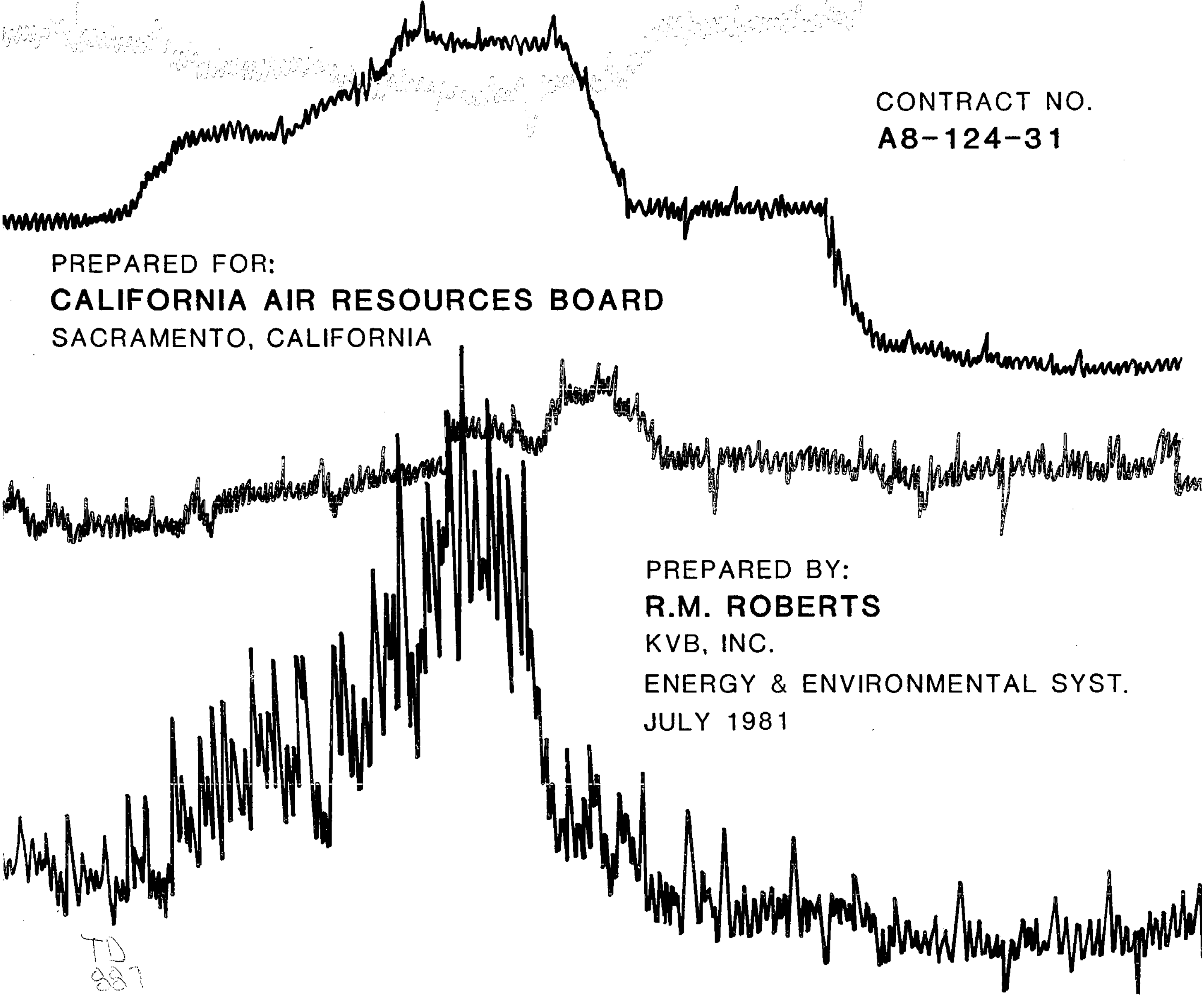
DEVELOPMENT OF EMISSION FACTORS FOR REACTIVE HYDROCARBONS USED IN PESTICIDE FORMULATIONS

KVB13 5809-1256

FINAL REPORT



CONTRACT NO.
A8-124-31

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CALIFORNIA AIR RESOURCES BOARD
SACRAMENTO, CALIFORNIA

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This report was submitted in fulfillment of ARB Contract No. A8-124-31, "Development of Emission Factors for Reactive Hydrocarbons Used in Pesticide Formulations," by KVB, Inc. under the sponsorship of the California Air Resources Board and the University of California. Work was completed 31 October 1980.

ABSTRACT

A program was conducted to determine the amounts of hydrocarbons emitted when selected pesticides are applied to various substrates. An initial laboratory effort was made to establish the relative evaporation rates of 20 test materials under different environmental conditions. Selection of the test candidates, 12 petroleum-based, 6 synthetics, diesel oil #2, and a reference oil (dodecane), was based on usage within the state.

In subsequent field tests, four of the more volatile, predominantly petroleum products and DEF-6 were applied at appropriate coverage rates. Since drift could not be successfully monitored, emissions resulting from that effect could not be included. Using continuous measurement technique, emissions could only be measured when carrot oil was applied.

The results demonstrated that the test configuration employed was not sufficiently sensitive to adequately characterize the volatilization of pesticides under field conditions. With the test arrangement employed, the hydrocarbon concentrations of most pesticides evaporated in the field chamber were below detectable levels and could not be successfully nmonitored, against a (smog) background of several ppmc. The additional hydrocarbons that were undoubtedly released can only be quantified by more sensitive test techniques.

Also included in the study was consideration of techniques for reducing drift and otherwise minimizing volatilization of applied pesticides.

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OVERVIEW

1.1 INTRODUCTION

In agricultural operations, organic pesticides are commonly grouped into two broad classifications. The first comprises formulations in which the active ingredient is a synthetic organic chemical, such as malathion or carbaryl, in a suitable solvent or diluent powder. The other class of organic pesticides are non-synthetic in nature and consist of petroleum refinery mixtures usually with a percent or two of added emulsifier, typically dodecylbenzenesulfonic acid. The non-synthetic hydrocarbon pesticides vary considerably in volatility and aromaticity depending on intended function. This may range from complete herbicide activity (e.g., weed oils) to insect control in leafed trees (e.g., foliar spray oils). A discussion of the types and quantities of non-synthetic hydrocarbon pesticides used in the state of California is contained in a recent report to the ARB by Eureka Laboratories (Ref. 1).

Because the non-synthetic hydrocarbon pesticides may constitute a significant source of hydrocarbon emissions, the behavior of these materials in agricultural use needed to be determined. Thus, the purpose of this study was to determine experimentally the volatilization characteristics of selected pesticides under conditions approximating actual use conditions. While emphasis was placed on the non-synthetic hydrocarbon pesticides, other materials were considered. Those synthetics having significant volatilities were included, as well as those specialized materials that are used to condition crops (e.g., cotton defoliation), causing emissions of photochemically active hydrocarbons (ethylene) from the plant itself.

The scope of work for the program was broken down into five tasks or work areas. These can be synopsized as follows:

Task I - Select representative pesticide formulations for study on the program. The list of items selected for study should include:

(1) formulations that contain volatile reactive hydrocarbons and that are extensively used in California during the smog season; (2) formulations that contain volatile reactive hydrocarbons and that are used extensively over short time durations or in localized areas of California; and (3) formulations that cover a range of suspected volatilities.

Task II - Determine the rate of evaporation of the selected formulations under different environmental conditions using a suitable laboratory device. Variables should include temperature, wind velocity, relative humidity, and presence of soil.

Task III - Design and fabricate a test device that will then be used to measure the emission rates of five selected pesticides when applied to standing crops under actual field conditions. Testing should aim at evaluating the effect of differences in average prevailing temperature, wind speed (controlled), and soil moisture. As an adjunct to this task, consideration (including cost impact) will be given to techniques that will reduce emissions associated with pesticide applications releasing large quantities of hydrocarbons to the atmosphere.

Task IV - Using the available literature, and the Task II evaporation rate test results, estimate the amount of hydrocarbon emitted in the aerosol drift occurring during application. Mode of application will be taken into account, at least semi-quantitatively, as well as the use of adjuvants.

Task V - Develop emission factors for the candidate pesticides under different modes of applications based on the results obtained in Tasks II, III and IV.

1.2 SUMMARY AND CONCLUSIONS

1.2.1 Summary of Results

A. Task I - Candidate Pesticides Selection--

This task was eliminated from the contract by the initial ARB Research Contract Manager (RCM) as being satisfied by another ARB research contract then being conducted by Eureka Laboratories, Inc. That group accordingly submitted a list of non-synthetic candidate materials that would be appropriate for testing on the program. The list was refined by the program staff to eliminate items no longer offered and those which constituted redundant rebrands (identical materials on the list carrying different labels). Since no synthetics were nominated, the program staff produced recommendations for this requirement. The final ARB-approved list of test-worthy candidates then became:

Brand or Generic Name	Pesticide Category
Non-synthetics:	
ARCO Weed Killer "A" Lite	Non-selective Weed Oil (aromatic)
Beacon Weed Killer #5	Selective Weed (carrot) Oil
Chevron Weed Oil	Non-selective Weed Oil (aromatic)
Diesel Oil #2	Non-selective Weed Oil
Gavicide Super 90	Narrow-Range Oil
Keen-Kil Weed Oil #20	Selective Weed (carrot) Oil
Keen-Kil Weed Oil #40	Non-selective Weed Oil (aromatic)
Leffingwell Uni-Par	Narrow Range Oil
Leffingwell Unicide-60	Light-Medium Oil
Leffingwell 90-Par	Narrow range but unclassified
Moyer Weed Killer #20	Non-selective Weed Oil (straight run)
Orthol K Ready Mix	Light Medium Oil
Volk Supreme	Unclassified Foliar Oil
Synthetics:	
Dacthal	Preemergence Herbicide
Methomyl	Insecticide
Molinate	Selective Herbicide
Toxaphene	Insecticide
Kelthane	Miticide
DEF-6	Defoliant
Reference:	
Dodecane	--

B. Task II - Laboratory Volatilization Tests--

All of the materials tabulated above were tested in a laboratory wind tunnel to determine relative volatilization rates. These tests were done at three wind speeds (5.5, 2.5, and 0 mph), three temperatures ranging from 55° to 96°F, at two relative humidities, and with and without soil present. The last test variable involved the addition of conditioned soil in a few-fold weight excess to the pesticide film contained in a small evaporation pan.

Four of the synthetics and six of the non-synthetics showed such low volatilization rates as to eliminate them from consideration for field testing. These were:

- Dacthal
- Gavicide Super-90
- Kelthane
- Leffingwell 90
- Leffingwell Unipar
- Leffingwell Unicide
- Methomyl
- Orthol K Ready Mix
- Toxaphene
- Volk Supreme

Those ten materials for which evaporation curves could be constructed exhibited volatilities that can be arranged as follows:

TABLE 1-1. RELATIVE EVAPORATION RATES OF THE MORE VOLATILE CANDIDATE MATERIALS

CONDITIONS: 72°F, 2.5 mph wind; 52-54% R.H.

Test Material	Time Required To Evaporate 20%
Beacon Weed Killer No. 5	3 min.
Keen-Kil Weed Oil No. 20	4 min.
Dodecane	1.7 hrs.
DEF-6*	1.8 hrs.
Diesel Oil #2	2.2 hrs.
Chevron Weed Oil	3.5 hrs.
Moyer Weed Killer No. 20	3.8 hrs.
ARCO Weed Killer "A" Lite	10 hrs.
Keen-Kil Weed Oil No. 40	12 hrs.
Molinate	19 hrs.

*Weight loss is probably exclusively from the xylene solvent and not the active ingredient.

The presence of soil in low ratios (<5.0 soil:pesticide), produced large increases in the evaporation rate of all the Table 1-1 test materials except diesel oil #2. Changes in relative humidity appeared to have no effect on evaporation rate. Differences in temperature produced changes in evaporation rate of the reference material, dodecane, that corresponded reasonably well with the Clausius-Clapeyron predicted values. Wind speed effect was pronounced when comparing stagnant evaporation rates with those evidenced at 2.5 and 5.5 mph. The differences in the dynamic test at these speeds varied as the samples fractionated and probably involves very complex relationships. In the case of the reference material, a pure chemical, the rates were constant to sample depletion. Dodecane evaporated just about twice as fast in a 5.5 mph wind than in the 2.5 mph wind. With less volatile materials, wind speed did not exhibit such a direct effect on evaporation rate.

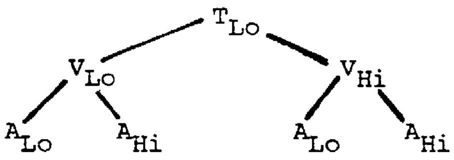
C. Task III - Field Emission Measurements--

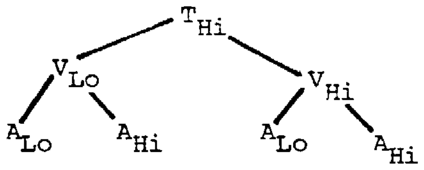
Acquisition of a field site resulted in access permission being granted for space use at the University of California South Coast Field Station (UCSCFS) near the El Toro U.S. Marine Corps Air Station (MCAS-El Toro). A large field test chamber was built. This basically consists of a Tedlar-skinned rectangular structure [10 (w) x 10 (h) x 20 (l) - ft], fitted with a rail-riding spray boom. At one end of the chamber a blower assembly is attached and a wind screen at the other (open) end. Photographs of this device are shown later in Figure A-4. The test chamber is moved down field on wooden rails designed to rest in the bottoms of the standard furrow pattern. Instrumentation included a recorder-equipped Century OVA Total Hydrocarbon (THC) analyzer, a hygrothermograph, an evaporimeter and assorted other measuring devices. The entire system was designed to operate independent of any umbilical services other than a 600 ft. water hose.

Five pesticide/crop combinations were specified by the Research Contract Manager for testing. These were:

Crop	Pesticide
Weeds	ARCO or Chevron Weed Oil
Cotton	DEF-6
Carrots	Beacon No. 5 or Keen-Kil No. 20
Citrus Trees	Orthol K Ready Mix Light, Medium or Leffingwell Unicide 60
Undesignated Row Crop	To be specified

The battery of tests to be performed would follow, as weather permitted, this general matrix:





Where: T = Temperature
V = Wind Speed
A = Application Rate

Special tests involving the measurements of pesticide emissions from very wet plots and natural emissions from untreated fallow plots were also planned.

Following system check out, which occasioned considerable modification and rework, testing was initiated on weeds. Recommended coverage with ARCO weed oil was put down while an induced draft was drawn through the spray chamber by the fan. The exhaust was continuously monitored for THC. With the exception of a possible initial, very brief manifestation, no hydrocarbons above background level were discerned. Repeating the test with the more volatile weed oils, Chevron Weed Oil and diesel oil #2, produced about the same results. Reducing the rather high wind speed (5.0 mph) specified by the

ARB Research Contract Manager to 2.5 mph also did not promote positive results.

Calculations were then made using pesticide vapor pressure data that had just become available as a result of Eureka Laboratories studies on CARB Contract No. A7-173-30. Three cases were evaluated, (Appendix B). The results of two (Cases 1 and 2) were based on the use of Hartley's equation. The last case (Case 3) was merely an extrapolation of the evaporaton rate data developed in Task II. The results shown in Table 1-2 indeed suggest that the average emission levels would probably be below detection limits for the test configuration employed.

Two ad hoc tests were then run in which the sampled exhaust stream was passed through charcoal traps. These were extracted and analyzed by gas chromatography over the distillation range. Differentiation between the exhaust and inlet air streams was inconclusive.

Applications of Beacon Weed Killer #5 produced monitorable THC traces which could be followed for up to several hours before extinction occurred. The data showed a brief, high initial level of emissions that checked reasonably well with what Hartley's equation would predict. Within minutes, however, the THC levels decayed rapidly to less than 10 percent of the onset concentration.

In the nine carrot oil tests conducted, the amount of material accounted for in the exhaust stream ranged from 3 to 14 percent of the amount applied. These results are based on measureable emissions. There is no question but that additional hydrocarbons were released, the quantities of which can only be dimensioned by more sensitive test techniques.

Application of a cotton defoliant (DEF-6) on row plants in lint also failed to provide detectable hydrocarbon emissions. According to Texas A&M researchers, the cotton plant reacts to the defoliant to produce ethylene gas. This phytogenic and photochemically reactive olefin reaches peak generation rates 4 to 5 hours after defoliant application. The levels released are, however, quite low.

TABLE 1-2. CALCULATED EXHAUST THC CONCENTRATIONS FOLLOWING THE APPLICATION OF ARCO WEED OIL IN THE FIELD TEST APPARATUS
CONDITIONS: WIND SPEED = 5.0 mph; temp.=86°F
SOURCE: APPENDIX B

Case	Basis of Calculation	Source of Vapor Pressure Data	Calculated Exhaust Hydrocarbon Level, ppb*
1	Hartley's Eq.	Ref. 1	8.2
2	Hartley's Eq.	Calc'd. from ARCO data	140-590†
3	Task II Results	N.A.	14.5-26.1§

*Expressed as the material itself and not methane.

†The range corresponds to the low and high end vapor pressures of the oil.

§The lower value was derived using the MW given in Ref. 1; the higher value is based on an MW derived using the ARCO data.

Testing on fallow ground and with citrus trees was not attempted. There proved to be no point in doing the former since before pesticide application, there were no differences noted in inlet/outlet THC readings regardless of what was in the chamber. Thus if fallow soil emitted hydrocarbons, the test configuration could not detect such emanations. Citrus oil application was forgone since all of the foliar sprays on the candidate list were seen in Task II to be so much less volatile than the unmonitorable materials already tested in Task III that it would be pointless to try.

A final aspect of Task III was to consider options that would result in the reduction of emissions from pesticide during and after application. The obvious caveats were reviewed--avoidance of high temperatures, windy or unstable weather, and mechanisms promoting drift. Substitution of synthetic pesticides for petroleum-type pesticides was suggested but, being beyond program purview, was not explicitly detailed. Particular focus was placed on the inductive electrostatic sprayer invented by Dr. E. Law of the University of Georgia. This device, now under commercial prototyping and evaluation by FMC, could significantly reduce pesticide consumption and the propagation of aerosol drift. Other drift abating techniques were considered in the next task.

D. Task IV - Estimation of Evaporation from Drifted Pesticide--

A review of the literature was made to ascertain typical drift fallout patterns and persistence of small droplets that might produce greater vapor releases. A crude model was then proposed in which it was demonstrated that the evaporation of volatile pesticide areosols (<10 μm dia.), under even ideally stable conditions, would be complete within 25 ft. of the application point in a 2.5 mph wind. Less volatile materials, such as Chevron Weed Oil, would probably fall out before losing 15 percent of their weight unless turbulent conditions operated.

In considering techniques for abating drift, the work of U.C. Davis researchers was cited. They demonstrated that selected adjuvants could significantly reduce (to 90 percent) the formation of fine (evaporation-prone) aerosol particles, but had little effect on the amount of aerosol that fell out within 1000 to 2600 ft. of application. Deflector type (KGF) nozzles and low pressure micro-jet (MF) nozzles were shown to produce drastic reductions in drift. For example, within 328 ft. of application, fallout from the former was only 0.1 percent that produced by an 80 degree fan-type nozzle (8003).

E. Task V - Development of Emission Factors--

Field work produced monitorable emissions only in the case of carrot oil and these did not include lingering subbackground releases. Because of this, reliable emissions factors could not be obtained.

1.2.2 Conclusions

A. Relative Volatilities--

Based on the materials tested and the procedures employed, a wide range of volatilities is represented in non-synthetic pesticides. This ranges from 1.5 Torr (72°F) for the light ends of carrot oil to values probably well below 1×10^{-5} for Volk Supreme. In fact, some synthetics (e.g. molinate) exhibit vapor pressures that fall in that broad range. Thus, in considering these materials as area sources of air pollution, consideration of the more volatile materials should be prioritized.

B. Suitability of the Test Configuration--

The results obtained clearly demonstrate that the test configuration employed was not sufficiently sensitive. Evaporation rates for most pesticides are so low that continuous monitoring against a (smog) background of several ppm is not practical. Through the extrapolation of the results obtained with carrot oil, it is now appreciated that a better approach is to concentrate the pesticide vapors on suitable traps using very large volumes of air. Because the results obtained on this program do not provide adequate information as to how long evaporation goes on at the subbackground or subtle levels, the tests will probably have to be conducted over fairly long periods of time.

C. Drift Evaporation and Control--

Evaporation of aerosolized pesticides is much more rapid than from the fallen out phase. Reduction of drift is therefore highly desirable in terms of reducing air pollution (not to mention pesticide savings and reduction in damage to adjacent crops and animals). Techniques are available for radically reducing drift and should be considered by the agricultural community. These include the hardware and adjuvants discussed in part 1.2.1-D of this section.

1.3 RECOMMENDATIONS

1.3.1 Emissions Testings with Increased Sensitivity

Additional field testing should be done to quantify the total long-term/subtle emissions from the applications of the more volatile non-synthetic pesticides, including carrot oil. The plan outlined in Appendix C would implement this recommendation even though slanted to the evaluation of drift control techniques. It would be highly desirable, however, that prior to attempting such relatively expensive field tests, which may then still produce inconclusive results, that preliminary laboratory testing be done to demonstrate a justification for proceeding with field work.

1.3.2 Evaluate Drift Control Techniques

The various techniques available or in development for reducing drift have been evaluated largely in terms of fall-out patterns rather than evaporative effects. Again, the plan presented in Appendix C would permit the evaluation from an air pollution perspective of devices known to produce significant reductions in airborne pesticide losses.

SECTION 2.0

TASK I - SELECTION OF TEST PESTICIDES

2.1 SELECTION PROCESS

2.1.1 Non-Synthetic Pesticides

Candidate pesticides believed by the ARB staff (Ref. 2) to be important sources of hydrocarbon emissions are listed in Table 2-1. This list, together with any suitable candidates the contractor might nominate, was to serve as the basis for the selection process. The task was deleted from the contract by ARB because of related work performed on another on-going ARB contract at Eureka Laboratories. That work, which subsequently has been reported in Ref. 1, was aimed at developing an estimated inventory of hydrocarbon emissions from the applications of non-synthetic pesticides in the state. Eureka's Leung had obtained usage data for this class of substances and, using rough volatility indices, had calculated emission estimates.

The ARB Research Contract Manager (RCM) therefore obtained from Eureka for this program a rough working list of manufacturers and trade name groups that figured prominently in the non-synthetic pesticide market. This was subsequently referred back to Eureka for detailing. A list of candidates was then prepared by Eureka. The program staff interacted in this effort, suggesting elimination of products that were merely relabelled versions of other items already listed (called "rebranding"). Also some of the pesticide candidates were found to have been discontinued items for various reasons, including business closure. A final group of twelve non-synthetic pesticides thus eventuated and was approved by the RCM. At his request, diesel oil No. 2, was also added to the list. Diesel oil is sometimes used as a weed killer.

TABLE 2-1. CALIFORNIA AIR RESOURCES BOARD CANDIDATE PESTICIDES LIST

SYNTHETIC PESTICIDES

D-D Mixture
DNBP
Carbaryl
Ordram
Parathion
Toxaphene
Folex-R
Choropicrin

DEF
Malathion
Endosulfan
Diazinon
Dursban
Kelthane-R
Methomyl
Telone-R

NONSYNTHETIC PESTICIDES

Pesticide Use Report Classification	Manufacturer's Trade Name
Aromatic Petroleum Solvent	Chevron Aquatic Solvent 3501
	WFSI Weed Killer 31
	B.F. Weed Oil - 711
Mineral Oil	Super C
	Soilserv Crop Oil
	Chemurgic Spray Oil
Petroleum Distillates	Knox Pyronyl Oil Conc. No. 3610
	GB-1111
Petroleum Hydrocarbons	Arco Weedkiller "A"
	Richfield Weed Killer "A", 10 and 20
	Best Weed & Grass Killer
	Bardon Super "77" Weedkiller
	Beacon Selective Week Killer 5
	Beacon Shure Kill Weed Oil
	Dio-Kil Weed Oil
	Merit Weed Killer 20
	Weed-A-Rest Oil Spray
	Spray Moore S Weedkiller
	Keen-Kil Weed Oil No. 20, 40 and 60
	General Contact
	Max-Kill Weed Oil
Petroleum Oil, Unclassified	Kleenup Ready-Mix Dormant Oil Spray
	Orthol-K Ready-Mix Light and Medium Supreme Oil
	Diazinon Spectrum 415
	Chevron Weed Oil
	Chevron Aromatic Oil "A"
	Unicide 60 and 75
	Uni-Par
	Supreme Spray
	Soluble Summer Oil
	Summer Oil Emulsion
	Super 94
	Herbidical Oil
	MEWCO Brand Summer Oil
	Russell Chemical Emulsible Spray Oil Medium
Petroleum Oil, Unrefined	Orthol-K Light Medium 92

2.1.2 Synthetic Pesticides

Inclusion of some synthetics on the list was also desired, although it was recognized that the vapor pressures would likely be quite low, at least in comparison with some of the petroleum pesticides. One item specified for study emphasis by the RCM was a cotton defoliant. Folex was initially suggested but later dropped in favor of DEF-6, which is far more popular among cotton growers. The ARB's interest in such products is to determine the extent to which the plant itself emits hydrocarbons upon being "treated" with the defoliant. The defoliation process not only facilitates cotton gathering but causes the boles to erupt quickly, producing clean, white lint. At the same time, however, the plant reacts to the defoliant by releasing ethylene, a highly photochemically reactive gas.

The selection of additional synthetics was done solely on the basis of statewide consumption rates and product volatility, rather than application effects and characteristics. The selection was done by the program staff. This was necessary because Eureka Laboratories' experience with synthetic pesticide usage had been localized (Fresno County) rather than statewide as has been their experience with petroleum-based pesticides.

Using the Pesticide Use Report, a listing of the seventeen synthetic pesticides (fumigants excluded) consumed in amounts exceeding 200 tpy in 1978 was tabulated vs vapor pressure (see Table 2-2). It should be pointed out that the usage rates and vapor pressures are for the active ingredient and do not include diluents or solvents.

From the seventeen synthetic pesticides shown on Table 2-2, five were selected for inclusion on the list of test materials. The selection was done so as to feature the more popular materials while covering a wide, yet practical range of volatilities. The materials selected, which include four of the top five and none below the twelfth most popular, are listed here in order of their vapor pressures (which, unfortunately, are not all at the same temperature).

TABLE 2-2.

LISTING OF SYNTHETIC PESTICIDES USED IN 1978 IN AMOUNTS EXCEEDING 400,000 LBS. (FUMIGANTS EXCLUDED) RANKING IS BY USAGE RATE

Pesticide	Synonyms & Trade Names	Lbs/Yr	Vapor Pressure*, torr
Molinate	Hydram, Ordram	1,276,803	$5.6\text{X}10^{-3}$, 25 °C
Toxaphene	Several	1,025,098	0.3, 25 °C
Kelthane-R	Dicofol, DTMC	1,004,828	$5.7\text{X}10^{-7}$, 20 °C
Propargite	Comite, Omite	986,335	$1\text{X}10^{-7}$, 25 °C
Methomyl	Lannate	955,028	$5\text{X}10^{-5}$, 25 °C
Carbaryl	Sevin	928,196	$4\text{X}10^{-5}$, 25 °C
Captan	Orthocide 406	891,030	$1.5\text{X}10^{-5}$, 25 °C
Paraquat	Dexthrone, etc.	680,898	Probably very low
Dimethoate	Cygon, De-fend	584,108	$8.5\text{X}10^{-6}$, 25 °C
Acephate	Orthene, Orthan	571,355	$1.7\text{X}10^{-6}$, 24 °C
Maneb	MEB, Manzate	505,188	Negligible
Dacthal	Dimethyl-chlorthal	495,626	0.001, 20 °C†
DNBP	Dinoseb etc.	497,770	$2.2\text{X}10^{-3}$. 20 °C
2,4-D (dimethyl amine salt)	Weed-B-Gon	465,689	$1\text{X}10^{-10}$
MCPA (butoxy ethanol ester)	- - - - - - -	445,564	$1\text{X}10^{-6}$†
Malathion	Several	427,509	$4\text{X}10^{-5}$, 30 °C
Methyl Parathion	Several	412,432	$9.7\text{X}10^{-6}$, 20 °C

* Source: Eureka Labs Fresno County Study

† KVB estimates based on Eureka Labs data or reference materials

TABLE 2-3. ADDITIONAL SYNTHETIC PESTICIDE TEST CANDIDATES

Pesticide	Vapor Pressure, Torr (°C)
Toxaphene	3×10^{-1} (25)
Dacthal	1×10^{-3} (20)
Molinate (liquid)	6×10^{-3} (25)
Methomyl	5×10^{-5} (25)
Kelthane	6×10^{-7} (20)

2.2 CHARACTERISTICS OF THE CANDIDATE PESTICIDES

2.2.1 Overview

The overall list of pesticide test candidates is shown in Table 2-4 together with some brief generic information. This is further detailed by the following capsule discussions for each of the pesticides.

The text is organized into subsections on synthetic and non-synthetic pesticides. Because all of the former categories were potential candidates for field testing (Task III), application information is included. For synthetics, only DEF was considered for field usage; the other five were to be subjected only to laboratory evaporation tests and in the pure (nonformulated) form. Thus, application information is included only for DEF-6, with limited comments provided for the other synthetic pesticides. Application information, where provided, was generally obtained from the pesticide marketer and label specifications accompanying samples.

2.2.2 Characteristics of the Non-synthetic Candidate Pesticides

A. ARCO Weed Killer "A" Lite--

This weed oil is a heavily aromatic, higher-boiling petroleum mixture containing a small amount of emulsifier. The ARCO product specifications for this material are shown in Table 2-5. Being a nonselective herbicide, it is

TABLE 2-4.

TASK II
PESTICIDE TEST CANDIDATES

Test Material	Designation	
	California Dept. Agriculture	Manufacturer's*
Non Synthetic Pesticides		
1. ARCO Weed Killer "A" Lite		Nonselective contact type aromatic petroleum herbicide
2. Beacon Selective Weed-killer No. 5		[Carrot oil]
3. Chevron Weed Oil		Light bodied highly aromatic petroleum oil
4. Gavicide Super 90	Unclassified	Narrow boiling range oil for dormant fruit trees
5. Keen-Kil Weed Oil #20		[Carrot oil]
6. Keen-Kil Weed Oil #40		General contact aromatic petroleum oil
7. Leffingwell Uni-Par†	Unclassified Narrow range	[Narrow boiling range oil for fruit trees]
8. Leffingwell Unicide 60	Light Medium	[Light medium foliar (summer) insecticide]
9. Leffingwell 90-Par	Unclassified (Emulsifiable)	[Narrow boiling range oil for fruit trees]

TABLE 2-4. (Continued)

	Designation	
Test Material	California Dept. Agriculture	Manufacturer's*
Non Synthetic Pesticides		
10. Moyer Weedkiller 20		[Aromatic herbicide]
11. Orthol-K-Ready Mix Light Medium	Light medium	[Light medium foliar (summer) insecticide]
12. Union Oil Diesel Oil #2		[Nonselective herbicide]
13. Volck Supreme (Chevron U.S.A.)		Contact insecticide/foliar or dormant
Synthetic Pesticides - Formulated Form		
14. DEF-6	Restricted	Cotton defoliant
Synthetic Pesticides - Pure Form§		
15. Toxaphene		
16. Dachtal		
17. Molinate		
18. Methomyl		
19. Kelthane		

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* When a manufacturer's label or correspondence provide no product classification, KVB has assigned the designation shown in brackets.

† May be Item No. 11 rebranded.

§ Obtained from Chem Service Inc., West Chester,PA

TABLE 2-5. MANUFACTURER'S PRODUCT SPECIFICATIONS FOR ARCO WEEDKILLER "A" LITE

SOURCE: ARCO PETROLEUM PRODUCTS CO., LOS ANGELES, CA.

SPECIFICATION CODE	ARCO Weedkiller "A" Lite
Gravity, °API, Typical	Record
Flash, °F (°C), Minimum	150 (66)
Color, Maximum	4.0
Sulfur, W %, Typical	1.20
Pour, °F (°C), Typical	-10 (-23)
Viscosity at 100°F (37.8 °C)	
Kinematic, cSt	3.65 Maximum
Saybolt, SUS	38.0 Maximum
Hydrocarbon Distribution V %	
Aromatics, Minimum	60
Olefins, Typical	--
Paraffins, Typical	--
Distillation, °F (°C)	
IBP, Typical	Record
10 V%, Recovered	450-500 (232-260)
50 V%, Typical	520 (271)
90 V%, Typical	595 (313)
EP, Typical	750 (399) Maximum
Appearance	Bright
Odor	Pass

used in non-cropped areas primarily, although weed kills in citrus orchards and vineyards can be made so long as foliar contact with the cultured crop is avoided. It is effective against most annual and many perennial weeds. Best results are obtained when the weeds are small and succulent. ARCO weed killer can be safely used as pre-emergence weed killer for such row crops as sweet-corn, onions and tomatoes. This emulsible weed oil may be diluted with up to two parts of water. Application rates, excluding water, range from about 20 (pre-emergence use) to 150 gallons/acre (perennial grasses).

B. Beacon Selective Weed Killer No. 5--

This product is one of the several offered by various companies that is referred to by farmers as a "carrot oil". It is relatively low boiling (300-400°F), straight run distillation cut from a crude unit. Designated as a mineral spirit, it is not highly aromatic and can be tolerated by some cash crops, such as carrots. It is typically applied for weed control where the row crop is a few weeks emergent. Beacon Oil Company advised that their weed killer No. 5 has a flash point above 100°F and a specific gravity of 43-44° API. When used on carrots application rates between 50 and 100 gallons per acre (undiluted) are recommended by the seller.

C. Chevron Weed Oil--

The characteristics and utilization of this product are essentially the same as those already discussed for ARCO Weed Killer "A" Lite. This is brought out when the typical test data supplied by Chevron (Table 2-6) are compared with those shown for the corresponding ARCO product (Table 2-5). Both products are higher boiling fractions produced by refinery reformers which convert naphthas rich in cycloalkanes to corresponding and other aromatics by catalytic dehydrogenation.

The justification for including two such similar products on the candidate list of test pesticides was indeed to determine to what degree that similarity actually operated. The results of the Task II work vindicated the decision. The evaporation rate of the Chevron product was found to be considerably faster than that of the ARCO weed oil.

TABLE 2-6. TYPICAL PROPERTIES OF CHEVRON WEED OIL

SOURCE: CHEVRON RESEARCH CO., EL SEGUNDO, CA

Gravity, °API	29.0
Gravity, Specific at 60°F	0.8816
Pounds Per Gallon at 60°F	7.34
Flash Point TCC °F	154
Flash Point TOC °F	170
Aniline Point °F	103.5
Kauri Butanol Value	61.2
Reid Vapor Pressure, Lbs.	0.4
Threshold Limit Value, ppm	50
Composition - Volume %	
Benzene	0.0
Toluene/Ethylbenzene	0.0/0.0
Xylene & C_8 + Aromatics	63.6
Naphthenes	29.0
Paraffins	7.4
Color Saybolt	-16
Distillation, D-86, °F	
Initial Boiling Point	383
10% Recovered	439
50% "	518
70% "	566
90% "	624
Dry Point	648
Spontaneous Ignition Temperature °F	500
Freezing Point °F	<-17
Molecular Weight, Average	195
Solubility Parameter	8.5
Refractive Index 20°C	1.5152
Thermal Conductivity, 60°F Btu/hr/ft/deg F	0.076
Heat of Vaporization, Btu/lb	107
Heat of Combustion, Btu/lb	18099
Vapor Pressure, Torr	<1

D. Diesel Oil No. 2--

This material was included in the list of pesticide candidates by the RCM because it was believed to be used in significant quantities for agricultural weed control. Although many brands exist, the material selected for use on the present program was Union Diesel #2. This was done merely because the diesel oil supply closest to the program office happened to be a Union Oil Co. station.

Union Diesel #2 is an ASTM Grade 2-D diesel fuel for engines in industrial and heavy mobile service. It is widely used in automotive type diesel engines. Typical inspection test data provided by the Union Research Center, Brea, are shown in Table 2-7.

TABLE 2-7. TYPICAL INSPECTION TEST DATA FOR DIESEL OIL NO. 2

SOURCE: UNION RESEARCH CENTER, BREA

Parameter	Value
Gravity, °API @ 60°F	33
Flash Pt, PMCC, °F	190
Distillation, °F	
IBP	375
10%	460
50%	525
90%	600
EPt	640
Viscosity	
SVS @ 100°F	37.6
Cs @ 100°F	3.5
Sulfur, Wt. %	0.2
Cloud Pt, °F	10
Pour Pt, °F	0
Color, ASTM	1.0
Ash, Wt. %	nil

E. Gavicide Super 90--

This product is offered by Puregro Company, Los Angeles. The material is a narrow-range oil insecticide containing one percent emulsifier. It is derived from the raffinate from the solvent extraction process in the aromatics recovery unit of a refinery. The raffinate or solvent (phenol) insoluble fraction is rich in paraffins. This is dewaxed and then distilled. The cut used for Gavicide Super 90 is in the higher boiling range as is seen in the following table:

TABLE 2-8. TYPICAL PROPERTIES OF GAVICIDE SUPER 90-- PETROLEUM BASE OIL

SOURCE: PUREGRO COMPANY, LOS ANGELES, CA.

Parameter	Typical Test Value
Gravity, °API @ 60°F	32
Viscosity, SSU/100°F	90
Distillation @ 10 Torr	
Mid-boiling Point, °F	436
10-90% range, °F	50
Paraffinicity, % Cp	62
Pour Point, °F	20
Unsulfonated Residue, %	93
Chemical Composition of Base Oil, wt. %	
Total Saturates	82.5
Total Monoaromatics	11.9
Total Diaromatics	2.5
Total Triaromatics	1.1
Total Pentaaromatics	1.2
Total Sulfur Compounds	0.8

Gavicide Super 90 is formulated as a "fast break" spray oil. This is an emulsion that is very unstable so that on contacting the target the components separate rapidly, the water dropping off to leave the oil on the contacted area. This requires that it be agitated while being applied but permits the use of much diluent water (1 to 6 gallons of oil per 100 gallons water).

The manufacturer's recommended use of Gavicide Super 90 is on deciduous trees in dormant, delayed dormant or summer applications for the control of mites and scale insects. Tree types for which its use is suggested on the PureGro lable include: apples, almonds, apricots, cherries, nectarines, olives, peaches, pears, plums, prunes, and walnuts. Recommended application rates range from 1 to 6 gallons/acre.

F. Keen Kil Weed Oil No. 20--

This material is marketed by Keen Incorporated of Long Beach. It is generically a selective weed oil having the characteristics and application specifications described earlier for Beacon Selective Weed Killer No. 5 (Sec. 2.2.2-B), another "carrot oil." Neither contain emulsifiers (are applied undiluted) and are the lowest boiling petroleum-base pesticides considered on the present study.

Keen Kil Weed Oil No. 20 is actually a finished refinery product, designated as mineral spirits. It is used also as a garage cleanup solvent, paint thinner and for other similar applications. Keen Inc. indentified a specific petroleum company product which they relabelled as Keen Kil Weed Oil No. 20. The typical properties of that product were obtained from that petroleum company and are shown in Table 2-9. For proprietary reasons, the source is not identified.

TABLE 2-9. TYPICAL PROPERTIES OF KEEN KIL WEED OIL NO. 20

SOURCE: CONFIDENTIAL

Parameter	Value
Gravity, °API @ 60°F	47.1
Color, Saybolt	+30
Kauri-butanol No.	44.6
Aniline pt., °F	111.5
Flash pt., T.C.C., °F	106
Distillation, °F	
IBP	310
10%	327
30%	335
50%	343
70%	353
90%	373
EPt	384
Paraffins + naphthenes, Vol.-%	76.1
C_8 + aromatics, Vol.-%	23.9

G. Keen Kil Weed Oil No. 40--

This material is a general contact, non-selective weed oil. It is a refinery catalytic reformer product to which a small amount of emulsifier (0.5%) has been added. Being a highly aromatic, higher boiling oil, it is thus similar in usage and application amounts to those of ARCO and Chevron weed oils. It is not, however, a rebrand of either of those products. The refinery producing the weed oil supplied typical properties data. These, however, were contained on a Material Safety Data Sheet and are thus not as detailed as those shown for other of the preceding products. The data are as follows:

TABLE 2-10. TYPICAL PHYSICAL DATA FOR KEEN KIL WEED OIL NO. 40--
PETROLEUM BASE OIL

SOURCE: CONFIDENTIAL

Parameter	Value
Specific gravity, 60°F	0.946
Boiling Pt range, °F	437-700
Vapor density (air=1)	7.1
Flash Point, PMCC, °F	220
Color	Dark Liquid
Vapor Pressure @ 100°F, mm Hg	<0.5

H. Leffingwell Uni-Par--

This material, a narrow range fruit tree insecticide, is offered by the Leffingwell Chemical Co., Brea.

The product, as seen in Table 2-11, is a predominately saturated petroleum mixture to which 2% emulsifier has been added. Uni-Par is primarily used as a foliar spray for control of mites and scale on citrus, avocado, and deciduous fruit trees (apples, apricots, cherries, peaches, pears, plums, prunes). It is also used for dormant and past dormant applications with or without dissolved synthetic pesticides such as parathion and diazinon.

Dilution with water is usually recommended, the rate ranging from 1 to 1.5 gallons per 100 gallons of water. Application rates (based on oil volumes) recommended by Leffingwell start at about 1/2 gallon (dormant grapes) to up to 20 gallons/acre (citrus and avocado).

TABLE 2-11. TYPICAL CHEMICAL AND PHYSICAL PROPERTIES OF LEFFINGWELL UNI-PAR -- PETROLEUM BASE OIL

SOURCE: LEFFINGWELL CHEMICAL CO., BREA, CA.

Parameter	Value
Distillation range, °F	650-690
Viscosity @ 100°F, SSU	68
Specific gravity (water=1)	0.865
Average M.W.	310
Chemical Composition, Wt.-%	
Paraffins	62
Naphthenes	32
Aromatics	6
Unsulfonated residue, wt. %	93

I. Leffingwell Unicide-60--

This spray is a foliar or summer insecticide oil for use against scale and mites on fruit trees. Classified as a light medium petroleum pesticide, it is similar to Leffingwell's Uni-Par, both containing predominantly saturated hydrocarbons from the higher boiling range. In the case of Unicide-60, the distribution of paraffins and naphthenes is about equal, while Uni-Par is richer in paraffins. This can be seen from the following table.

TABLE 2-12. TYPICAL CHEMICAL AND PHYSICAL PROPERTIES OF LEFFINGWELL UNICIDE-60 -- PETROLEUM BASE OIL

SOURCE: LEFFINGWELL CHEMICAL CO., BREA, CA.

Parameter	Value
Distillation range, °F	575-690
Viscosity @ 100°F, SSU	69-74
Specific gravity (water=1.0)	0.877
Average M.W.	290
Chemical Composition, wt. %	
Paraffins	48
Naphthenes	48
Aromatics	4
Unsulfonated residue	92

Unicide-60 contains one percent emulsifier and its recommended dilution rate is between 1 to 1.8 gallons per 100 gallons of water. Application rates for citrus ranging from 6 to 54 gallons of oil per acre. When used on other type fruit trees (peaches, nectarines, plums, prunes, olives, and walnuts) incorporation of synthetic pesticides, such as Parathion, Sevin or Trithion, is recommended by Leffingwell.

J. Leffingwell 90-Par--

This insecticide is similar to Leffingwell's Uni-Par except that the distillation range occurs at a somewhat higher temperature. Although the range reported by Leffingwell is the same for both products (40°F), 90-Par does not bear the California Department classification of Narrow Range Oil. This is perhaps because the California Narrow Range Citrus Spray Oil specificaton calls out a distillation characteristic that this oil does not fulfill. The two narrow-range oils (415- and 440-types) require that the 50 percent distillation point occur within ±3 and ±6°F, respectively of the typing temperatures, 415 and 440°F. The label information designates the product as an unclassified emulsifiable oil. Recommended use of the spray follows essentially that for Uni-Par. Suggested application rates for citrus are somewhat lower (12-15 gallons oil/acre), but the same for stone fruit, almonds, apples, pears, olives and grapes. Typical test characteristics for 90-Par are shown in the next table.

TABLE 2-13. TYPICAL CHEMICAL AND PHYSICAL PROPERTIES OF LEFFINGWELL 90-PAR -- PETROLEUM BASE OIL

SOURCE: LEFFINGWELL CHEMICAL CO., BREA, CA.

Parameter	Value
Distillation range, °F	670-710
Viscosity @ 100°F, SSU	90
Specific gravity (water=1.0)	0.867
Average M.W.	320
Chemical Composition, wt. %	
Paraffins	62
Naphthenes	NA*
Aromatics	NA*
Unsulfonated Residue	93

*NA = not available

K. Moyer Weed Killer No. 20--

This Moyer Chemical Co. spray is a non-selective weed oil. Unlike the other non-selective weed oils discussed earlier, which are highly aromatic, Moyer Weed Killer No. 20 is a straight run, high boiling cut obtained from the crude unit vacuum tower. Its chemical composition is thus variable, depending on feed stock properties. For this reason, only typical physical properties are shown in the next table. These were provided to Moyer by the major petroleum refinery furnishing the product. About one percent emulsifier is added to the oil to permit water addition. Moyer, however, does not recommend a mixture ratio greater than 1:2 of water to oil. Use of the Moyer Weed Oil follows those specified for the aromatic weed killers offered by ARCO and Chevron.

TABLE 2-14. TYPICAL PHYSICAL PROPERTIES OF MOYER WEED KILLER NO. 20 -- PETROLEUM BASE OIL

SOURCE: MOYER CHEMICAL CO.

Parameter	Value
Distillation Range, °F	437-700
Vapor Pressure @ 100°F, mm Hg	<0.5
Vapor density (air=1.0)	7.1
Specific gravity (water=1.0)	0.946
Appearance	Dark Liquid

Application rate is somewhat less, however, with 15 to 20 gallons/acre recommended for general uses. The Moyer spray is also suggested for use at about the same rates (10 to 20 gallons/acre) on dormant overwintering strawberries where weed control is required.

L. Orthol-K-Ready Mix Light Medium--

This is a product of the Chevron Chemical Co. designed to conform with the California classification for light medium citrus foliar (summer) insecticides. It is actually a blend of two refinery products to which 0.55 Vol. % emulsifier and 0.2 Vol. % n-butyl alcohol (coupling agent) has been added. Chevron specifications for the blended petroleum base oil are given in the following table.

TABLE 2-15. TYPICAL CHARACTERISTICS OF ORTHOL-K-READY MIX LIGHT MEDIUM -- BLENDED PETROLEUM BASE OILS

SOURCE: CHEVRON CHEMICAL CO., RICHMOND, CA.

Parameter	Value
Distillation Recovery, @ °F 55%	636*
Viscosity @ 100°F, SUS	65
Specific gravity (water=1.0)	0.871
Flash point, °F	300
Pour Point, °F	-25 (Max)
Color (ASTM D-1500)	0.5
Unsulfonated Residue Vol-%	92

*California state specification for light medium oil sprays

This Orthol-K product is low in aromatics, as evidenced by the high unsulfonated residue value. The small amount of emulsifier used coupled with a recommended high aqueous dilution rate (1 to 2-1/4 gallons oil per 100 gallons water) is intended to create a fast-break effect on the target surface. Continuous agitation is required during application to maintain the unstable emulsion.

The primary use for Orthol-K ready mix light medium is for mite and scale control on citrus. Although Chevron does not recommend application rates, it does suggest the user follow state guidelines. The Division of Agricultural Sciences of the University of California (Ref. 3) specifies applications of 30 to 35 gallons diluted spray per mature orange tree and 20 to 25 gallons per mature lemon tree. This would be equivalent to 0.15 to 0.68 and 0.10 to 0.56 gallons of straight oil per each type tree, respectively, based on Chevron's dilution instructions and the range of strengths suggested for controlling the different types of scales and mites.

M. Volck Supreme--

This is a product of Chevron Chemical Co. A specially refined phytonomic oil contact insecticide, it is used on plants in foliage or the dormant stage. The petroleum material used in formulating this product is Turbine Oil Base Light (TOBL) to which is added 1.5 percent emulsifier, 0.5 percent isobutanol and a trace of blue-green dye. The TOBL content comprises the difference of 98 percent. Chevron's raw material specification for the particular TOBL used in Volck Supreme is shown in Table 2-16. Although no distillation specifications are included, the material was described by Chevron representatives as having very low volatility. The high unsulfonated residue required suggest an oil of low aromaticity.

