior to aerial spraying (Holty, 1970). Since there had been no ground spraying since the summer of 1966, this would indicate that malathion was not degrading in the environment as fast as anticipated. This is important since it is then possible for the spring runoff to carry significant quantities of the pesticide and its degradation products into streams and rivers in the area. Retention of the malathion appears to depend on

the amount of rainfall, and the summer of 1966 had been very dry. During the wetter summer of 1967, the post-spray soil samples showed a rapid drop in the level of malathion except at sampling sites in "mucky" soils which also increased noticeably in moisture as the amount of rainfall accumulated (Figure 1).

Very little has been known about the aqueous photodecomposition of malathion and nothing was known of its vapor phase stability under atmospheric conditions and exposure to sunlight prior to this study.

It has been found that many common pesticides exhibit their principal electronic absorption maxima in the region between 220 and 440 nm (Table 1).

TABLE 1. UV Absorption Maxima of Selected Herbicides in Water

| Common Name | Chemical Name | Absorption Maximum (nm) |
|-------------|---|-------------------------|
| Simazine | 2-chloro-4,6-bis (ethylamino)-s-triazone | 220 |
| 2,4-D | 2,4-dichlorophenoxyacetic acid | 220,230,283 |
| 2,4,5-T | 2,4,5-trichlorophenoxyacetic acid | 220,289 |
| IPC | Isopropyl N-phenylcarbamate | 234 |
| Monuron | 3-(4'-chlorophenyl)-1,1-dimethylurea | 244 |
| Propanil | 3'-4'-dichloropropionanilide | 248 |
| Dicryl | 3',4'-dichloro-2-methylacrylanilide | 258 |
| Amiben | 3-amino-2,5-dichlorobenzoic acid | 297 |
| DNBP | 4,6-dinitro-2- <i>sec</i> -butylphenol | 375 |
| Trifluralin | α,α,α -trifluoro-2,6-dinitro-N,N-di- <i>n</i> -propyl- <i>p</i> -toulidine | 376 |

Energy from the sun is a reasonable source for carrying out numerous photochemical reactions among these pesticides. At the earth's mean solar distance, the energy amounts to $\sim 0.14 \text{ W/cm}^2$ which is equivalent to 1170 W on each square yard. However, only about two-thirds of this energy reaches the earth's surface, the rest being absorbed, scattered, and reflected by the atmosphere. Very short wavelength ultraviolet is effectively absorbed by the ozone in the atmosphere and a wavelength of 286.3 nm is the shortest ever recorded at the earth's surface. The solar energy may be considered negligible below $\sim 295 \text{ nm}$ and the maximum total energy is found at 540 nm.