Recommended dilution rates for Volck Supreme are from 0.83 to 1.25 gallons per 100 gallons of water for tractor applications to about twice that oil strength for airborne spray equipment. For the control of many insect pests on various crops, use of synthetic pesticides (e.g., Parathion, Toxaphene, Kelthane) in combination with the supreme spray is recommended. This is the case for alfalfa, dormant or delayed dormant fig trees, dormant grapes, all types of citrus, and leafed walnuts. For most other deciduous tree applications, Volck Supreme can be used without synthetic reinforcements, regardless of stage. This recommendation applies to almonds, apples, apricots, cherries, nectarines, peaches, pears, plums, and prunes.

2.2.3 <u>Characteristics of the Synthetic Candidate Pesticides</u>

A. Def-6--

This cotton defoliant is produced by the Chemagro Agricultural Division of Mobay Chemical Corp. The active ingredient is S,S,S,-tributylphosphorotrithioate (70.5%), the balance consisting of xylene solvent (~20%), emulsifier, synthesis impurities, etc. The synthesis of the trithioate involves the reaction of n-butyl mercaptan with phosphine. The former reagent is of course the principal ingredient of skunk scent, thus rendering the defoliant esthetically repulsive when mercaptan residues are high. Mobay's present product contains about 100 ppm of n-butyl mercaptan and is labeled as a "low odor formulation." Formerly, the mercaptan level exceeded one percent.

TABLE 2-16. RAW MATERIAL SPECIFICATION FOR VOLCK SUPREME -- PETROLEUM BASE OIL

SOURCE: CHEVRON CHEMICAL CO., RICHMOND, CA

Parameter	Min.	Max.	Typical
Specific Gravity (water = 1.0)	--	--	0.85-0.86
Unsulfonated Residue, Vol. %	92	--	--
Flash Point, COC, °F	380	--	--
Viscosity, Kin., @ 100°F, cS	29.7	32.0	--
Viscosity, SUS @ 100°F, sec	140	150	--
Viscosity Index (ASTM D-2270)	90	--	--
Sulfur, ppm	--	20	--
Color (ASTM D-1500)	--	0.5	--
Pour Point, °F	--	+20	--
Neutralization No., mg KOH/g	--	0.03	--

The effect of the defoliant on cotton plants is not a perceptible process until just before leaf drop occurs. In about 4 to 7 days following application the fields will turn slightly grayish, but the leaves will remain otherwise green and healthy looking up to the time they fall. On completion of defoliation, which may take up to 14 days in cool weather, picking is done. Defoliation with DEF-6 does not kill the plant or even supress second growth.

Spray application can be directed over the entire plant to produce complete defoliation or at the bottom leaves only (bottom defoliation). The latter practice is observed because the cotton boles mature first at the bottom and are thus more susceptible to loss from rot and exposure. Bottom defoliation promotes aeration and sunlight contact of the bottom boles, increasing lint yield. If desired, the bottom can even be harvested separately by removing the top 8 to 12 rows of spindles from the picker. Following this the normal complete defoliation routine and harvest of top boles can then be done.

DEF-6, like other formulations containing the tributylphosphorotrithioate, can be emulsified in water or dissolved in diesel oil. The latter arrangement is preferred if cooler weather persists, a condition that inhibits the efficacy of the defoliant. Mobay's recommended application rates for DEF-6 are as follows:

TABLE 2-17. MANUFACTURER'S RECOMMENDED APPLICATION RATES FOR DEF-6 ON COTTON FIELDS

Crop	Pints DEF-6 Per Acre	Water Diluent, Gals* Aircraft	Ground Rig	Effect
Cotton	1.33 to 2	5 to 10	15 to 25	Complete Defoliation
Cotton	1 to 1.5	N.A.	10 to 15	Bottom Defoliation
Rank Cotton	3	5 to 10	15 to 25	Complete Defoliation

*If diesel oil is used, the suggested solvent volumes for complete defoliation of cotton are 3 to 5 gals for aircraft applications and 5 to 20 gals for ground rigs. The amount of DEF-6 would remain the same as shown above.

B. Dacthal--

This herbicide is the dimethyl ester of tetrachloroterephthalate. A more common name, according to the Nanogen Index (Ref. 4), is dimethylchlorthal. The name, Dacthal, which is used in the Pesticide Use Reports, is actually a trademark name, as are the competitive products DCPA, and DAC-893. The material finds general agricultural use as a pre-emergence herbicide.

C. Kelthane--

Chemically, this non-systemic acaricide is 1,1-bis (p-chlorophenyl)-2,2,2-trichloroethanol. It is thus the DDT molecule to which a hydroxyl group has been added to the bridge methylene carbon atom. Like Dacthal, Kelthane is also a trademark name, dicofol being regarded as the common name (Ref. 4). Other label names used for this material are Keltane, FW-293, and DTMC.

Its principal use is in the control of mites and ticks. While highly toxic to these arachnida, Kelthane shows little effect on members of the class insecta.

D. Methomyl--

This insecticide is chemically 1-(methylthio)ethylideneaminomethylcarbamate. It is also offered under the label names Lannate and duPont 4179. Methomyl controls a number of insects on several row crops and is also used as an aphicide and nematocide. The chemical is soluble in water but does slowly hydrolyze to 1-(methylthio)ethylidenehydroxylamine and N-methylcarbamic acid or the second order degradation products thereof. This instability could lead to the formation of products that are more volatile than the parent compound. Thus, if hydrolysis occurs in moist air, the evaporation rate of methomyl could appear to increase with time.

E. Molinate--

This material is used as a selective herbicide. Its primary use in California is for the control of broadleaf grasses in cereals, especially rice. Molinate, which is also offered under the tradenames Hydram, Ordram and R-4572 is, like Methomyl, also a water soluble (sparingly) carbamate. The proper chemical designation for Molinate is S-ethyl-N,N-hexamethylenethiocarbamate. Hydrolysis should lead to the formation of the volatile ethyl mercaptan and the intermediate degradation product, N,N-hexamethylenecarbamic acid. This could result in an increase in the apparent evaporation rate of the neat material if hydrolysis occurs.

F. Toxaphene--

This chlorinated hydrocarbon is a mixture of camphenes containing 67 to 69 percent chlorine. The product thus predominates in isomers of octochlorocamphene. A number of trademark names are used for Toxaphene, including Alltox, Estonox, Chem-Phene, Genephene, Gy-Phene, Phenacide, Phenatox, Toxadust and Toxaspra.

Toxaphene is a powerful contact and stomach insecticide that also exhibits some acaricidal activity. The pesticide is nonsystemic and exhibits little or no phytotoxicity. It is, however, rather toxic to mammals and very toxic to fish.

SECTION 3.0

TASK II - LABORATORY VOLATILIZATION TESTS

3.1 OBJECTIVES

The purpose of the present task was to determine the relative evaporation rates of the candidate materials under various environmental conditions. The tests would be performed under laboratory conditions without attempting to reproduce field effects. Using the results obtained, decisions could be better developed in the selection of materials for Task III field testing. The variables of interest would be: (1) temperature; (2) wind speed; (3) relative humidity; and (4) substrate composition.

Weather being such a critical factor, serial sequencing of the tasks could not be arranged. The field test effort (Task III) was actually started before Task II, then terminated for the winter when Task II was then begun. Task II was then completed before resumption of field work.

3.2 LABORATORY SYSTEM USED FOR VOLATILIZATION TESTS

3.2.1 Functional Characteristics

The wind tunnel assembled to follow the evaporation rates of the candidate test materials is shown in Figure 3-1. Wind speed variation is provided by the two speed fan in the air conditioner. The air conditioner serves as the air mover for the train, the blowers in the evaporative cooler being disconnected as unnecessary. Trimming wind speed to desired set points (2.5 and 5.0 mph) is effected by opening a damper on the side of the duct housing the recording hygrothermograph (Weathertronics Model No. 5020). Temperature control in the subambient direction is provided by the air conditioner and in the elevated range by the electric element air heater. The design goal was to run tests at 55, 72 and 95°F.

Variation of relative humidity is accomplished by use of the evaporative cooler. The air heater corrects the temperature drop resulting

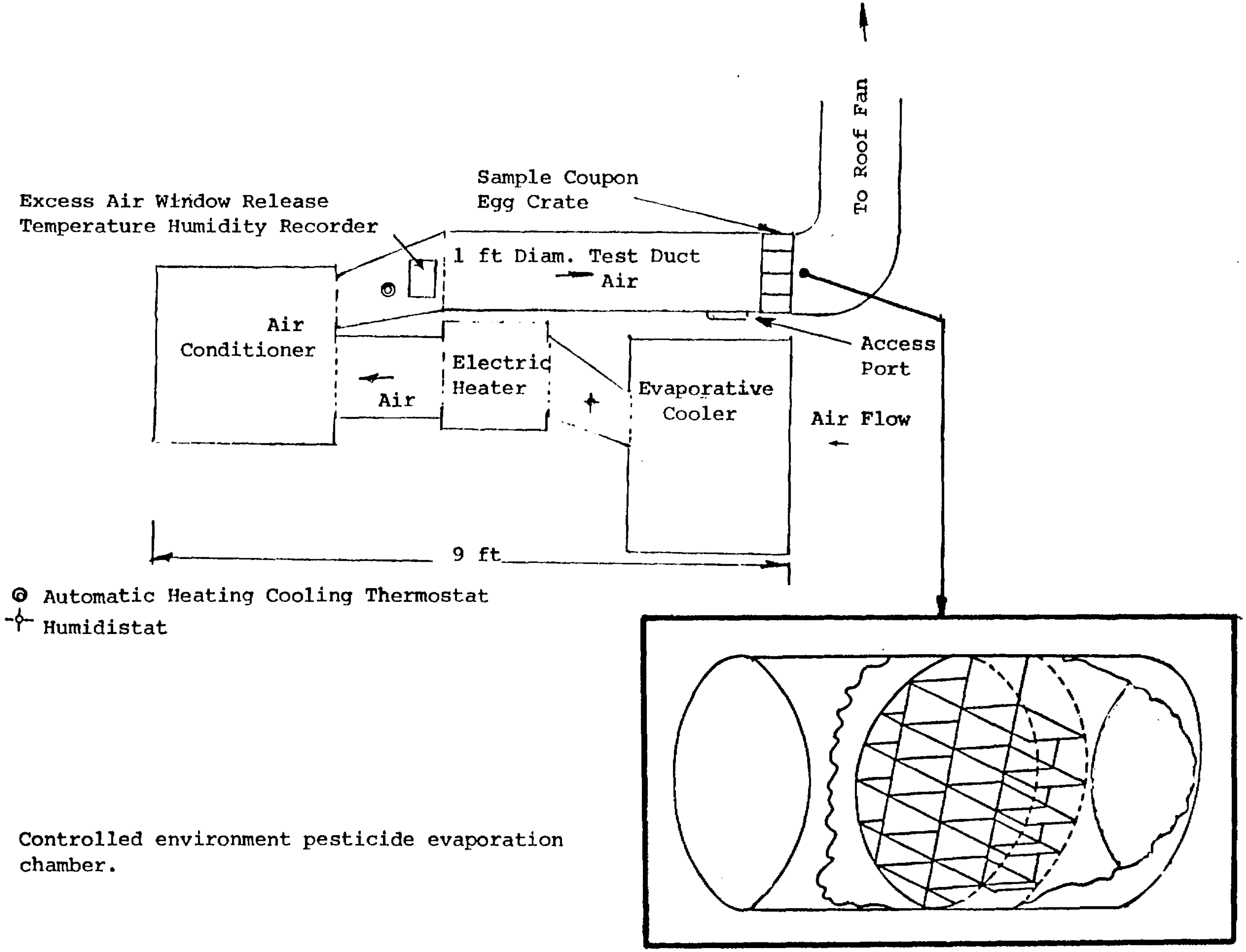


Figure 3-1. Controlled environment pesticide evaporation chamber.

while the air conditioner moves the air in the train. No set points were specified for relative humidity.

The first component in the train is an ordinary roof-type evaporative cooler (Artic Circle Model AS330A) of about 20 cu. ft. volume. Because the blower was of no functional use, it was disconnected. The water pump is actuated by a humidistat (Honeywell Model H600A 1014), the sensor of which is located in the duct between the evaporative cooler and the air heater. The latter (Hunter Heater Model 33037) is rated at 4 kilowatt (17 amps at 240 Vac). Temperature control is effected by a thermostat (Honeywell Model T678-A-1478), the sensitive element being situated downstream of and also controlling the air conditioner. The latter (Whirlpool Model AGF-1 854) is rated at 12,000 Btu/hr and provides two fan speeds, both fortuitously close to the desired set points when driving the entire wind tunnel. The low fan wind speed produced is 2.5 mph in the egg crate, which is the lower set point. The high speed position moves the duct air through the sample trays at 5.5 mph, which is close enough to the desired set point of 5.0 mph to use without attempting to bleed off duct air.

Directly downwind of the air conditioner is a box-shaped structure in which are installed a spring-wound, recording hygrothermograph (Weathertronics Model 5020), an air filter and the thermostat sensor. The chamber is large enough to permit installation of a wet and dry bulb thermometer to verify the accuracy of the hygrothermograph.

The samples to be evaporated are placed in the individual cells of the egg-crate structure situated in the exhaust duct of the wind tunnel. An access door is provided downwind of the egg-crate so that individual samples can be removed without disturbing the air flow through the structure. The egg-crate provides sections for over forty sample evaporation trays. Thus all nineteen candidate pesticides and a reference material (dodecane) can be simultaneously run in duplicate.

The exhaust gas duct, shown in Figure 3-1 in vertical termination, actually was modified to a straight-run configuration. Blowing the duct gas into the ceiling fan proved inefficient since the DEF-6 was smelled by otherwise disinterested coworkers. The modified ducting flowed the exhaust gas into a large spray booth (no longer in use). This diminished awareness of the DEF-6 presence and facilitated anemometer readings at the end of the pipe. The anemometer used is a Biram type (Davis Instrument Mfg. Co. Model 3996K90).

The performance characteristics observed in operating the wind tunnel are shown in Table 3-1. Measured wind speeds are not given since they were consistently 2.5 and 5.5 mph, depending on set point. Temperatures and R.H. values achieved were reasonably close to set point except in the case of the high humidity runs. There, the air heater obviously proved incapable of driving the temperature of the higher heat capacity fluid to the desired set point. This compromised somewhat but did not preclude comparisons of high and low relative humidity test results in which a temperature differential of about 10°F prevailed. This is discussed later in subsection 3.4.

3.2.2 Test Approach

The basic plan for determining the evaporation rates of the test candidate pesticides was to follow weight loss with time. The material would be introduced onto a suitable plate or pan configuration, then installed with the other samples into the wind tunnel egg crate at some set of environmental conditions. The individual (duplicate) samples would be withdrawn periodically for weight checks then returned to the wind tunnel. It was recognized, however, that removal of samples for weighing could influence the results since brief changes in environmental conditions would occur during each weighing. This would probably only be noticeable with the more volatile pesticides such as carrot oils. If problems were noted in handling such materials in the above-described manner, then an alternative technique would be applied. This would consist of loading the egg crate with multiple samples of the volatile oil such that each would be reweighed only once. The samples would be withdrawn sequentially in time until all desired data points for the test time frame had been acquired. The two weighing procedures just discussed are hereinafter referred to as the "single-pan/multiple reweighings" and "multiple-pans/single reweighing" techniques.

The amount of oil to be applied to the evaporation stages followed two directions. In the cases of all the petroleum-based pesticides, the amount of liquid applied fell within the recommended range of coverage (gals/acre)

TABLE 3-1. LABORATORY WIND TUNNEL PERFORMANCE CHARACTERISTICS

Nominal Control Setting			Number of Tests	Results			
				Maximum Range of Control Cycle		Avg. Value For Tests	
Temp, °F	Wind, mph	R.H., %		Temp, °F	R.H., %	Temp, °F	R.H., %
72	2.5	Uncont.	8	8±1	-	72.4±0.7	-
72	2.5	75	2	2±0	8±1	62.5±0.5	73.7±0.3
72	5.5	Uncont.	2	8±0.5	-	73.0±0.0	-
55	2.5	"	3	4±1	-	56.1±1.9	-
95	2.5	"	5	6±0.5	-	95.6±0.3	-

recommended by the vendor. In the case of the synthetics, this was not practical since the usage rates are much lower. This would necessitate the use of such small amounts that normally expectable gravimetric errors could easily exceed the actual weight change. The loading was therefore arbitrarily set at 60 mg on each stage. This is equivalent to 3.1 mg/cm^2 or 275 lbs/acre.

Four of the six synthetics are solids at room temperature. Molinate is a liquid at that temperature while DEF-6, a formulation, is a solution of the trithioate pesticide in xylene. In order to distribute the solid pesticides on the stages, they were first dissolved in a suitable volatile solvent. Following evaporation and formation of a finer crystalline process, the stages were weighed. Acetone was used to dissolve Toxaphene, while dichloromethane was used to dissolve Methomyl, Dacthal and Kelthane.

3.3 PRELIMINARY WIND TUNNEL TESTING

3.3.1 Test Objectives

A number of preliminary tests were run in the wind tunnel. These were done in order to (1) characterize the system; and (2) to establish the proper procedures for performing the evaporation tests. These included the following specific studies:

- Selection of evaporation stage material and configuration.
- Comparison of single pan/multiple reweighings vs. multiple pans/single reweighing techniques.
- Determination of flow characteristics in sample egg-crate.

3.3.2 Selection of Evaporation Stage Material and Configuration

The original proposed plan was to use thin teflon slabs as the evaporation stages. This choice was prompted by the inertness of the material but did not anticipate poor wettability. The applied oils were found to bead badly. Glass (microscope slides) was found to promote the same effect, although to a lesser degree. Cytological microscope slides were therefore tested. This type of slide is fully etched on the upper side but smooth on the under side. An applied droplet of oil was found to contact very nicely, spreading evenly over the entire etched surface. Invariably, however, the surfactant-containing film crept down the edge of the slide and wetted points on the supporting platform. It was therefore decided that devices with slight rims should be used. Polypropylene (P/P) pharmaceutical vial caps were initially selected for this purpose. The caps used on 12 dram pill boxes are 2.125 in. diameter with two annular rims. The outer rim thus can serve as a grasping surface for forcep handling. The inner rim, 0.125 in. inset from the outer, can serve as retainer for the test oil. The height of the inner rim is 0.187 in. The area of the inner circle is 2.40 sq. in. (15.5 cm^2).

Introduction of the pesticide into the "pan" is done with a drawn-tip (capillary) glass tube. After the approximate correct weight is added, the oils all spread very rapidly, forming an even, flat film that covers the entire bottom of the pan.

Initial testing of P/P pans was done using diesel oil No. 2 as the evaporated liquid. In these tests, a comparatively fast evaporation rate occurred, which, after the first hour, decayed to a slower rate for the balance of the test. It was feared that this effect might be caused by the solution of the oil in the plastic pan. A verification test was therefore run using galvanized metal pans of about the same dimensions. The results, plotted in Figure 3-2, show that the unanticipated evaporation curve rate shift was real and not introduced by the P/P pan. This was further demonstrated when distillation data provided by Union Oil Co. was plotted (Figure 3-3) to show the same characteristic.

Before adopting the round P/P evaporation pan, studies were also made of square stainless steel (SS) pans. The purpose was to detect any aerodynamic differences introduced by the two shapes. The SS pans, incidentally, were handmade by program staff and were far from perfect test shapes. The results obtained with the SS pans were badly scattered, although generally fitting the pattern shown in Figure 3-2. Given equal rim heights, it was concluded that shape was not critical, but that structure uneveness does cause poor reproducibility.

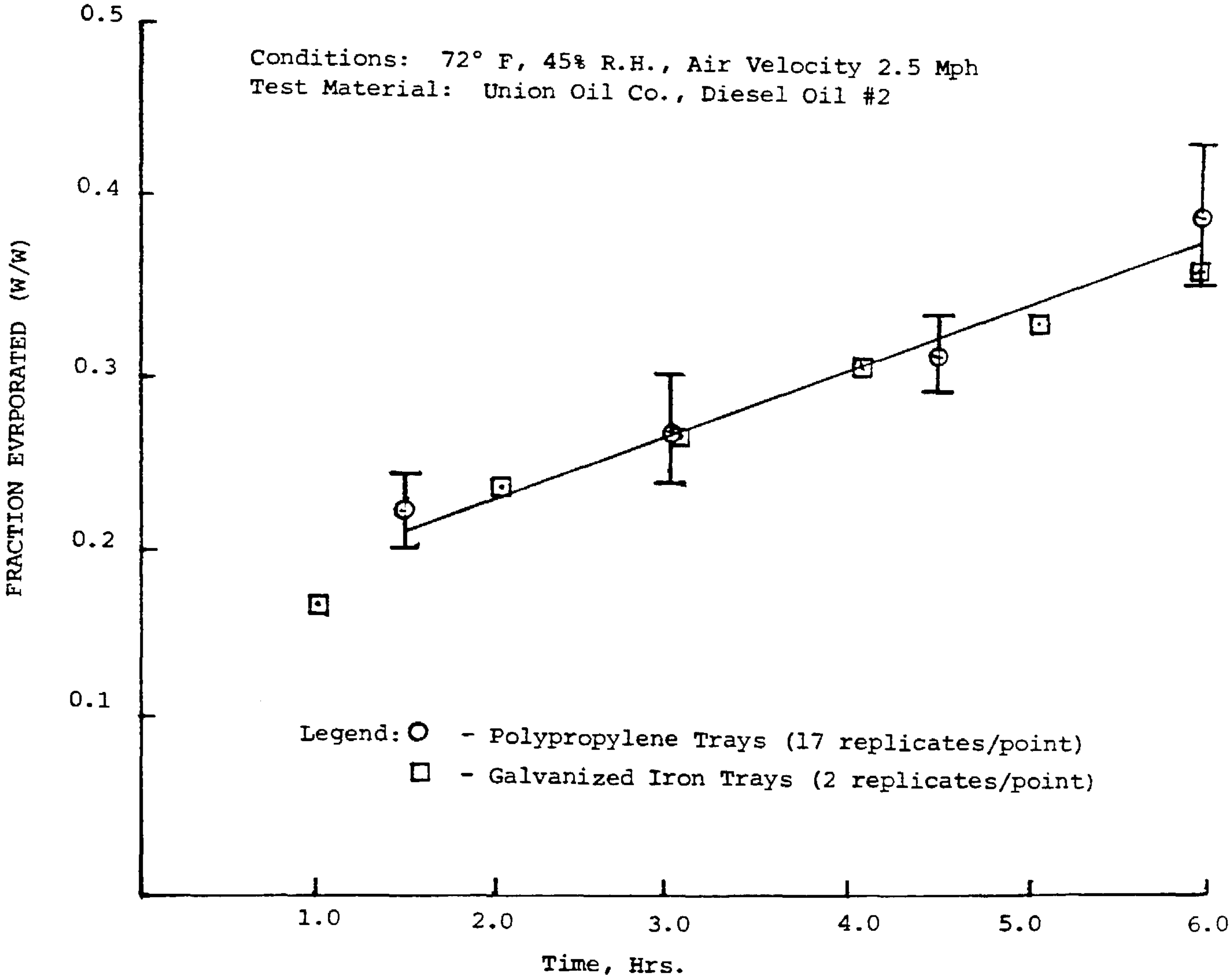


Figure 3-2. Comparative results using polypropylene and metal trays in evaporation tests.

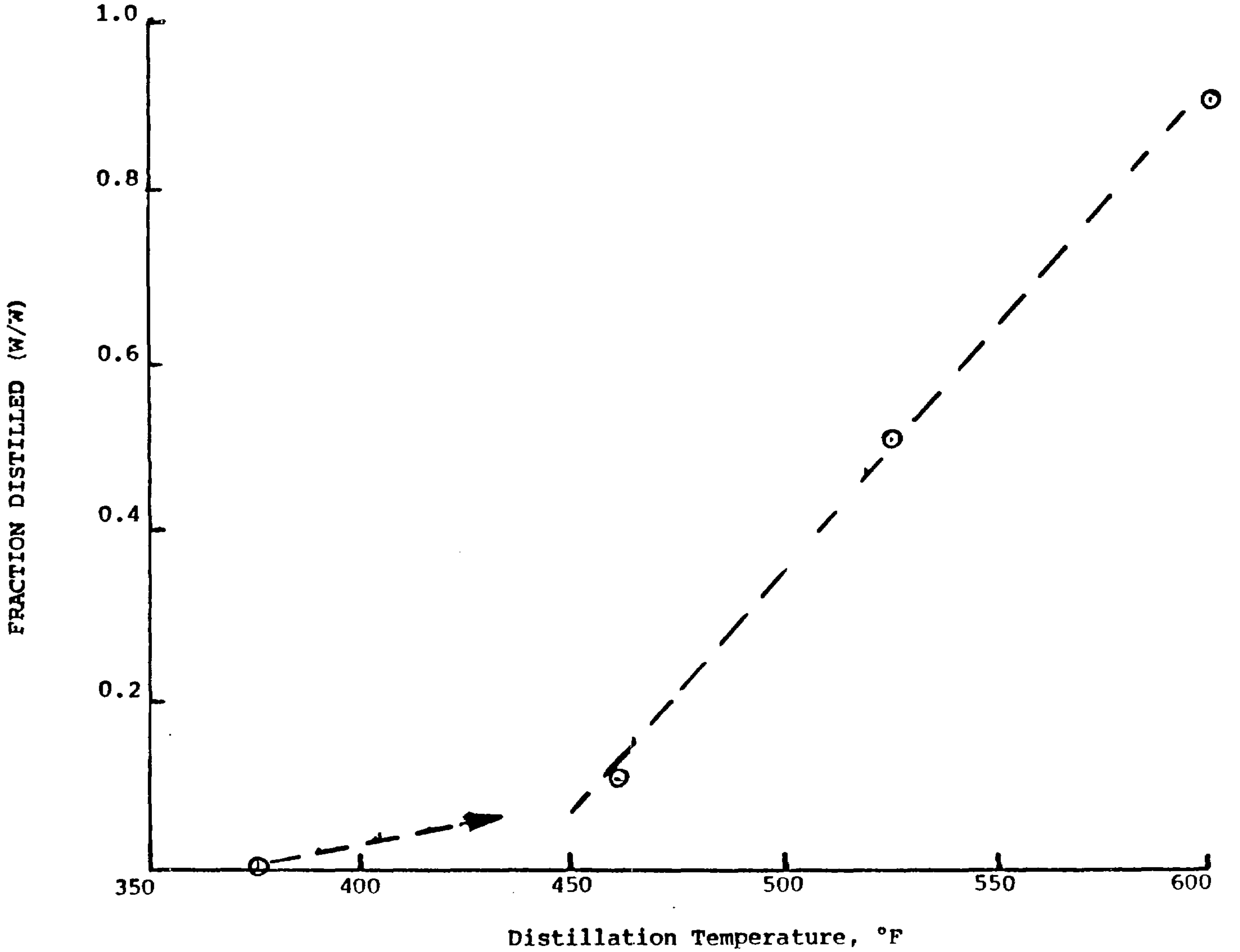


Figure 3-3. Distillation characteristics of Union Oil Co. diesel oil #2.

3.3.3 Comparison of Single Pan/Multiple Reweighings vs. Multiple Pans/Single Reweighings

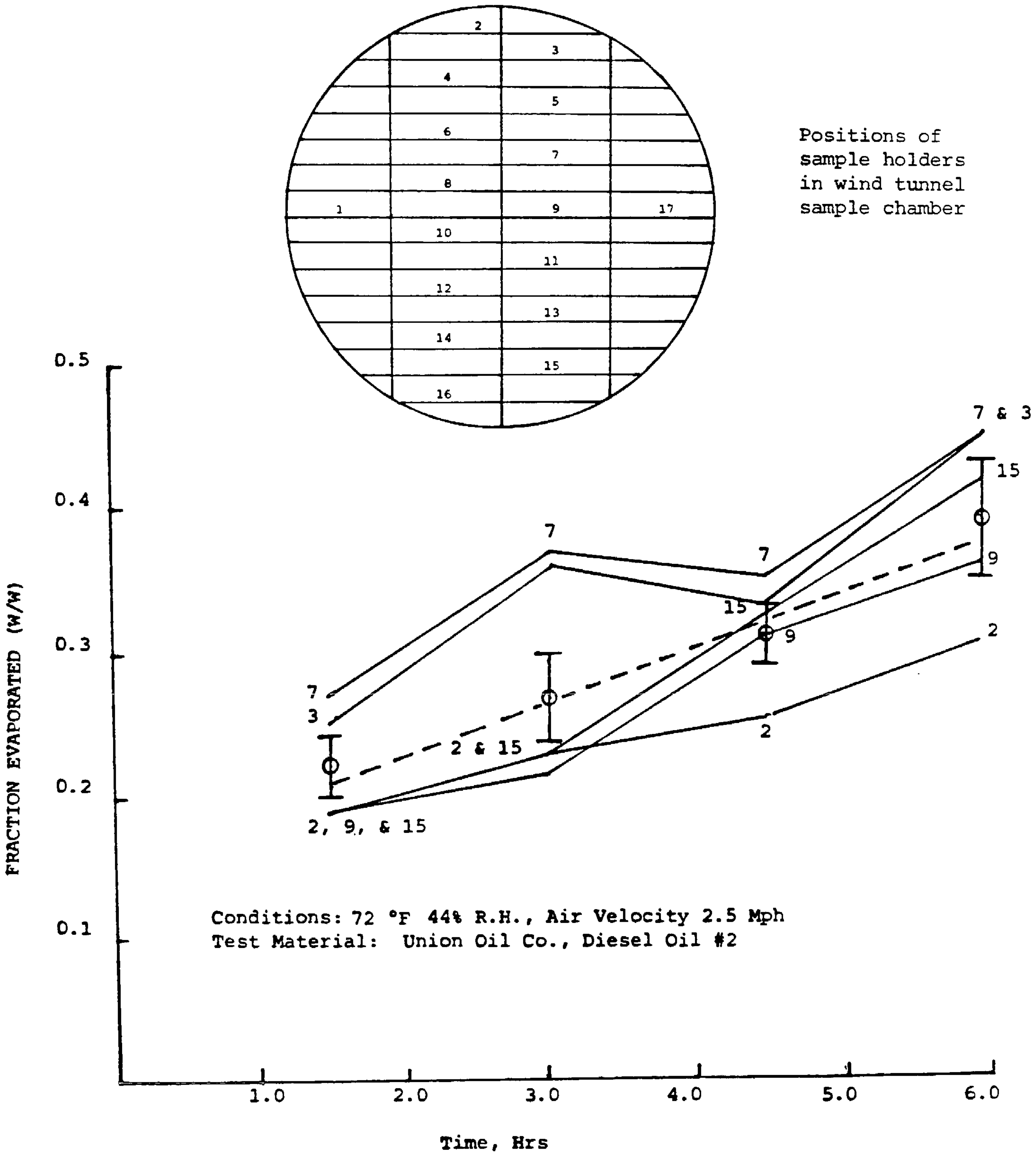
This test work was aimed at evaluating the effect of removing the test pans for periodic reweighings during a test run. Evaporation rate will obviously change when moving the pans from the wind tunnel to the analytical balance. Since, however, the evaporation rates would be expected to be quite slow, considering the physical property data shown earlier in Section 2.2, this effect might be imperceptable.

Verification was done by placing a number of pans containing the same oil in the egg-crate and then removing individuals at prescheduled intervals to develop a time-based evaporation rate curve. In that way, only one pan would be used (and discarded) for each data point. Thus, the time lost for weighing the pan would occur only after the initial reweighing and just before the final reweighing.

For these tests, the most volatile pesticides were selected. These are diesel oil No. 2 and the two carrot oils--Keen-Kil No. 20, and Beacon No. 5. Because the last two oils appear to be very similar in properties, only Keen-Kil No. 20 was tested. In testing the diesel oil No. 2, the results obtained by the multiple pan/single weighing technique overlaid nicely those obtained by the single pan/multiple weighings (Figure 3-2). On the run with the Keen-Kil No. 20, however, the evaporation rate proved to be so fast that it was obvious that the multiple pans/single weighing technique would have to be used. A comparison test with the single pan/multiple weighings approach was not even attempted.

3.3.4 Determination of Flow Characteristics in Sample Egg-Crate

A test was performed in the wind tunnel to determine if even air flow occurs throughout the cellular pattern of the egg-crate sample holder. Seventeen P/P pans were used. These, however, were for 8 dram pharmaceutical pill vials unlike the larger 12 dram type described in Subsection 3.3.2 and provided only a single, shallower rim. The pans were filmed with diesel oil No. 2 (avg. 4.4 mg/cm^2 or ~50 gal/acre) and installed in the egg crate in the pattern shown in Figure 3-4. The tunnel was then run so that each sample installed had a total residence time of 6 hours. Weighings were made every



Positions of sample holders in wind tunnel sample chamber

Conditions: 72 °F 44% R.H., Air Velocity 2.5 Mph
Test Material: Union Oil Co., Diesel Oil #2

Figure 3-4. **Results of tests to demonstrate even air flow through sample chamber.**

1.5 hrs. The results are shown in Figure 3-4 together with cell positions that exhibited questionable behavior. Of the five, only position 2 is actually of concern. Positions 9 and 15 fell in the pattern half of the time while the pans in positions 3 and 7 can be disregarded since both had been dropped on the floor during the weighing process. It was therefore concluded from these data that the two uppermost cells might have slower air flows than the rest of the structure and should not be used.

3.4 PESTICIDE EVAPORATION TESTING AND RESULTS

3.4.1 Test Plan

The test plan observed in the pesticide evaporation testing was to consider thirteen petroleum-based pesticides, six synthetic pesticides, and the reference material dodecane. The last item was included as having a volatility representative of the high ends of the very volatile pesticides (carrot oils) and the low ends of the intermediate petroleum cuts (diesel oil, Chevron and Arco weed oils).

The tests to be run can be categorized as follows:

- Temperature varied tests at intermediate wind speed (2.5 mph) and actual humidity. Set points: 55°, 72°, and 95°F.
- Wind-speed varied tests at intermediate temperature (72°F) and actual humidity. Set points: 0.0, 2.5, and 5.5 mph.
- Humidity varied tests at intermediate temperature (72°F) and intermediate wind speed (2.5 mph). Set points: actual and high R.H.
- Soil-effect testing at intermediate temperature (72°F) and wind speed (2.5 mph), and actual humidity.

3.4.2 Temperature Varied Tests

The results of the temperature-varied runs are shown in Figures 3-5 through 3-14. Because one rerun was necessary, two sets of conditions resulted. The low temperature averaged 54.5°F in 4 of the tests and 59.5°F in the others. The high and intermediate temperatures averaged the same in all tests. The variation in relative humidity was merely a temperature dependent effect and apparently not accompanied by any condensation. The absolute vapor

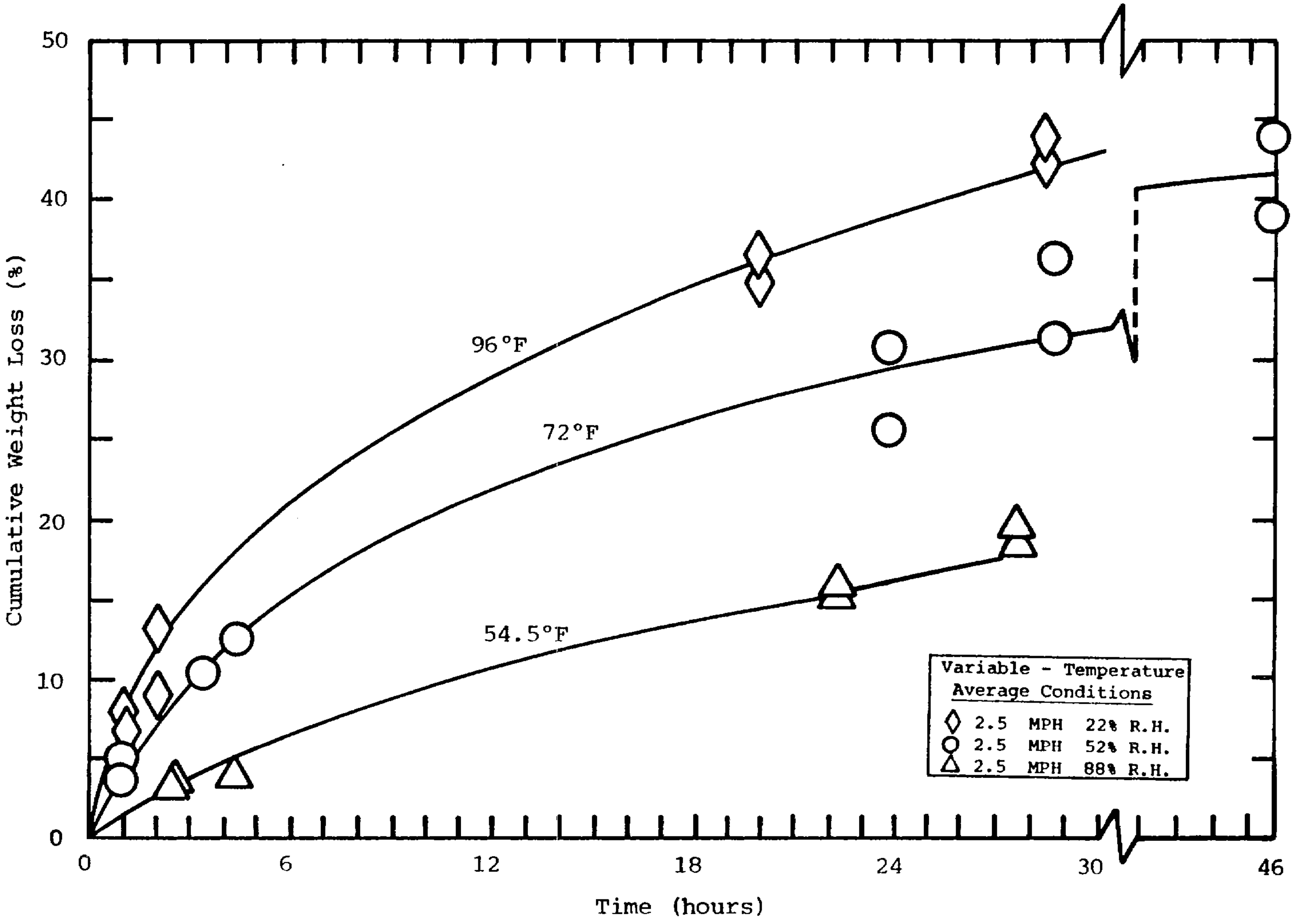


Figure 3-5. Pesticide Evaporation Rate Test: ARCO Weed Killer "A" Lite - Temperature Varied.

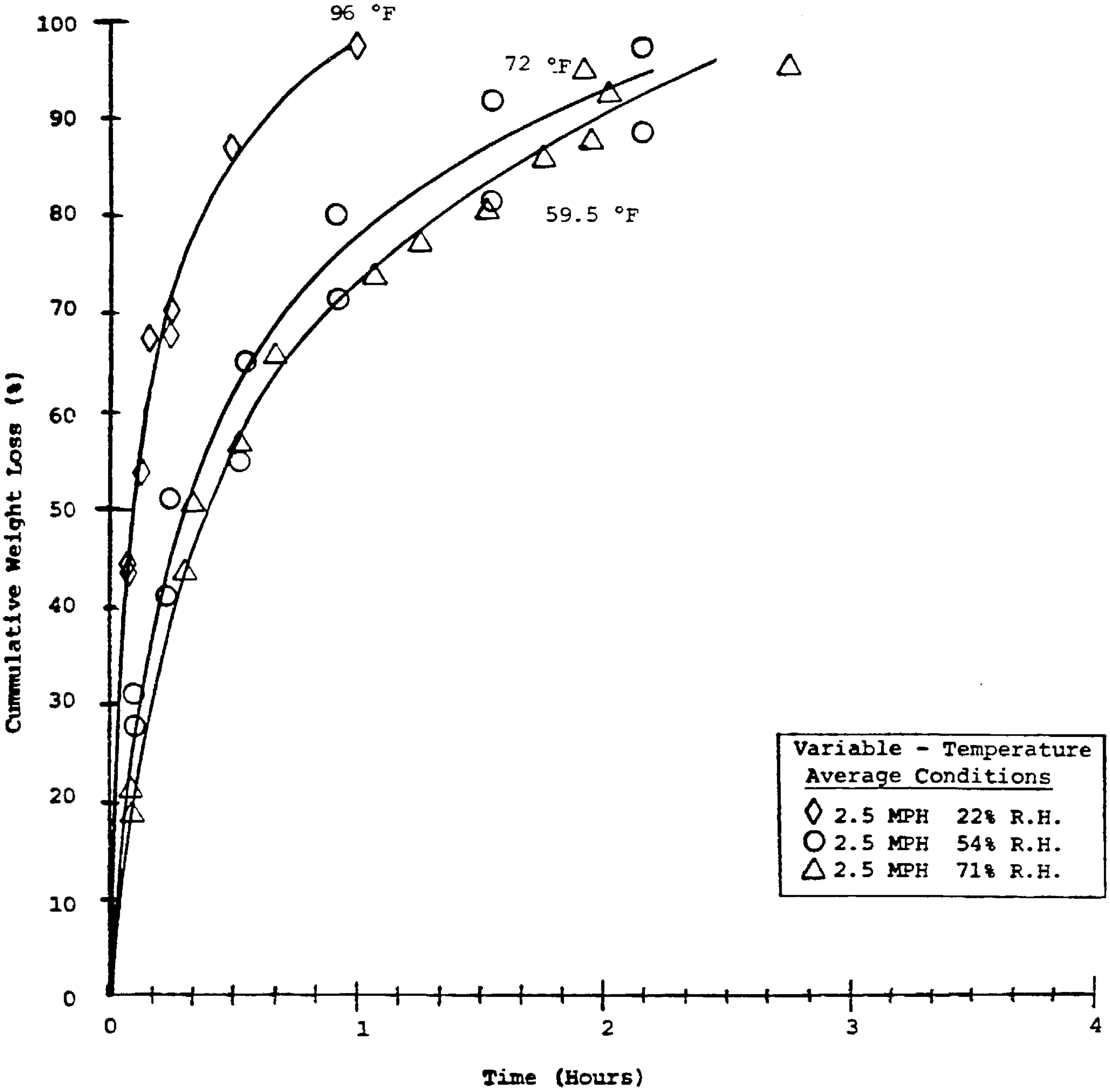


Figure 3-6 . Pesticide Evaporation Rate Test: Beacon Weed Killer #5 - Temperature Varied.

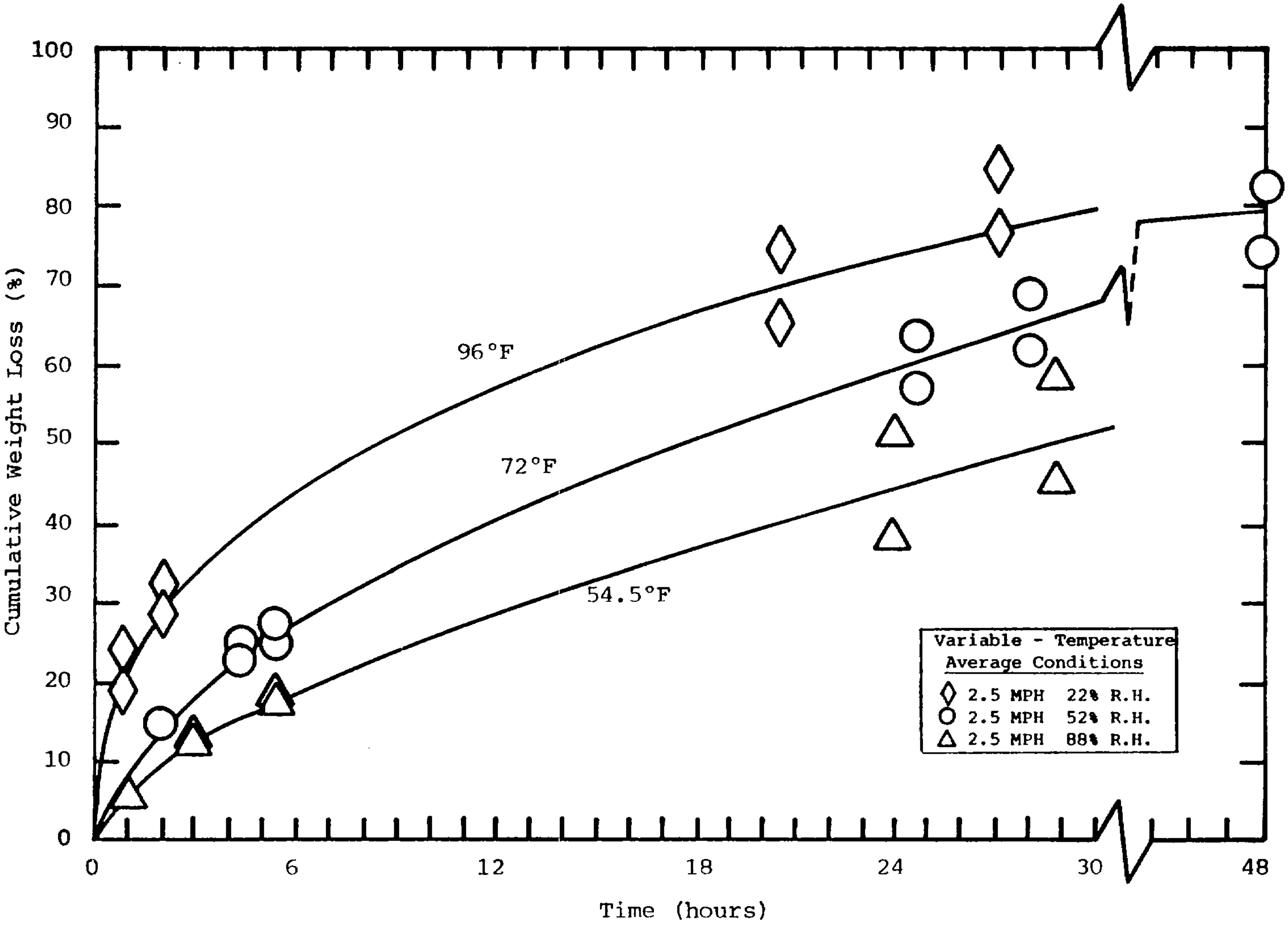


Figure 3-7. Pesticide Evaporation Rate Test: Chevron Weed Oil - Temperature Varied.

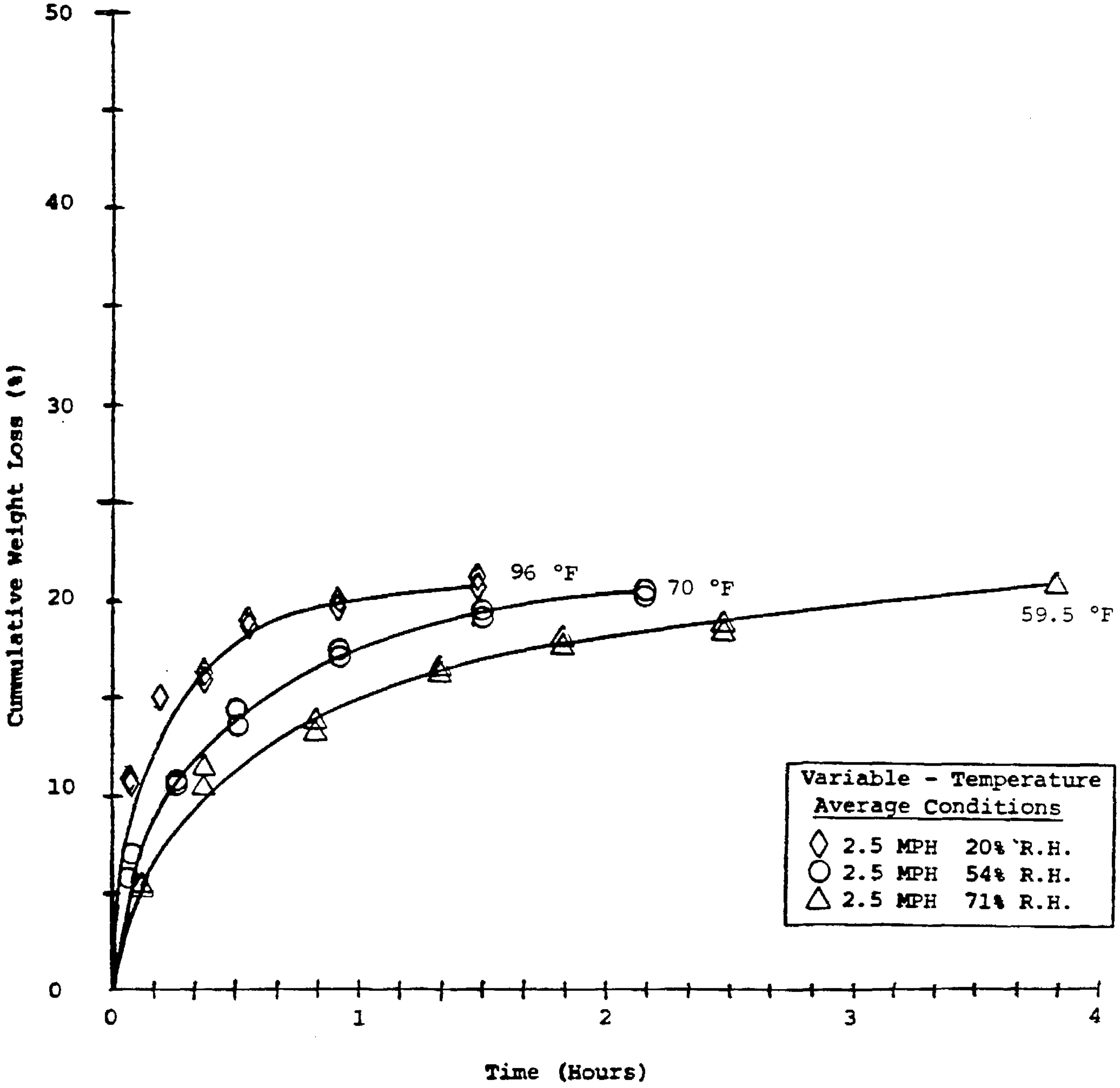


Figure 3-8. Pesticide Evaporation Rate Test: DEF 6 - Temperature Varied.

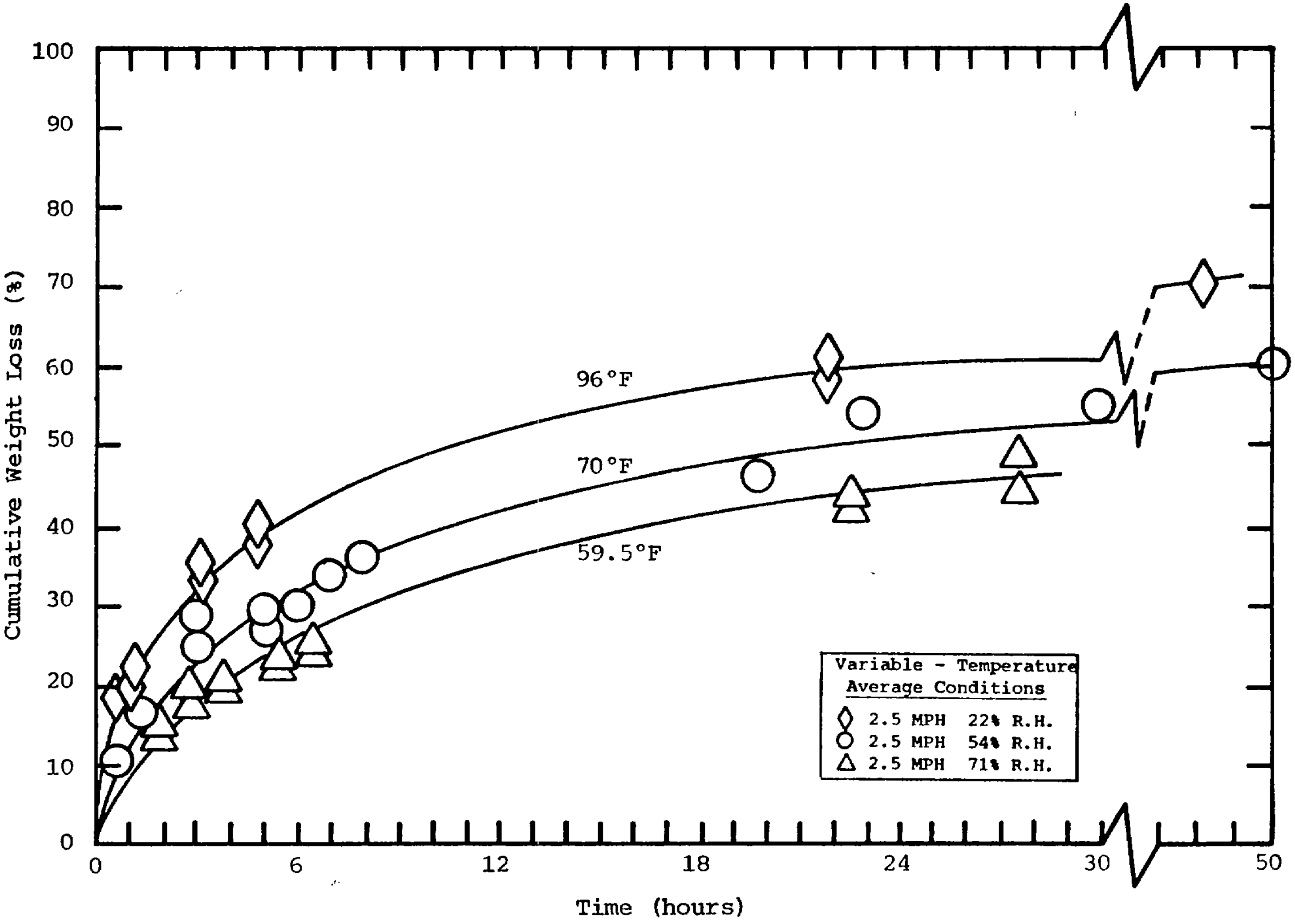


Figure 3-9. Pesticide Evaporation Rate Test: Union Diesel Oil #2 - Temperature Varied.

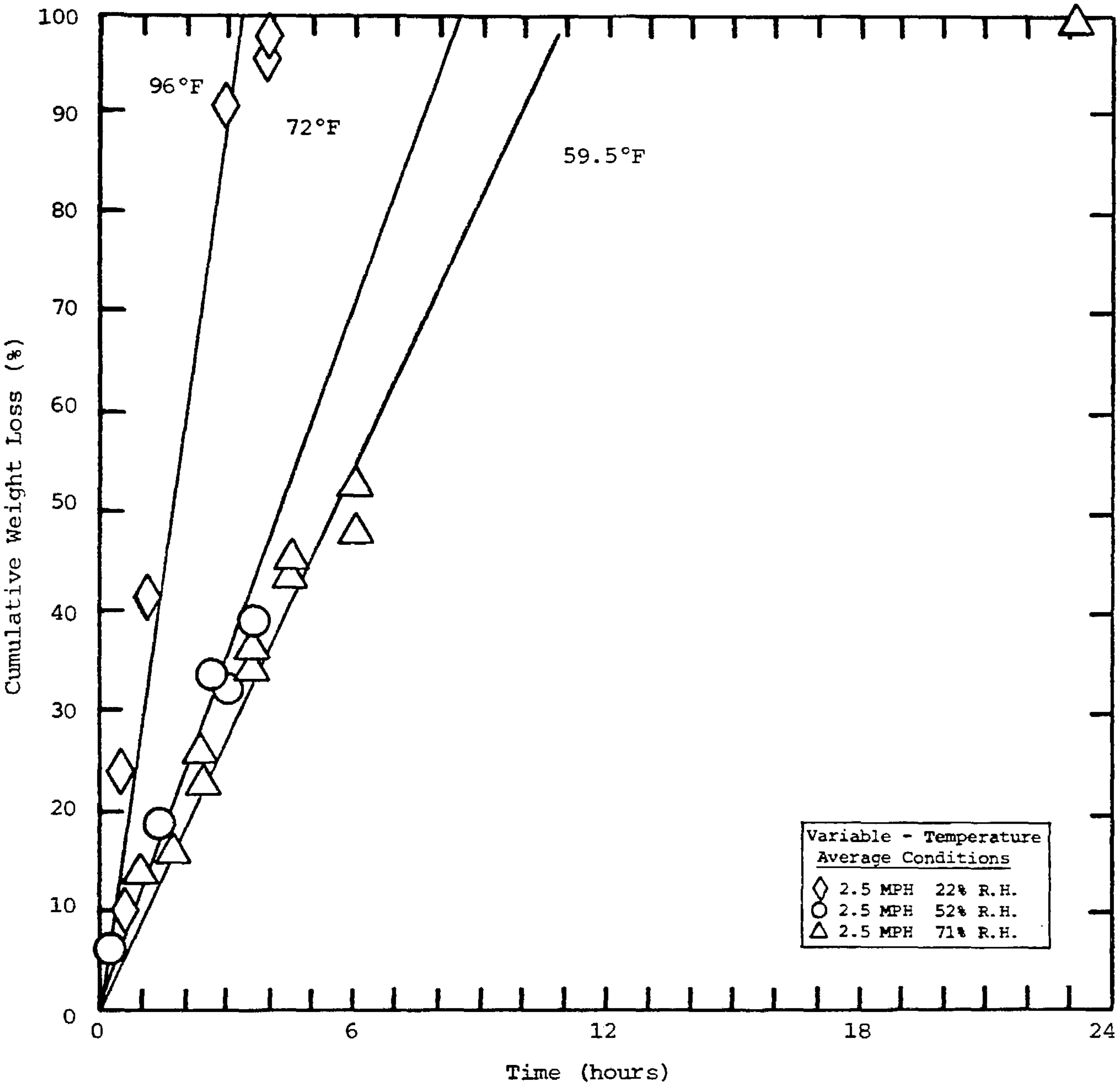


Figure 3-10. Pesticide Evaporation Rate Test: Dodecane - Temperature Varied.

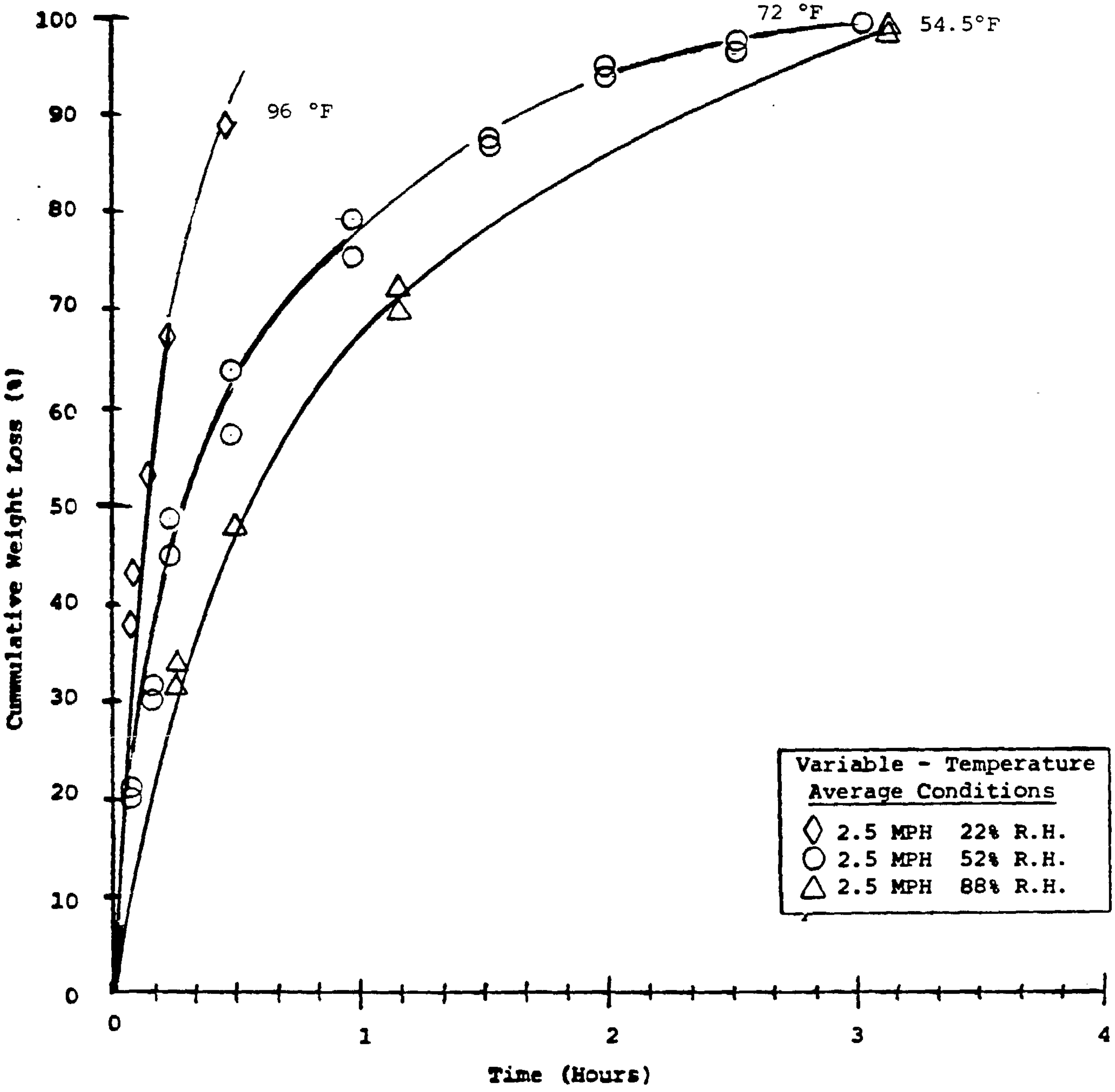


Figure 3-11. **Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #20-** Temperature Varied.

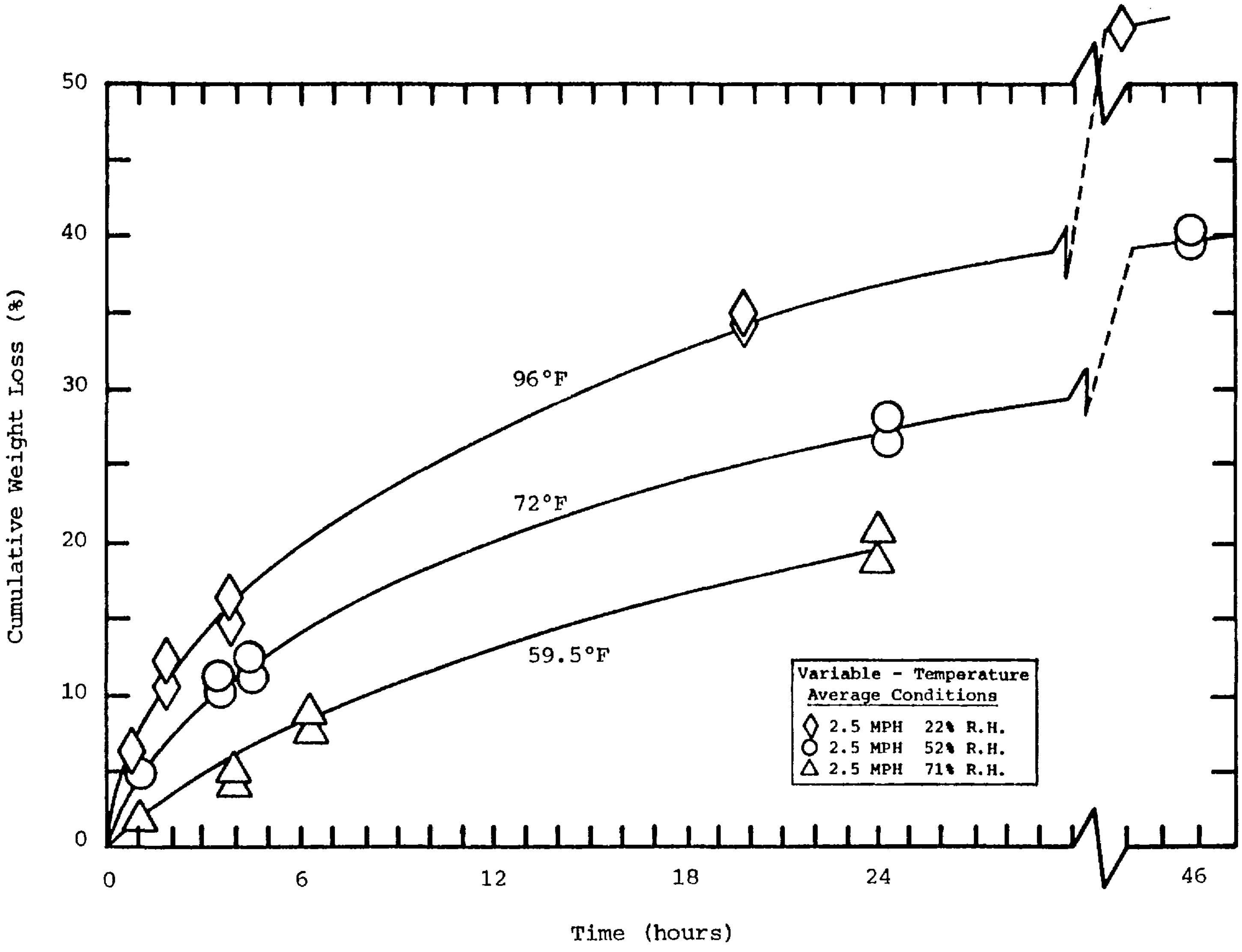


Figure 3-12. Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #40-Temperature Varied.

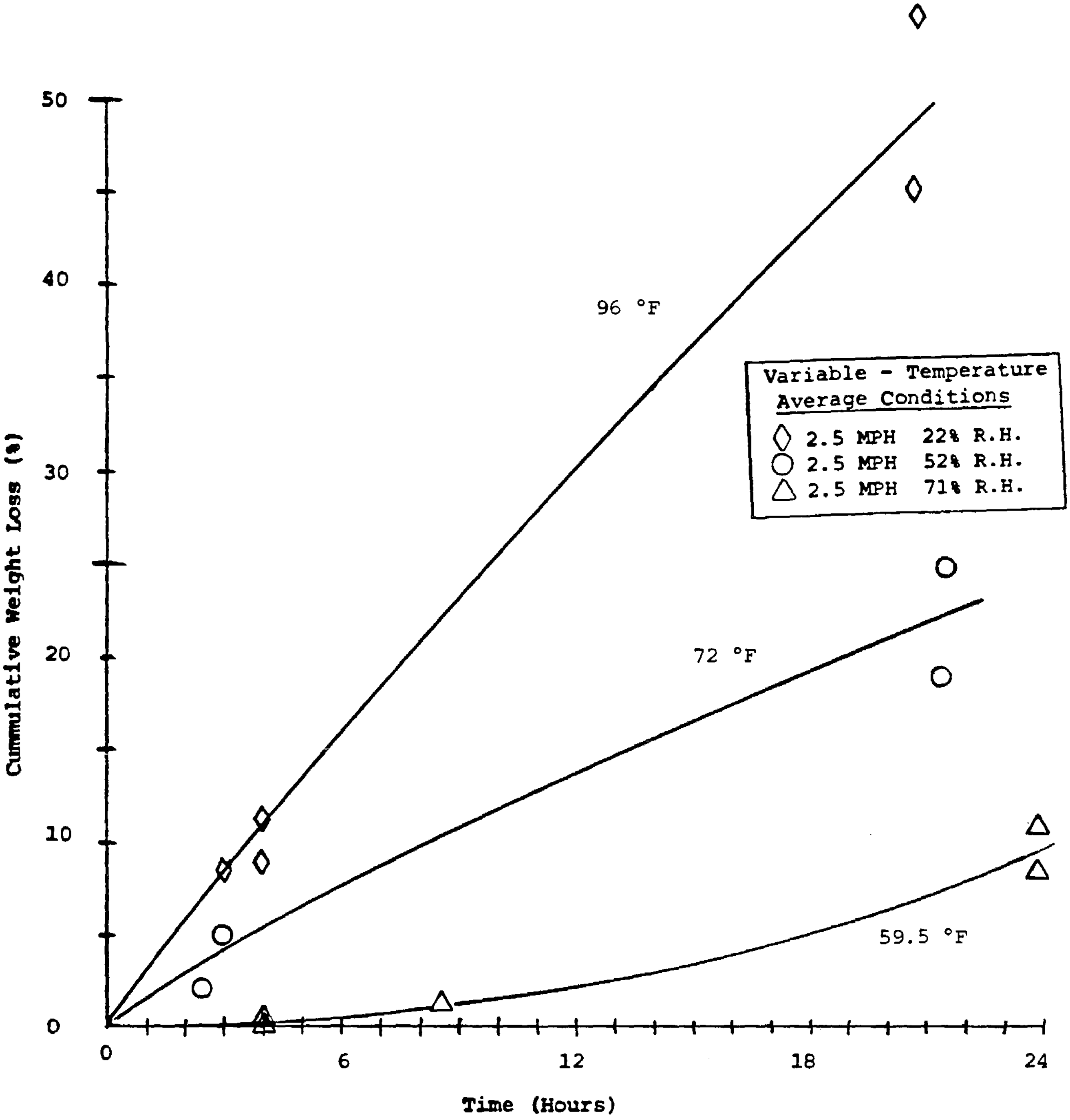


Figure 3-13. Pesticide Evaporation Rate Test: Molinate - Temperature Varied.

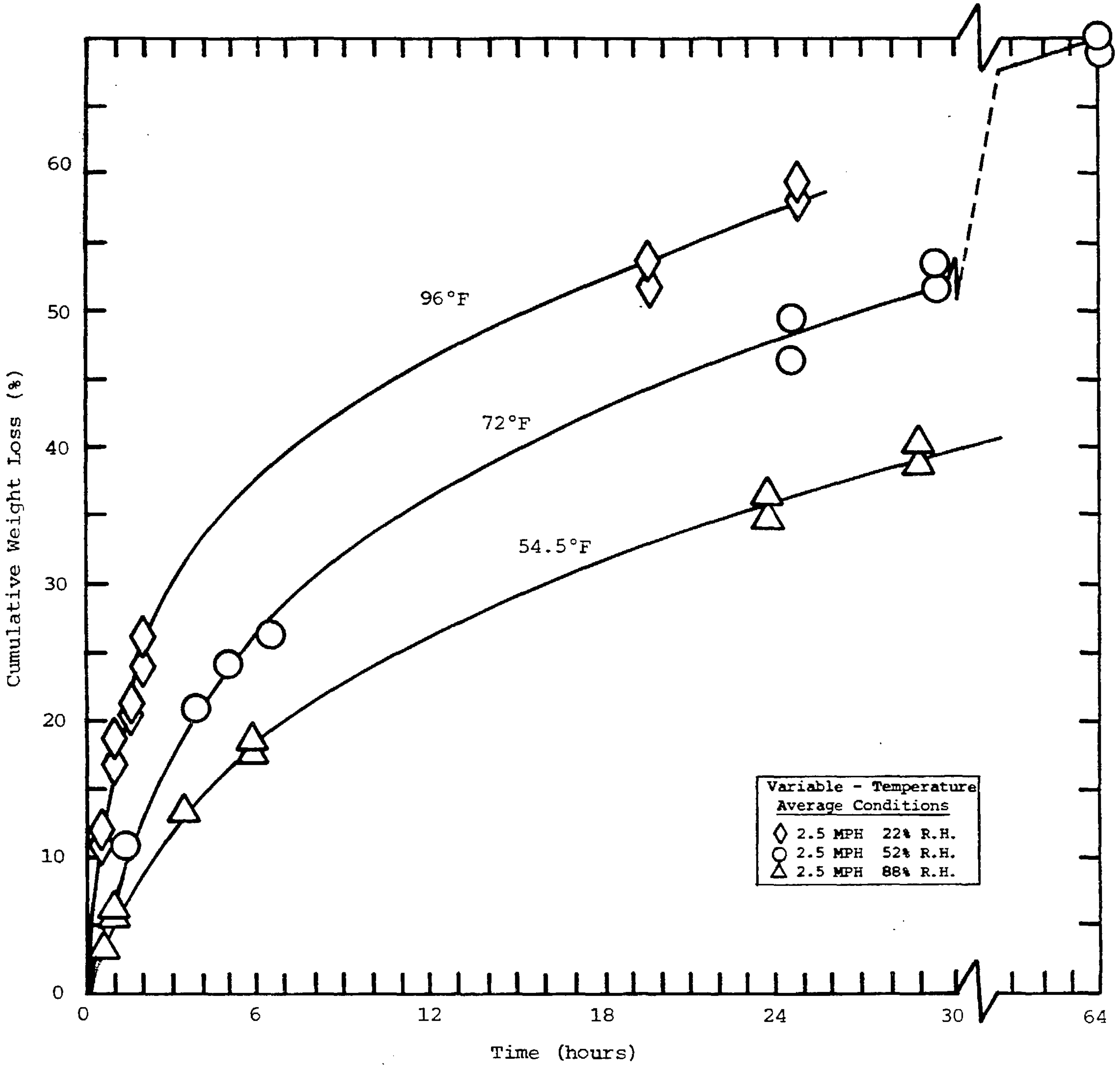


Figure 3-14. Pesticide Evaporation Rate Test: Moyer Weed Killer #20 - Temperature Varied.

pressure of water at all three temperatures in the set in which the low temperature was 54.5°F calculated out at 9.8 ± 0.4 Torr (or 9.6 ± 0.4 g water/m^3). In the other set (low temperature averaging 59.5°F), the corresponding value calculated from the average R.H.'s recorded is 9.9 ± 0.4 Torr.

It will be noted that curves for only half the test substances are included. This is because the other ten materials evidenced very slow or imperceptible evaporation rates. In some cases, weight changes showed little dependence on temperature, suggesting that the effect was not promoted by simple evaporation. The results obtained with these ten low-volatility pesticides are shown in Table 3-2.

Returning to the more volatile materials, the reference material exhibited a linear evaporation. This would be expected of a pure substance. This was not the case with the petroleum-based pesticide materials, all of which exhibited rate changes, which probably correspond with the distillation characteristics of the oils. Molinate, a pure synthetic pesticide exhibited a linear evaporation curve, except for a possible increase in rate occuring at the lowest temperature. This effect, if real, could suggest decomposition of the test substance into more volatile fragments. As discussed earlier (Subsection 2.2.3-E), Molinate is a hydrolyzable carbamate and it might degrade in moist air to form ethyl mercaptan and, possibly, an N,N-hexamethylene carbamate. Such a decomposition would thus cause an apparent increase in the evaporation rate.

It might also be noted that although Molinate, a liquid, exhibited a measureable evaporation rate, two other synthetics that did not, Toxaphene and Dacthal, actually have higher vapor pressures (see Table 2-3). These more volatile pesticides are, however, both solids. The heats of sublimation are typically much higher for solids than are the heats of vaporization of liquids of corresponding molecular weights. This probably accounts for the results obtained. Surface areas were also different, but probably larger in the case of the solids.

TABLE 3-2. WEIGHT LOSS OF PESTICIDES EXHIBITING LOW VOLATILITY

	Nominal Test Temperature			
	72 °F		95 °F	
Pesticide	Δt, Hrs.	% Wt.Loss	Δt, Hrs.	% Wt. Loss
Dachthal	22	0	19	2-3
Gavacide-90	140	0	18	0
Kelthane	20	3	21	3-4
Leffingwell 90	142	0	18	0
Leffingwell Unipar	138	0-4	23	4
Leffingwell Unicide*	118	15	24	8-9
Methomyl	19	4	22	1-2
Orthol K Ready Mix†	118	11	24	9-10
Toxaphene	118	0	18	5-6
Volk Supreme	138	0	23	2-3

* At 24 hrs., weight loss was 8%, stabilizing at 15% after 99 hrs.

† At 24 hrs., weight loss was 6%, stabilizing at 11% after 99 hrs.

Another comment concerning the synthetics goes to DEF-6 behavior (Figure 3-8). This is the only formulated synthetic pesticide tested; the other five synthetics were all pure materials obtained from Chem Service Inc., West Chester, Pennsylvania. DEF-6 contains about 20 percent xylenes as solvent. The evaporation curves merely reflect the loss of that solvent, upon completion of which no detectible loss of the active ingredient could be measured.

In evaluating the results obtained with the reference material, dodecane, calculated vapor pressure ratios were compared with the evaporation rates measured. Assuming that the heat of vaporization for dodecane (11,857 cal/g-mole @ 20°C) is constant over the range of test temperatures, one can apply an approximate integration of the Clausius-Clapeyron equation, viz:

$$\log P_2/P_1 = \frac{\Delta Hv}{2.3R} \frac{T_2 - T_1}{T_2 T_1}$$

one then calculates dodecane vapor pressure ratios for the high to intermediate and high to low test temperature of 2.39 and 3.88, respectively. These ratios compare reasonably well with the corresponding ratios of the slopes (evaporation rates) of the isotherms shown in Figure 3-10, which are 2.4 and 3.4, respectively.

3.4.3 Wind-Speed Varied Tests

The results obtained in the previous (temperature-varied) test done at 72°F and 2.5 mph air velocity were compared with the wind speed set at 0 and 5.5 mph. The still air test could not be done in the wind tunnel because the hygrothermograph and the egg-crate were several feet apart. Both were removed and placed in a draft-proof wooden box in an air-conditioned room. The resulting average temperature (70°F) proved slightly lower than that (72°F) recorded in the wind tunnel tests conducted in a 2.5 mph wind.

Conversely, the test run at 5.5 mph in the wind tunnel produced an average test temperature (74°F) slightly higher than that obtained in the 2.5 mph test. This was doubtless due to the inability of the air conditioner to maintain the same temperature at twice the mass throughput rate of fairly warm ambient air.

The results obtained are shown in Figures 3-15 through 3-24. In all cases, except with DEF-6, the expectable large differences are noted in the gas-phase, diffusion-controlled (0.0 mph air movement) and the flow-induced turbulent processes at 2.5 and 5.5 mph wind speeds. In the case of DEF-6, a binary solution is involved in which one component (xylene) is far more volatile than the other (the trithioate). Thus, diffusion of the solvent through the depleted liquid/gas interface also influences evaporation rate. The marked differences in loss rates with stagnant and moving air are thus significantly diminished in the case of DEF-6.

Similarly, the evaporation rates of the only pure volatile substances tested, dodecane and Molinate about double (x 2.2 and x 1.6, respectively) as the wind speed is increased from 2.5 to 5.5 mph. This is hardly true of the petroleum oils, with volatilities on either side of that of dodecane. The latter, of course, exhibits a homogeneous liquid phase that is not influenced by depletion/diffusion effects as with petroleum oils containing hydrocarbons having a range of volatilities.

As in the one case seen in the temperature-varied tests (see Figure 3-13), evidence of Molinate decomposition was again noted. In the highest wind speed test, there appears to be an increase in evaporation rate in what was a good isothermal run. The hydrolytic stability of this pesticide was discussed in the previous subsection.

Again, only half of the candidate pesticides are represented in the graphs shown in Figures 3-15 through 3-24. The reasons are the same as given in the previous section covering temperature-varied testing. The other ten materials showed low volatilities that did not significantly increase with wind speed. In fact, the difference was less in going (essentially at 72°F) from 2.5 to 5.5 mph wind speed than from 72°F to 96°F at the same (2.5 mph)

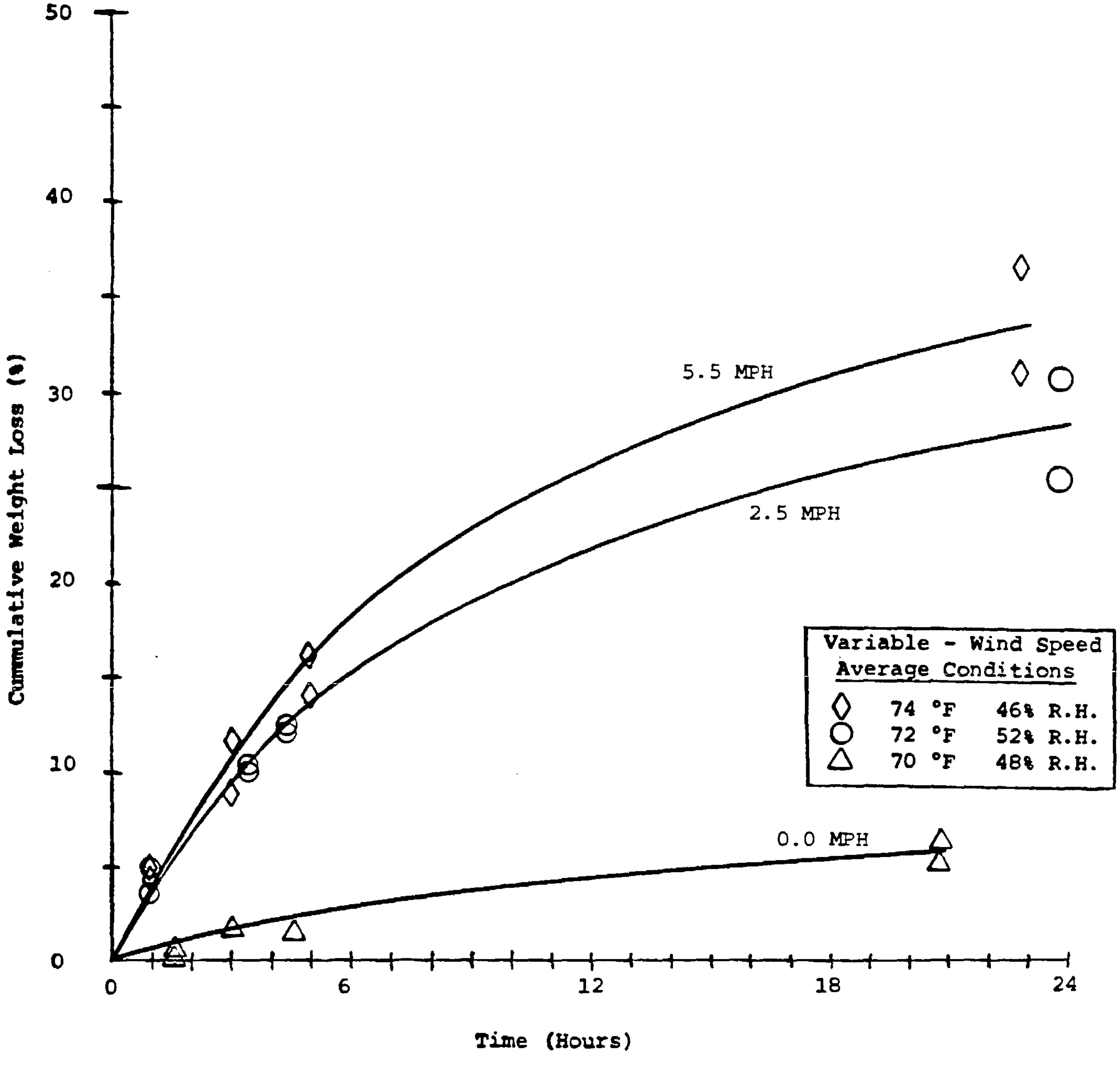


Figure 3-15. Pesticide Evaporation Rate Test: ARCO Weed Killer "A" Lite - Wind Speed Varied.

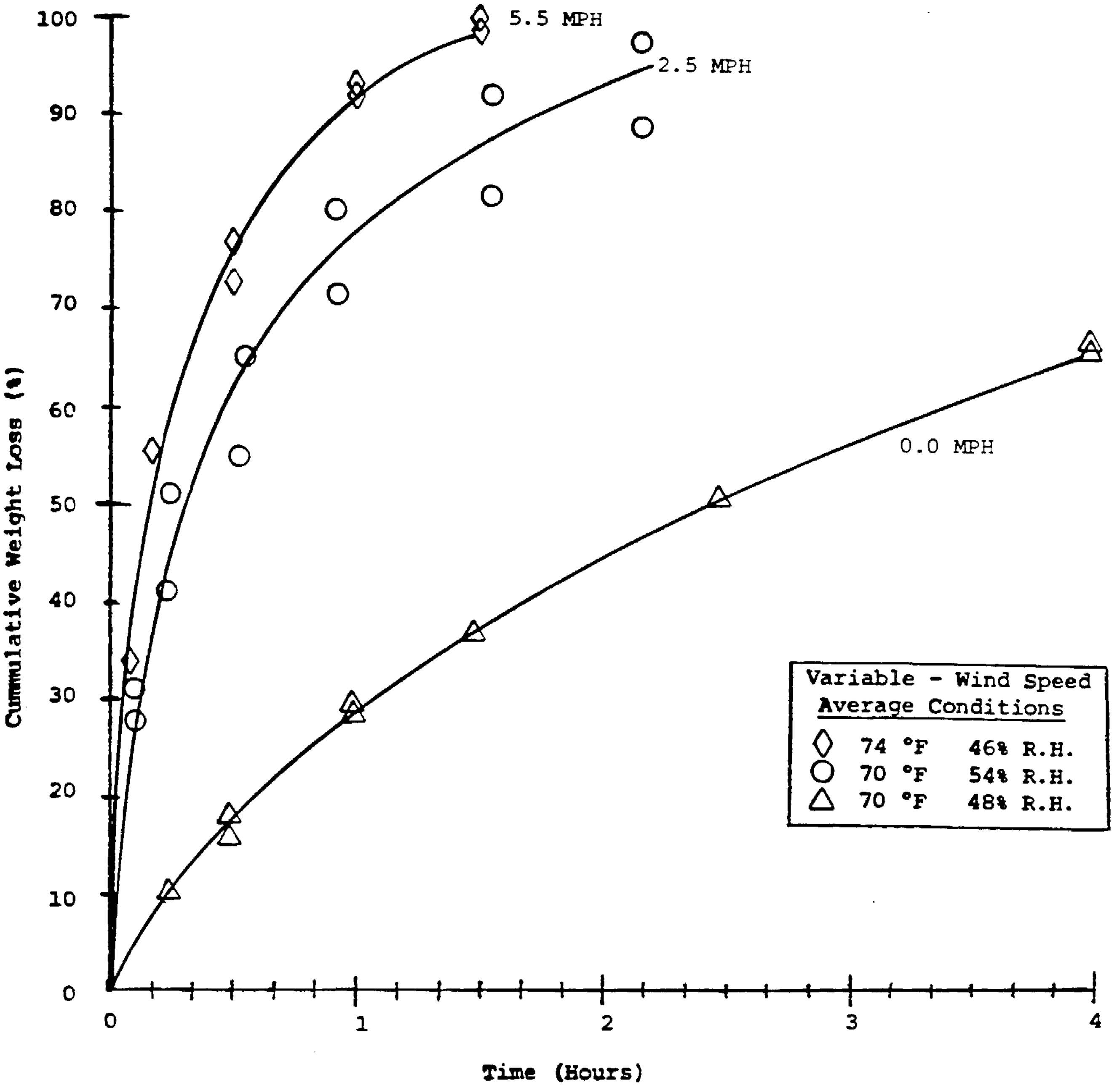


Figure 3-16. Pesticide Evaporation Rate Test: Beacon Weed Killer #5 - Wind Speed Varied.

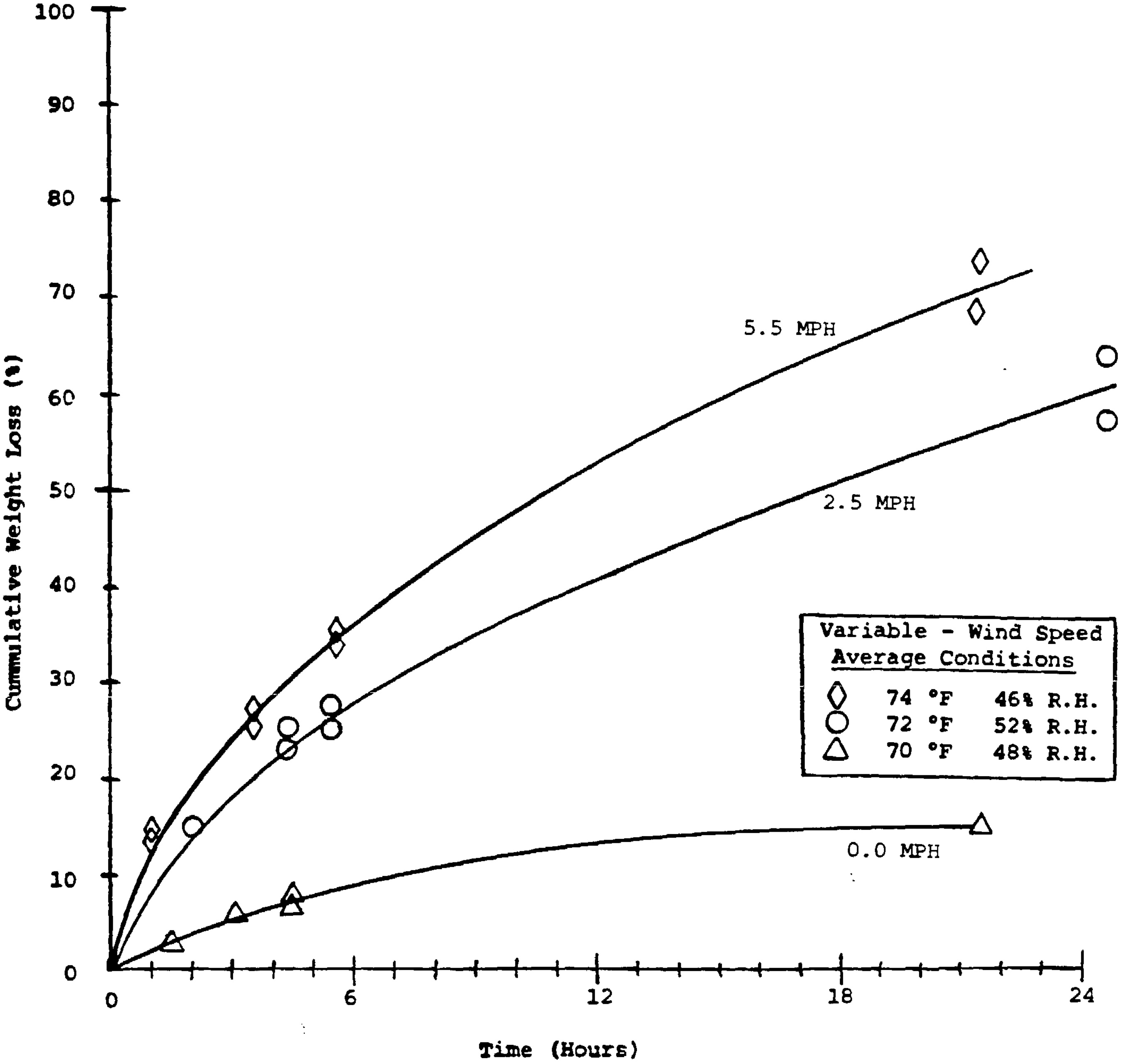


Figure 3-17. Pesticide Evaporation Rate Test: Chevron Weed Oil - Wind Speed Varied.

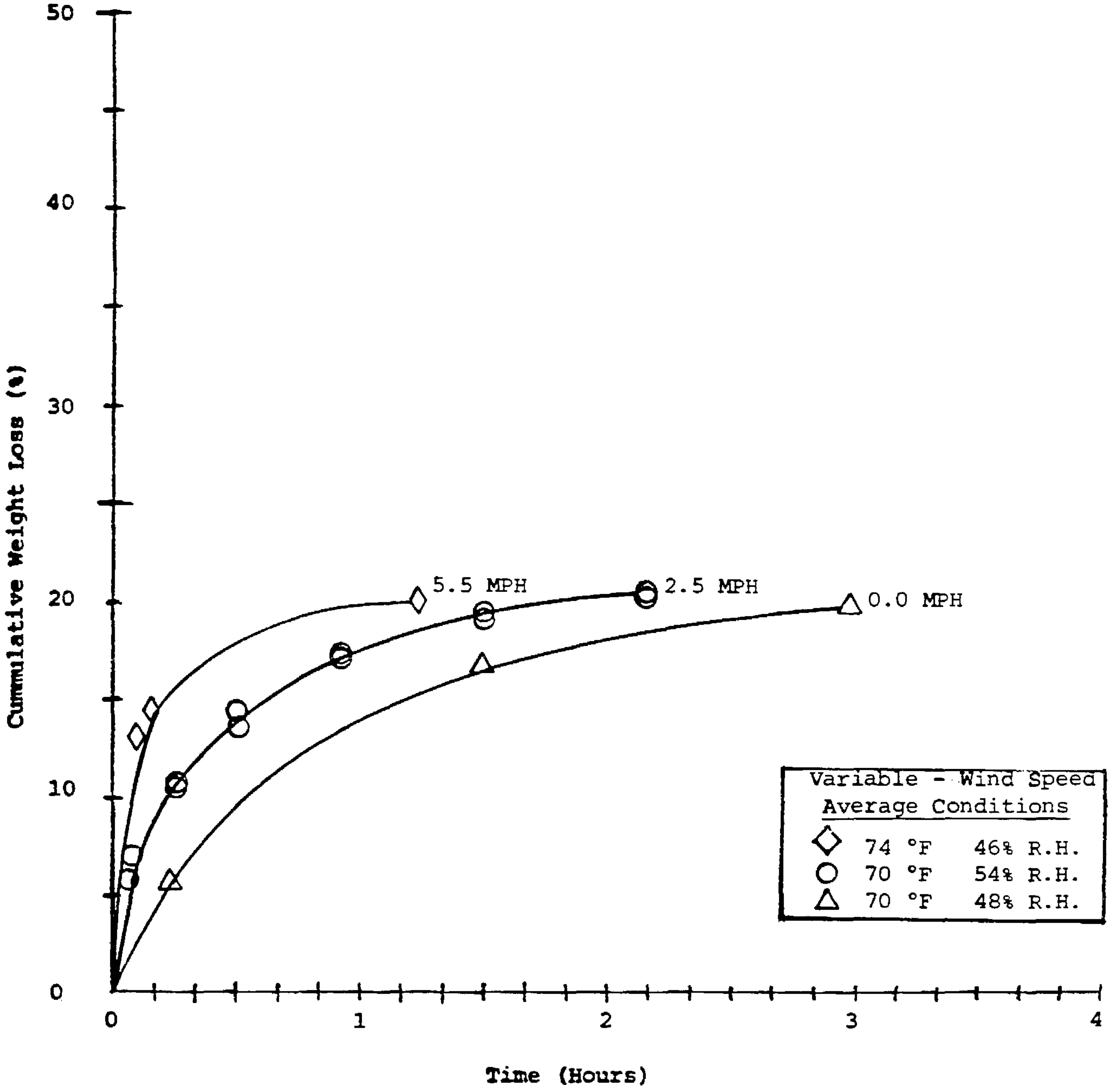


Figure 3-18. Pesticide Evaporation Rate Test: DEF 6 - Wind Speed Varied.