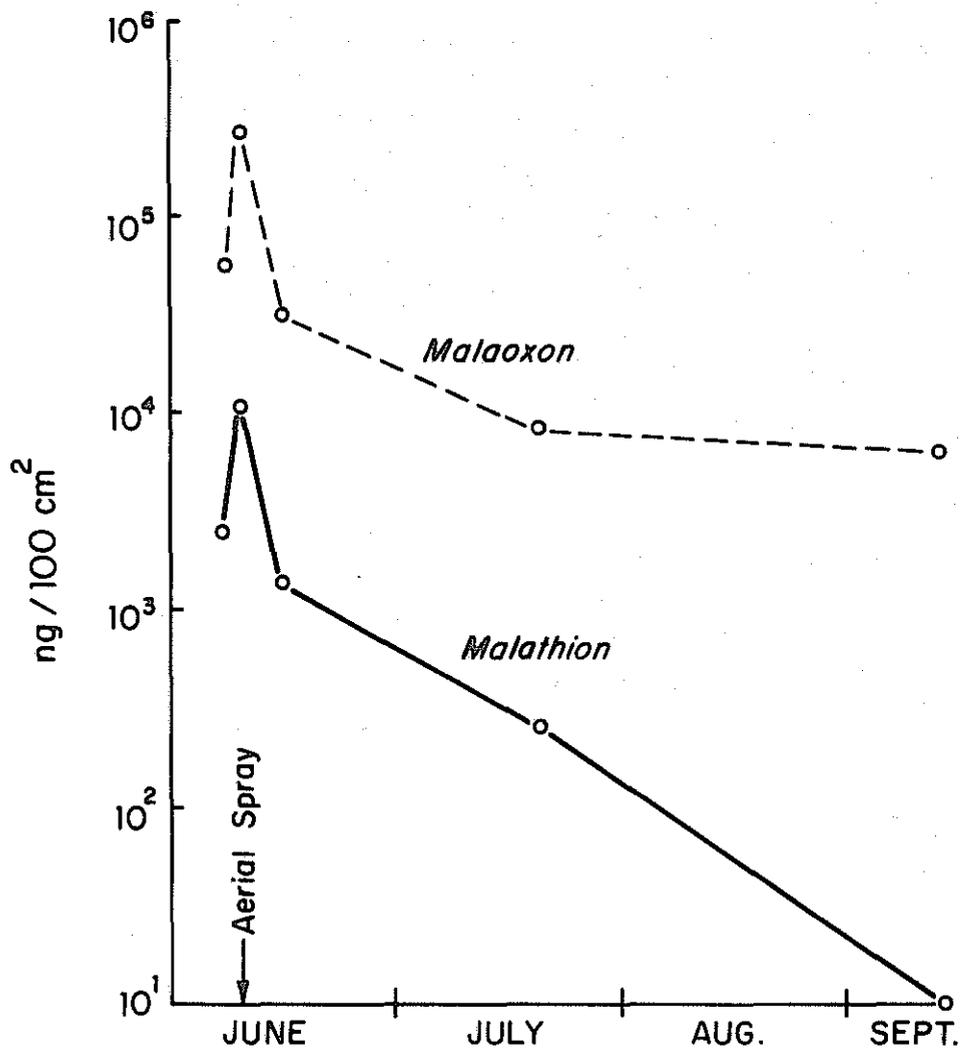


Figure 1: CONCENTRATION OF RESIDUE RECOVERED FROM SAMPLES OF THE SURFACE CENTIMETER AT MURPHY DOME EAST-1967

Dispersion of ultraviolet light in the open sky may equal or surpass the energy from direct radiation. The shorter the wavelength, the greater the dispersion. Long days with high dispersion often produce more total light energy than shorter days with greater heat and more intense direct sunlight. Thus, it is interesting to note that Alaska, in the late spring and summer, may receive more light energy than Honolulu, New York, or Los Angeles (U. S. Department of Commerce, 1966).

While the photochemistry of pesticides in organic and aqueous solutions has been the subject of a variety of investigations, there are almost no reported vapor phase photochemical studies. That the vapor phase photochemistry may be even more interesting and at least as important as the liquid phase work, is indicated by the recently reported irradiation of 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane (DDT) vapor, yielding unsuspected polychlorinated biphenyls as products (Maugh, 1973). DDT in solutions (including water) or as a thin film is essentially inert to sunlight, but when DDT vapor, in the presence of a large excess of air, was irradiated with light in the region 290 to 210 nm, Moilanen and Crosby found that DDT was very slowly converted to 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethane (DDD) and about 15 times more rapidly to 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene (DDE). After four days of irradiation, as much as 34% of the DDT was converted to DDE and about 2% of DDD. Further experiments showed that DDD is inert to ultraviolet radiation, but that, under the same conditions, DDE is converted to at least nine other products, including 4,4'-dichlorobenzophenone and several chlorinated biphenyls.

In spite of the high molecular weight and low vapor pressure of these pesticides, their rate of evaporation from aqueous solutions can be surprisingly high. This is due to the high activity coefficients of these compounds in water which cause unexpectedly high equilibrium vapor partial pressures and high rates of evaporation from aqueous solutions of compounds such as hydrocarbons, and chlorinated hydrocarbons which are of low solubility (Mackay and Wolkoff, 1973).

The major route by which chlorinated hydrocarbons are transported is apparently through the atmosphere. Concentrations of pesticide residues of 104-229 ppt (parts per trillion) have been found in rainwater

in England (Frost, 1969) and Peterle (1969) has reported DDT concentrations of 40 ppt in meltwater from Antarctic ice. Some of these contaminants are applied by spraying techniques with the possibility of direct evaporation. However, most are used as solids, liquids, or wettable powders in which transport to the atmosphere can take place by natural evaporative processes when exposed to the atmosphere.