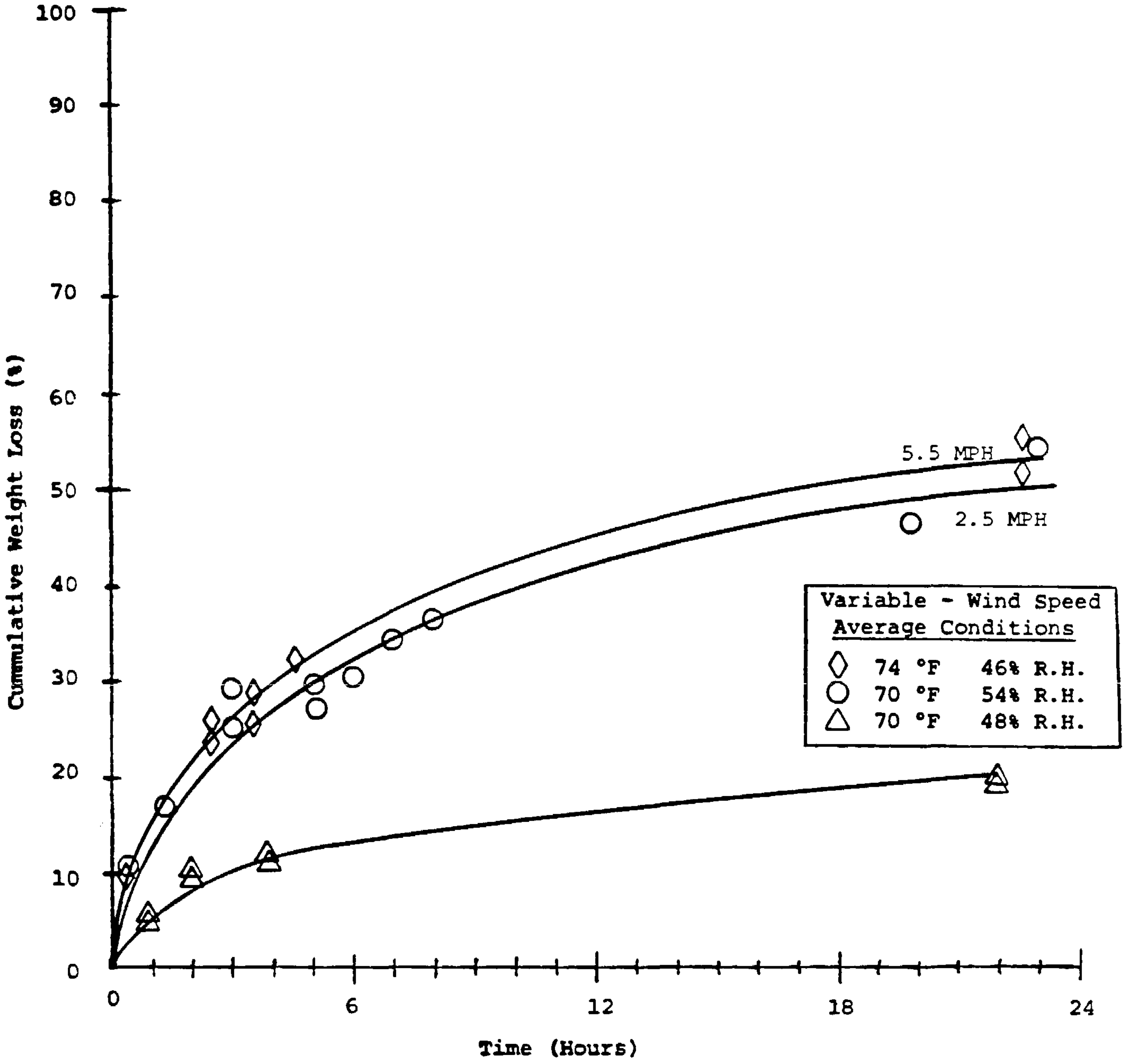


Figure 3-19. Pesticide Evaporation Rate Test: Union Diesel Oil #2 - Wind Speed Varied.

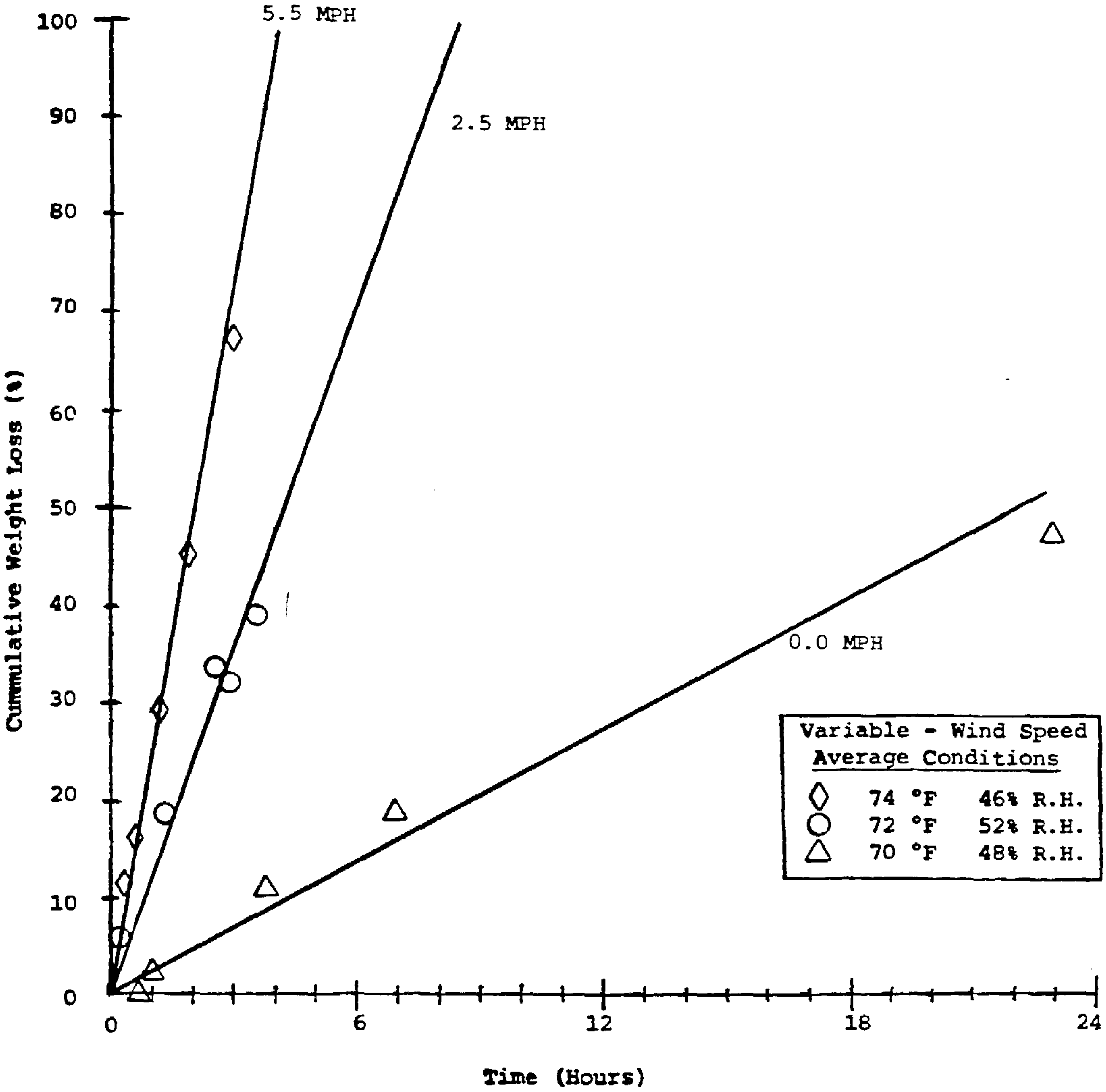


Figure 3-20. Pesticide Evaporation Rate Test: Dodecane - Wind Speed Varied.

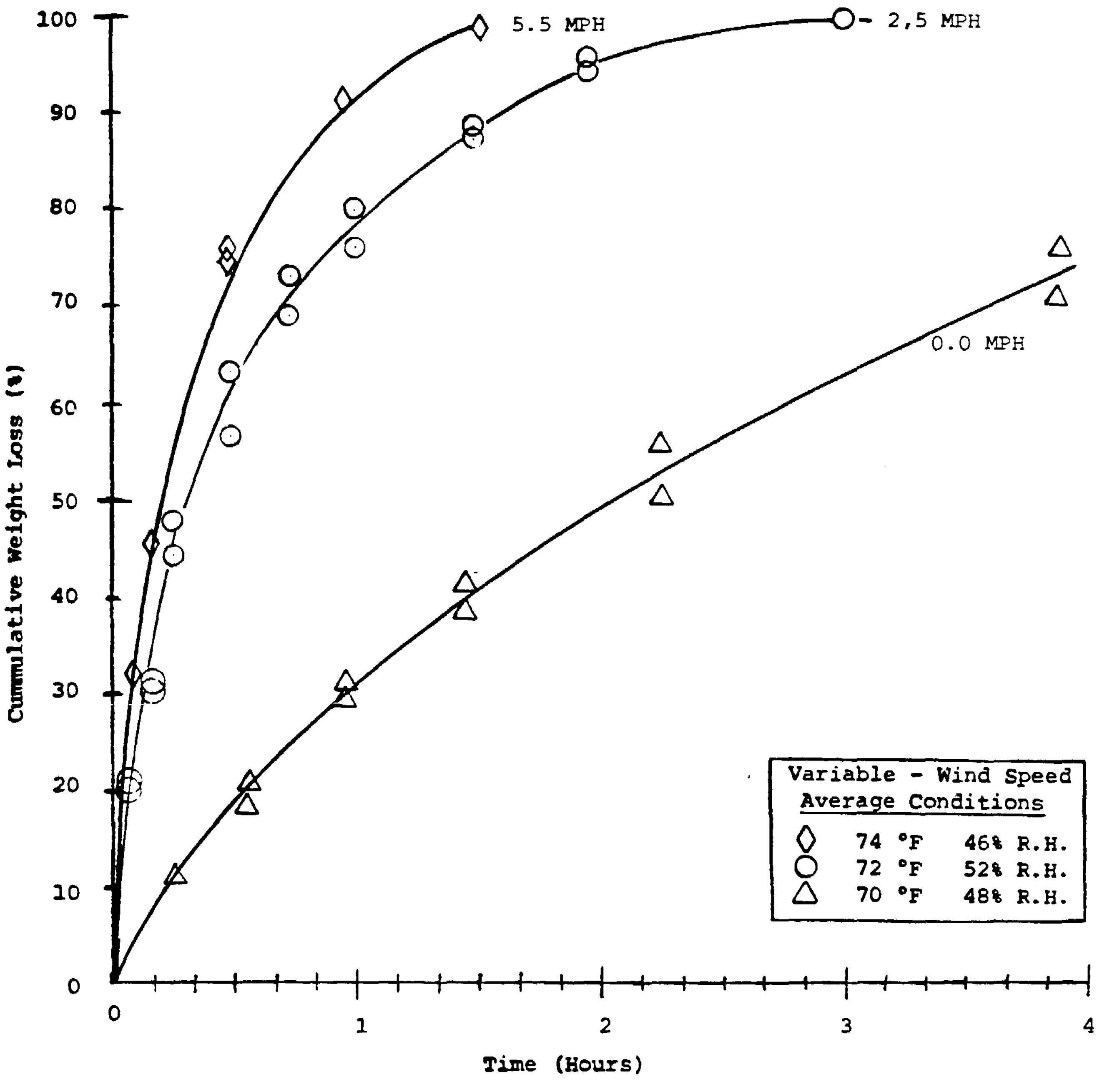


Figure 3-21. Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #20 - Wind Speed Varied.

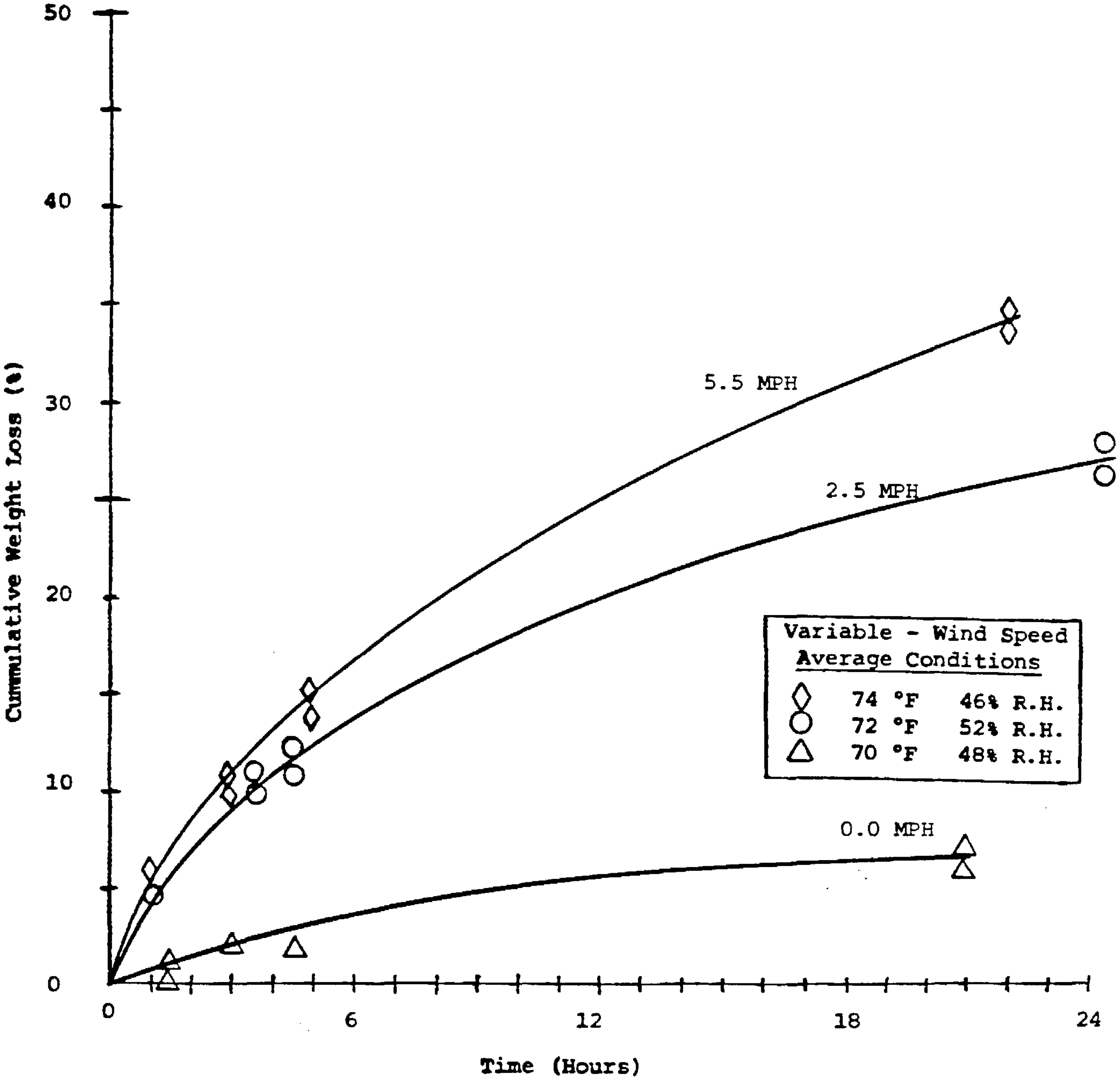


Figure 3-22. Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #40 - Wind Speed Varied.

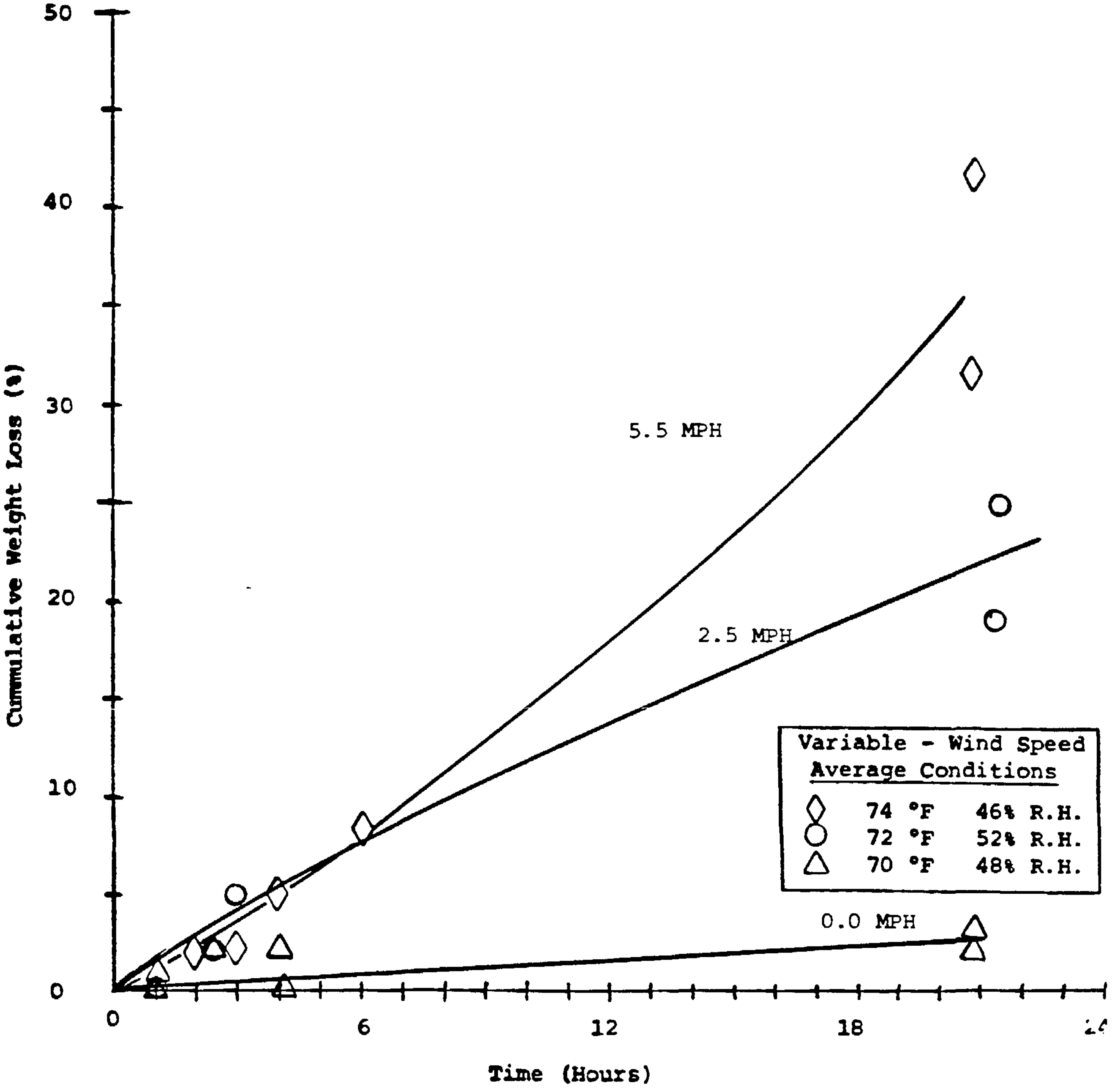


Figure 3-23. Pesticide Evaporation Rate Test: Molinate- Wind Speed Varied.

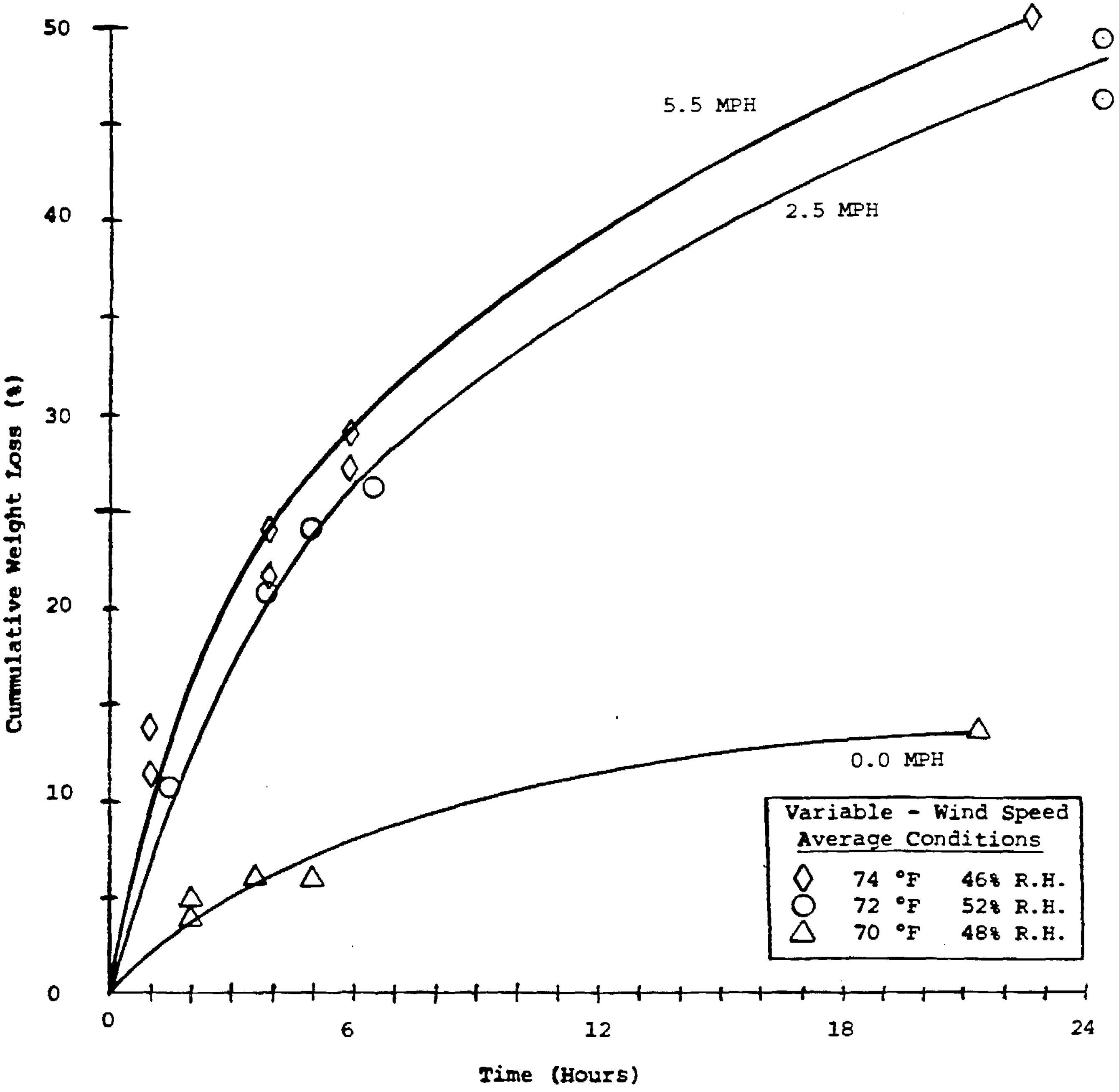


Figure 3-24. Pesticide Evaporation Rate Test: Moyer Weed Killer #20-Wind Speed Varied.

wind speed. The results for the other ten low volatility pesticides are given in Table 3-3. As in the temperature varied tests, differences noted for those pesticides evidencing small losses (Leffingwell Unicide and Orthol K Ready Mix) did not appear to be influenced by the varied test parameter.

3.4.4 Relative Humidity Varied Tests

Evaporation rates of the candidate pesticides at higher relative humidity are shown in Figure 3-25 through 3-34. Most of the curves obtained show a consistent offset suggesting that the lower R.H. air causes a more rapid evaporation of the samples. In fact, however, the test conditions did not prove to be isothermal as initially preset. The difference in evaporation noted is thus probably due only to the difference in temperatures of the runs. This can be seen by overlaying the 72 percent R.H. curves (63°F) on the family of curves for the corresponding pesticides shown in Figures 3-5 through 3-14. The curves situate about where they would be expected to, based on temperature. It is thus likely that, in the present test context, R.H. has little if any effect on evaporation rate of hydrocarbons.

3.4.5 Soil-Effect Testing

To determine what effect the presence of a soil would have on the evaporation rate of the candidate pesticides, a special set of tests was run. The soil used was taken from the University of California South Coast Field Station near El Toro. This is the site where the Task III or field test work was done. Soil in that area is typical farm land soil fairly rich in adobe. The soil was ground and sieved, the 30 to 45 mesh cut being saved. This was then conditioned in the wind tunnel for 21 hours at an average temperature and R.H. of 72°F and 45 percent, respectively.

The test procedure consists of filming the pans in the usual way with the liquids, then sprinkling two to four hundred mg of soil evenly over the entire film. The tared pan is weighed both after the pesticide and the soil are added. In the case of the solids, the material is added to the tared pan which is then weighed. The soil is then introduced, the pan reweighed and then about 500 µl of the appropriate dispersion solvent is introduced. (See last paragraph of subsection 3.2.2).

TABLE 3-3. WEIGHT LOSS AT TWO WIND SPEEDS OF TEN PESTICIDES EXHIBITING LOW VOLATILITY

	Wind Speed			
	2.5 mph		5.5 mph	
Pesticide	Δt, hrs	% Wt. Loss	Δt, hrs	% Wt. Loss
Dacthal	22	0	5.5	0
Gavicide-90	140	0	5.5	0
Kelthane	20	3	5.5	0
Leffingwell 90	142	0	6	0
Leffingwell Unipar	138	0-4	5.75	0
Leffingwell Unicide	24	8	22.5	7
Methomyl	19	4	20	1
Orthol K Ready Mix	24	6	22.5	6
Toxaphene	118	4	44	4
Volk Supreme	138	0	46	0

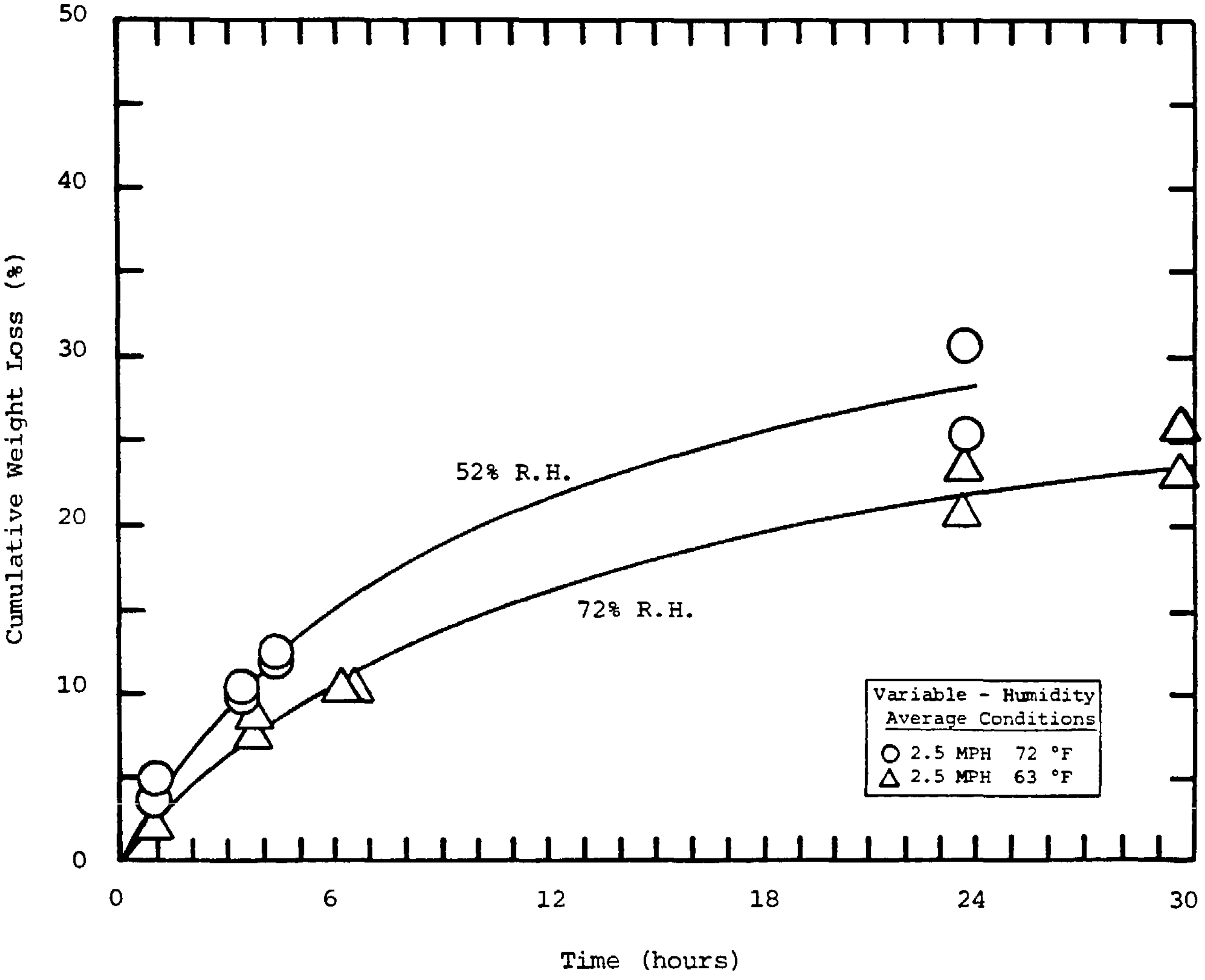


Figure 3-25. Pesticide Evaporation Rate Test: ARCO Weed Killer "A" Lite - Relative Humidity Varied.

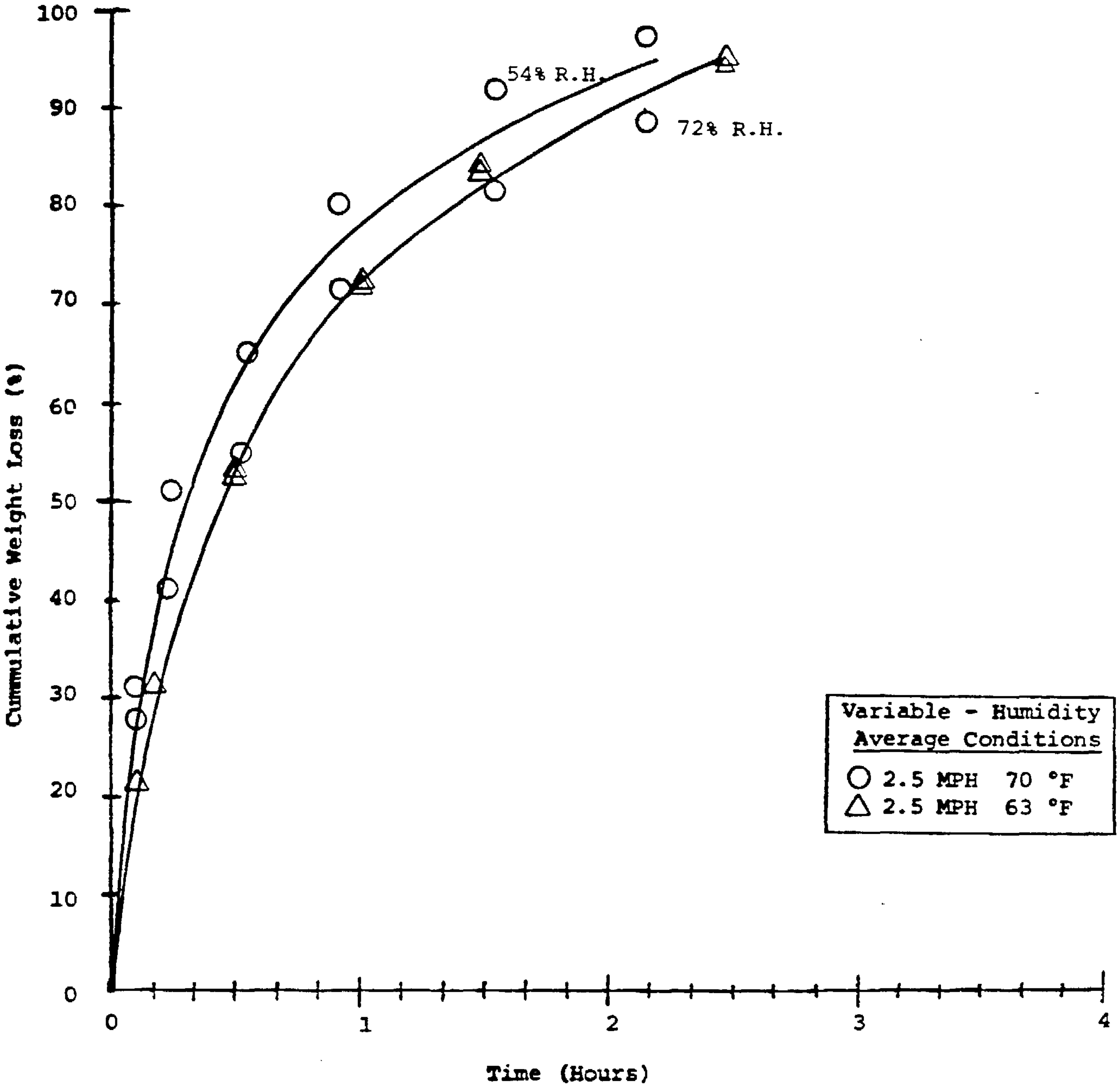


Figure 3-26. Pesticide Evaporation Rate Test: Beacon Weed Killer #5 - Relative Humidity Varied.

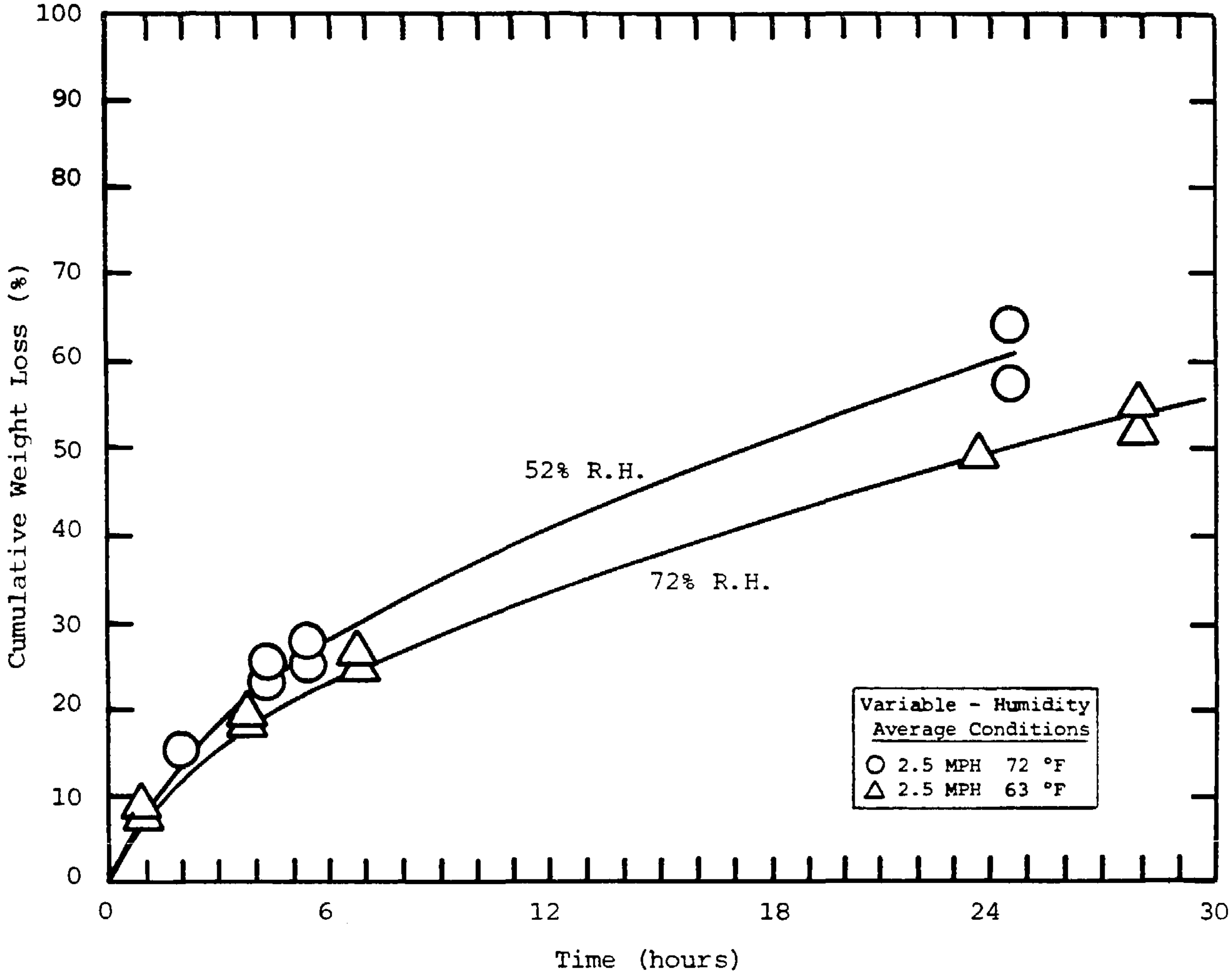


Figure 3-27. Pesticide Evaporation Rate Test: Chevron Weed Oil - Relative Humidity Varied.

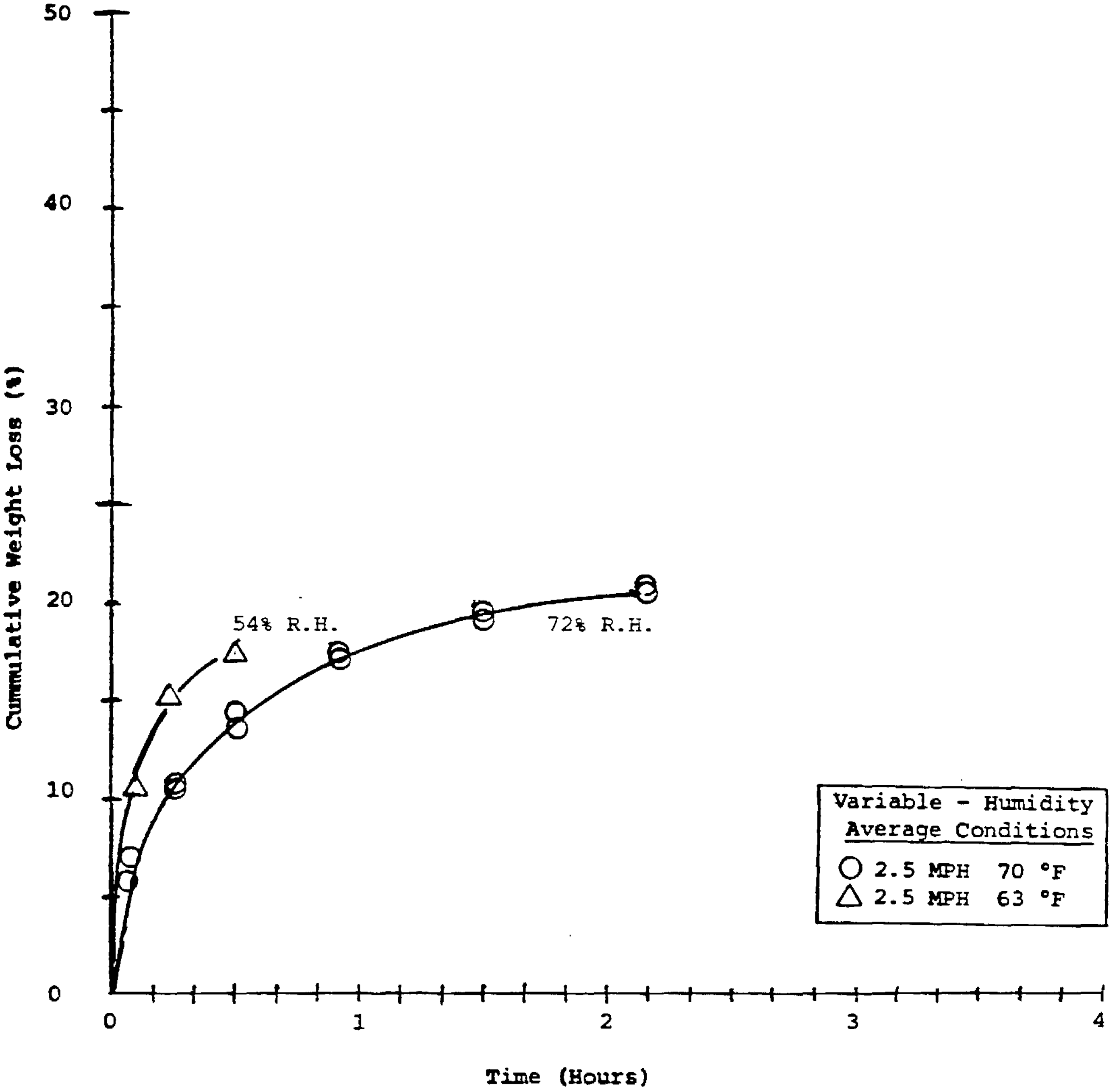


Figure 3-28. Pesticide Evaporation Rate Test: DEF 6 - Relative Humidity Varied.

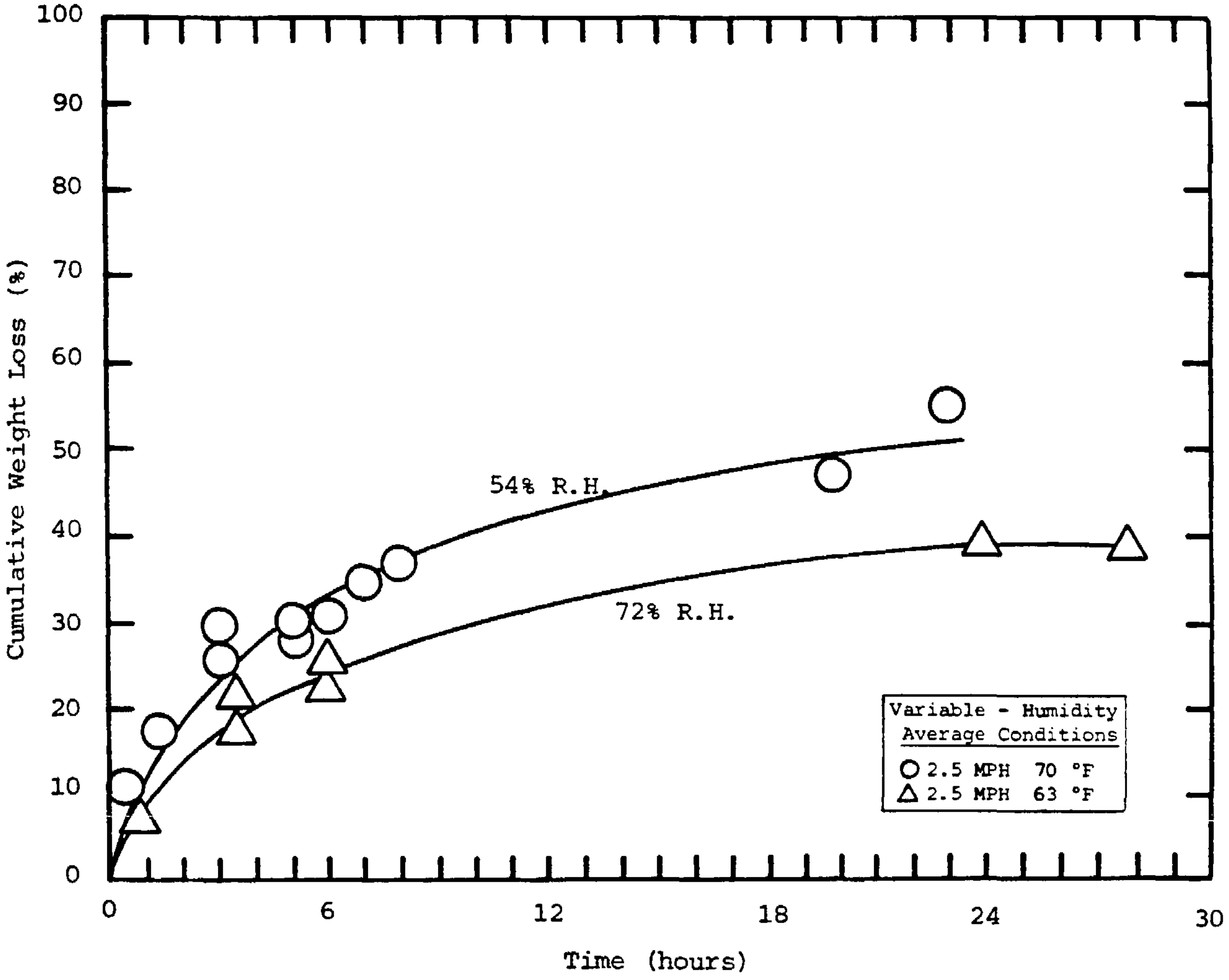


Figure 3-29. Pesticide Evaporation Rate Test: Union Diesel Oil #2 - Relative Humidity Varied.

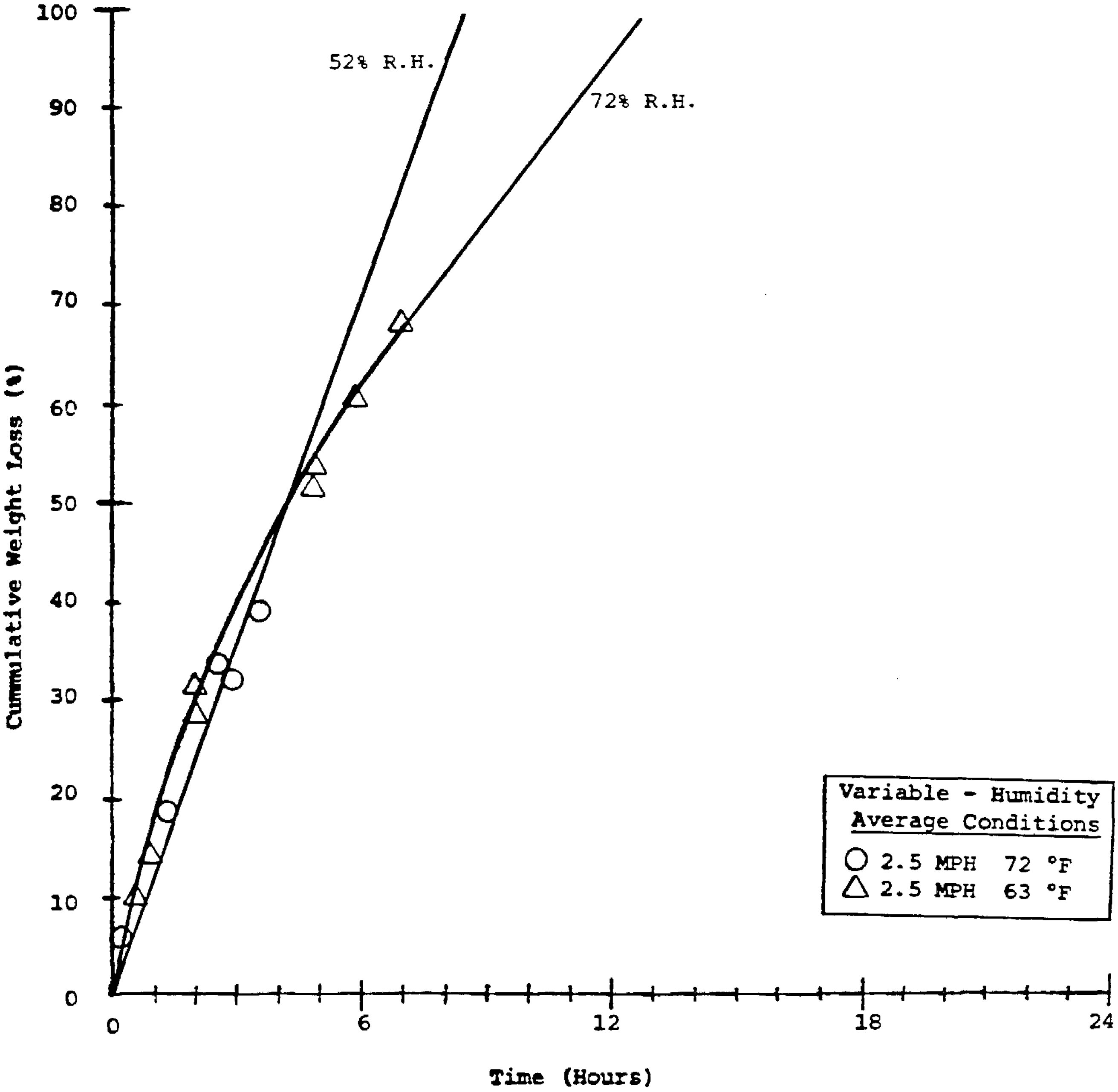


Figure 3-30. Pesticide Evaporation Rate Test: Dodecane - Relative Humidity Varied.

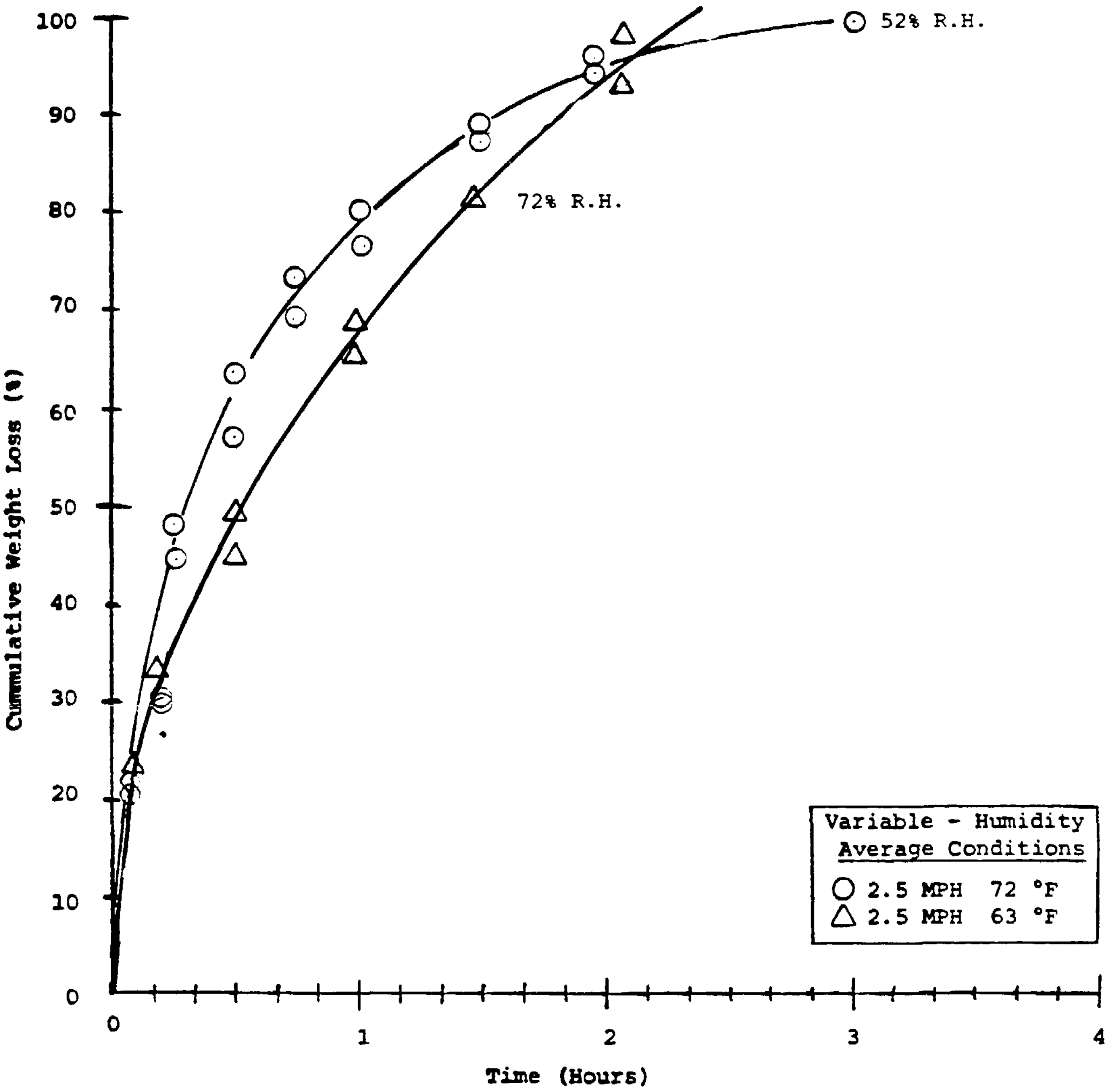


Figure 3-31. Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #20 - Relative Humidity Varied.

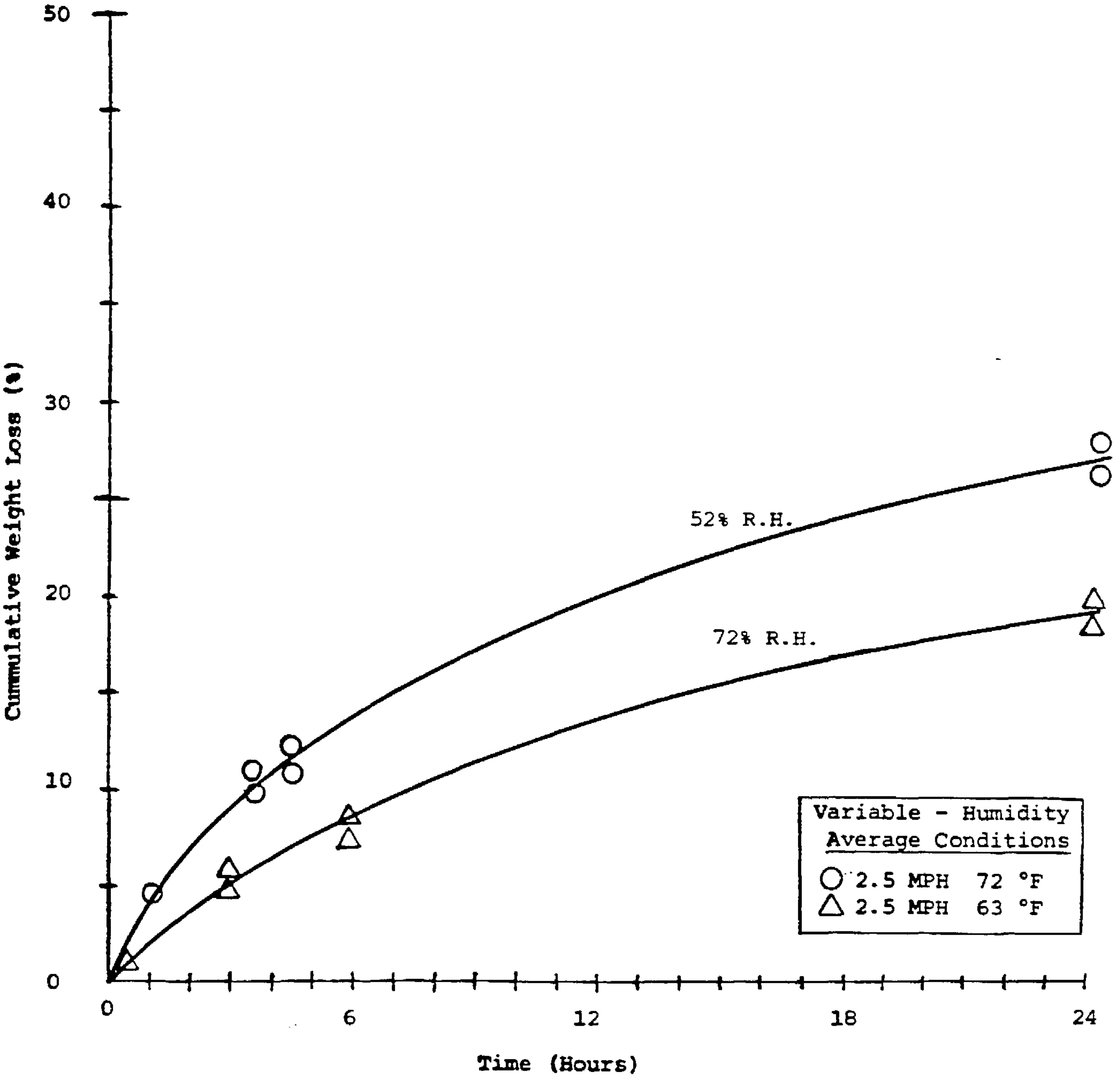


Figure 3-32. **Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #40 -** Relative Humidity Varied.

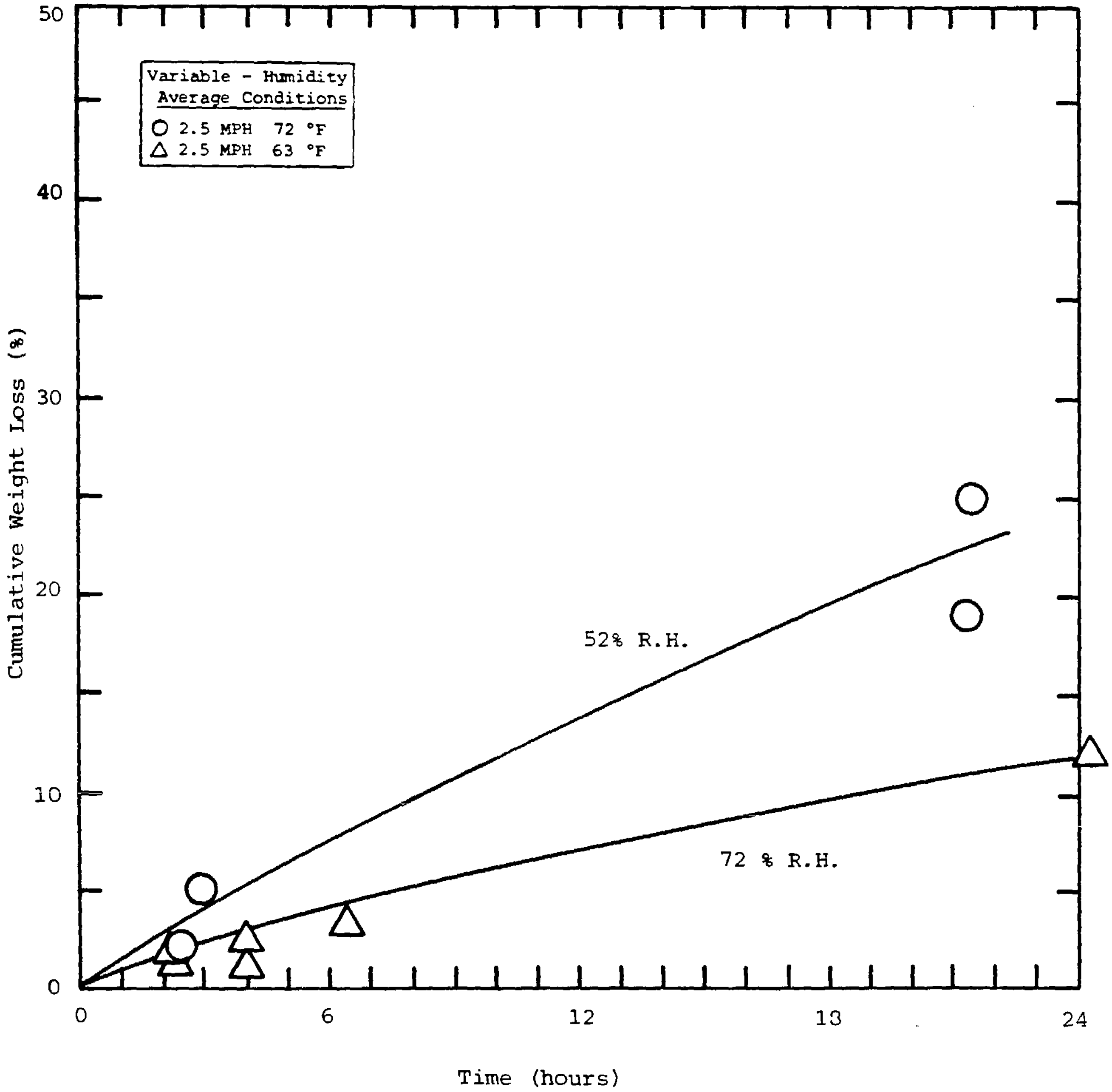


Figure 3-33. Pesticide Evaporation Rate Test: Molinate - Relative Humidity Varied.

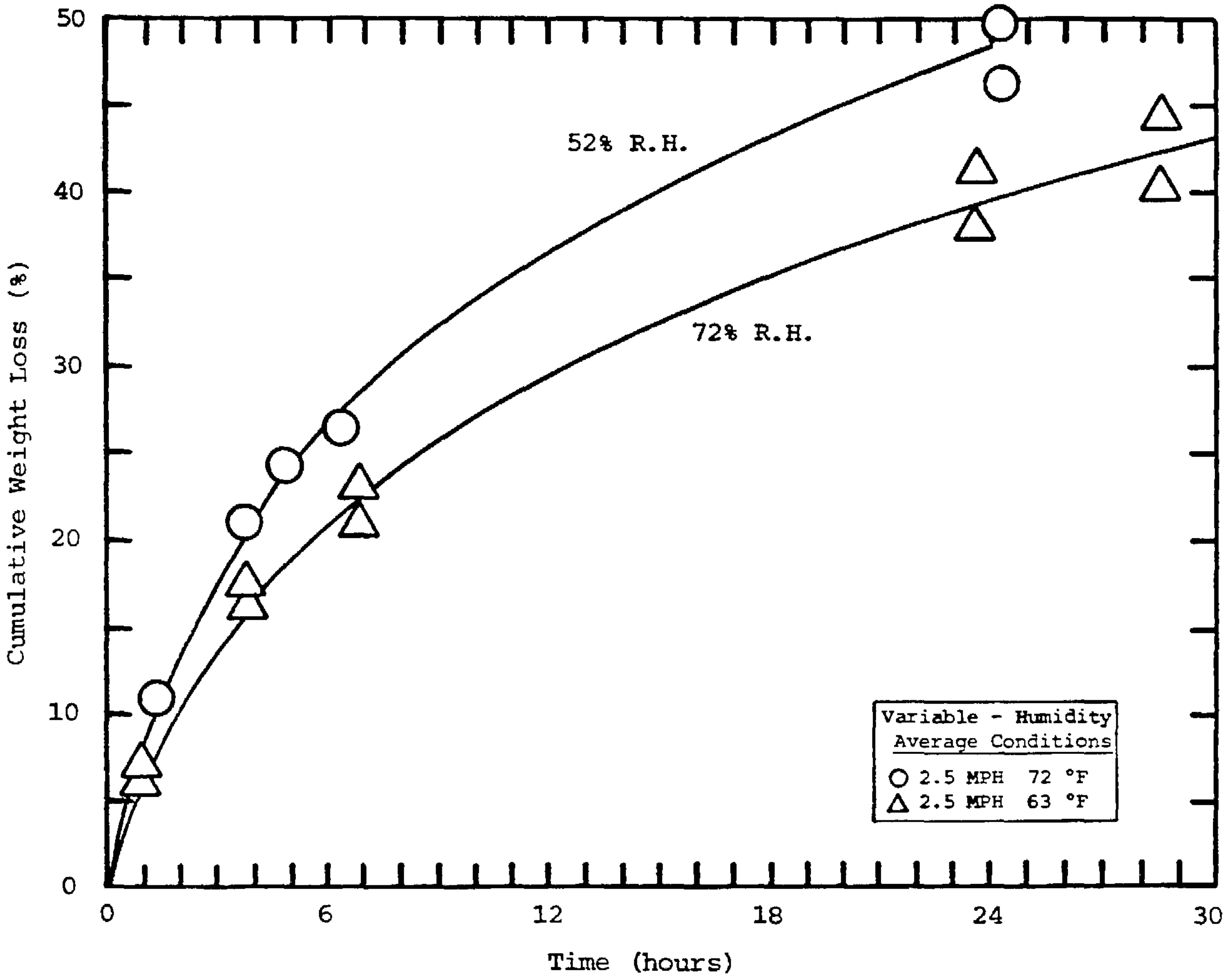


Figure 3-34. Pesticide Evaporation Rate Test: Moyer Weed Killer #20 - Relative Humidity Varied.

Because the amount of pesticide placed in the pan was intended to correspond with recommended farm-usage rates, the ratio of soil to pesticide weights varied. These ratios are shown on the evaporation curves that resulted (Figures 3-35 through 3-44).

The purpose of the tests was to determine if soil exerted a strong influence (e.g., chemisorptive adsorption) on retarding the evaporation rates of the test materials. The results clearly indicate that this is not the case. It would appear that any adsorptive process operating is more than offset (except in the inexplicable case of diesel oil) by the increase in surface area produced on wetting. This of course applies only to a superficial zone and does not consider the possible effect of a capillary soil sink of infinite depth.

The average conditions for the soil conditioning (72°F; 45% R.H.), and the two tests shown in Figure 3-35 (soil present-75°F; 39% R.H., soil absent-72°F; 52% R.H.) were not perfectly matched. The soil blank, however, showed less than a 1 percent weight loss in the "soil present" test and the 3°F difference in average temperature for the two runs would hardly account for the fourfold increase in evaporation rate of dodecane. It is thus safe to conclude from these results that, in context of the test configuration, the presence of soil did not inhibit the evaporation process.

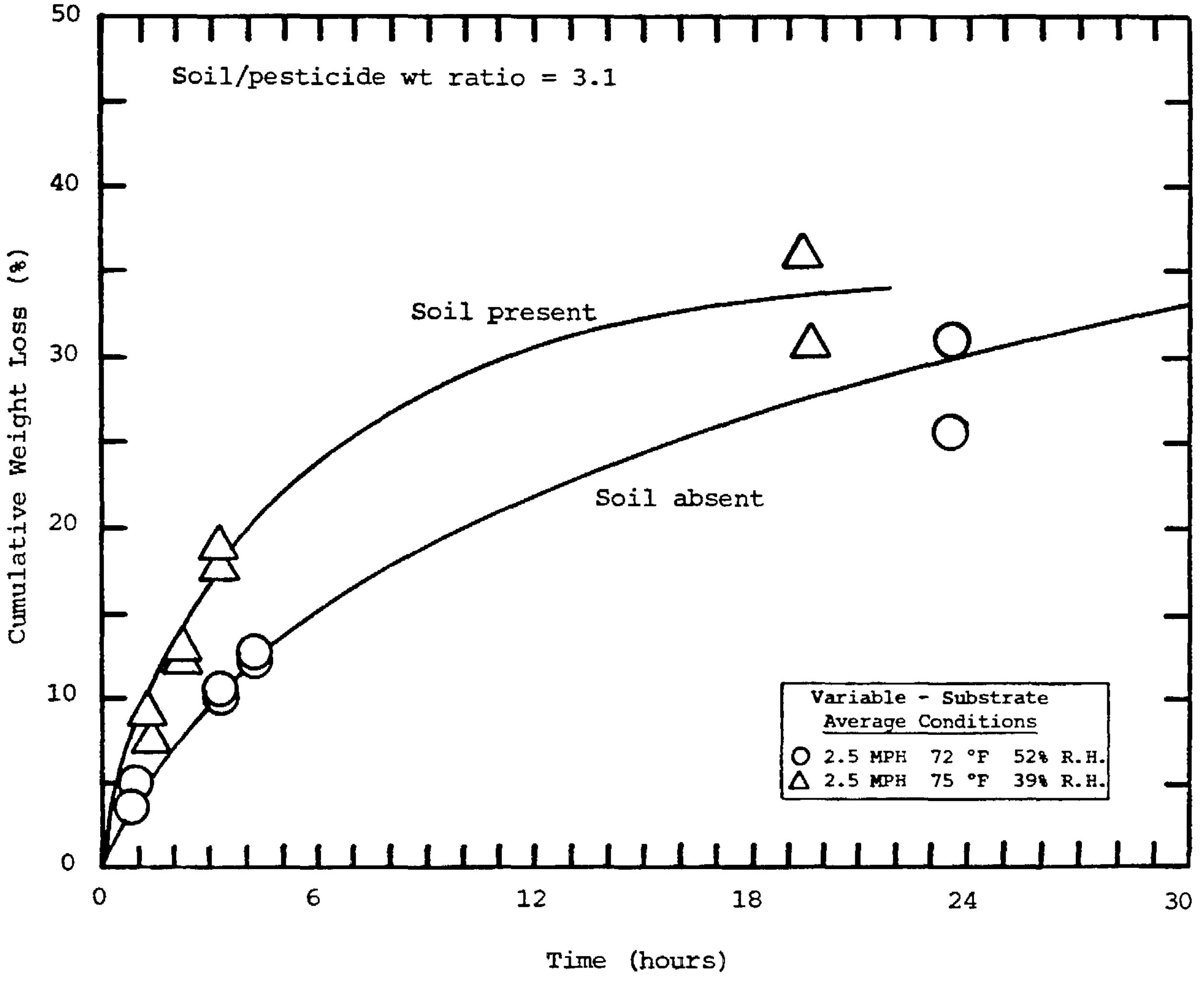


Figure 3-35. Pesticide Evaporation Rate Test: ARCO Weed Killer "A" Lite - Soil Effect.

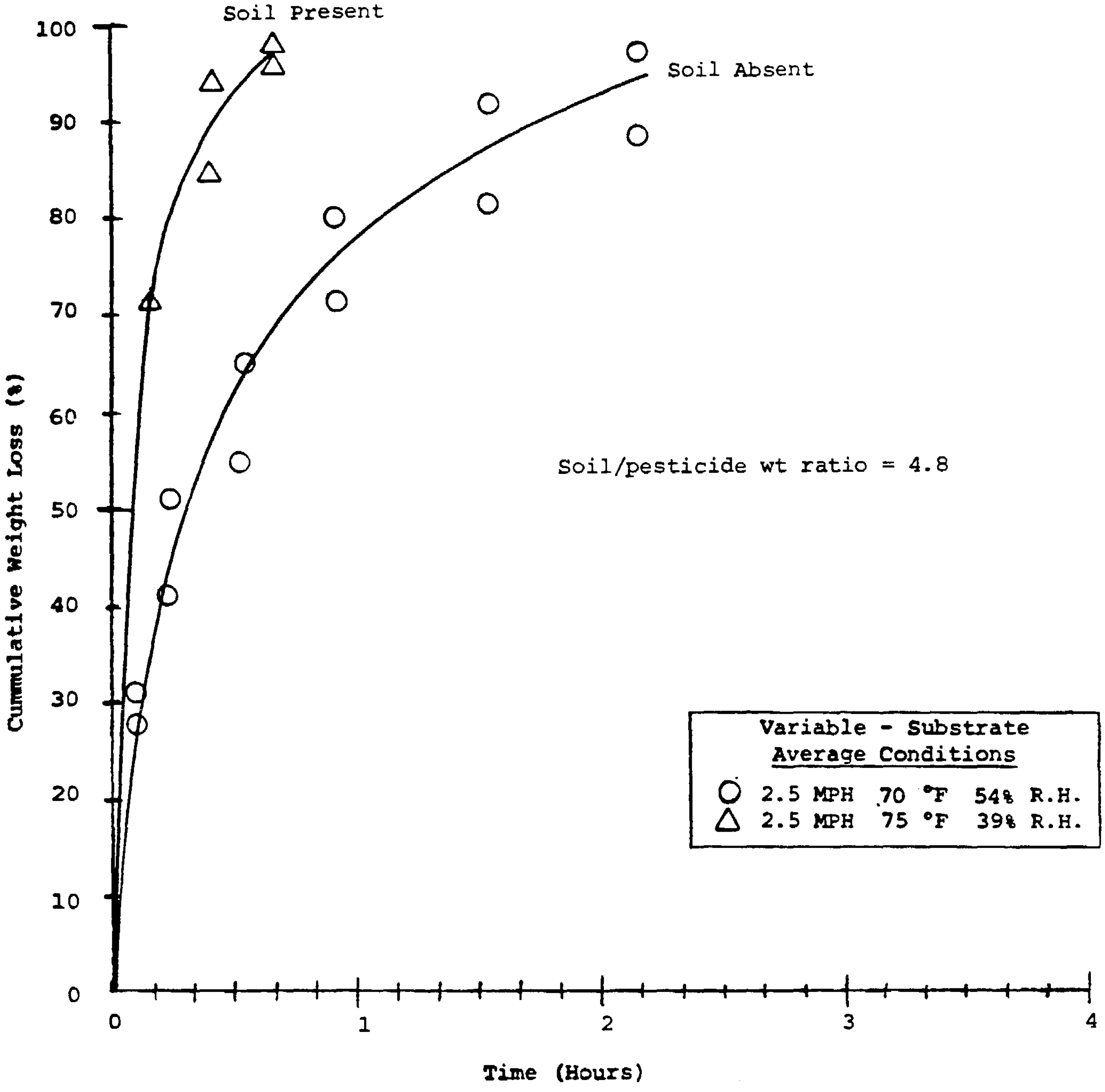


Figure 3-36. Pesticide Evaporation Rate Test: Beacon Weed Killer #5 - Soil Effect.

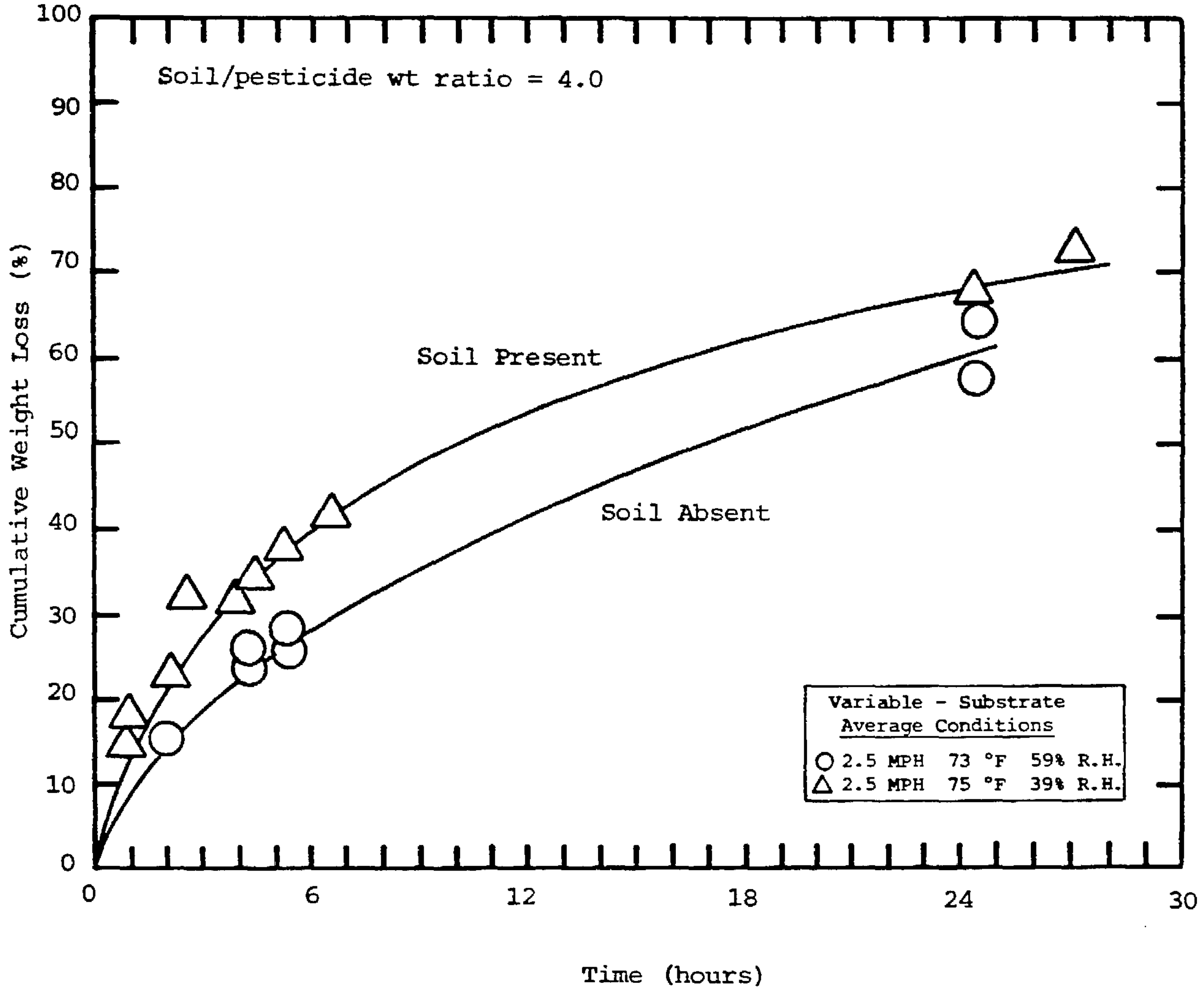


Figure 3-37. Pesticide Evaporation Rate Test: Chevron Weed Oil - Soil Effect.

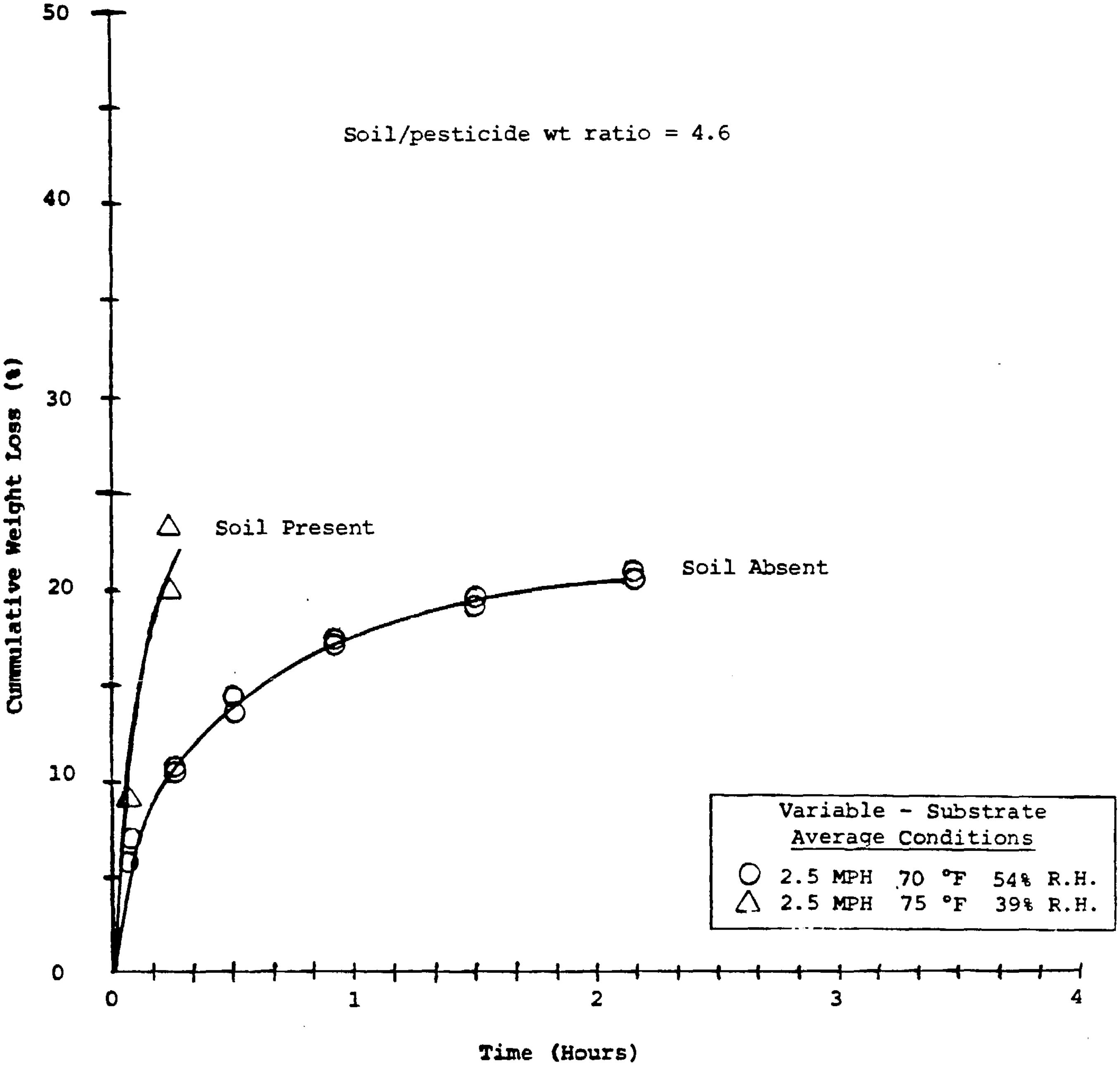


Figure 3-38. Pesticide Evaporation Rate Test: DEF 6 - Soil Effect.

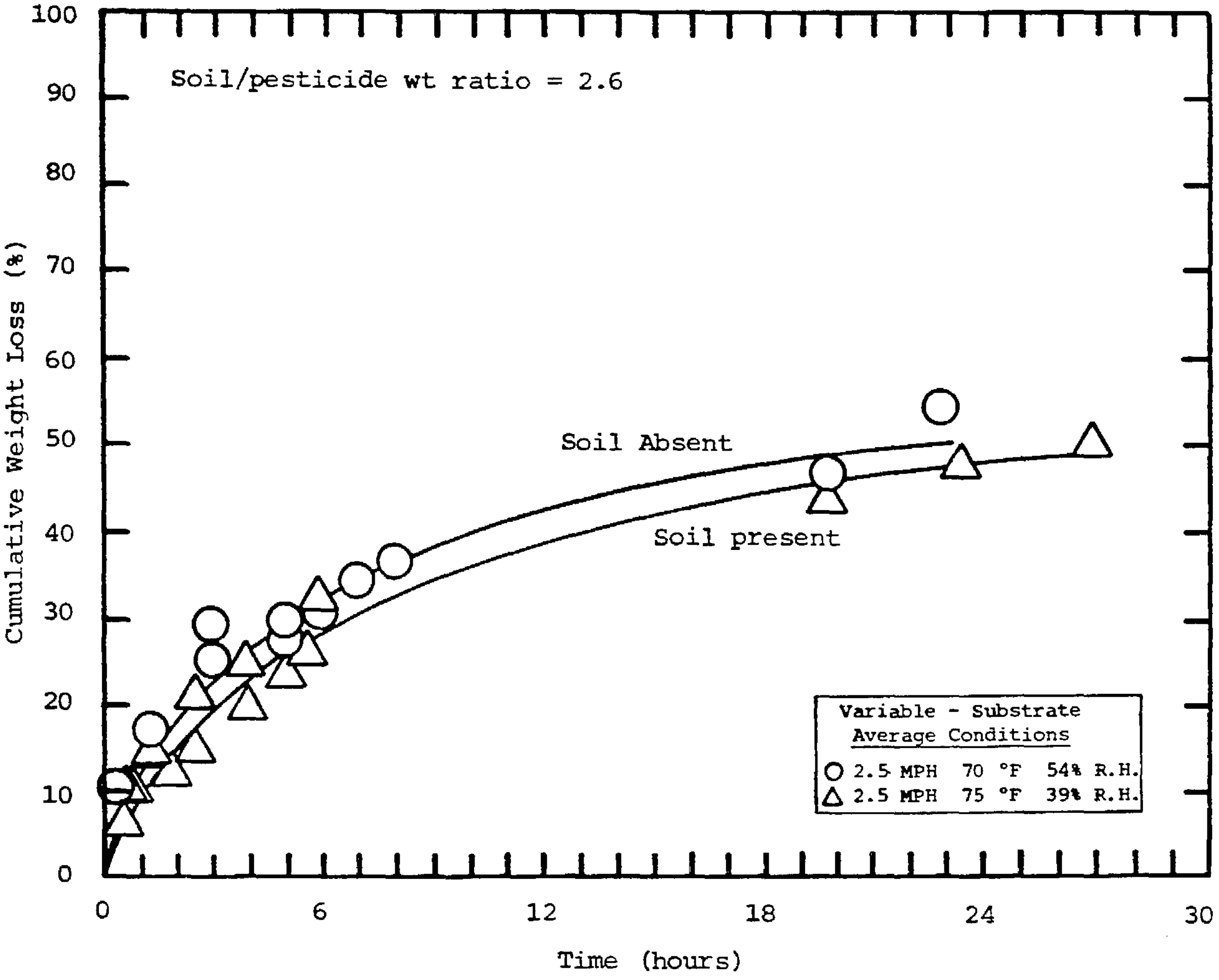


Figure 3-39. Pesticide Evaporation Rate Test: Union Diesel Oil #2 - Soil Effect.

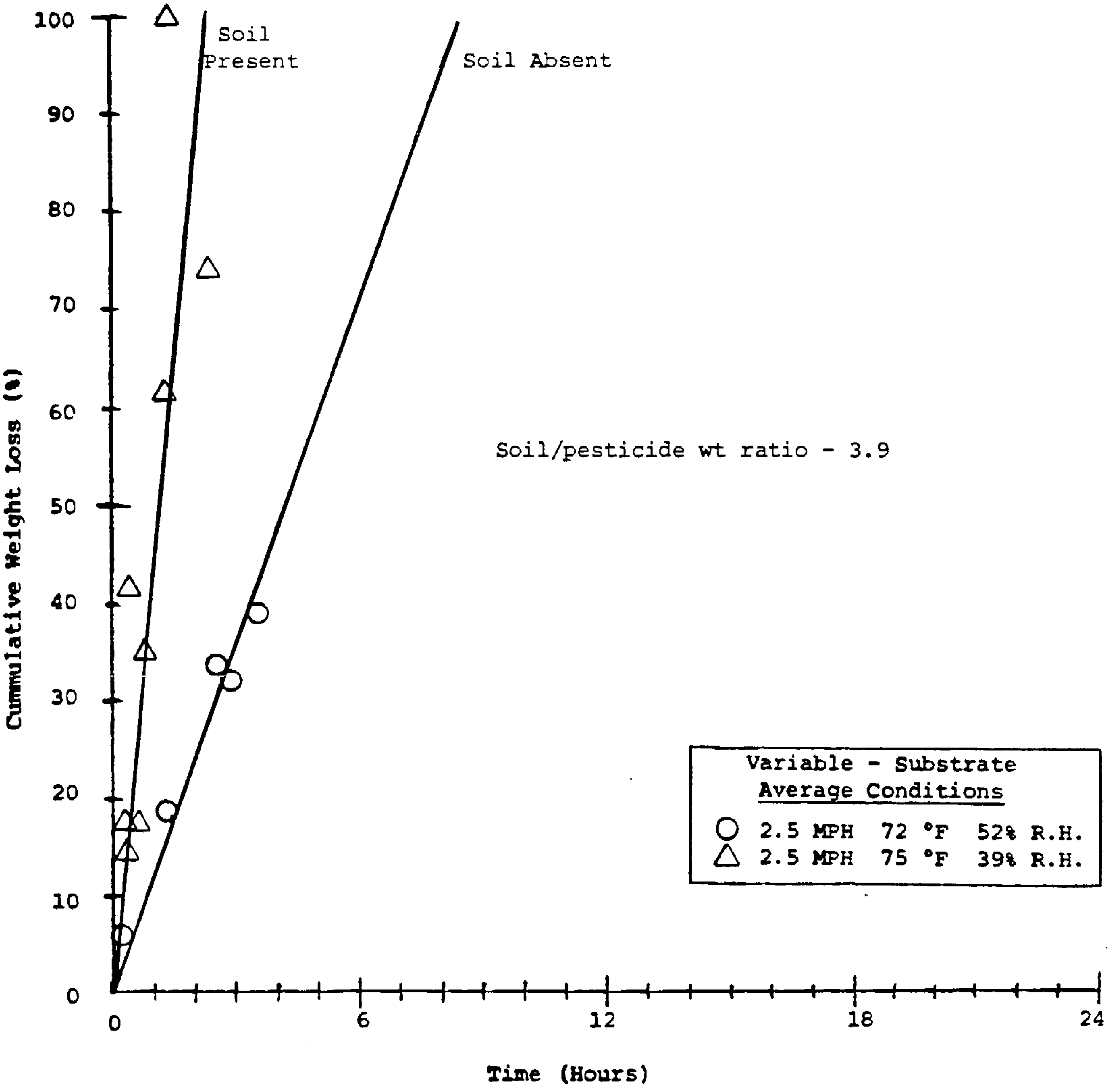


Figure 3-40. Pesticide Evaporation Rate Test: Dodecane - Soil Effect.

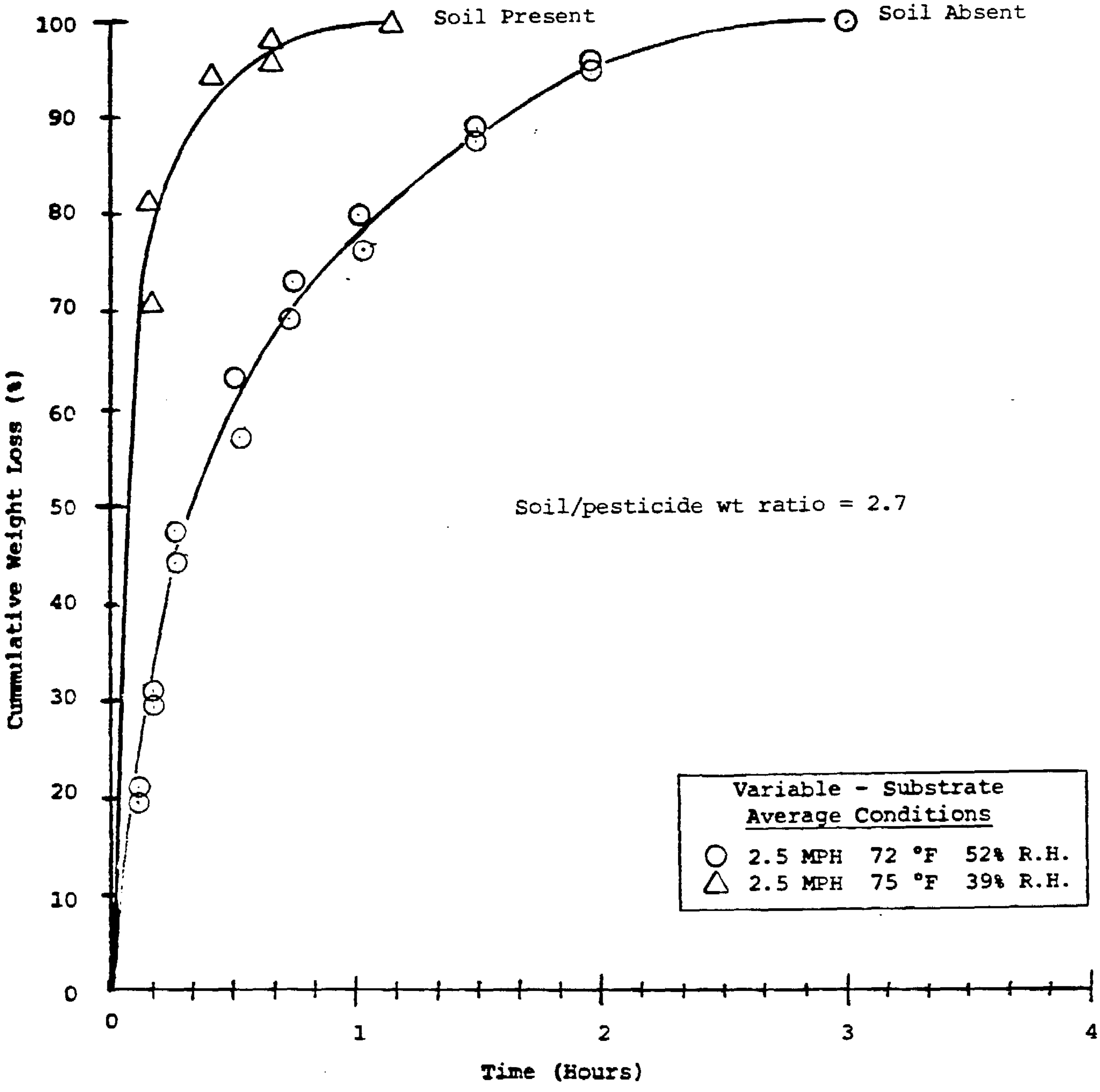


Figure 3-41. Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #20 - Soil Effect.

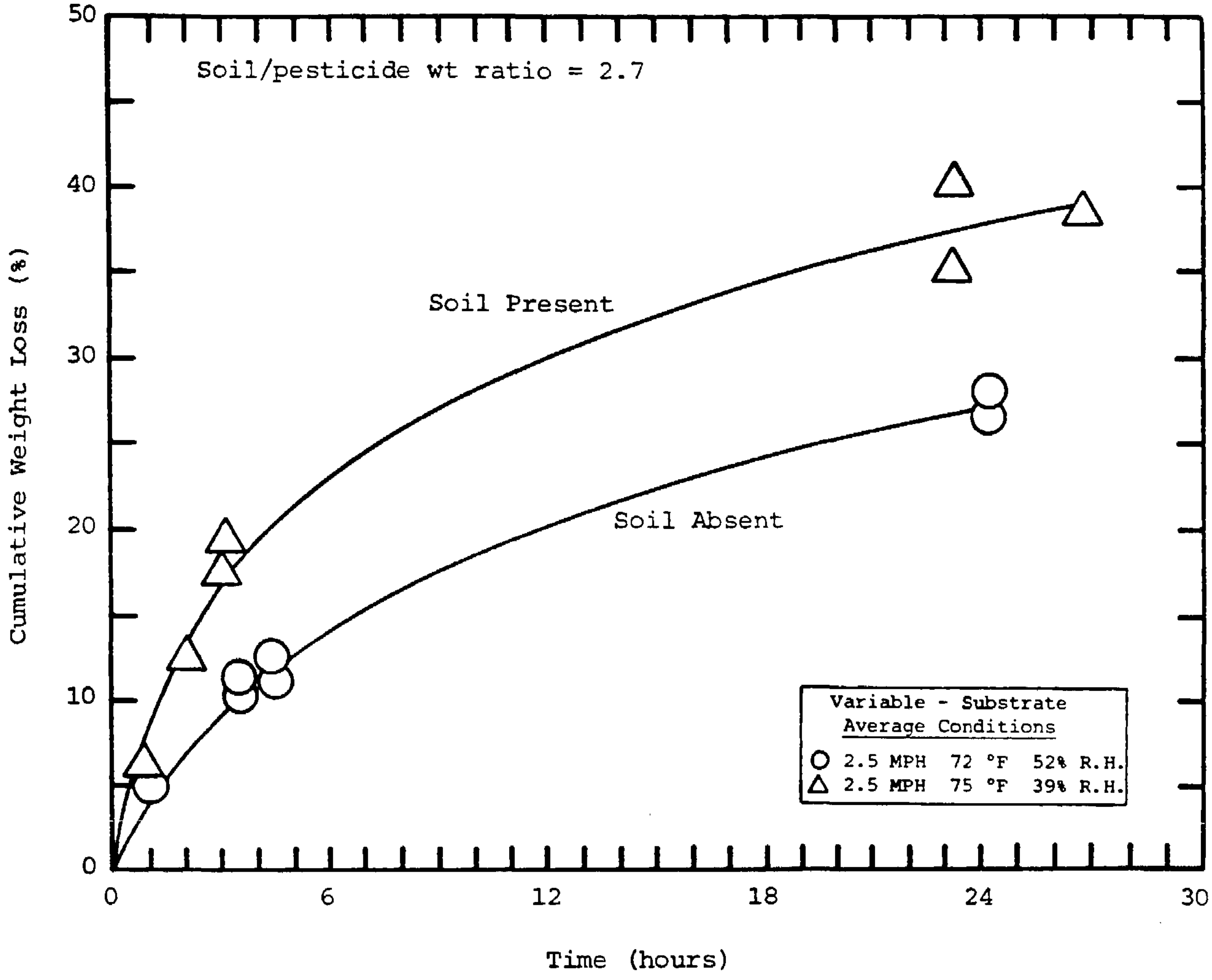


Figure 3-42. Pesticide Evaporation Rate Test: Keen-Kil Weed Oil #40 - Soil Effect.

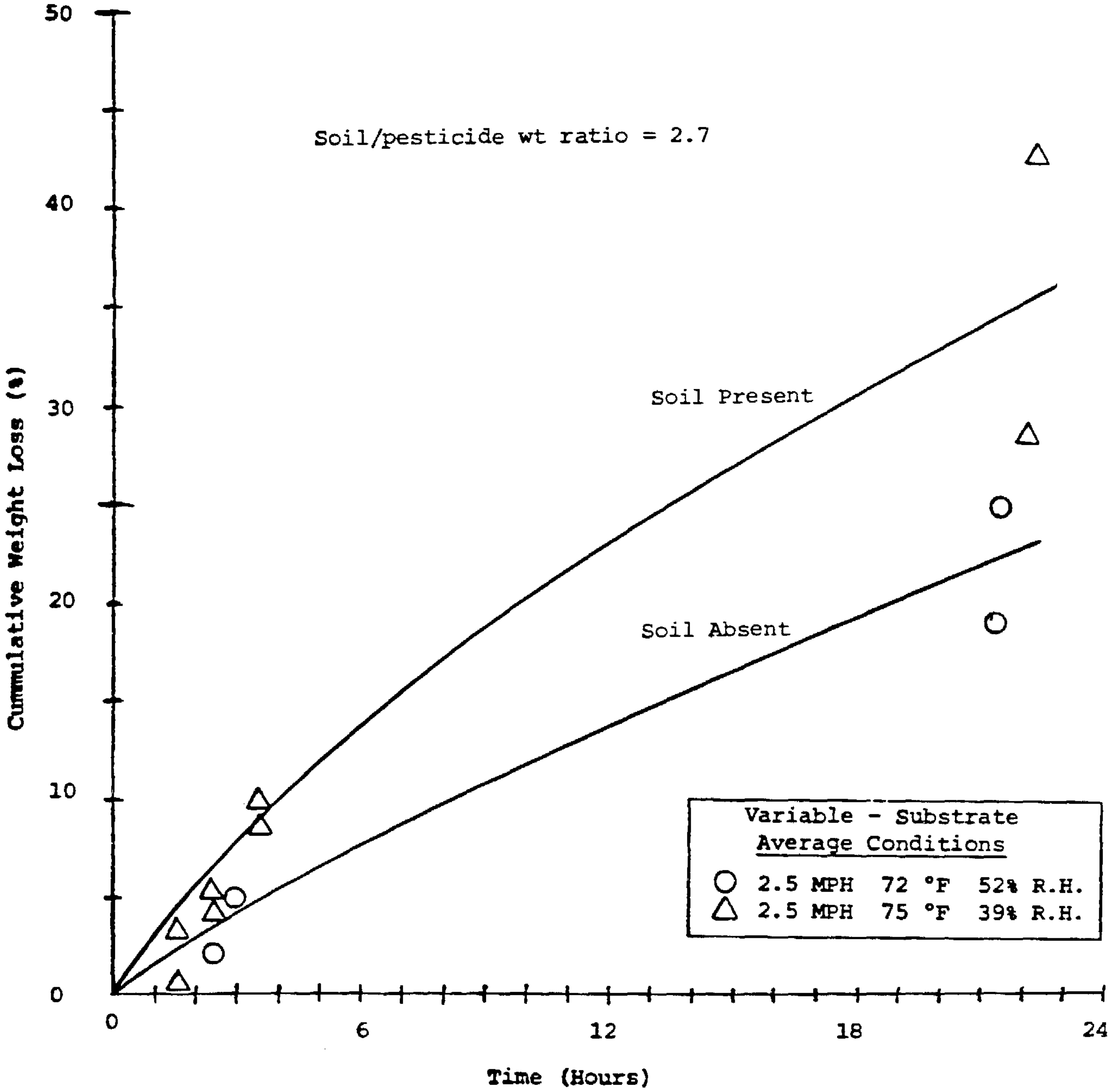


Figure 3-43. Pesticide Evaporation Rate Test: Molinate - Soil Effect.