Predictions of evaporation parameters and rates for various compounds based on the equations developed by Mackay and Wolkof (1973) are shown in Table 2. This table shows the value of the dimensionless quantity, $\tau E/G$, which is a measure of the time required for evaporation for each compound (where one considers G grams of water containing m_i grams of the compound i which may be present either as a solution or as a separate phase and from which E g/day of water evaporates); F , the fraction of the mass of i present which is evaporated when 0.01% of the water is evaporated; and τ , the "half life" of the compound in aqueous solution for a depth of water L of 1 meter.

It is, therefore, readily apparent that a large percentage of the world's accumulated production of pesticides spends a significant amount of time in the vapor phase. Photochemical decomposition of these vapors, which may also be photosensitized by organic (e.g. ketones) or inorganic (e.g. mercury) atmospheric contaminants, remains a virtually unresearched, vitally important area for study.

TABLE 2. Evaporation Parameters and Rates for Various Compounds at 25°C

| Compounds | Solubility mg/l | Vapor Pressure mm Hg | τ E/G | F % | τ for L=1 meter |
|--|----------------------|-------------------------|----------------------|--------|-------------------------|
| Alkanes | | | | | |
| n-Octane | 0.66 | 14.1 | 1.2×10^{-7} | >99 | 3.3 sec |
| 2,2,4-Trimethylepentane | 2.44 | 49.3 | 1.3×10^{-7} | >99 | 4.1 sec |
| Aromatics | | | | | |
| Benzene | 1780 | 95.2 | 7.0×10^{-5} | 62 | 37.3 min |
| Toluene | 515 | 28.4 | 5.8×10^{-5} | 70 | 30.6 min |
| o-Xylene | 175 | 6.6 | 7.4×10^{-5} | 61 | 38.8 min |
| Cumene | 50 | 4.6 | 2.7×10^{-5} | 92 | 14.2 min |
| Naphthalene | 33 | 0.23 | 3.3×10^{-4} | 19 | 2.9 hr |
| Biphenyl | 7.48 | 0.057 | 2.5×10^{-4} | 24 | 2.2 hr |
| Pesticides | | | | | |
| DDT | 1.2×10^{-3} | 1×10^{-7} | 1.0×10^{-2} | 0.7 | 3.7 days |
| Lindane | 7.3 | 9.4×10^{-6} | 7.9×10^{-1} | 0.009 | 289 days |
| Dieldrin | 0.25 | 1×10^{-7} | 2.0 | 0.004 | 723 days |
| Aldrin | 0.2 | 6×10^{-6} | 2.6×10^{-2} | 0.3 | 10.1 days |
| PCB's | | | | | |
| Aroclor 1242 (C ₁₂ H ₇ Cl ₃) | 0.24 | 4.06×10^{-4} | 6.8×10^{-4} | 9.7 | 5.96 hr |
| Aroclor 1248 (C ₁₂ H ₆ Cl ₄) | 5.4×10^{-2} | 4.94×10^{-4} | 1.1×10^{-4} | 46 | 58.3 min |
| Aroclor 1254 (C ₁₂ H ₅ Cl ₅) | 1.2×10^{-2} | 7.71×10^{-5} | 1.4×10^{-5} | 39 | 1.2 min |
| Aroclor 1260 (C ₁₂ H ₄ Cl ₆) | 2.7×10^{-3} | 4.05×10^{-5} | 5.5×10^{-5} | 72 | 28.8 min |
| Other | | | | | |
| Mercury | 3×10^{-2} | 1.3×10^{-3} | 3.4×10^{-5} | 87 | 17.9 min |

Note: The vapor pressure of malathion at 20-25°C has been reported to be 40×10^{-6} mm Hg and water solubility is 145 ppm.

SOURCE: Mackey, D., and Wolkoff, A. W. (1973). Environ. Science and Technology. 7:611-614.

OBJECTIVES

The objective of this research was to extend our qualitative and quantitative knowledge about the persistence and photodecomposition of malathion. Specifically the objectives were to:

1. Study the aqueous photodecomposition of malathion in degassed and oxygenated solutions using a variety of irradiating wavelengths and ambient conditions.
2. Study the aqueous photodecomposition of malathion-clay complexes.
3. Study the vapor phase photodecomposition of malathion over aqueous solutions.
4. Conduct field studies of environmental decomposition and loss of malathion from representative Alaskan soil plots.