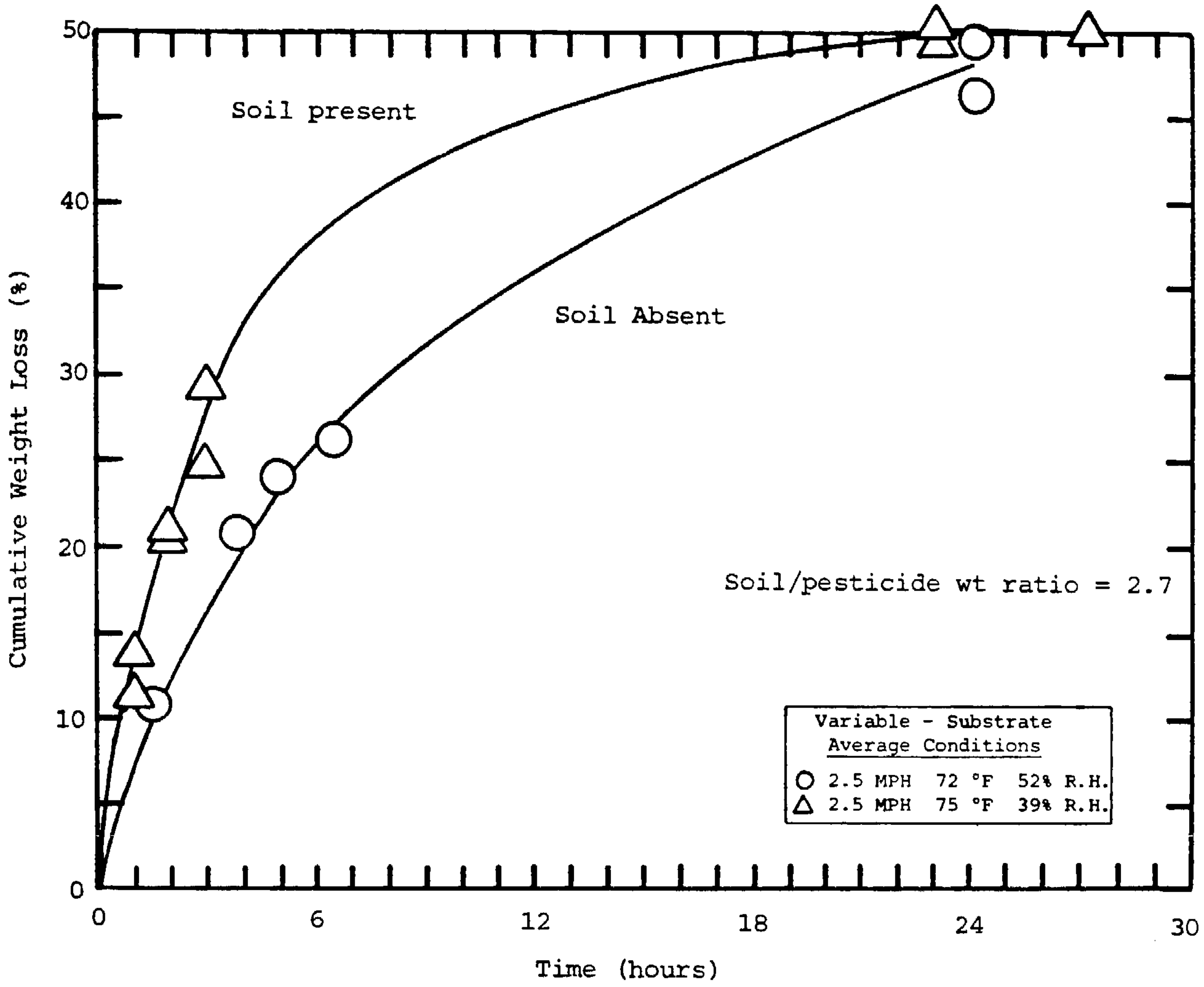


Figure 3-44. Pesticide Evaporation Rate Test: Moyer Weed Killer #20 - Soil Effect.

SECTION 4.0

TASK III - FIELD EMISSION MEASUREMENTS AND EVALUATION OF CONTROL OPTIONS

4.1 FIELD EMISSION MEASUREMENTS

The results demonstrated that the test configuration employed was not sufficiently sensitive to adequately characterize the volatilization of pesticides under field conditions. With the test arrangement employed the hydrocarbon concentrations of most pesticides evaporated in the field chamber could not be successfully monitored given the high prevailing background hydrocarbon concentrations and the limited sensitivity of the continuous total hydrocarbon analyzer. The test results are inconclusive and should not be used for developing pesticide emission factors until the results are confirmed by more sensitive testing.

In order to emphasize the inconclusive nature of the test results, details of the experiment and the results are contained in Appendix A.

The Air Resources Board intends to engage the University of California at Davis (USD) to conduct experiments to measure emissions from essentially the same pesticides as studied in this program but to use GC/MS techniques to attempt to make the measurements more accurate and sensitive. These UCD experiments should confirm or deny the results obtained here. Only if confirmed by UCD or others, should the results presented here be used for emission factors.

4.2 EVALUATION OF CONTROL OPTIONS

Effecting some kind of control over emissions from carrot oil or any non-synthetic oil, if it is found to be an air pollution source, can take several forms. An obvious one is to apply pesticide only at reduced temperatures. This is already mandated by regulation. It is not clear, however, whether this actually reduces emissions or merely prolongs the process.

Another obvious approach is to substitute a pesticide that does not emit much organic vapor. Synthetic pesticides generally have much lower vapor pressures than non-synthetics and are usually far more potent. Thus the small amount of organic solvent carrying the synthetic should not prove as problematic even if more volatile than what it replaces. An example is the DEF-6 used on the present program. This was applied at a rate of four pints/acre. If all the xylenes in the solvent evaporated, the release would only amount to about 0.8 lb/acre.

DEF-6 is, of course, no substitute for carrot oil. It is not, in fact, within the purvue of the present program to make specific recommendations as to what might constitute suitable substitutes for pesticides that have been or may be proved to be problems as area source emitters. Such questions of any called-for pesticide substitutions clearly lie with the crop specialists.

Another aspect to the matter of emission control is drift control and spray optimization. It would appear from the present field studies that soil contact retards the emissions of hydrocarbons from applied pesticides. This effect would not be available to the drifted pesticide aerosol. Until it settles, it would evaporate at a much faster rate. Thus, minimization of drift is a desirable goal both from an air pollution reduction standpoint as well as economy (pesticide loss and pesticide damage to continguous life forms.)

Maybank and Yoshida (Ref. 5) have organized the techniques for reducing drift into four categories. The first group involves consideration of factors that increase drift distance. These include the reduction of the nozzle height over the target, and avoiding windy or turbulent conditions. These are common sense requirements that most applicators observe. The second category are procedures for lowering evaporation. This is achieved through the use of low volatility carriers (of synthetic pesticides) and the addition of evaporation suppressants to aqueous emulsions. The effectiveness of adjuvants is discussed in Section 5.0.

The third category of drift minimizing techniques goes to methods that will reduce the amount of small droplets produced by the sprayer. This includes nozzle design, changing the physical properties of the emulsion, using invert emulsions and so on. This area is also addressed in Section 5.0.

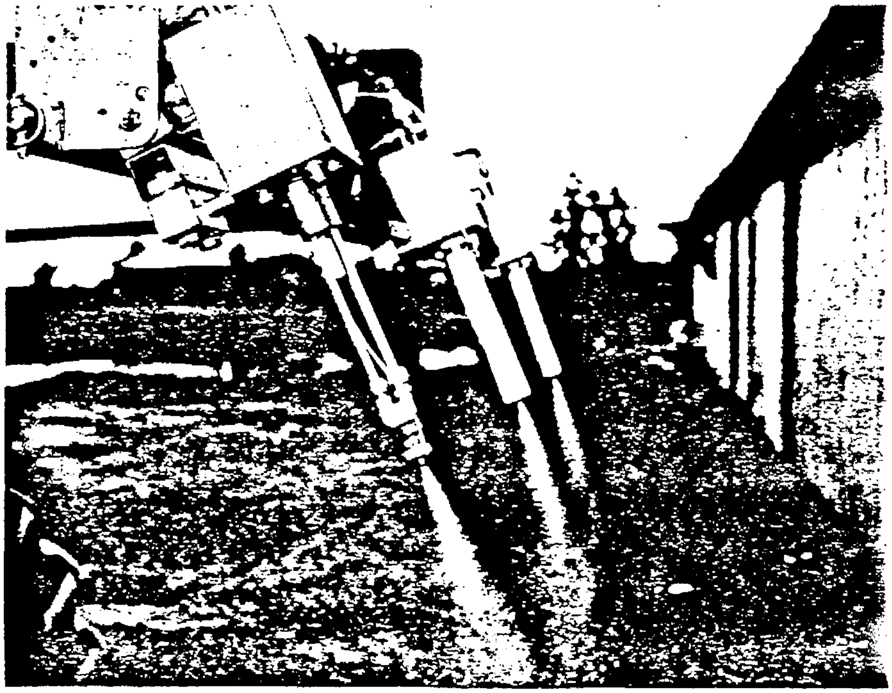
The last group of procedures defined by Maybank and Yoshida involve sprayer configuration in which small droplets are not prevented from forming but are prevented from leaving. This includes the incorporation of cowling devices, installing aspirators around the nozzles, or by promoting coalescence through aerodynamic design. These factors are expressed in a number of sprayer systems already commercially offered.

Of particular interest in the minimization of drift and the reduction of overspray is the electrostatic sprayer. This potential device was developed by Dr. Edward Law of the University of Georgia and is now being studied for possible incorporation into a commercial configuration by FMC.

The use of the Law spray system realizes an almost 100 percent vegetation contact with little material being lost to the ground or into drift. Moreover, the aerosol, which is of a finer size than standard nozzles produce, reaches under the plant canopy to areas most likely to be insect infested. Figure 4-1 is a photograph of the hybrid electrostatic nozzle apparatus. Figure 4-2 diagrams the principle of operation of the system.

Electrostatic spray equipment has been used by industry for quite some time. Most home appliances are painted by that process. In this type of aerosol application, the spray (and often the equipment lines and containers) are charged to as high as 100,000 V. As the charged particles travel toward the grounded target piece, they are uniformly attracted to the entire surface. The result is a very even coating of flat areas.

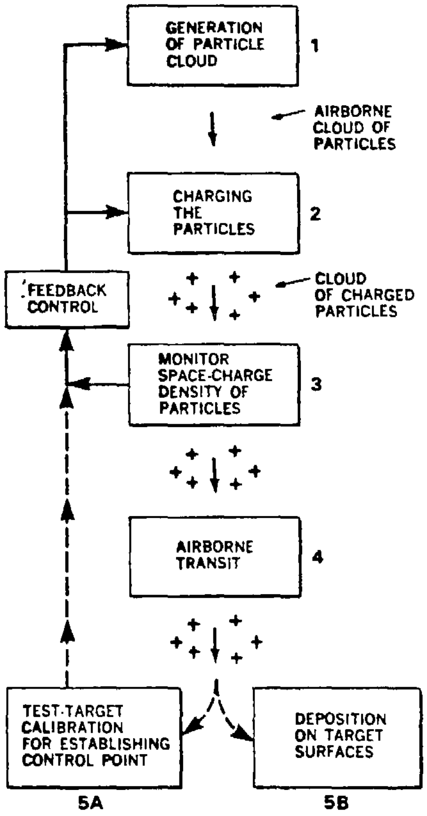
The Law spray nozzle is based on electrostatic-inductive charging rather than the industrial ionized-field method just described. This followed from the finding that the ionized-field method works poorly out-of-doors, and in fact, pointed leaves discharge the spray cloud like lightning arresters. The Law invention does not require that the particles come in contact with an electrode to be charged. Instead, charge is inductively acquired from a



Hybrid sprayer nozzles are mounted on tractor boom at test farm. Individual power supplies for each electrostatic nozzle are located in box at base. High-voltage lead can be seen on unshielded nozzle in foreground.

Figure 4-1. Hybrid electrostatic nozzle apparatus.

How the system works



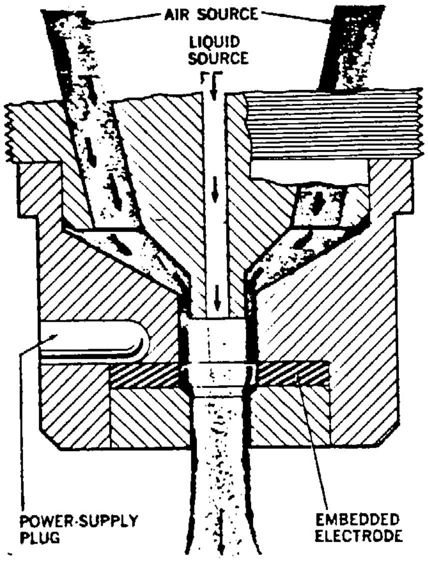
Cloud particles are generated by nozzle (1) and charged as they leave orifice (2). Monitoring electrode built into nozzle will continuously measure space-charge density of the cloud (3) and send correction data back to the power supply. Air pressure (4) carries particles toward test probe (5A) inserted in the earth by the operator. Spraying at different intensities will establish control point to indicate that a maximum amount of spray is reaching the target (5B). Once established, the correct setting will be maintained over varying conditions in the field by the monitoring electrode.

Figure 4-2. Principle of operation of the Law electrostatic spray nozzle.

washer-like electrode embedded in a dielectric epoxy nozzle-orifice cap (see Figure 4-3.) By combining a commercially available nozzle for mixing air and liquid with the Law orifice cap, two other aspects of spray optimization result: particle sizing and effective air delivery to the nozzle.

Testing of the hybrid spray nozzle demonstrated that the most effective spray applications resulted when comparatively low volatages (1 to 2 kv) were employed. Because power consumption is actually quite low, fairly compact power supplies can be used.

A requirement of the present program has been to estimate costs for evaluating alternative strategies of pesticide application that would reduce emissions. It is uncertain that the Law device will do that since its optimal use would be with row crops using foliar sprays. This would dictate the preferred use of synthetic pesticides. Whatever pesticide is applied, however, the Law device would certainly reduce pesticide usage. Conventional nozzle overspray can range up to 40 percent. Thus, if subtle hydrocarbon emissons are associated with any pesticide application, significant reduction would likely accrue if the amount of pesticide employed is reduced. This cannot be guaranteed, however, since some forms of foliage may exhibit little ability to inhibit, through absorption, pesticide evaporation. On soil, however, even if wasted there, the pesticide is retained. The only way to resolve the matter is through actual testing. Appendix C presents an abbreviated test plan for evaluating the Law device (against conventional nozzles) in the field test chamber using a sampling configuration offering greatly enhanced sensitivity.



Air is forced into nozzle at about 40 psi and flows in around liquid source. Electrode to charge particles is separated from the liquid by about 0.050 inch. Air forms boundary layer between liquid and channel wall of nozzle, keeping electrode region dry.

Figure 4-3. Cross-section of Law electrostatic spray nozzle.

SECTION 5.0

TASK IV - ESTIMATION OF EVAPORATION OF DRIFTED PESTICIDES

5.1 OBJECTIVES

The intent of this task is to estimate the amount of hydrocarbon volatilized after the pesticide mixture is discharged from the application equipment but prior to reaching the receptor surface. This should include a comparison of the range of efficiencies of various application equipment and effects of adjuvants. The undertaking was to rely on published data and involve no laboratory verification.

5.2 APPROACH TO THE QUESTION

The loss of volatile material from the spray process between the nozzle and the receptor involves two aggregates of liquid. The first is the sprayed material that hits target and is retained and that which fails of the immediate receptor, drifting downwind as aerosol. Travel time in the latter plume is figured in minutes, while that of the straight-line contact process is figured in milliseconds. Moreover, the particle size of the drifted material must be smaller in order for it to be lost. Thus, airborne time and surface area both point to the drift as undergoing evaporative loss before fallout. Consideration of the question was therefore limited to drifted pesticide.

Because the extent of drift loss is dependent on many factors, assumptions are necessary in order to establish a scenario that can be examined mathematically. For this purpose, the work of Yates and his U. C. Davis coworkers, N. B. Akesson, R. E. Cowden, and D. Bayer, was reviewed. Yates not only experimentally studied the drift effects in the field but showed the influence exerted by the platform used (aircraft, helicopter, or tractor) and the use of adjuvants and different nozzle configurations. This work will be specifically referenced as this exercise is developed. A ground application scenario will be used since it conforms with the scope of the present work.

Given, then, a drift process of a definite magnitude and particle size distribution, evaporation rates are estimated using data acquired in Task II of this program. The results are then treated from the perspective emissions reduction possibilities as quantified by Yates.

5.3 ESTIMATED EVAPORATIVE LOSSES OCCURRING IN DRIFTED PESTICIDE AEROSOL

The amount of pesticide that impacts the intended receptor is influenced by a number of factors. These include application rate, the viscoelastic properties of the pesticide mixture, the type of dispersion produced by the application device, the height of the boom or nozzle array, wind speed, and other atmospheric conditions. Of these, particle size distribution, wind speed, and atmospheric stability are generally the most important parameters in terms of drift (Ref. 6). According to Furmidge (Ref. 7), a droplet size less than 100 µm approaches the ideal when applying pesticides in a range centering on 8 gals/acre. He also shows, however, that drift travel distance increases exponentially as the volume mean diameter of the droplets fall below 200 µm and approach 20 to 30 µm. Akesson and Yates (Ref. 8) have determined, for example, that a 400 µm spray drop traveling downward 10 ft. in a 3 mph wind would drift only 8.5 ft. before precipitating while aerosols 100 µm, 10 µm, and 2 µm would drift as far as 48, 4500, and 110,000 feet, respectively.

In studies of the application of the weed killer, Glyphosate, the same authors, with Bayer, reported (Ref. 9) measured both fall-out rates and air concentration of the drifted aerosolized aqueous pesticide solution applied. In a ground application (6 mph, 3 ft. nozzle height) on a flat dry field in short dry grass, 4.5 lbs/acre were used in a 8.5 mph wind. Fall out (collected on mylar sheets) was measured on the wind from 25m out to 1000 m from the sprayed area, the swath running perpendicular to the wind direction. An extrapolation of the U. C. Davis authors' data roughly suggests a drift deposit of 0.1 lb/acre (at 15 feet - an arbitrary boundary limit) to negligible at 6 miles.

They found that the regression curves calculated for their fallout data followed the general form:

$$\text{Log } R = b_o + b_1, (\log d) + b_2 (\log d)^2$$

Where R is the fallout concentration per unit area, d is the distance downwind, and b_o, b_1, and b_2 are regression coefficients. The same relationship was observed for the airborne concentrations.

Using the extrapolation of the curve mentioned above, and starting at 15 ft. from the swath, an integration of the fallout was made out to 328 ft. (100 m). Levels beyond that were quite small and can be ignored. It was found that 0.33 percent of the applied material had drifted and precipitated (0.0121 lbs in the area out to 328 ft. vs. 3.75/acre applied). The fallout would be much larger if the 15 ft. next to the swath were included, but it was not measured by the U.C. Davis workers and the extrapolation already used here would doubtless become even more imprecise if extended up to the edge of the swath.

The air borne concentration of pesticide was found to be much higher (expressed as lbs/acre), some 60 times at 328 ft. where the first hi vol sampler was located. The level was equivalent to 0.0223 lb/acre if precipitated, which is almost twice that which had precipitated to that point from 15 ft. of the target swath. It is this airborne material that is of interest in the present context. What had fallen out up to 328 ft. not only represented a smaller fraction of the total but the precipitation time (about 26 sec at the given wind speed) was rapid enough to entail probably only minor evaporation of a petroleum-type pesticide. The same data of Yates and coworkers also showed convergence in the sampled pesticide air concentration, suggesting negligeable fallout beyond 0.62 mile (1 km).

Given the above findings, a scenario was therefore attempted. It should be recalled that the purpose of this is not to speculate on what typically evaporates from drift during any given field application. The objective is to construct a plausible case, then demonstrate what emission-reductions might be realized using the U. C. Davis data involving adjuvant and nozzle variables.

Let us assume an aromatic weed oil, such as Chevron Weed Oil, is being applied in a 2.5 mph wind at 30 gals/acre. Air temperature is constant at 70°F. With the equipment used, 2 percent of the oil is lost in drift. This would include 1 percent in the 15 ft. zone adjacent to the swath, 0.33 percent in the adjoining fields to 328 ft. out and 0.67 percent still airborne at 328 ft.

The particle size distribution of the drift still aloft should range from 10 μm down. The average aerosol diameter is 5 μm. Thus for every acre of weeds treated we have 0.20 gal. airborne in that form. Let us also assume stable atmospheric conditions prevail, so that turbulence is minimal.

In Figure 3-17, the evaporation rate of Chevron Weed Oil is shown at zero wind speed. Under entirely nonturbulent conditions, an airborne droplet carried by the wind should evaporate at about the same rate. The curve is for a 15.5 cm^2 sample area in which 102 ± 0.6 mg of material was evaporated. From Figure 3-17 it can be seen that only about 15 percent of the sample was lost, but the initial 5 hr. weight loss was about 100 $\mu\text{g/cm}^2\text{-hr}$.

We will assume that 15 percent wt. loss is therefore maximum and that the droplet precipitates after that takes place.

Neglecting droplet surface area decreases with 15 percent volume reduction (~10%), the evaporation rate from 0.20 gal. of drift dispersed as a 5 μm aerosol would be

$$\underset{\text{No. of droplets}}{\frac{0.20 \times 6 \times 3785}{\pi\,(5 \times 10^{-4})^{3}}} \quad \times \underset{\text{Area per droplet, cm}^2}{\pi(5 \times 10^{-4})^2} \times \underset{\text{Evap. Rate, lbs/hr}}{\frac{100}{10^{6} \times 453.6}} \quad = \quad \underset{\text{lbs/hr}}{2.00}$$

Since the amount aloft that has evaporated is only 0.226 lb. (15 percent x 0.20 gal. x 7.54 lb/gal), evaporation will have occurred within 6.8 seconds or within 25 ft. of the edge of the swath.

The balance of aerosol would continue to drift and, according to Figure 3-17 would not evaporate much further unless turbulent conditions occur. If this is the case, precipitation will be less likely to occur

(Ref. 10), and the evaporation of the less volatile oil constituents will take place. If we assume that practically all of the drift has settled with 6 miles of application, it would have been aloft 2.5 hrs.

Considering a more volatile pesticide, such as a carrot oil, the evaporation rate in stagnant air is 27 times greater per unit area than the Chevron Weed Oil. Furthermore, the decay in evaporation due to fractionation (enrichment in heavy ends) is not great. Thus, aerosol droplets in the size discussed here would evaporate completely over the same 25 ft. distance.

5.4 EFFECT OF SPECIAL SPRAY TECHNIQUES ON REDUCING DRIFT

As discussed in Subsection 4.2, a number of techniques may be considered for minimizing drift. The farmer does not want to waste his pesticide and he does not want to damage bordering, possibly sensitive crops. The entire slant of the work of Yates and his colleagues has been aimed by these considerations.

The Law electrostatic spray nozzle (see Subsection 4.2) has been evaluated and claimed to produce almost zero drift. It is still in prototypic form, however, and the future commercial availability or expectable field performance of the device on different crops is still not definite.

Yates and his coworkers have conducted investigations on other nozzle forms and on adjuvants for the suppression of drift. In working with low pressure, deflector type (KGF) nozzles (Ref. 11) and low-pressure micro-jet nozzles (Ref. 12), the U.C. Davis scientists observed considerable drift reduction (Ref. 9). The KGF nozzle, which is suitable in tractor applications, was particularly impressive. In applications compared with standard 8003 type (80° fan-nozzle) and sprays with and without adjuvant, the KGF produced fall-outs of undoped pesticide at 66 and 328 feet downwind that were 0.1 and 2.8 percent, respectively, of the average for the 8003 nozzle when the latter was spraying with and without thickener. The airborne drift from the KGF nozzle at 328 ft. was 1.75 percent of the average produced by the 8003 nozzle (with and without thickener).

The low pressure micro-jet nozzle (MF) is best suited for helicopter applications. These were used by Yates et al on an airfoil-shaped manifold with 60 0.71 mm-ID tubes molded to the trailing edge. The angle of the boom was carefully adjusted in flight to align the jets with the airstream. The aircraft was held below 45 mph air speed to reduce air shear.

The helicopter-mounted MF nozzles produced more drift fallout than the tractor-mounted KGF nozzles but developed less airborne drift (at 328 ft. downwind). Both nozzles were decidedly superior to all other nozzles tested with or without adjuvants being used in the other nozzles. At 328 ft., the MF produced only 0.15%, coincidentally in both cases, of the average fallout and airborne drift measured at 328 ft. out for a jet-type (D-4) nozzle spraying with and without a thickener. It is thus clearly obvious that the use of nozzles designed to minimize drift will produce that desired result with impressive effectiveness.

In testing adjuvants, Yates and his coworkers (Refs. 9 and 13) did not observe quite as dramatic benefits in drift abatement that was demonstrated by the low pressure nozzles. Two of the materials initially tested were a polyvinyl polymer (Nalco-trol, Nalco Chemical Co.) and an experimental hydroxyethyl cellulose buffer system designated HEC/B (Union Carbide Corp.).

Field drift tests measured fallout and air levels downwind of various aerial applications of oil-in-water emulsion (O/W), the two adjuvants and three types of atomization. Employing high-shear nozzles but low air shear, air concentrations from Nalco-trol were 70 percent those from O/W, although fallout was not significantly changed at 1000 and 2600 ft. Atomization with a high air shear gave very high levels of drift (fallout and airborne) for all three preparations. Thus, that type of atomization should be avoided in all cases.

The application with both minimum air and nozzle shear produced minimum drift for all fluids. In comparison with the O/W standard, both adjuvants significantly reduced drift air concentrations (to 10 to 70 percent of that produced by O/W) but not fallout, at all downwind points tested. It is thus clear that adjuvants will reduce drift when conventional nozzles are correctly used but that the use of the low pressure, low drift nozzles described above would render the use of anti-drift adjuvants unnecessary.

SECTION 6.0

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APPENDIX A

FIELD EMISSION MEASUREMENTS

APPENDIX A

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FIELD EMISSION MEASUREMENTS

A-1.0 OBJECTIVES

The primary objective of this task was to determine the rate of release and the approximate total pesticide volatilized after realistic application to actual crops. The effects of variations in temperature, wind speed, soil moisture, and application rate would be evaluated for various combinations of pesticide/crop types. To be included in the test plan would be the application of: (1) a cotton defoliant; (2) carrot oil; (3) a non-selective weed oil; (4) a citrus miticide.

A mobile or portable field test device would be constructed that would contain the application event and permit a continuous monitoring of hydrocarbons out of the chamber under known flow conditions. The originally proposed structure is drawn in Figure A-1. While this design was considerably modified, as will be seen in the next subsection, the drawing does depict the conceptual intent.

A secondary objective of this task was to evaluate possible control options that might serve to reduce the release of hydrocarbons when pesticides are used (see Sec. 4.2).

A-2.0 SITE ACCESS ARRANGEMENTS

Access to an operating farm would be necessary in order to conduct the envisioned tests. This would require a cooperative arrangement wherein the necessary horticulture would be furnished by the host-operator and tracts would be made available for the test work. Another requirement would be adequate security. The equipment would have to be left in the field for a long period of time and would be vulnerable to vandalism and theft. In the interest of logistics and cost effectiveness, the test work would preferably be performed close to the contractor's home base in Irvine. Fortuitously, the

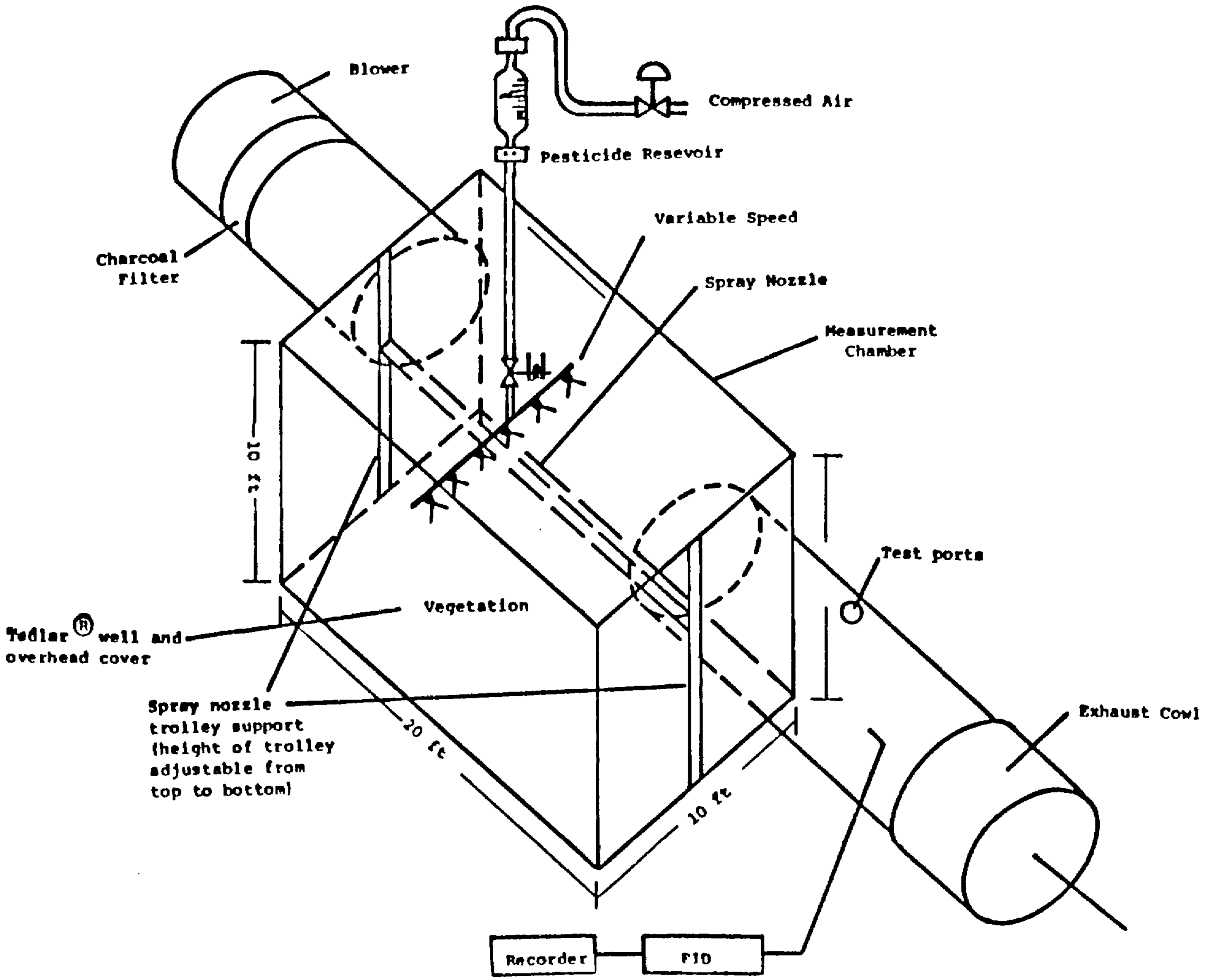


Figure A-1. Field emissions measurement apparatus - proposed conceptual design.

area is a rich farming region capable of producing all of the crops of interest, including cotton.

Three farm operators were contacted. These were the Irvine Co., the Orange Coast Junior College, and the University of California South Coast Field Station. The Irvine Co., which works or leases most of the farmland in Orange County, felt that the proposed test work would be incompatible with their own, highly-organized operations and could not suggest a secure area (none of their fields are fenced). The Orange Coast Junior College, which maintains an impressive level of agricultural activity (its founding purpose) at its Costa Mesa campus, showed considerable interest in the project. Access, however, would have required leasing campus acreage which would first have to be declared surplus. This involved such a legally complicated process that both sides agreed to abandon the scheme.

The third site investigated was the University of California South Coast Field Station (UCSCFS) which is in unincorporated Orange County land near the El Toro U.S. Marine Corps Air Station (see Figure A-2). It is a well-fenced, shrubbery and tree screened plot located on a dead-end road that is lightly traveled. The farm is divided into comparatively small road-separated tracts that permit limited-scale experimental work while still using conventional farm equipment.

The UCSCFS Supervisor, Dr. Randy Keim, expressed interest in the project and initiated inquiries within the University. It was determined that access to any University field station is contingent on the existence of interest in the work by technically appropriate faculty members. Such individuals could then arrange access as academic sponsors of the study but would be expected to offer technical comment.

The RCM had early on identified Dr. Walter J. Farmer as a highly knowledgeable expert in pesticide transport phenomena. A meeting was therefore arranged with him and his colleagues, Drs. W. F. Spencer and M. M. Cliath. This proved to be a very fruitful meeting in which the entire scope of the program was reviewed. Thus, when academic sponsorship was later solicited, Dr. Farmer graciously acquiesced to serve in that capacity. He then quickly arranged access to the field station. A grant in aid was

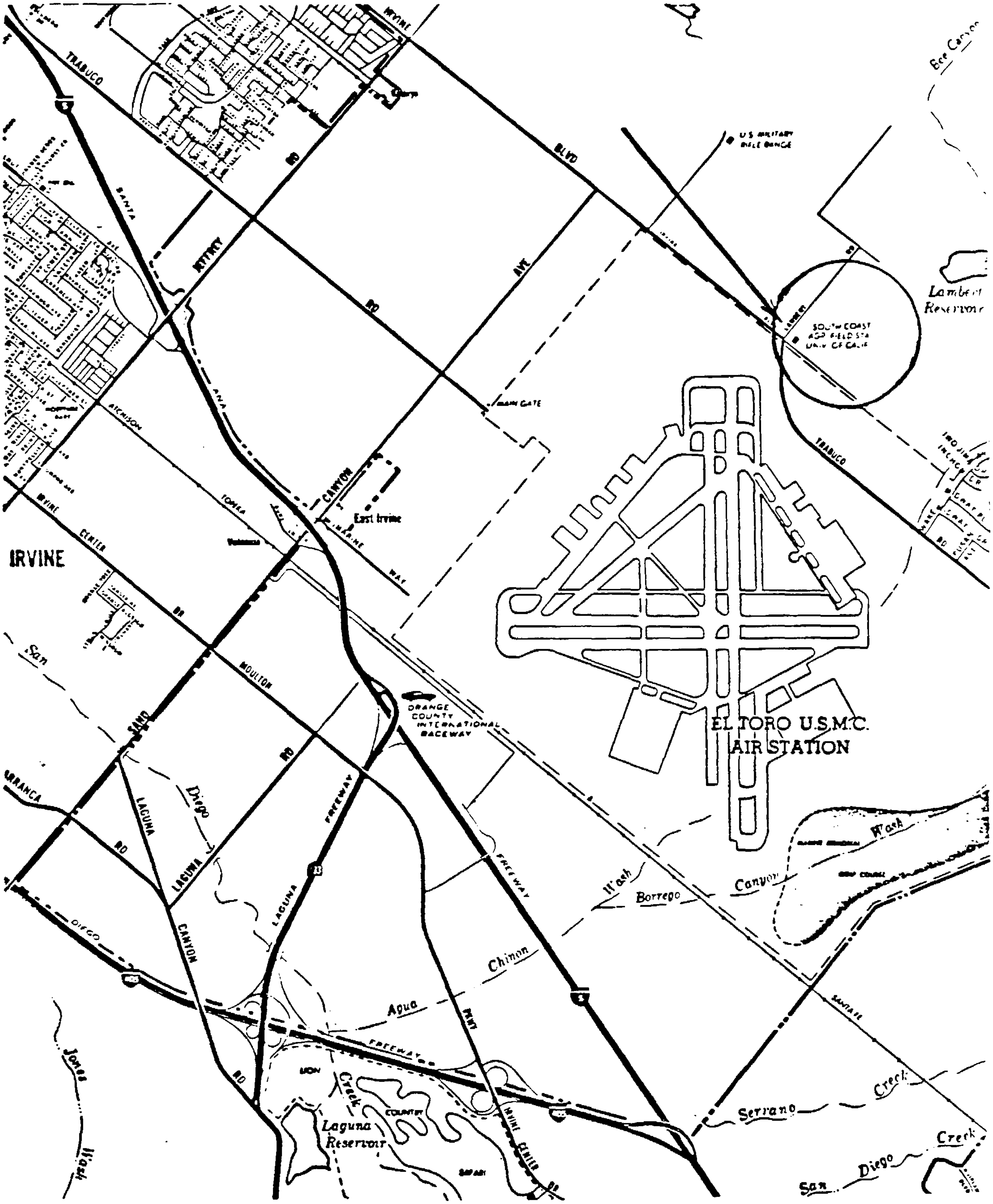


Figure A-2. Proposed test site for Task III operations.

tendered to the University to cover Dr. Farmer's participation and the labor costs of the field station personnel for the planting and culture of the target crops.

A-3.0 FIELD TEST APPARATUS DESIGN, FABRICATION AND PRELIMINARY TESTING

A-3.1 Functional Requirements

Operating in the field over furrowed row crops (and weeds) involves testing without service utilities other than irrigation water. The apparatus must not only encapsulate a sprayable plot but must provide its own power, water and gas supplies. The chamber must also be portable or moveable so that after an area is treated, it can be moved on to a new test plot. Finally, the system must be capable of applying pesticide to the target crop in a realistic manner and be so designed that it itself does not compromise the consequent effects.

This was the design philosophy reflected in proposing the configuration shown in Figure A-1. Air would be drawn through a transparent chamber and be reduced to zero hydrocarbons by passage through a charcoal filter. The main chamber would contain the weeds or row crops and a device for applying pesticide to these targets at about tractor speed. After the air had passed through the chamber at speeds up to 5 mph (as specified by the RCM), it would pass through an exhaust duct where it would be monitored for total hydrocarbons. Other instrumentation would be installed or brought into the chamber to monitor temperature, R.H., wind rate and water evaporation rate.

A-3.2 Preliminary Design Decision

Need for several changes in the originally proposed test chamber design became evident. Since air velocities of up to 5 mph were specified, throughput in the 2000 cu.ft. main chamber would be 44,000 cu.ft./min. This would require a fairly large fan and a charcoal bed of larger cross section than the chamber itself. The mobility of the latter was highly questionable, so the concept of precleaning the input air to furnish zero background was dropped. Differential measurement of input/output air was considered preferable. Also, the direction of the fan was reversed so that air leakage from the envelope, particularly along the base would be precluded. Since suction would be used, one end of the chamber could then be left open, provided adequate shielding from off-prevalent winds was provided. The configuration decided upon is shown in Figure A-3. This design was followed essentially in fabrication, except that the use of plywood for the wind shield was dropped. Heavy polyethylene film mounted on a metal and wood frame was used. Also, two smaller (6' x 12') wind screens, similarly constructed, were added. These are attached to the large wind screen at about 45° relative to the side of the chamber. It should be pointed out that while polyethylene was selected for the wind screens, the main envelope chamber would be shrouded in Tedlar, a more non-adsorptive film. It was expected that some spray would contact the chamber walls, but not the wind screens.

The original plan for powering the structure was to use a field generator. This was sized and the rental cost found to be prohibitive. It was, therefore, decided to drive the fan with an alternator-equipped tractor engine. The latter device is a small, air-cooled, gasoline engine sometimes mounted on tractors for general utility needs - driving saws, pumps, etc. All other power would be taken from a heavy duty automobile battery that would be charged by the tractor engine alternator.

Mobility of the device would be created by installing wheels on the bottom of the frame. These would rest in wooden, U-shaped tracks. On finishing work at one test plot, additional tracks would be set out. After removing all guy-wires and the wind screens, the device could then be hand-pushed to the next location. On long moves or angled turns, the main envelope would be light enough to be carried by 6 or 8 men, while the heavier end-assembly could be moved by a fork-lift truck.

A-3.3 Test Chamber Fabrication

Elements of the test chamber were constructed at the yard of KVB's test facilities in Santa Ana. The various sections were then transported to the UCSCFS by a crane-equipped machinery-moving truck. Actual assembly was then done in the middle of the actual 4-acre test area (in Fields 47 and 48) assigned by the University. A portable generator was used to power drills and

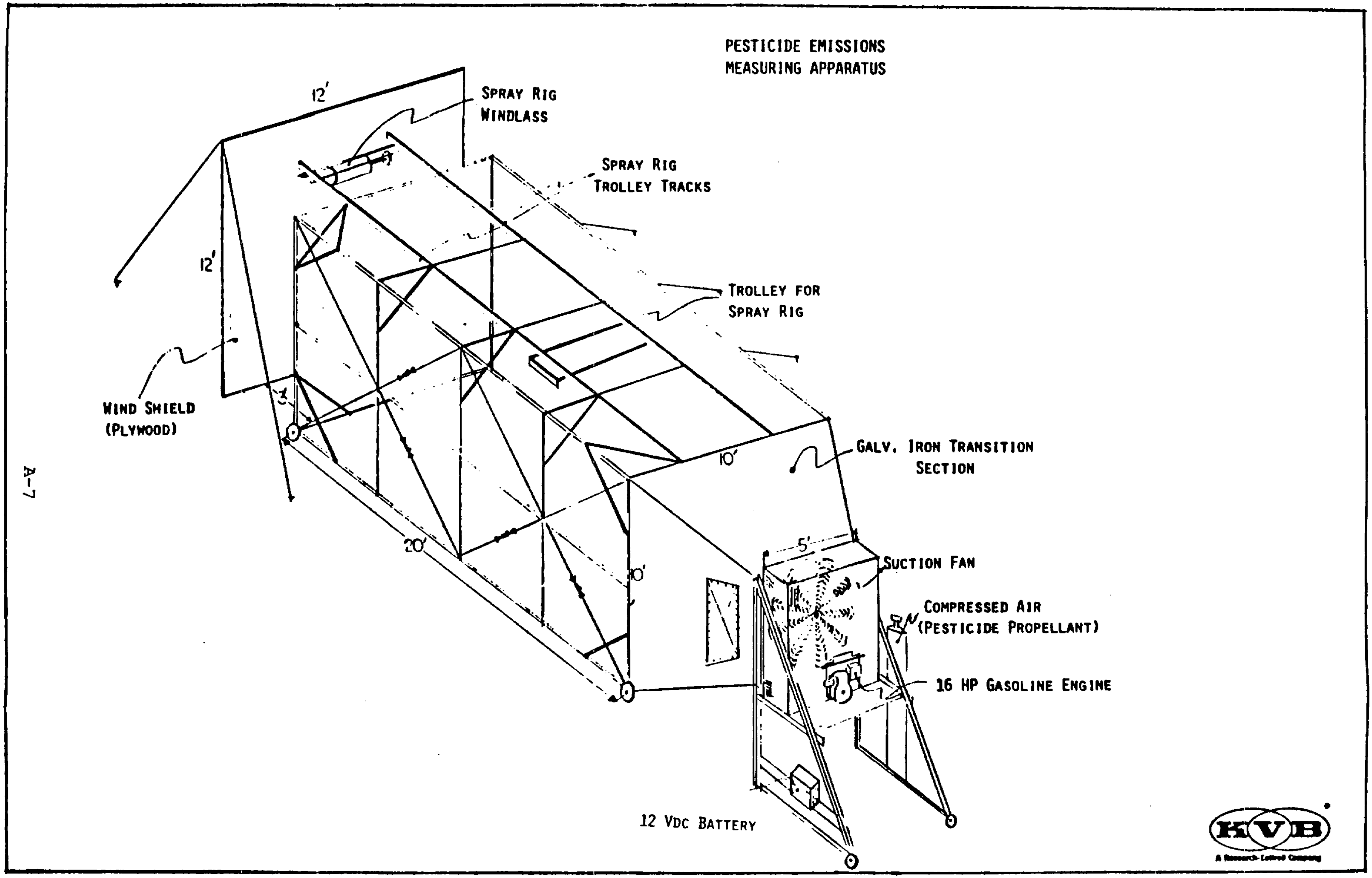


Figure A-3. Pesticide emissions measuring apparatus - final conceptual design.

other 110 VAC electrical devices needed for the work. The finished test chamber is shown in Figure A-4a through d.

A-3.4 Details of Test Chamber Components

The overall chamber can be considered as (and dismantled into) six components:

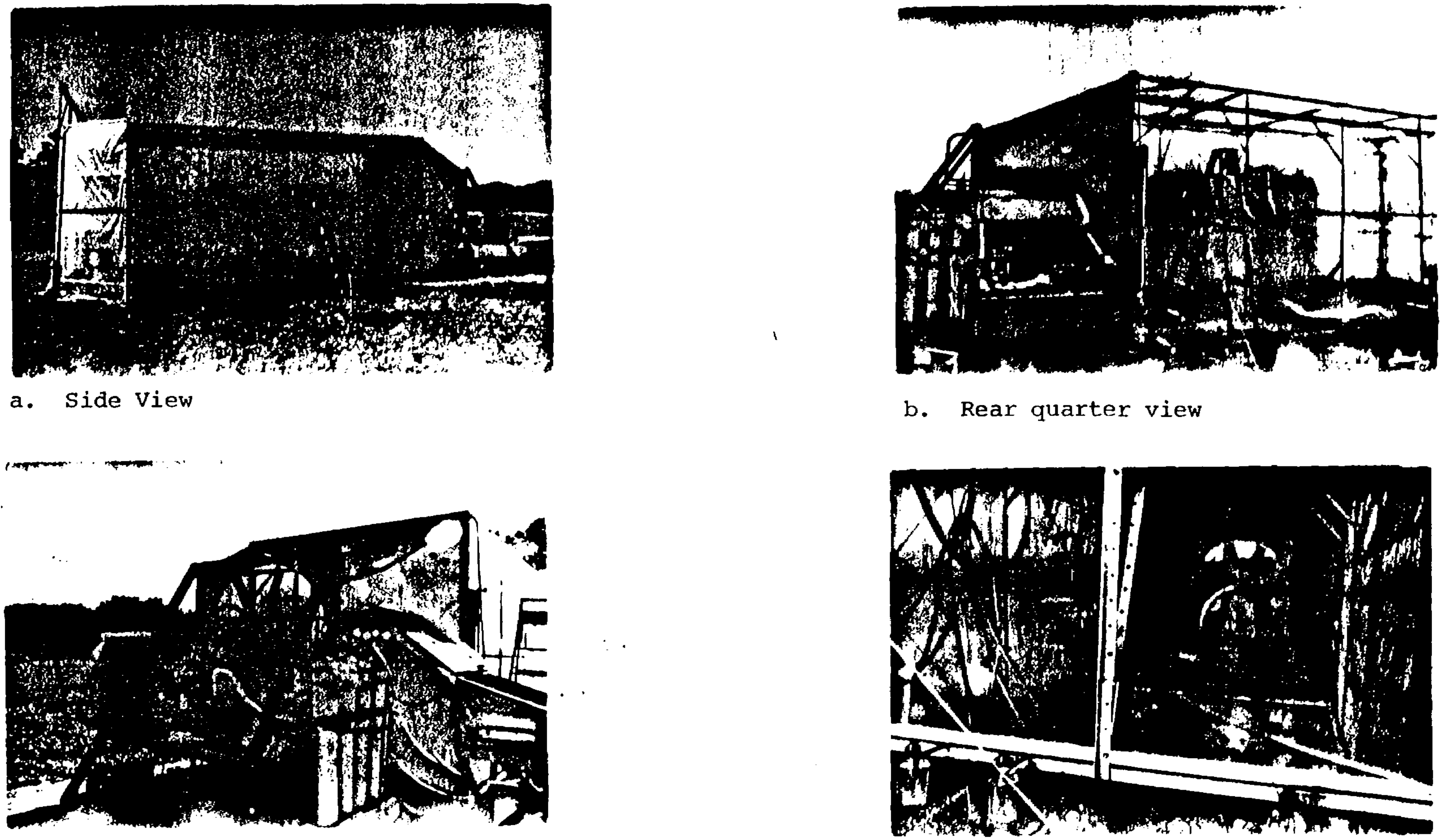
- windscreens (3)
- main envelope
- end (fan) assembly
- rails
- instrument station
- instrumentation
- ancillary equipment

A. Wind Screens--

These polyethylene-covered panels stand two feet higher than the chamber. Wooden frames are covered on both sides with 6 mil film; angle-iron (1 x 1 x 1/8"-inch) forms a complete frame on each. The center panel is 12 x 12-ft. while the side panels are 6 x 12-ft. The panels are free standing, held in place by four guy wires per panel. The side panels are attached to the middle panel with bailing wire.

B. Spray Chamber--

This chamber is open at either ends and on the floor. Framing is of 1 x 1 x 1/8-in. and 1-1/2 x 1-1/2 x 3/16-in. angle iron. Strengthening of this light frame is realized by use of 1/8-inch aircraft cable in diagonal runs, tightened by turnbuckles. The frame rests on six 4-inch, rubber-tired wheels. The Tedlar skin consists of 10 x 10-ft. panels of 4 mil film. The side panels are heat-sealed together to form single side pieces, while the "roof" is two pieces to allow rain drainage through the overlap strip. The side panels are seamed top and bottom into which 20-ft. x 1/4-in. iron rods are inserted. The panels are then secured permanently at the top by wiring the rod to the frame. At the bottom, wire is led through spaced, small holes



a. Side View

b. Rear quarter view

c. Rear view

d. Spray assembly.

Figure A-4. Pesticide emissions measuring apparatus - actual. KVB13-5809-1256 in the Tedlar and over the rod. These wires are then nailed to the underlying wooden track to furnish a taut skin effect. Between tests, the side panels are rolled to the top and furled there until testing resumes. This practice was instituted after a gale gusting to 47 mph badly damaged the structure on 11 December 1979.

The spray apparatus, which can be seen in Figure A-4d, consists of a set of rails, a trolley connected spray boom, a windless, switching mechanism, calibrated pesticide reservoir, and compressed gas source. All except the last item are mounted on the spray chamber frame. The trolley rails run the full length of the top of the frame and extend beyond the spray chamber about 2-feet.

The end of the rails are connected by an angle iron on which is mounted the windlass (a 12 Vdc automobile starting motor). The shaft of the windlass is fitted with a 6-inch pulley wheel over which is reeved a nylon rope. The latter runs to a pulley at the extreme other (fan) end of the chamber, thence to the trolley where both ends of the rope are secured, creating an endless loop. The spray boom consists of two aluminum angle irons between which the nozzle pipe nipples are inserted at any desired intervals or quantities (up to about twelve). The boom is attached to the trolley by the A-frame arrangement made of perforated angle aluminum. By selecting the matching holes on this frame, the nozzles can be adjusted to any desired height.

The nozzles obtained were of the flat spray tip variety (Spraying Systems Co. Unijet) designed to furnish a spray angle of 50 degrees at 40 psi reservoir pressure. A selection of tips was acquired to furnish, at pressure, flows ranging from 0.20 to 1.0 gpm per head. All nozzles were fitted with strainers and diaphragm check valves. The latter ensure drip-free shut off and require application of 7 psig pressure before opening. Standard pesticide hose was employed to connect the nozzles to the manifold (3/8-inch hose) and reservoir (1/2-inch hose).

The pesticide reservoir consists of a 4-ft. piece of 1-1/2-inch galvanized iron pipe. To this was fitted a parallel run of boiler sight glass and a calibrated scale. The bottom of the reservoir was fitted with a solenoid valve (Spraying Systems Co. P/N 11438-22) to which the hose to the spray boom manifold was connected. The top of the reservoir is terminated in a T-arrangement comprised of a quick-opening and a gate valve. The latter is used to relieve pressure on the reservoir and to fill it. The quick opening valve controls the line from the pressurizing source, a cylinder of compressed nitrogen.

In test operations, the trolley is moved to the end of the rails at the fan housing. Bottles are wired under each nozzle and the test pesticide is pressurized into the system at low pressure. This forces air out of the hoses, priming the lines. The solenoid valve is then closed. A switch is then thrown which activates the windlass. The spray apparatus moves about 5-ft., attaining full speed (about 6 mph), when it actuates a limit switch. This reopens the solenoid so that spraying commences. About 5-ft. from the end of the rail, the trolley trips a second limit switch. This closes the solenoid on the pesticide reservoir and deenergizes the windlass. A spray pattern of about 10 x 14-ft. results.

Sampling lines for extracting air samples entering and leaving the spray chamber were 0.25-in. O.D. teflon tubing of 0.03 in wall thickness. The originally planned output air sampling arrangement consisted of an isokinetically-sized orifice located in front of the fan's hub. Teflon tubing was then run from that point through the wall of the transition section into the instrumentation station. The tubing was heat-traced by lagging it close to, but not touching, the exhaust line of the tractor engine. The latter, which replaced the factory-installed exhaust and muffler assembly, consisted of a 1-1/2 in. flexible copper line led through the transition section wall (to heat the sampling line) and then back outside to a point in the exhaust stream. Insulation consisted of fiberglass and heavy aluminum foil. The intended purpose of this arrangement was to collect drift aerosol, then volatilize it so that it would be pumped to the detector along with hydrocarbon vapors.

The background sampling lines are run out to two mid-height points on either vertical angle irons forming the open end of the spray chamber. These are tied so that equal length runs are used. Switching from input to output air is effected using quick opening toggle valves.

C. End (Fan) Assembly--

This assembly consists of a transition section of galvanized iron that connects the end of the spray chamber with the fan housing and an A-frame on wheels that holds the fan housing, fan, tractor motor, gasoline supply and various other components. The transition section is a square pyrimidal frustum, reducing the 10 x 10-ft. spray chamber end to a 5.5 x 5.5-ft. opening at the fan housing. The exhaust assembly (Airmaster fan P/N H60B04) consists of a pulley-driven, eight bladed fan (60-in. tip to tip). At a top-recommended fan speed of 505 rpm, rated throughput is 48,830 cfm at zero static pressure (7.5 h.p. motor recommended). That is equivalent to a wind speed through the spray chamber of 5.5 mph. Pulley drive is furnished by a tractor engine via a pair of v-belts. The engine selected is a Briggs & Stratton Model 32 6437, a four-cycle, horizontal crankshaft 16 h.p. (@ 3600 rpm) gasoline engine equipped with an alternator. Because the tank provided with the engine is too small for extended-duration test needs, an external gasoline source was provided. This consisted of a 55 gallon drum. Gasoline flow between the drum and the engine carburetor is promoted by an in-line automotive fuel pump. Starting energy is obtained from a heavy duty automobile battery, which also is the energy source for the windlass, the pesticide reservoir solenoid, and some of the instrumentation. Charge on the battery is maintained by the tractor engine alternator. After long downtimes, the battery occasionally required help from the battery in the van used to transport personnel and equipment to the site. Also attached to the A-frame supporting the fan housing were the various compressed gases needed in the field. As many as 6 cylinders were in use at a time.

The A-frame itself was constructed of 3 x 3 x 1/4-in. angle iron. It is supported by four 5-in. solid filled-plastic wheels. These are situated closer together than those under the spray chamber, thus necessitating the laying of a separate set of tracks. Unlike the spray chamber, movement of the end-assembly is not a simple matter of pushing the device along tracks. In its normal interlock with the spray chamber, the end assembly must be raised about 6 inches in the air. This is done by cranking continuous thread studs through bolts welded to the frame. These contact steel plates laid in the wooden track and lift the wheels into the air. The galvanized iron transition section is connected to the fan housing by a hinge at the top. As the assembly is raised the transition section slowly closes over the mating edge and bottom sections of the fan housing. When this closure is complete and the rollers on the bottom of the mouth of the transition section are just touching the rails, interlock can be effected.

To move the device, the reverse procedure is necessary. The wheels are lowered to the tracks and the transition section is tilted up on its hinge and propped out from the fan housing with a 2 x 4-in. board.

D. Rails--

Five sets of 14-ft. rails were made. These are 2 x 6-in. boards on top of which 3/4-in. deep grooves were produced by nailing 1-1/2 x 3/4-in. wood strips flush to the edges of the underlying, larger board. On moving the spray chamber and/or the end assembly, rails were butted up to those already supporting the structures. The assembly was then pushed onto the newly positioned rail and so on. Because the end assembly is narrower gauge than the spray chamber, the same rails cannot be used for both. The gauge (10 ft.) of the spray chamber is such that the rails lie in the bottom of furrows if the furrows were produced by standard equipment.

As pointed out earlier, this technique was used only to move the rigs down row. When longer hauls were involved, UCSCFS and KVB personnel moved the equipment by brute force and a fork lift truck.

E. Instrument Station--

This consisted of a lean-to cabinet mounted on four legs. It is the object (lid open) to the far right of Figure 4-4c. This served as secretary and storage or operating platform for most of the instrumentation used.

The structure is equipped with vent panels on either side and is weather-proofed with a heavy polyethylene shroud. Holes are provided in the bottom to permit insertion of gas hoses. Moving this piece of field furniture requires the services of two strong men.

F. Instrumentation--

All the measurement equipment used on this field program is 12 Vdc or spring-driven. The inventory of items used is as follows:

- Total hydrocarbon analyzer/gas chromatograph
- Strip chart recorder
- Anemometer
- Hygrothermograph
- Evaporimeter

Other items used included a volt-ohm meter, stop watch, hypodermic syringe, bubble buret, other graduated glassware. The characteristics of the primary instrumentation employed is developed in Table A-1.

G. Ancillary Equipment--

This consisted of calibration and functional gases, safety equipment, motor van, assorted hand and power tools (ac and dc), lumber, solvents, and messing gear.

A-3.5 Preliminary System Testing

A. Spray Rig--

Spray action was observed using, initally, water in the reservoir. Initial trials demonstrated that the track alignment was poor and that the entire track installation had to be strengthened. This was done by installing two pieces of 1-1/2 x 1-1/2 x 3/16-in. angle iron over the tracks and the intervening roof frame and locking the entire framework together with bolts. This greatly improved the performance of the spray rig.

Timing runs made on the spray rig showed it to be traversing with the nozzles-open for 1.5 ± 0.1 sec. The pattern put down reached from edge to edge (10 ft.) of the spray chamber and repeated within a few inches either way

TABLE A-1. CHARACTERISTICS OF INSTRUMENTATION USED IN THE TASK III FIELD WORK

ITEM	MANUFACTURER & MODEL NO.	POWER SOURCE	DESCRIPTION
Total Hydrocarbon Analyzer/Gas Chromatograph	Century Systems OVA-128	12Vdc	Portable organic vapor detection system based on flame ionization detector. Equipped with optional GC function, including back-purge modality. Sensitivity (for CH_4) rated at 0.2 ppm capable of internal or external battery and hydrogen operation. On program external, longer-lasting sources used. Three sensitivity settings: 0-10, 0-100, and 0-1000 ppm.
Strip Chart Recorder	Esterline Angus 401B	12Vdc	Variable speed (1.5-300 cm/hr), variable sensitivity (1m-100v), single channel, recorder with conventional (ball-point) writing mode. Capable of internal or external battery operation; latter used on program. Step response time 1 sec. full scale.
Anemometer	Davis Instrumentation Co. no P/N	None Required	Hand-held, turbine-type (Biram) revolution counter.
Hygrothermograph	Weathertronics 5020	Spring Wound	Recording weather station. Bimetallic strip thermometry and human-hair humidity sensing element. Seven day operation possible.
Evaporimeter	Weather Measure E801	Spring Wound	Recording water evaporation rate instrument. Wick principal operation with float to follow water level change. Seven day operation possible.

of 14 ft. This is equivalent to a delivery speed of 6.4 mph and an application area of 140 sq.ft.

B. Isokinetic Sampling System--

A run was then made to determine the behavior of the system with a petroleum oil. Diesel oil #2 was used at an application rate of about 25 gallon/acre and the fan drawing a wind of about 5 mph. Very erratic behavior of the OVA hydrocarbon analyzer was noted. A low total hydrocarbon (THC) reading drifting from 10 to 20 ppm was obtained that did not change much when the sampled air was shifted from input to output. The sampling line was checked for condensate but none was found. Diesel oil was found, however, in the in-line, sintered metal filter in the internal plumbing of the OVA. It was concluded that in this cold portion of the delivery system the oil had condensed or had otherwise been trapped. Thus situated, it contaminated the sampled air drawn into the detector.

Since it was physically impossible to heat trace the internal plumbing of the OVA, it was decided that measuring drift would be impractical with the equipment available. The resulting action consisted of: (1) reversing the direction of the sampling probe so that only vapor would be collected; (2) thoroughly cleaning the OVA; and (3) operating future sprays with the fan initially off, turning on the tractor engine after the drift had settled in the chamber (ten minutes was subsequently allowed for this).

C. Air Movement in Envelope--

Orientation of the field rig was in accordance with the furrowing direction observed in Field 48 at the UCSCFS. This is in parallel to Lambert Road (Figure A-2). The El Toro U.S.M.C. Air Station runways can be visualized as a compass rose; the longest runways are exactly North-South and are intersected by three runways that are exactly East-West. The aerology station at that station advised that the prevailing wind is from 270° (true) or out of the west at from 8 to 10 mph. Santa Ana winds (largely winter phenomena) are from 030° to 090° (true) and feature gusts from 20 to 80 mph.

The test rig was therefore installed with its axis aligned with the furrows Southwest to Northeast and the end (fan) assembly situated at the lee end. The prevailing wind would thus be on the quarter of the structure, if we

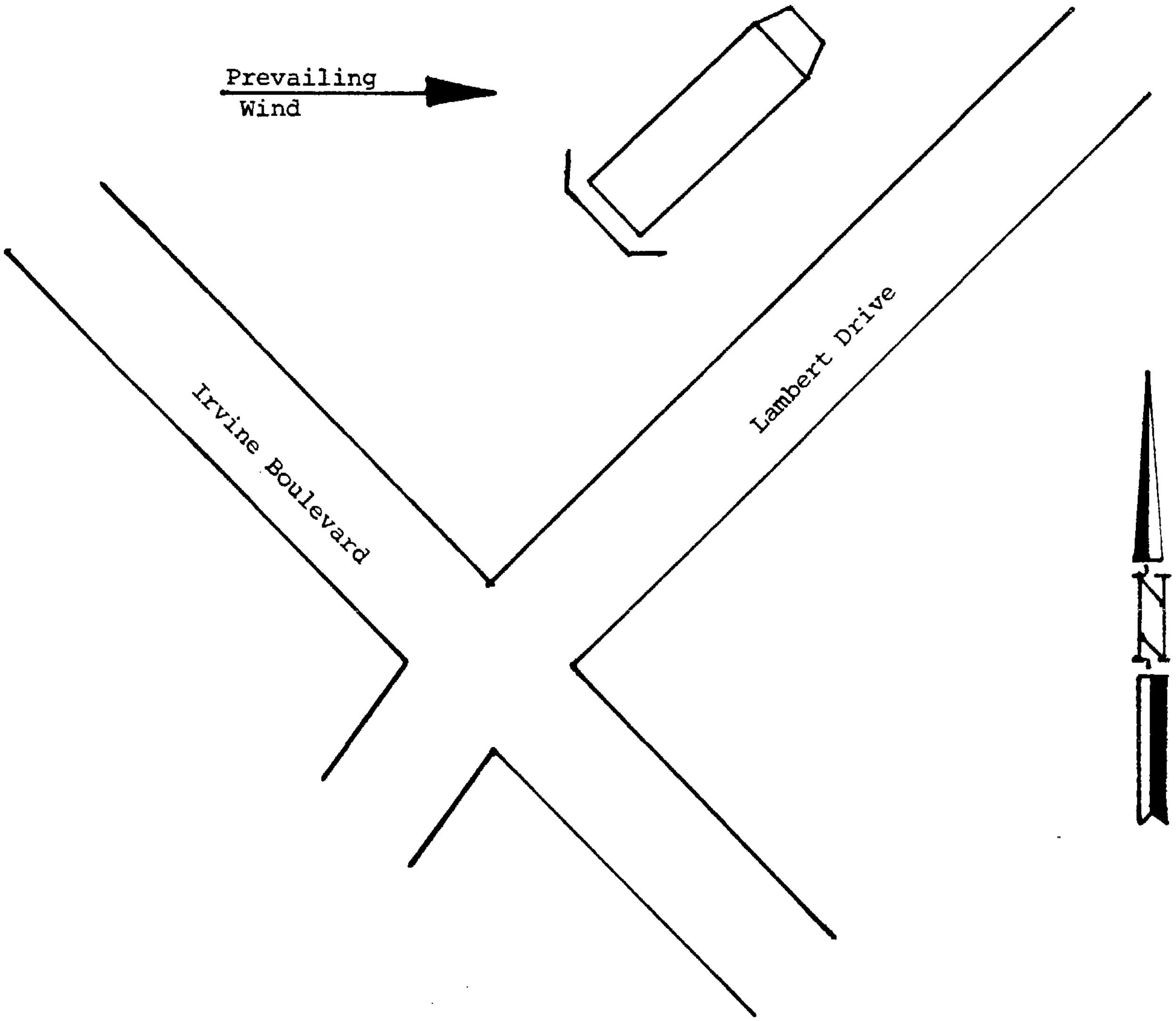


Figure A-5. Wind orientation of the pesticide emissions measuring apparatus.

consider the wind screens as figuratively comprising the stern of the arrangement. This is diagrammed in Figure A-5.

Because the prevailing winds were stronger than the test wind speeds sought (up to 5 mph), the air movement inside the chamber was measured. At the dead center of the 10 x 10 x 20-ft. spray chamber, considerable variation in wind movement was noted. During a single, one minute anemometer reading with the fan operating to produce a 2.5 mph wind, excursions ranging from up to four times the intended fan-induced speed to reverse flow occurred. The time-averaged readings did not, however, deviate anywhere that much from set point. Locating the anemometer at different locales within the chamber produced possibly different patterns with more even flows being observed as the fan was approached. Because of the state of air movement in the chamber, it was decided that frequent readings would be taken and then averaged to express wind speed for any given run. The sampling point used would be the center of the plane comprising the vertical midsection of the spray chamber. Thirty three averages of triplicate readings taken at that point with the fan set to provide a 2.5 mph wind produced a grand mean of 2.53 mph. The average deviation was ±0.45, with extremes of measurement (triplicate averages) at 0.92 and 4.50 mph. These readings were made on five different days from early morning to late afternoon.

D. Adequacy of Hydrocarbon Sampling Arrangement in Spray Chamber--

Because the air flow in the spray chamber proved quite irregular and recognizing that pesticide vapor concentrations would diminish vertically, non-uniform distribution of these concentrations at the plane of sampling probe was expected. Installation of air-mixing baffles and/or multi-orifice sampling arrays were therefore considered. To justify the effort, however, tests were first conducted to determine if actual concentration discontinuities could be demonstrated.

The test consisted of spraying the floor of the spray chamber with a hydrocarbon oil and then moving the end of the sampling line from point to point on the safety grid just in front of the fan. This was first done using diesel oil #2 and the fan set to produce a nominal 5 mph wind in the chamber. An equivalent of about 25 gal/acre was put down on the dominant creepers (blue bells) then covering about 75 percent of the spray plot. Aside from an initial, brief OVA reaction, the THC readout was otherwise not clearly distinguishable from background. These results obviously promoted concern that went beyond the objectives that were immediately implicit in the test itself. This observed lack of system sensitivity is considered in some detail in subsequent sections of this report.

The test was continued using a more volatile oil--Shell Mineral Spirits 120. Coverage was about the same as for diesel oil and an OVA response above background was recorded. This differential ranged up to almost 10 ppm (as CH_4) initially with a decay to about 1 ppm when the test was discontinued after about an hour. During this period, the sampling-line probe was moved to five equidistant different points vertically spaced from the bottom to the top edges of the circle described by the fan blades. Each point was monitored several minutes, after which the probe was manually shifted to another station, this selection being random. Since the objective was to determine any differences in the exhaust plane where the probe would be situated, all measurements were differential. After initial span and zero calibrations, the background was tested but not again until the test was finished. Considerable instrument drift occurred during the test (which was typical) so that the record obtained was not useful beyond the purposes of this particular test. The average chart readings obtained at the various stations over about one hour of monitoring are shown in Table A-2.

It was concluded from these results that the position of the air-sampling probe was not critical and that adequate mixing did occur within the chamber.

A-4.0 PESTICIDE APPLICATION AND THE MONITORING PROCEDURES

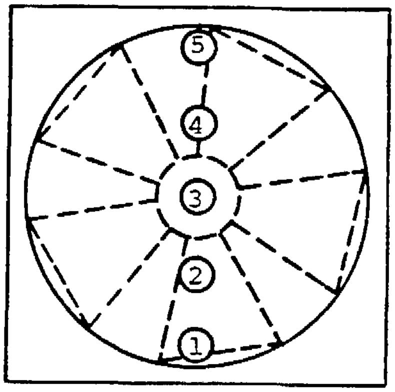
A-4.1 Scope of Planned Testing Activities

A rather ambitious test plan was initially proposed that would include the performance of some 59 tests. Forty of these were to be routine tests in which each of five pesticide/crop combinations would be evaluated under eight different combinations of conditions. These would involve the following

TABLE A-2. RELATIVE HYDROCARBON READINGS RECORDED AT DIFFERENT POINTS IN THE SAMPLING PROBE PLANE OF THE FIELD APPARATUS EXHAUST SYSTEM

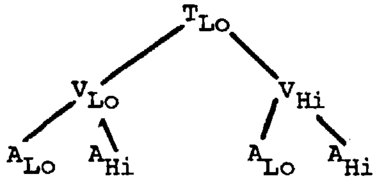
Position Sampled (See Inset)	Avg. Relative THC* Chart Readings, Scale Divs	Read Out Trend
3	55	
5	50	Increasing
1	65	THC†
5	70	
	Off Top Scale	Reset on Scale
2	50	
1	35	Decreasing
3	20	THC†
	Off Bottom Scale	Reset on Scale
5	55	
4	50	Slowly
2	52	Decreasing
3	45	THC†

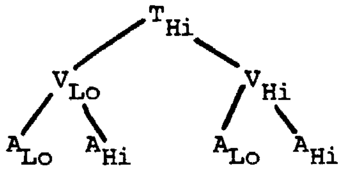
*In chronological order
†Including instrumental drift



variables: (a) low and high average temperature (weather permitting); (b) two wind speeds (approximately 2.5 and 5.0 mph); and (c) two application rates (approaching the extremes of the range normally recommended for agricultural purposes).

Thus the battery of tests for each pesticide/crop combination would be according to this matrix:





Where: T = temperature
V = wind speed
A = application rate

The five pesticide/crop combinations tentatively decided upon were as follows:

Crop	Pesticide
Weeds	ARCO or Chevron Weed Oil
Cotton	DEF-6
Carrots	Beacon No. 5 or Keen Kil No. 20
Citrus Trees	Orthol K Ready Mix Light, Medium or Leffingwell Unicide 60
Undesignated Row Crop	--

Besides the above tests, five tests with no pesticide used would be made over fallow ground under various temperature and wind conditions. The purpose of these tests would be to establish what, if any, hydrocarbon emissions were released by the soil itself.

Fourteen additional other tests were also defined and were designated "special tests." These were to involve the variation of such parameters as soil moisture, nozzle height, nozzle spray angle, and applicator speed. Except for the first variable, soil moisture, all were deleted by the RCM early on the program as being of secondary importance. New requirements were substituted; water evaporation rate would be monitored, if practical, and the soil moisture content in the test plot would be determined before and after each test. A third additional procedure was suggested by Chevron Research Corp. observers. They suggested a small evaporation pan, identical with that used in the Task II laboratory evaporation tests, be filmed with test pesticide and be installed in the spray chamber during test runs. It would be located out of the reach of the spray pattern and would be weighed before and after the test so that the results could be correlated with the laboratory test results and what occurred during the test itself. This suggestion could not be implemented because the small laboratory at the UCSCFS was not equipped with an analytical balance. The distance to the KVB lab (~10 mi) was too far for the procedure to be practiced with accurate outcome.

A-4.2 Field Test Procedures

Based on the results seen in the preliminary test efforts (subsection A-3.5) and early (aborted) testing, the following protocol was followed in the field tests:

A. Positioning the Field Emissions Measurement Apparatus--

The spray chamber is rolled over the test plot using the wooden rails. The end assembly is then rolled up to it and the frame jacked up off the wheels until the two assemblies match faces. They are then locked together. The wind screens are next raised and guy wired in place. The spray chamber is also guy wired and the furled Tedlar side panels lowered and fastened to the rails.

B. Pesticide Application Preparation--

The spray boom is hand-deployed to the open end of the spray chamber. The bottles are attached to each nozzle to catch clean-out liquid. The pesticide reservoir is drained of old test liquid and washed out with the current test pesticide and then topped. The reservoir is lightly pressurized (10 psig) and the solenoid communicating with the pesticide hose/manifold/nozzle arrangement is activated. Old pesticide and air in the lines is sprayed into the bottles, the contents of which are dumped outside the chamber into a sealable slop can. After clean-out and loading with new test liquid, the boom is returned to starting position. The reservoir is topped off and the level recorded using the graduated scale behind the boiler sight glass. Pressure on the reservoir is then adjusted to furnish the desired delivery.

C. Instrumentation Preparation--

The evaporimeter and hygrothermograph are set in a "dry" zone in the spray chamber. This is on a leveled board between the spray boom and the end assembly. A soil sample is next taken. A dozen or more scrapings of the top half inch of the surface are made until about a pound of soil is collected. Where furrows are present, equal amounts are sought from the tops and bottoms of these processes, since the moisture content is obviously higher in the latter zones.

The OVA is energized, calibrated with zero air and span gas (54.2 ppm methane in air) both from Scott Environmental. Readings are then made of THC at the fan probe and at the background or inlet air positions. Monitoring is then shifted to the fan probe.

D. Application and Monitoring--

The spray boom is energized and the pesticide pattern put down. All nozzles are checked by eye to insure that none are dripping. When this occasionally occurs, a drip bottle is immediately installed under the leaking nozzle, which is tightened only after the test is complete.

After allowing drift to settle, and not more than 10 minutes, the fan is started at the desired running speed. Because of instrument drift and variations in readings induced by turbulent air movement in the envelope, differential readings are taken. This is done by allowing the OVA to monitor first the fan probe then the intake air sampling probe. Each position is monitored several minutes, the differential between the best lines drawn through each trace being the THC ascribable to the pesticide. When this differential decays to an indistinguishable continuum, the test is terminated.

Anemometer readings in triplicate are taken shortly after the fan is started and periodically thereafter. To do this, the test technician enters the spray chamber and positions the hand-held Biram-type anemometer dead center in the plane describing the midsection of the spray chamber. Each replicate reading is integrated over a one minute period, using a stopwatch.

On the completion of the test, a final soil sample is taken, the records from the evaporimeter, hygrothermograph and the OVA are recovered.

A-4.3 Calendar Period of the Pesticide Testing

After the fabrication of the field rig in the summer and fall of 1979, preliminary testing and modification of the system ran into November of that year. Only three actual test runs were made that year, all with ARCO Weed Oil. Because of the negative results obtained and the fact that the previously fairly warm weather had finally turned to squalls and otherwise wintery times, testing was shut down until summer of the next year. The rig was left in the field and winterized by bagging and taping components in polyethylene film. All small moveables, such as instruments, gas cylinders, etc. were taken to storage.

When field testing was resumed in July 1980, the field rig was in a sorry state. A wind storm gusting to 47 mph, according to the Aerology Officer at the adjacent USMCAS El Toro, occurred December 11. While the rig had sustained little damage in a previous wind storm that peaked at 39 mph, the later storm created extensive damage. Furthermore, many components had weathered poorly, such that corroded wiring junctions, cracked hoses, etc. had to be repaired. This rework and recheck of the system delayed pesticide testing until late August. Testing was discontinued by October 1, 1980.

A-5.0 FIELD TEST RESULTS

A-5.1 ARCO Weed Killer "A" Lite

Three tests were run on this material on field weeds, dominated by creepers (blue bells). The first two tests were conducted with the sampling probe pointing into the fan-induced wind, which is to say, in the direction of the sprayed target vegetation. Aerosol collected in the air filter of the OVA analyzer and spoiled the test. In the second test, the sampling line was heat traced, but condensation or oil accumulation nonetheless occurred at the same point in the unheated portion of the sampling line. It was therefore decided that volatilization of drift particles for transport to the detector would not be practical. The sampling probe was therefore reversed and the drift allowed to settle in the chamber before activating the fan. The third test was conducted in this mode.

As in the previous two tests, the ARCO Weed Oil was applied straight (no water diluent) at a rate of 38.6 gals/acre. The wind velocity in the spray chamber was set at 5.0 mph. The average internal temperature during the interval monitored (50 min) was 72°F, the average R.H. was 9 percent (!) for the same period.

After the spray was applied, no change in THC reading over inlet air THC level was noted. It was concluded from this test that the material was too involatile to be detected by the test configuration being exercised.

Because vapor pressure data had just been compiled on non-synthetic pesticides by Eureka Laboratories (Ref. A-1), calculations were initiated to determine what levels of the ARCO Weed Oil might occur in the field apparatus. These calculations are presented in Appendix B. They involve three approaches. The first two cases involve the use of Hartley's equation (Ref. A-2 provides a review discussion of this and other empirical evaporation equations) incorporating Eureka Laboratories vapor pressure (Case 1) and vapor pressures derived from ARCO's typical distillation-range values for the product (Case 2). The third case was based on the results obtained in the Task II laboratory tests using the average molecular weights from both the Case 1 and 2 calculations. The results can be tabulated as shown in Table A-3.

These results were, of course, disturbing and were reported to the RCM (the Case 3 results being provided later, since Task II had not yet been begun at this point). The quandry was that a methane-calibrated THC analyzer (FID-type) would furnish readouts that would be 10 to 12 times higher than the tabulated concentrations because of the carbon number difference. In view of the field test results, the Case 2 values could not then be believed (since they would be easily discriminated from background on the OVA) nor could the

TABLE A-3. CALCULATED EXHAUST THC CONCENTRATIONS FOLLOWING THE APPLICATION OF ARCO WEED OIL IN THE FIELD TEST APPARATUS
CONDITIONS: WIND SPEED = 5.0 mph; temp.=86°F
SOURCE: APPENDIX B

Case	Basis of Calculation	Source of Vapor Pressure Data	Calculated Exhaust Hydrocarbon Level, ppb*
1	Hartley's Eq.	Ref. 1	8.2
2	Hartley's Eq.	Calc'd. from ARCO data	140-590†
3	Task II Results	N.A.	14.5-26.1§

*Expressed as the material itself and not methane.

†The range corresponds to the low and high end vapor pressures of the oil.

§The lower value was derived using the MW given in Ref. 1; the higher value is based on an MW derived using the ARCO data.

Case 1 results be proved since 8.2 x 12 ppb is marginally resolvable on an instrument such as the OVA. This situation thus lent impetus to the initiation of Task II so that the evaporation rates of the materials could be compared and the field test protocol perhaps revised to accommodate the problems recognized.

A-5.2 Chevron Weed Oil

Following the negative results obtained with ARCO Weed Oil, field testing was abandoned and the Task II work was initiated and completed. Since it was noted that the Chevron Weed Oil was clearly more volatile (see Figures 3-5 and 3-7) than the ARCO product, the former was first used when field testing was resumed the following year.

A single test was made on the product. Application was at 28.8 gals/acre undiluted. Weeds covered 80 percent of the target area and were a mixture predominated by blue bell and milk weed. The temperature at time of application was 70°F; R.H.=60 percent. The OVA showed some activity before the fan was turned on. These were sharp excursions of as much as 1 ppm above established background reflecting momentary gusting in the envelope. After fan initiation at reduced speed, a possible above-background differential of 0.1 to 0.2 ppm may have occurred for ten minutes or so. The instrument was, however, drifting badly so that such a small effect was not verifiable. The average wind speed in the envelope was 2.79 mph.

A-5.3 Diesel Oil No. 2

Because the test results with the Chevron Weed Oil were essentially negative, testing was resumed with the next more volatile material, diesel oil #2. An application rate of 31.2 gals/acre was calculated for an area with about 60 percent weed coverage. Air temperature in the envelope was slightly below 60°F and R.H. 93 percent.

On application, draft-promoted THC excursions again occurred in the ten minute drift-settling period before the fan was turned on. These ranged up to 5.5 ppm above background (2.3 ppm), but averaged about 2.5 ppm above background during the waiting period. With fan on, a THC spike occurred lasting about one minute and peaking at 1.2 ppm above background. The signal then decayed to background. In fact, the input air appeared to be 0.1 ppm richer in THC than the exhaust air. The average wind speed in the envelope was 2.88 mph during the test.

A-5.4 Chevron Weed Oil - Concentrative Sampling Tests

Because the results thus far obtained demonstrated that the emission rates of the materials were too low to discriminate from background, an alternative approach was investigated. This consisted of drawing streams of exhaust and inlet air through sorbent tubes. The contents were then extracted and analyzed by gas chromatography to estimate the two integrated catches.

The sampling arrangement consisted of two runs of 1/4-in. teflon tubing, essentially paralleling those used for continuous monitoring. Each connected with a charcoal sorbent tube (SKC West Jumbo, 1 gram), a needle valve and quick opening valve. The tubing runs were then joined at a T from which a single line led off to a dry gas meter (0.1 cu.ft./revolution) and a gas pump (Spectrex Model AS300). Flow through each was independently set at the same flow (1.62 ± 0.04 l/min.) and then total simultaneous flow through both was then measured (2.36 l/min.). The flow through each tube was then taken as half that amount (1.18 l/min.). Flow rates were checked on each set of sample/background sorbent tubes before and after exposure. No significant unbalances in total or individual flows were noted. Sorbent tubes were changed once an hour on the first day of testing and every two hours on the second day of running. The fan was allowed to run overnight at a nominal setting of 2.5 mph.

The conditions recorded or noted during the two consecutive tests made with Chevron Weed Oil are shown in Table A-4.

The exposed tubes were sent to Analytical Research Laboratories, Inc. (ARLI) in Monronia for analysis. The procedure followed was to extract each tube (fore- and backup-sections) with methylene chloride, then concentrate the extract for G.C. analysis. The range of interest was specified as from n-C_{10} to n-C_{20}. This was based on the results obtained at the CARB Haagen-Smit Laboratory, which analyzed the head vapors of the same material by GC/MS (Ref. A-3). The sample was characterized by the CARB analysts as

TABLE A-4. TEST CONDITIONS IN THE APPLICATION OF CHEVRON WEED OIL WHILE ACCUMULATING HYDROCARBON EMISSIONS ON SORBENT TUBES

Parameter	Test Run	
	1	2
Application Rate, Gal/Acre	32.9	44.4
Weed Coverage of Plot, %	60	70
Avg. Wind Speed, mph (n)*	2.2 ± 0.4 (10)	2.5 ± 0.2 (12)
Avg. Temp., °F (range)	69 (58-79)	67 (60-77)
Avg. R.H., % (range)	64 (45-90)	69 (48-87)
Avg. Water Evap. Rate, mm/day	†	5.0
Test Duration, hrs.	30	30

*Number of triplicate measurements made during the test.

†Instrumental malfunction.

predominating in alkyl naphthalenes but containing adequate n-alkane "markers" (several percent levels) in the range of interest at every carbon number above dodecane.

Because doubt still existed as to the catches that would be realized, the ARLI analyst was instructed to work initially only two sets of tubes from the first test run. Those were the set taken one hour immediately after spray application and the set taken during the last two hours of the 30 hour monitoring run.

The analytical approach, one constrained by economic factors, was to develop FID chromatograms over the area of interest. These would then be quantitatively expressed by applying stepped response factors for each group of peaks, fused or discrete, that occurred within each n-carbon number range. Reference chromatograms were run, of course, to establish both the elution volume of each of the n-alkanes used and their specific response factors.

Following an electronic integration, the mass yield of each carbon number group would be totalled. The yield from the exhaust air sorbent tube would then be corrected by subtracting out the background tube total yield.

Analysis was done on an OV-101 column. (1/8-in. dia. x 3 ft. (1)) loaded to 10 percent on 80/100 mesh Chromasorb W. A Hewlett-Packard gas chromatograph (Model H-P 5713) was used, temperature programmed from 120°C (5 minute dwell) to 270°C at 8°C/min. Flow rates in cc/min. were: helium-30; hydrogen-40; and air-300. The charcoal tubes were extracted with 2cc methylene chloride which was reduced in volume to 50 µl; 5 µl aliquots were injected.

Recovery tests were conducted by placing milligram quantities of the oil on the charcoal. The tubes were then extracted in the same manner as loaded tubes. After solvent removal, however, the yield was weighed back and corrected for a small blank effect. The recovery efficiency was found to be only 21 percent. A batch desorption was also tried as is done in determining adsorption isotherms. The purpose was to determine if the extraction technique itself was a limiting factor. The results obtained were essentially identical.

While the results obtained suggested that an alternate extraction solvent would have been preferred, the hydrocarbon catches found on the loaded tubes made this issue secondary in importance.

The results obtained with the field-exposed tubes indicated that little if any hydrocarbon material was collected on the charcoal traps. In the first hour tube sets, the mass yield was estimated at 2.1 μg in the exhaust air tube and 0.27 in the background tube. In the final 2 hour tube sets, the values were 0.21 and 0.38, respectively. The values for the first tube set can be worked to say that the yield was 25 $\mu g/m^3$, which corresponds to 3.9 ppb of dimethylnaphthalene, a reasonable choice for the average member of the mixture. While this agrees reasonably well with the value calculated by Hartley's equation (Case 1 of Appendix B = 8.2 ppb), the analytical value used to obtain it is hardly reliable. The sample to background ratio is less than 8.

To dimension the variation that one can expect in working with the charcoal tubes, two blanks were extracted. These produced yields based on the same G.C. technique of 0.31 and 4.6 μg. This demonstrated that the data obtained fell well within the error band of the measurement. The results also show that if the above blank values are typical, that the sample volumes would have to be increased by a factor of at least 10. This assumes, of course, that the values obtained for the first hour's run were near detection limit, an assumption that actually cannot be proved.

Analysis of the other sets of tubes was cancelled. Redesign of the sampling system to enable acquisition of hydrocarbon vapor from much larger volumes of sample gas was not attempted. Accumulative sampling with its attendent high laboratory costs was outside the scope of the program.

A-5.5 DEF-6

An important test in the mind of the program's first RCM was to measure hydrocarbons (predominantly ethylene) emitted by cotton plants sprayed by a defoliant. Such phytogenic emissions would be highly photochemically reactive.

Accordingly, UCSCFS personnel planted 1/3 acre of cotton (Delta Pine 70) in late spring 1979. It was hoped that the plants could be sprayed late that summer even though they had been planted too late to bloom that year. The presence or absence of boles was not considered important to the test. As it turned out, little spraying would be done the first year. The stand therefore overwintered, died back then crown sprouted the following spring. The crop bloomed and was bearing fully erupted bottom-boles when sprayed the following year.

Because the OVA has a GC capability, the feasibility of monitoring ethylene in that mode was investigated. The principal concern was the unusual gas-flow arrangement designed into the instrument. In normal survey-mode, the air sample passes through a gas loop in the GC valve and then runs to the detector, serving both as oxidizer and analyte carrier. Hydrogen fuel, on the other hand, flows through the GC columns (or unpacked tubing installed in their place) to the detector. When the GC valve is actuated, putting the instrument in the GC mode, the gas loop contents are carried onto the G.C. column with the hydrogen carrier. The sample air stream is simultaneously diverted into a charcoal bed where the air is theoretically reduced to zero THC before entering the detector as oxidizer minus analytes. This technique thus avoids the situation of attempting to see the GC partitioned components on top of a base line corresponding to their combined concentrations.

The drawback noted was that methane breaks through the charcoal air-cleaner about as fast as it is retained on the GC column. Since ethylene eluted immediately after methane, an unintelligible trace results which was additionally obfuscated by pneumatic transients caused by the backflush operation required in this chromatography. It was accordingly decided that continuous THC monitoring would have to be employed.

The conditions observed or recorded in the one spray run made were shown in Table A-5.

Again, no THC offsets from intake air quality were recorded in the exhaust air. The fan was allowed to run overnight with monitoring resuming the next morning, again with negative results.

An attempt was made to contact the previous RCM (now with Lake County Public Health Office) to obtain specific information as to the phenomenology of the ethylene release. Because he was unavailable at the time, the academic sponsor, Dr. Walter Farmer, was phoned. He suggested consultation with several workers at Texas A&M who had studied the phenomenon (Refs. A-4 and A-5). Dr. Morgan was reached. He advised that ethylene release typically peaked at about 4 to 5 hours following defoliant application and that the accumulated levels (using a stagnant air envelope over the test plant) would not likely exceed 10 ppb. He agreed that using the dynamic test configuration in operation at the UCSCFS would not likely result in the detection of the effect. Further testing was accordingly abandoned.

A-5.6 Beacon Weed Killer No. 5

Following what proved to be a series of negative tests, it was hoped that in working with a carrot oil, the most volatile of all the pesticides considered, positive results would be obtained. This expectation was rewarded. In all, eleven tests were conducted of which two were aborted due to equipment failures. The balance of the tests all produced exhaust emissions that could be monitoried above background. Unfortunately, the weather was rather monotonous and the hoped for variation in average temperature did not occur to any marked degree.

The test plot consisted of a field cultivated, seeded (Imperator 58-Champion Seed Co.) and irrigated by UCSCFS personnel. The plantings of twenty-foot sections were staggered in time so that the height of the young plants would be about the same in all tests. As it turned out, there was considerable natural variability and the plant height ranged from about 2 to 5-inches.

TABLE A-5. TEST CONDITIONS IN THE APPLICATION OF DEF-6 FOR THE DEFOLIATION OF COTTON PLANTS

Parameter	Calculated or Recorded Value (First Day)
Application Rate, pints/acre	4*
Avg. Wind Speed, mph (n)†	2.50 ± 0.06 (3)
Avg. Temp., °F (range)	72 (60-98)
Avg. R.H., % (range)	68 (26-92)
Test Duration, hrs.	20

*Dissolved in 13.5 gal. diesel oil #2 (per acre)

†Number of triplicate measurements made during the test

The spray boom was fitted with eight nozzles so that the pattern played on each side of the four berms treated. The variables exercised were application rate, fan speed, soil moisture, and (by afternoon or morning scheduling of the tests) temperature. The conditions prevailing during each of the nine tests are shown in Tables A-6 and A-7.

It will be noted that the wind speeds varied considerably from the set points of 2.5 and 5.0 mph. In tests 2, 5, 6, 8 and 9, the wind was atypically out of the North (into the fan), thus causing lower readings than normal. Thought was even given to the idea of moving one of the small wind screens to a short distance in front of the fan. Since, however, the wind was varying considerably, the idea was abandoned.

Following application and before the fan was turned on, THC readouts well above background were seen. Depending on air movement inside the chamber, excursions sometimes exceeding 100 ppm were recorded. After the fan was started, readings as high as 35 ppm above background were recorded, which decayed fairly rapidly.

As mentioned earlier, instrument drift was too rapid to allow reliable data reduction from continuous strip chart readouts. Although the recorder was used, as both a timing device and level recorder, the test data consisted of a series of points. These are traces of several minutes duration of the inlet air THC followed by a like dwell on the exhaust THC. The difference between the best straight lines through each trace then provided pesticide emission THC. Periodic span and zero checks were made to insure accuracy. Differential readings were taken only after the fan had been started.

The points for each run were then manually plotted to furnish integratable curves, with 1 cm = 1 ppm THC (as CH_4) on the ordinate and 10 min. on the abscissa. The under curve area was then determined using a polar planimeter (Los Angeles Scientific Instrument Co. Model L-30-B).

In reducing the integrated methane-calibrated OVA readings to mass release values, an average molecular weight or molecule had to be selected for the carrot oil. CARB's analysis of Beacon Weed Killer No. 5 (Ref. A-3) showed almost 90 percent of the material to range from C_9H_{12} (trimethylbenzene) to $C_{11}H_{24}$ (hendecanes). Because the amount of material accounted for in the

TABLE A-6. TEST CONDITIONS IN THE APPLICATION OF BEACON WEED KILLER NO. 5 ON CARROTS (EXCLUDING MOISTURE DATA)

Run No.	Test Code*	Appl. Rate, Gal/Acre	Avg. Wind Speed, mph (n)†	Test Duration, hrs	Average Chamber Temp., °F (Range, °F)
2	$A_LV_LT_L$	71	1.3 ± 0.8 (5)	2.3	66(60-72)
3	$A_HV_LT_L$	100	2.7 ± 0.6 (4)	2.8	73(72-76)
5	$A_HV_LT_H$	102	0.9 ± 0.8 (5)	2.5	80(78-82)
6	$A_LV_HT_L$	52	3.1 ± 0.8 (5)	1.9	76(70-80)
7	$A_HV_HT_H$	126	5.0 ± 0.5 (5)	2.5	77(75-79)
8	$A_HV_HT_L$	103	3.9 ± 0.5 (5)	2.5	70(63-70)
9	$A_LV_HT_H$	63	3.4 ± 0.7 (5)	2.9	79(77-81)
10	$A_HV_LT_H$§	113	2.8 ± 0.7 (7)	3.6	74(68-77)
11	Hi Soil H_2O	117	2.5 ± 0.9 (10)	5.4	77(68-78)

*A = appls. rate; V = wind speed; T = temperature. Subscripts denote high (H) or low (L) target conditions.

† - n is number of triplicate measurements made during a test.

§ - intent on test #10 ($A_LV_LT_H$) was not realized due to error.

TABLE A-7. MOISTURE DATA OBSERVED DURING THE APPLICATION OF BEACON WEED KILLER NO. 5 ON CARROTS

Run No.	Average Chamber R.H., % (Range, %)	Water Evaporation Rate, mm/day	Soil Moisture, %	
			Before Application	At Test Conclusion
2	65(51-89)	0.4	6.1	5.3
3	51(49-54)	4.3	5.2	4.4
5	37(31-44)	negl.*	5.6	5.7
6	46(40-54)	negl.	5.7	5.6
7	48(45-52)	negl.	5.5	5.3
8	52(44-70)	negl.	- (†)	-
9	42(37-47)	negl.	-	-
10	49(41-57)	3.2	-	-
11	45(36-54)	3.2	17.1	12.8

*It is believed that the evaporimeter malfunctioned during runs #5 through #9.
†Soil samples were improperly taken in runs #8 through #10.

tests was found to be low in trial calculations, it was decided to use n-nonane (C_9H_2) as the model. It represents the last material off in the first 25 percent distilled.

Correction of the methane-calibrated FID concentration levels involved the following adjustment:

$$C_{nonane} = \frac{C_{CH_4} \cdot R_{CH_4} \cdot MW_{CH_4}}{R_{nonane} \cdot MW_{nonane}} \qquad (1)$$

The R values are to correlate FID reponse factors for equal masses of an analyte. According to Esso Research's Dietz (Ref. A-6), these values are 0.97 and 0.98 for methane and n-nonane, respectively.

As developed in Appendix B, air flow through the test chamber is 8800 $\bar{V}$ cu.ft./min., where $\bar{V}$ is the average wind velocity in mph.