RESEARCH RESULTS

The research consisted of two related components: (1) field work on malathion persistence and decomposition on Alaskan soil test plots, and (2) experimental laboratory work to develop knowledge about the analysis of malathion and its photodecomposition products.

Two test plots were selected for field studies involving the environmental persistence of malathion. Each plot was 1 m² and both were in the Forest Soils Laboratory, Chena Hot Springs Road, Plot A. Both were located on the south side of a hill. One plot selected was beneath a stand of aspen trees and the other was beneath a stand of alder. Both plots were slightly sloping and flat.

Each plot was sprayed with 0.11 g of malathion in aqueous solution which is equivalent to a rate of 1 pound of malathion per acre. This is the usual rate applied in the interior of Alaska for mosquito control. Immediately after spraying, 4 cores were obtained using a 2-inch diameter hand corer. Each core extended from the surface down to the start of the inorganic soil layer and was divided into 3 distinct layers: (1) undecayed new leaves, (2) partially decayed vegetation, and (3) humus. Further samples were taken 2 days after spraying and then once a week until the ground froze. All samples were kept frozen until analyzed.

Malathion was removed from the samples by acetone extraction. It was found that 4 to 5 hours was the optimum time for refluxing. Samples were analyzed on a Hewlett-Packard Model 5730A gas chromatograph fitted with a ⁶³Ni electron-capture detector and a nitrogen/phosphorus detector. The best column for analysis was 3% DC-200 on 80/100 mesh Gas Chrom Q (6 feet by 1/8 inch I. D.).

Analysis of the samples taken 2 days after spraying indicated that virtually all of the malathion sprayed on the alder plot was still in the top layer of undecayed new leaves, with 2 of the 4 cores showing a trace of malathion in the middle (partially decayed vegetation) layer.

*The laboratory research and analysis desired for the project were severely restricted or curtailed by the extraordinary delay in receiving the gas chromatograph (Hewlett-Packard 5730A), whose sensitive nitrogen/phosphorus detector was essential to all of the analysis required. A major reason for this unavoidable and costly delay was the necessity for the amending of a Nuclear Regulatory Commission license to include and allow shipment of the chromatographic detector.

The remaining samples have not been analyzed and are stored in a freezer. The aspen plot showed 97% of the malathion still on the top layer and 3% in the middle layer. The top layer (undecayed new leaves) of the alder plot was about twice as thick as the corresponding layer of the aspen plot. No rain fell during the time the samples were collected.

Samples of Malathion-50 (50% malathion, 33% aromatic petroleum derivative solvent, and 17% inert ingredients, manufactured by the Ortho division of the Chevron Corporation) and Cythion (95% malathion and 5% inert ingredients, manufactured by the American Cyanamide Company) were purified by preparative gas chromatography with a Beckman GC-2 fitted with a column of 10% DC-200 on 80/100 mesh Gas Chrom Q and Chromasorb G or by fractional distillation through a Vigneux column at 0.1 torr. Analytical standards were prepared according to a procedure provided by American Cyanamide utilizing repeated recrystallization. Malathion prepared in this manner usually analyzed 99⁺ mole per cent by a cryoscopic method. These analytical samples were compared to standards obtained from the National Environmental Research Center, EPA, Pesticides and Toxic Substances Effects Laboratory (#4260).

Experimental photochemistry of the decomposition of malathion in aqueous and vapor phases could not be carried out during the project dates because of the late arrival of the analytical gas chromatograph required for the analysis. None of the gas chromatographs available were sufficiently sensitive to detect the photodecomposition products reliably. A number of samples were irradiated and a number of instruments tried, but none had the needed sensitivity to enable completion of the research objectives.

DISSEMINATION OF RESEARCH RESULTS

No papers or manuscripts have been prepared. The results thus far obtained will be made available to the state agencies expressing an interest in the research.

TRAINING

An advanced degree thesis was not prepared as part of this project because of the difficulty in obtaining the requisite instrumentation for carrying out the research.

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