The volumetric flow, therefore, of hydrocarbons (as n-nonane) is thus:

$$F^{v}_{nonane} = \frac{C_{nonane} \cdot 8800\,\bar{V} \times 28.32 \times 10^{3}}{10^{6}}, \text{ cc/min}$$

Introducing equation (1):

$$F^{v}_{nonane} = \frac{249V \cdot C_{CH_4} \cdot R_{CH_4} \cdot MW_{CH_4}}{R_{nonane} \cdot MW_{nonane}}, \text{cc/min}$$

or, $F^{v}_{nonane} = 3943\ C_{CH_4} \cdot \bar{V}/MW_{nonane}$, cc/min.

Assuming perfect gas behavior, the mass flow of nonane is:

$$F^{m}_{nonane} = \frac{MW_{nonane} \cdot 1.0 \cdot 3943 \cdot C_{CH_4} \cdot \bar{V}}{MW_{nonane} \cdot RT}, \text{g/min}$$

or $$F^{m}_{nonane} = \frac{48 \cdot C_{CH_4} \cdot \bar{V}}{\bar{T}}, \text{g/min}$$

The results of the graphing and integration of the data from the nine tests are summarized in Table A-8. The graphs are presented as Figures A-6 through A-14. The analysis of these data is discussed in Section A-6.0.

A-5.7 Citrus and Fallow-Ground Testing

These originally planned tests were not conducted, being considered pointless. In the case of citrus, all of the usable oils appearing on the candidate list are much less volatile than those already tested with negative results. Although application rates of citrus oils for the control of mite and scale is much higher than for weed oil use, this still would not promote the likelihood of vapor detection.

The testing of fallow ground was proposed by the academic sponsor to insure that any THC contributions from the soil itself would be taken into account. The sensitivity demonstrated by the test configuration employed was such that in repeated checks between inlet and exhaust THC levels, no defensible differentiation was recorded regardless of what was housed by the envelope.

A-6.0 DATA ANALYSIS

A-6.1 General Observations

It is very clear from the results obtained that the program objective of developing pesticide emission factors could not be achieved. Emissions were only detected in the case of carrot oil and in that case, it is uncertain as to whether all the emissions resulting from the applications were measured. Correlations were nonetheless attempted, yielding results that may have applicablity for conservative emissions estimating if they can be confirmed.

The evaporation characteristics noted in the field with carrot oil conformed with those seen by other investigators working with synthetic pesticides. The greatest loss occurs immediately following application. Gray and Weierich (Ref. A-7) estimated that 20 to 40 percent of s-ethyl-N,N-

TABLE A-8. HYDROCARBON RELEASES (EXPRESSED AS n-nonane) MEASURED DURING THE APPLICATION OF BEACON WEED KILLER NO. 5 ON CARROTS

Test No.	Test Condition Code*	Percent Applied Emitted+	Total Measured† Emissions, lbs. (as n-nonane)/acre
2	$A_LV_LT_L$	3.0	13.5
3	$A_HV_LT_L$	7.2	45.1
5	$A_HV_LT_H$	2.9	18.4
6	$A_LV_HT_L$	10.5	34.0
7	$A_HV_HT_H$	9.9	103.9
8	$A_HV_HT_L$	7.4	47.6
9	$A_LV_HT_H$	14.0	54.7
10	$A_HV_HT_H$	8.9	62.6
11	Hi Soil H_2O	6.9	50.3

*See footnote of Table A-6 for explanation of code.
†And was discernable above THC content of input air.

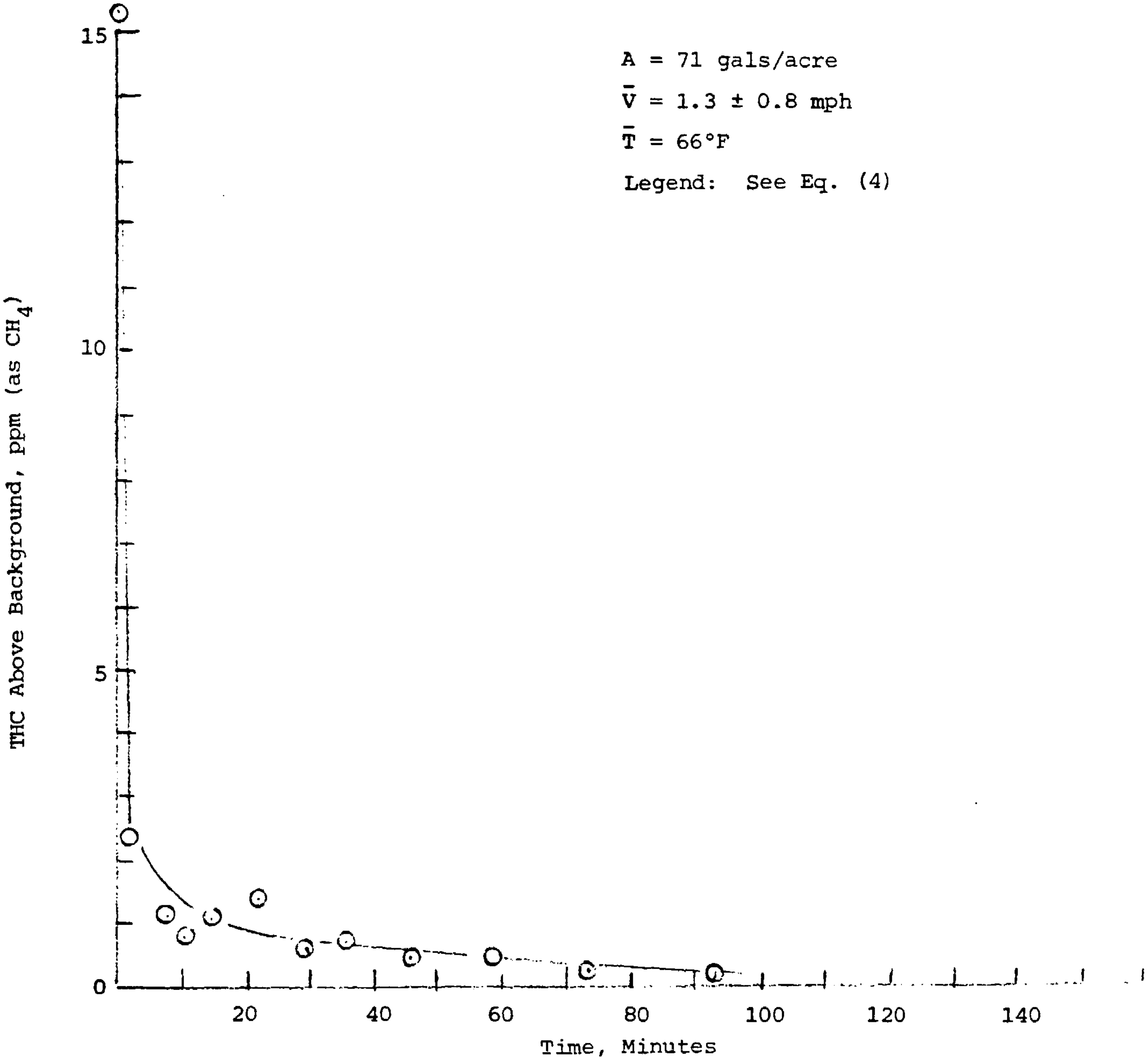


Figure A-6. THC Readouts of Carrot Oil Emissions - Run Number 2.

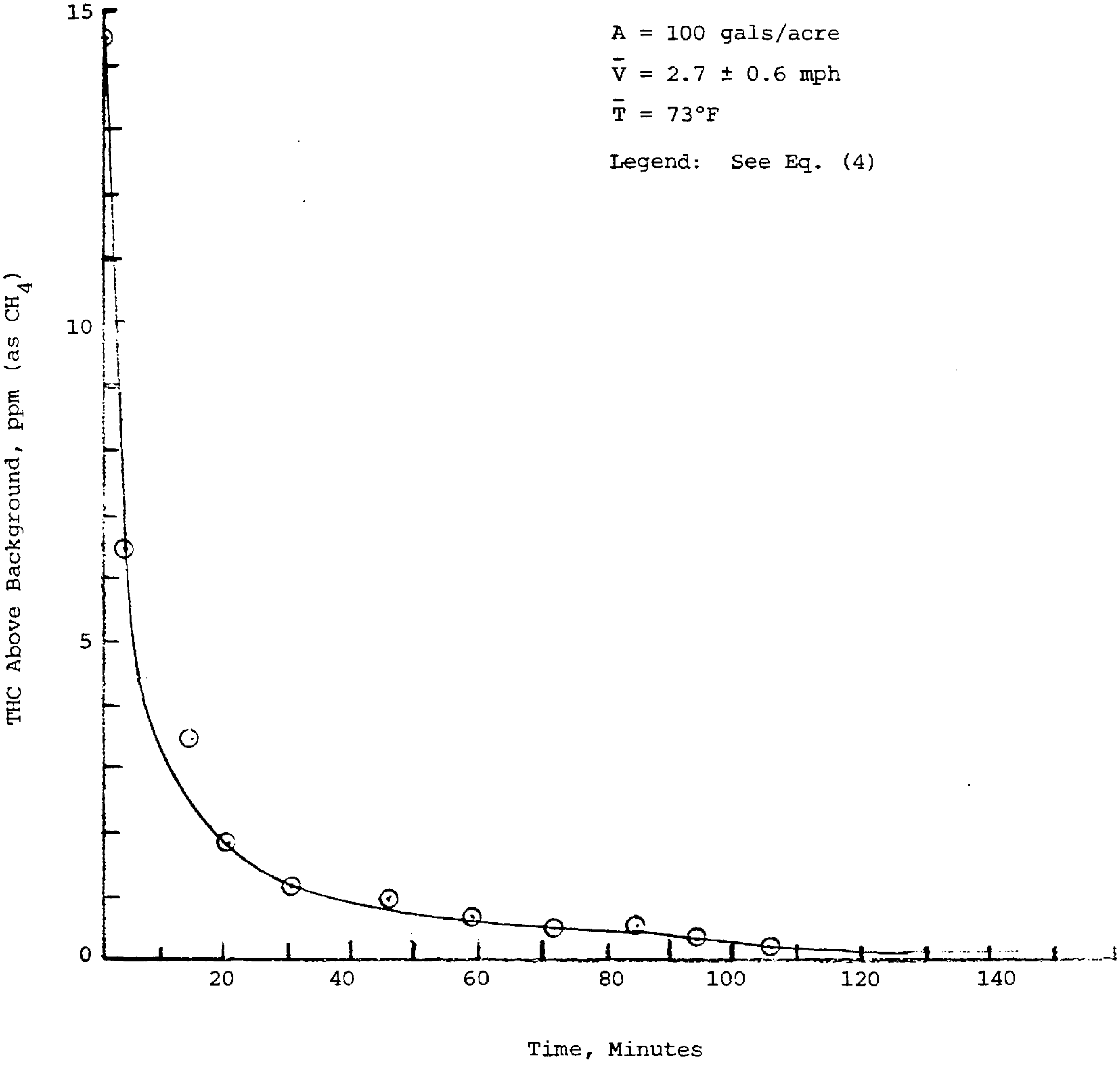


Figure A-7. THC Readouts of Carrot Oil Emissions - Run Number 3.

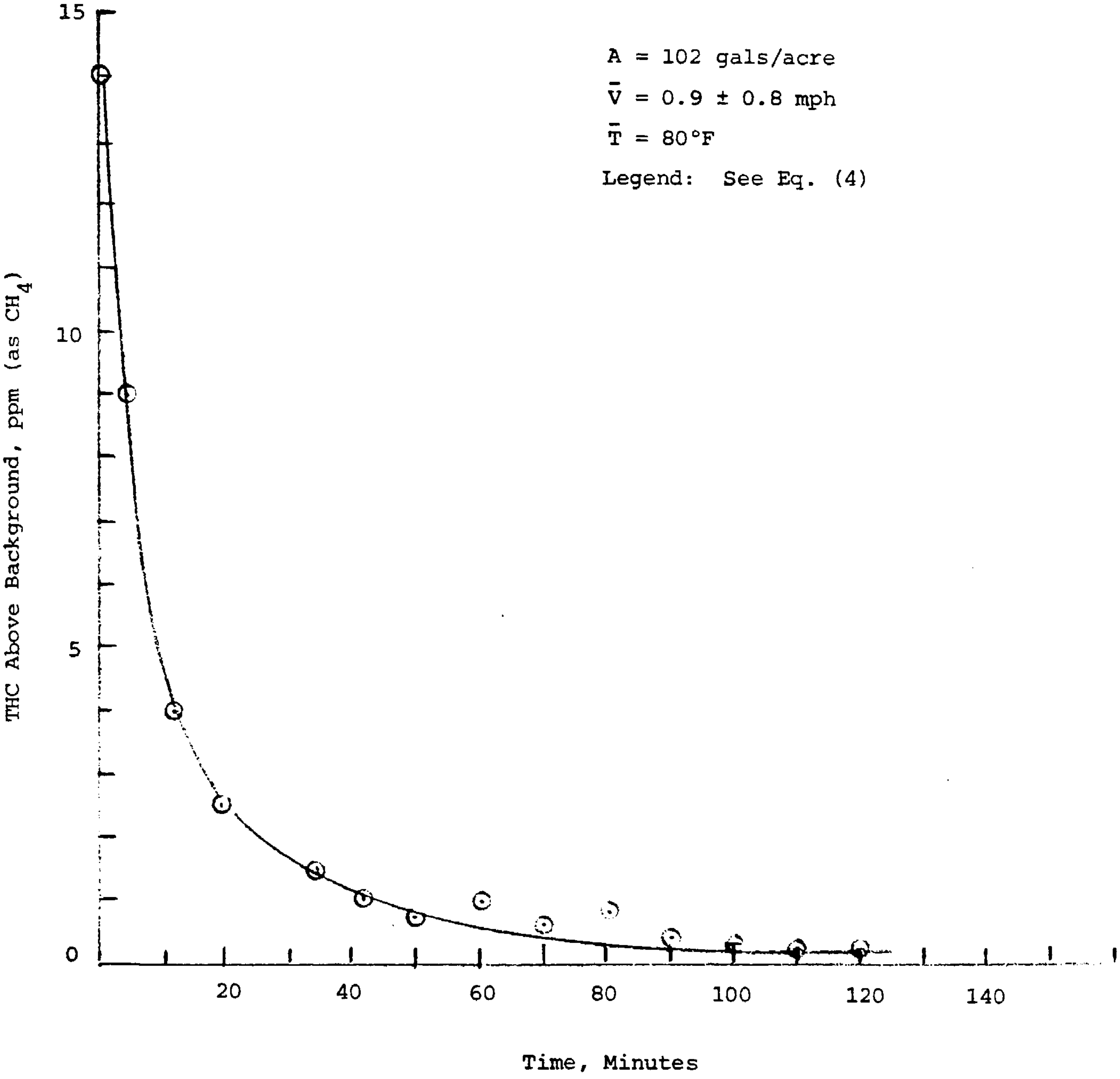


Figure A-8. THC Readouts of Carrot Oil Emissions - Run Number 5.

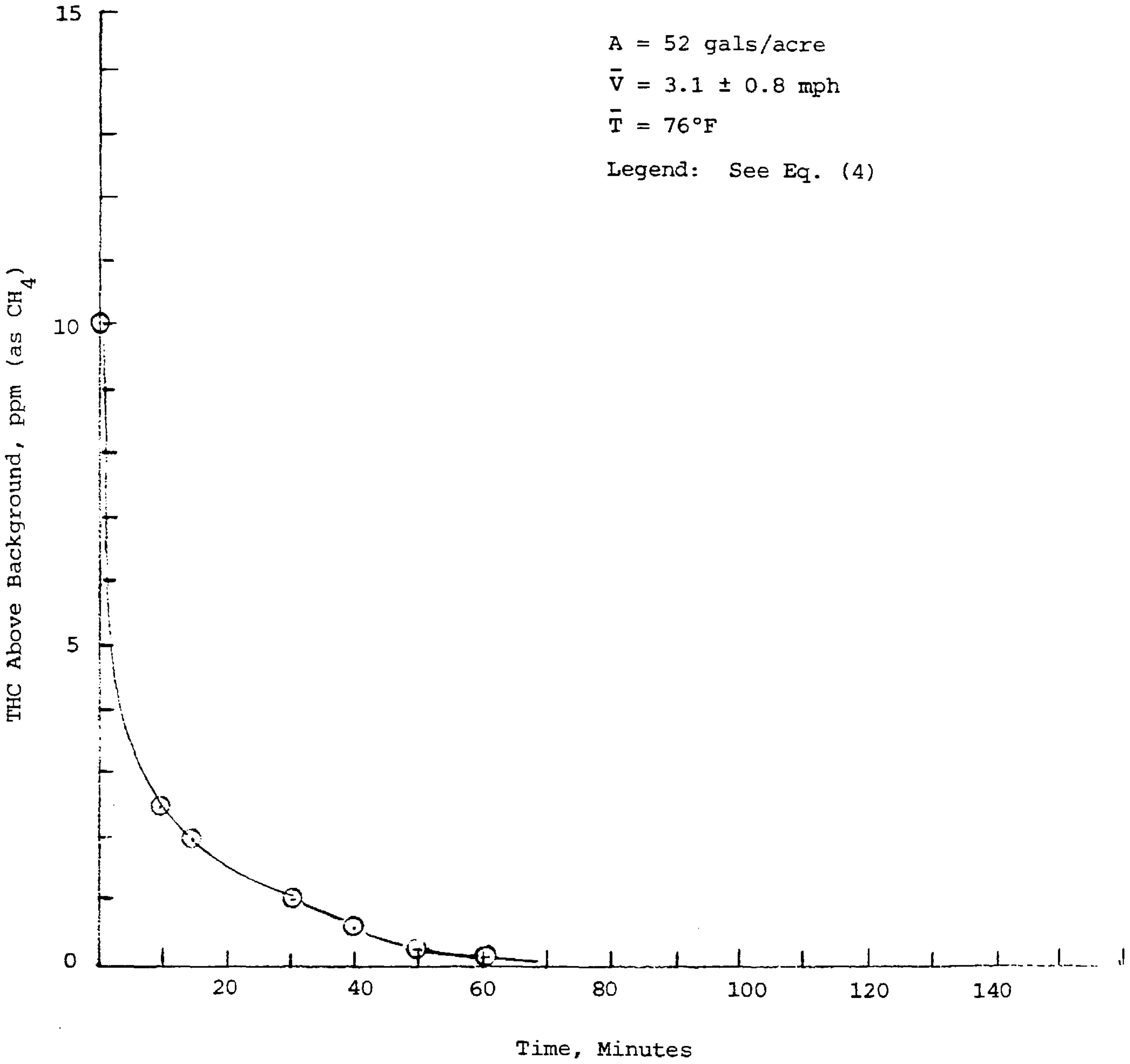


Figure A-9. THC Readouts of Carrot Oil Emissions - Run Number 6.

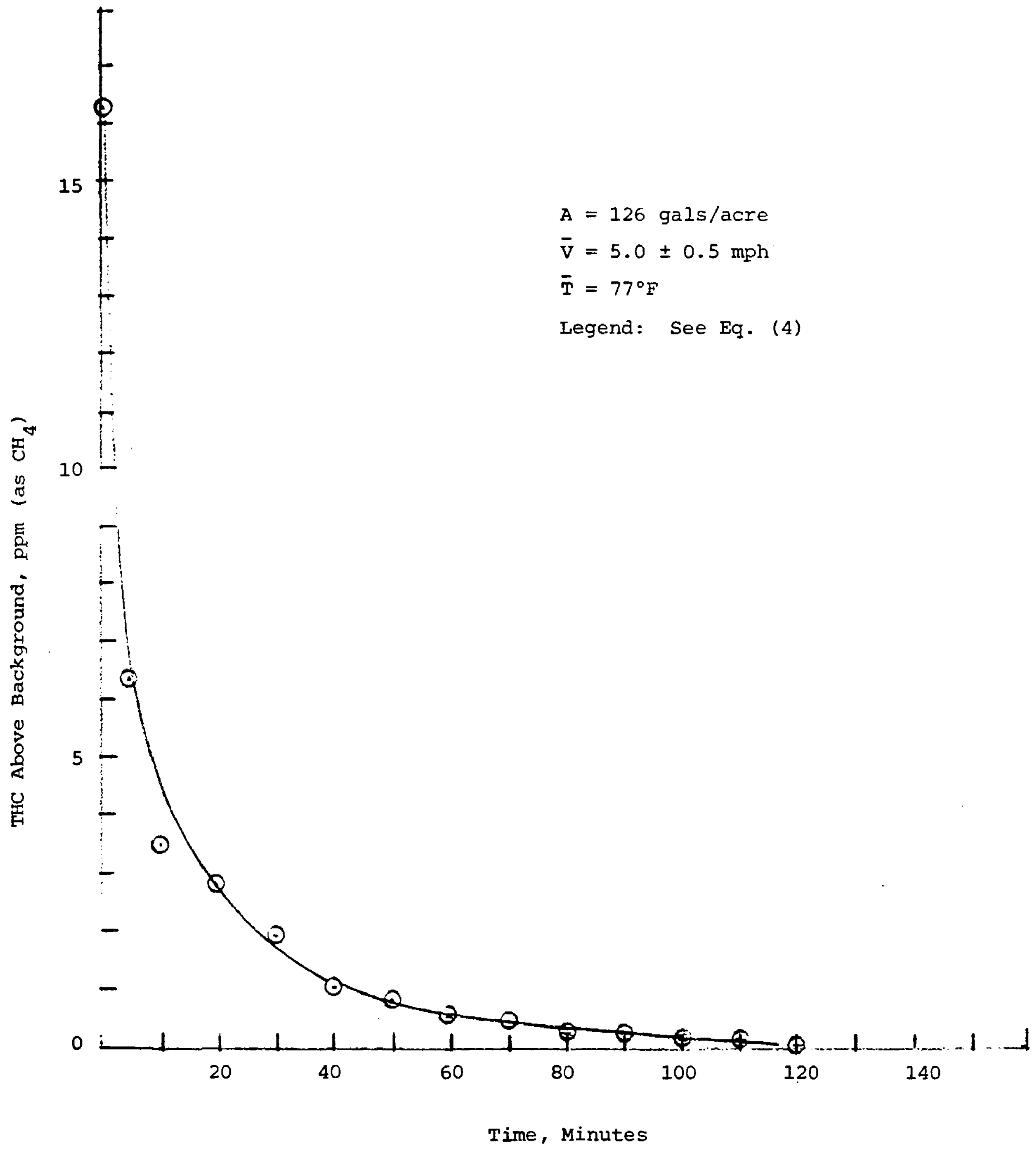


Figure A-10. THC Readouts of Carrot Oil Emissions - Run Number 7.

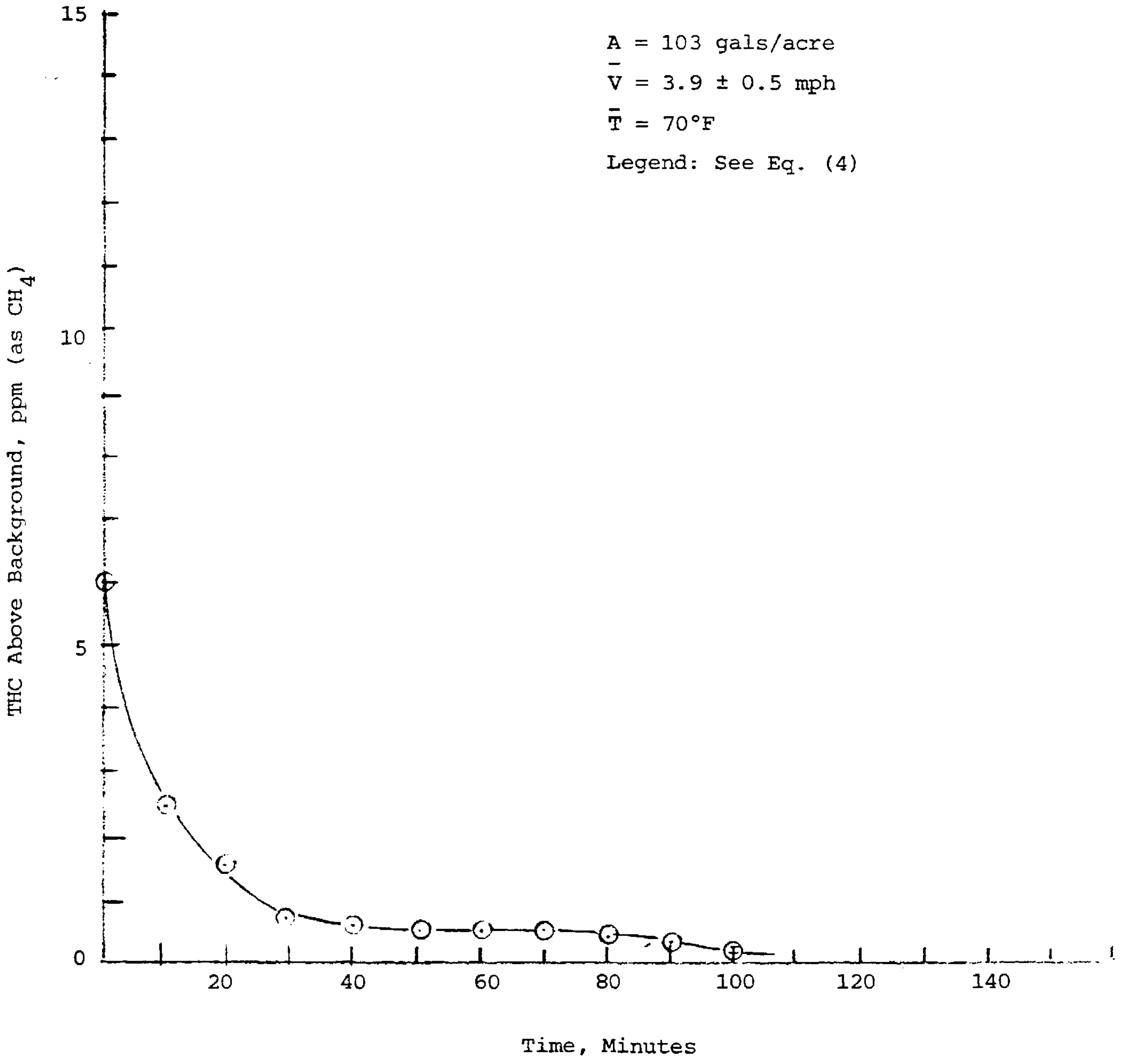


Figure A-11. THC Readouts of Carrot Oil Emissions - Run Number 8.

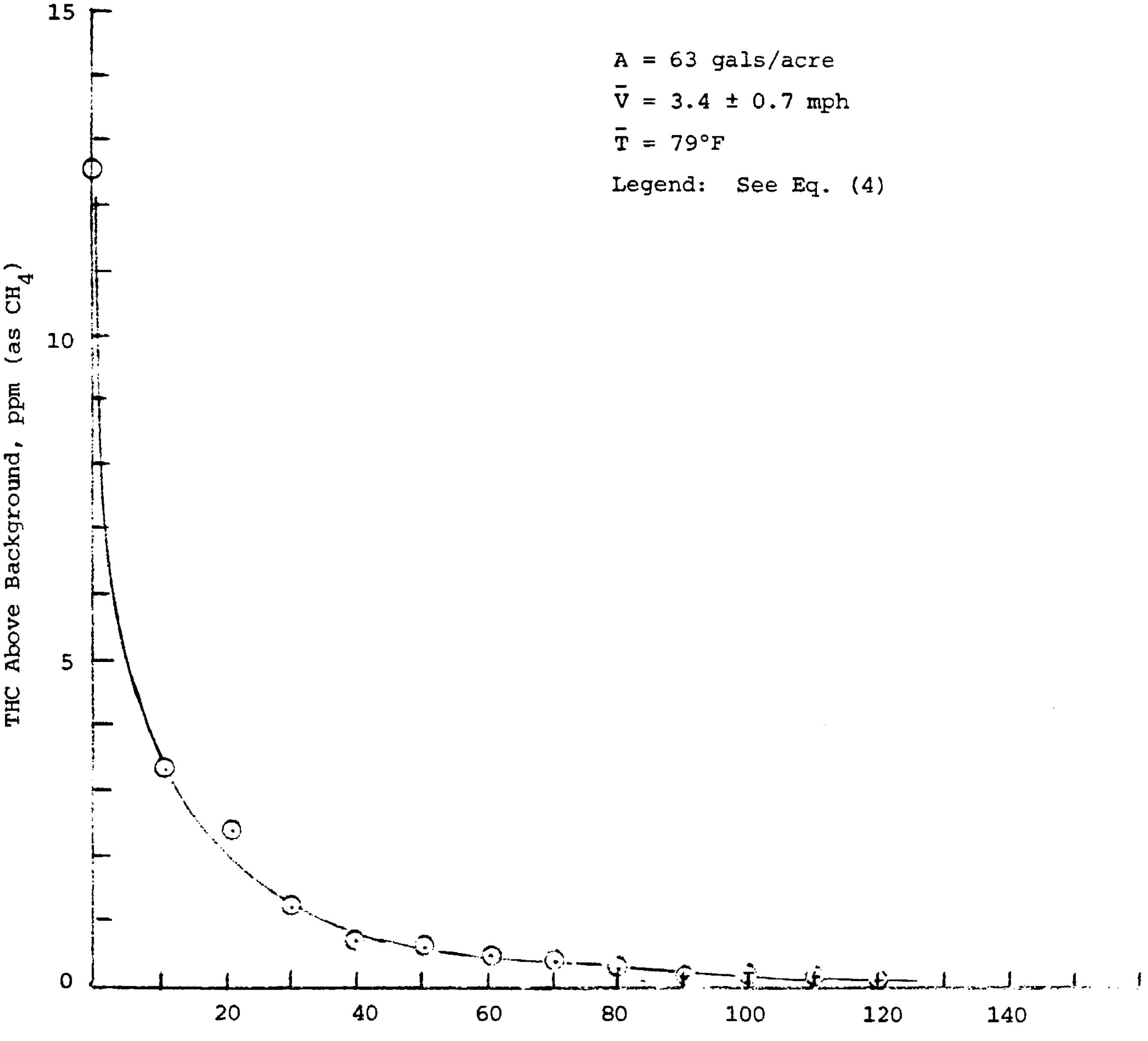


Figure A-12. THC Readouts of Carrot Oil Emissions - Run Number 9.

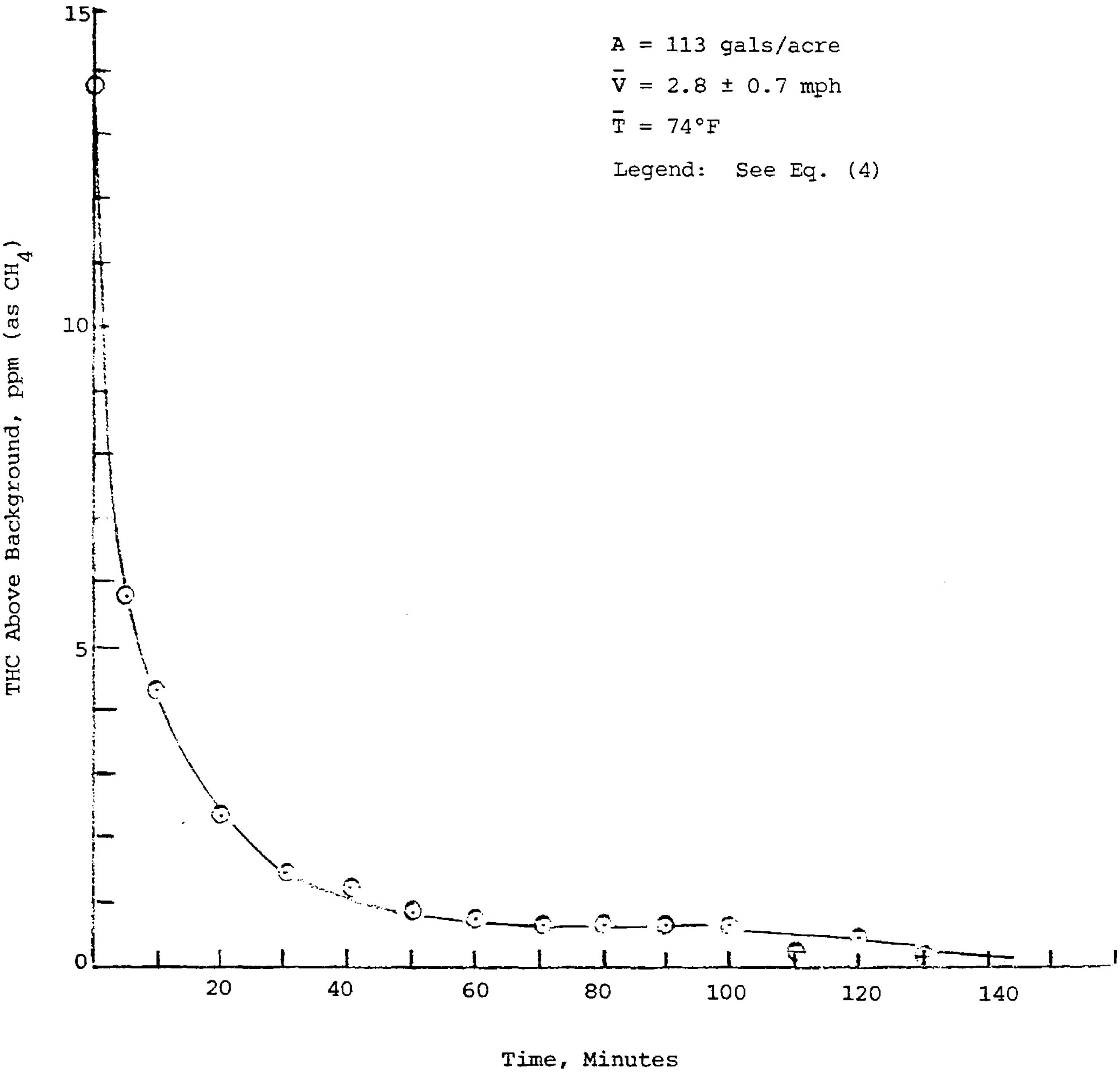


Figure A-13. THC Readouts of Carrot Oil Emissions - Run Number 10.

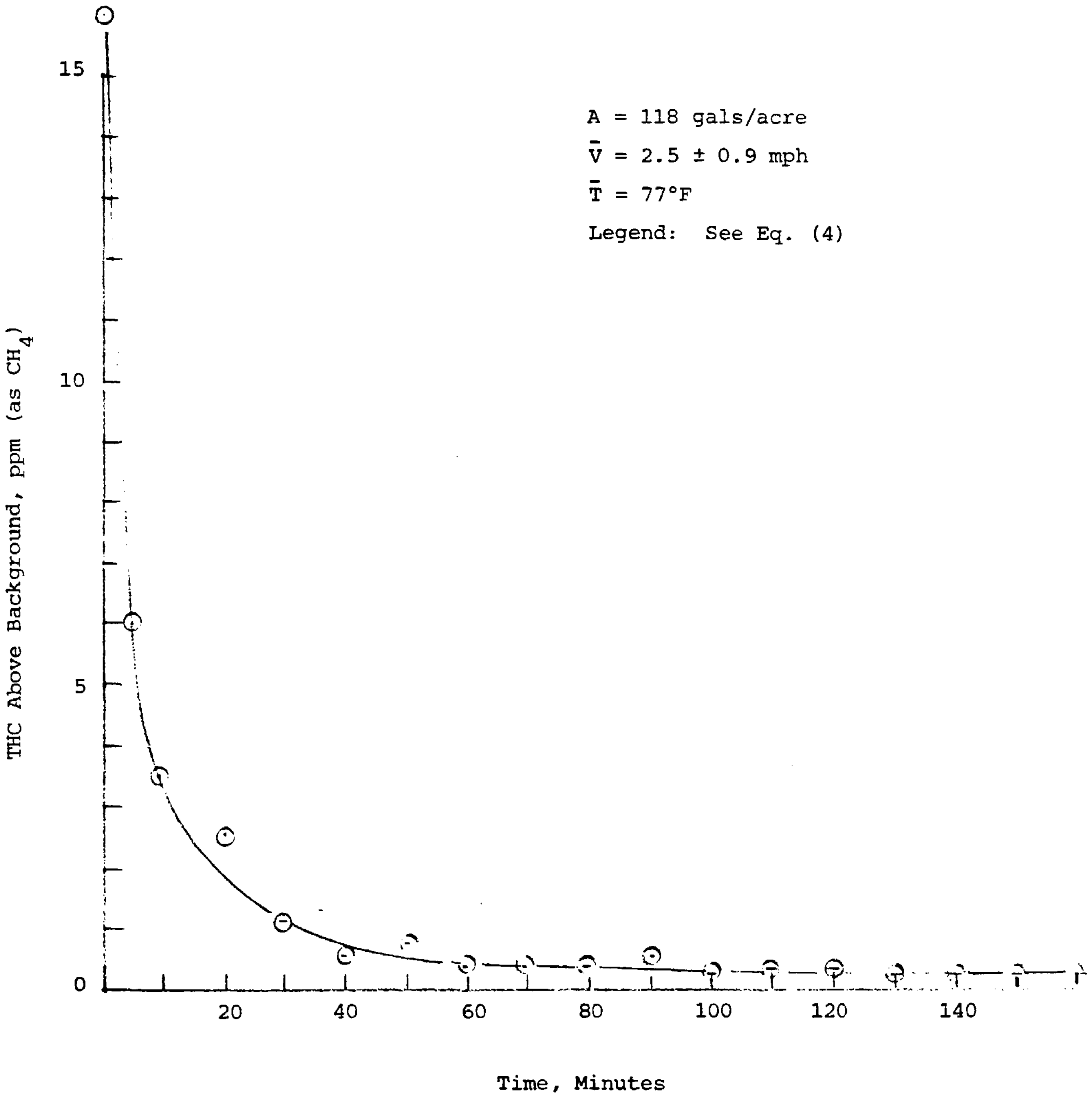


Figure A-14. THC Readouts of Carrot Oil Emissions - Run Number 11.

dipropylthiocarbamate (EPTC) was lost from the receptor plot within 15 minutes after application. Grover, et al. (Ref. A-8) found that 25 to 30 percent of butyl 2,4-dichlorophenoxyacetate vaporized within 30 minutes of application on a grassy plot. While the accounted recovery in the present testing did not range as high, the loss was clearly greatest in the first 20 to 30 minutes (see Figure A-6 through A-14). The difference in the amount evaporated, as mentioned earlier, could well have been influenced by the fact that the target area in carrot fields ready for weed killer is predominately soil. The phenomenon of evaporation seen in the present tests would appear to be one of rapid evaporation from a high surface-area substrate into which most of the oil has penetrated by capillary absorption. When the surficial layer is lost, then evaporation rate is controlled by the reverse capillary diffusion of the oil that replenishes the superficial layer.

A-7.2 Validity of Hartley's Equation

Considering the apparent affect of soil, it would then hardly seem likely that Hartley's equation (Eq. (1) Appendix B) would be appropriate for predominately soil targets. The equation compares open-pan evaporation of water with that of the applied pesticide, which is not in an open pan. In test #3, for example, the results of which are diagramed in Figure A-7, the evaporimeter showed a water evaporation rate of 4.3 mm/day.

If we consider the Beacon No. 5 carrot oil applied in terms of its analysis, as reported by CARB (Ref. A-3), we have a mixture ranging from about trimethylbenzene to n-hendecane (also called undecane). Using handbook values for vapor pressure, we can than estimate vapor pressures at the average test temperature of Run #3 (73°F or 296°K). Using the Clapeyron equation (Eq. (2), Appendix B), we find these to be 1.49 and 0.57 Torr for trimethylbenzene and n-hendecane, respectively. To avoid the complication of determining the vapor pressures of all the constituents, let us assume that the carrot oil has equimolar amounts of just the two compounds. The vapor pressure over the oil would then be 1.03 Torr (the average) when evaporation begins and about 0.57 Torr towards the end. The vapor phase would have an average molecular weight that would initially be the mean of those of the two compounds (M.W. = 138.3), slowly changing to that of hendecane as the more volatile trimethylbenzene is depleted. The actual weed oil would have about the same behavior. This assumes, of course, no reflux or any other effect that would produce fractionation. Taking the water evaporation rate at 51 percent R.H. and 73°F, we calculate a loss of 1600 lbs. H_2O/acre-hr. Plugging this and the vapor pressures of the organics into Hartley's equation, we find an initial pesticide evaporation rate of 421.1 lbs/acre-hr, decaying to 246.6 lbs/acre-hr (or 10.2 and 5.97 g/min, respectively). Using equation (3) of Appendix B, we find that the organic vapor level initially occurring would be 1.44 ppm, decaying to 0.74 ppm. Since 100 gal/acre was applied (or 673.5 lbs) in Run #3, all of the material would be gone in just two hours (673.5 x 2/(421.1 + 246.6)).

Converting the organic vapor levels to methane equivalents using Eq. (1) of this Appendix*, we would expect initial OVA readouts of 12.8 ppm, decaying to 5.4 ppm after 2 hrs. If we superpose these values over the results actually recorded for Run #3, the difference is marked (see Figure A-15). It is interesting to note, however, that the initial values plotted agree reasonably well. This is probably the only time a free-pan effect operates on the substrate. It would be interesting to compare Hartley's projections with results obtained with foliar targets where soil effect is less dominant.

A-7.3 Correlation Analysis

The results and observed conditions shown in Tables A-6 and A-8 were subjected to correlation analysis. The moisture parameters (soil moisture and relative humidity) were ignored. In the tests conducted, the soil moisture (except for Test 11 where wetting was deliberate) remained fairly constant through the testing, with on-shore morning fogs consistently ventilating the test site. The role of relative humidity is uncertain but should not have a pronounced effect. The average R.H. recorded was nonetheless not changing greatly from test to test.

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*The FID response factors for equal masses of n-hendecane and n-nonane are the same (0.98). Trimethyl benzene is 1.03. The initial mixture is taken as the average (1.00).

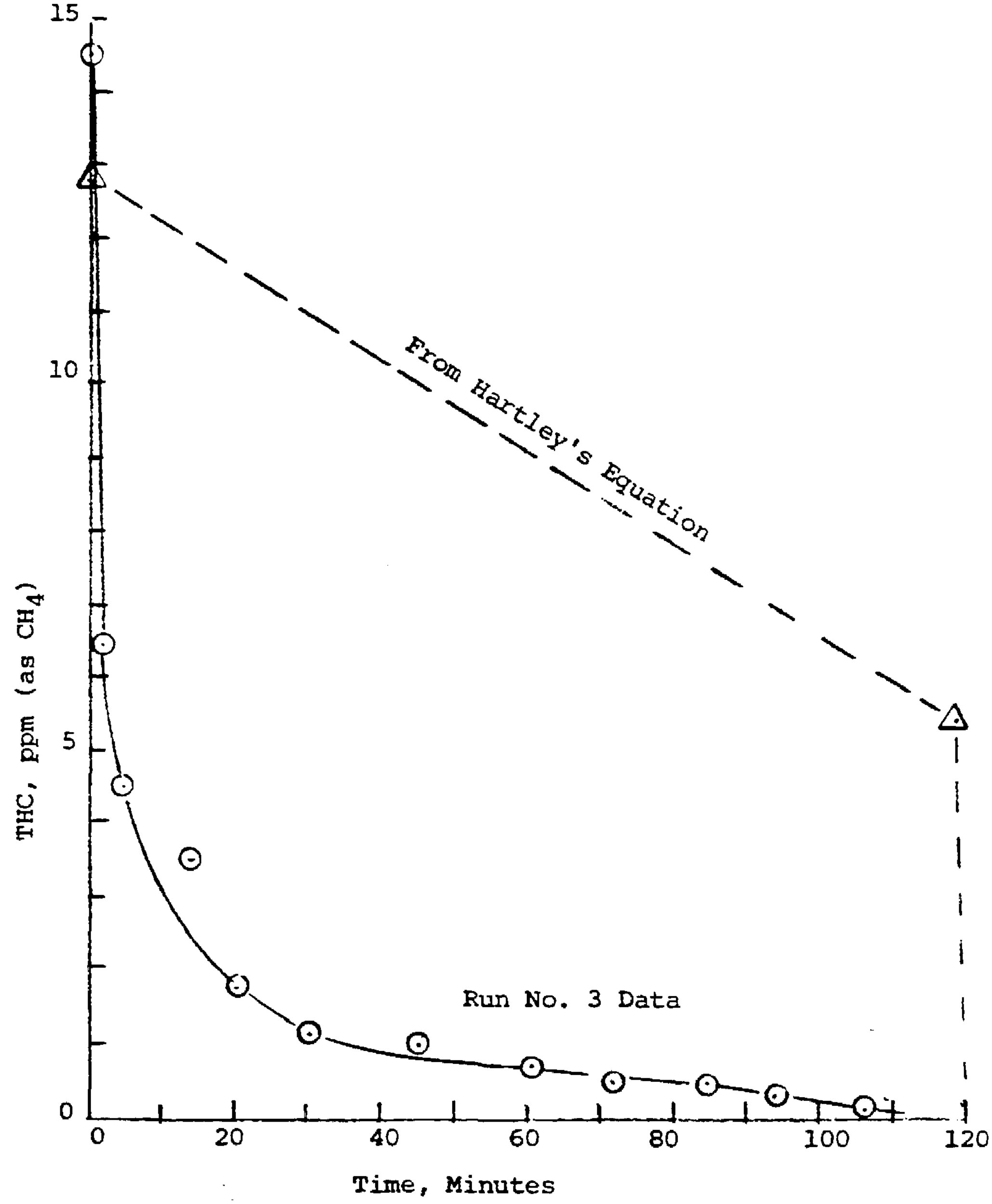

Figure A-15. Comparison of results of Run No. 3 with values obtained using Hartley's equation.

In considering the data obtained, Test No. 11 was omitted because there the surface soil moisture was considerably higher than what prevailed in the other tests. The approach used was to normalize the total measured emissions (Table A-8) for temperature differences using the Clapeyron term (See Eq. (2), Appendix B). That is:

$$E_n^T = E_m \cdot e - \frac{\Delta H_v(\bar{T}_m - T_r)}{R\ (\bar{T}_m \cdot T_r)} \qquad (2)$$

Where E_n is the temperature normalized and E_m the measured total emissions, lbs/acre (as nonane). The heat of vaporization (ΔH_v) was the average of n-hendecane and trimethylbenzene (11,100 cal/g-mole), although that of n-nonane (11,400 cal/g-mole) could also have been used. The temperatures (°K) are the average measured during the test ($\bar{T}_m$) and a benchmark temperature (T_r) within the test group. Run #2 had the lowest temperature (66°F) and was taken as the reference.

The next step was to normalize for wind effect. Figure 3-16 shows, in comparing the 2.5 and 5.5 mph, that the wind velocity will increase evaporation about 5 percent per mph increase. This neglects what may be a significant factor--the small temperature difference of the two curves. In any case, the wind normalization became:

$$E_n^v = [(\bar{V} - V_{lim})\ 0.05 + 1]^{-1} \cdot E_m$$

Where $\bar{V}$ is the average wind speed of the test and V_{lim} some low wind speed where linearity of the effect still operates. Wind speed for Run #5, the lowest, was used for this purpose. Thus the temperature and wind normalized emissions became:

$$E_n^{TV} = \frac{E_m \cdot e^{-f}}{[(\bar{V} - V_{lim})\ 0.05 + 1]} \qquad (3)$$

$$\text{Where,} \quad f = \frac{\Delta H_v(\bar{T}_m - T_r)}{(\bar{T}_m \cdot T_r)}$$

The values calculated for the emission terms are shown in Table A-9.

The E_n^{TV} numbers were then plotted on linear coordinates against application rates, the final remaining variable. The result is shown in Figure A-16. The least squares line offers a correlation coefficient of 0.62 and is expressed by the relationship

$$E_n^{VT} = 0.14A - 57.60 \qquad (4)$$

Where A is application rate, in lbs/acre rather than in gals/acre as used in Figure A-16.

TABLE A-9. WIND AND TEMPERATURE NORMALIZED EMISSIONS DATA FOR CARROT OIL TESTS

	Total Emissions, lbs/acre (as nonane)			
Test No.	Actually Measured	Temperature Normalized (E_m^T)*	Temp.&Wind Normalized (E_m^{TV})†	Application Rate (A), Gals/Acre
2	13.5	13.5	13.2	72
3	45.1	34.8	31.9	100
5	18.4	11.1	11.1	102
6	34.0	24.7	22.3	52
7	103.9	70.7	58.7	126
8	47.6	41.8	36.3	103
9	54.7	35.0	31.1	63
10	62.6	48.4	44.2	113
11	50.3	34.2	31.7	117

*See Equation (2)
†See Equation (3)

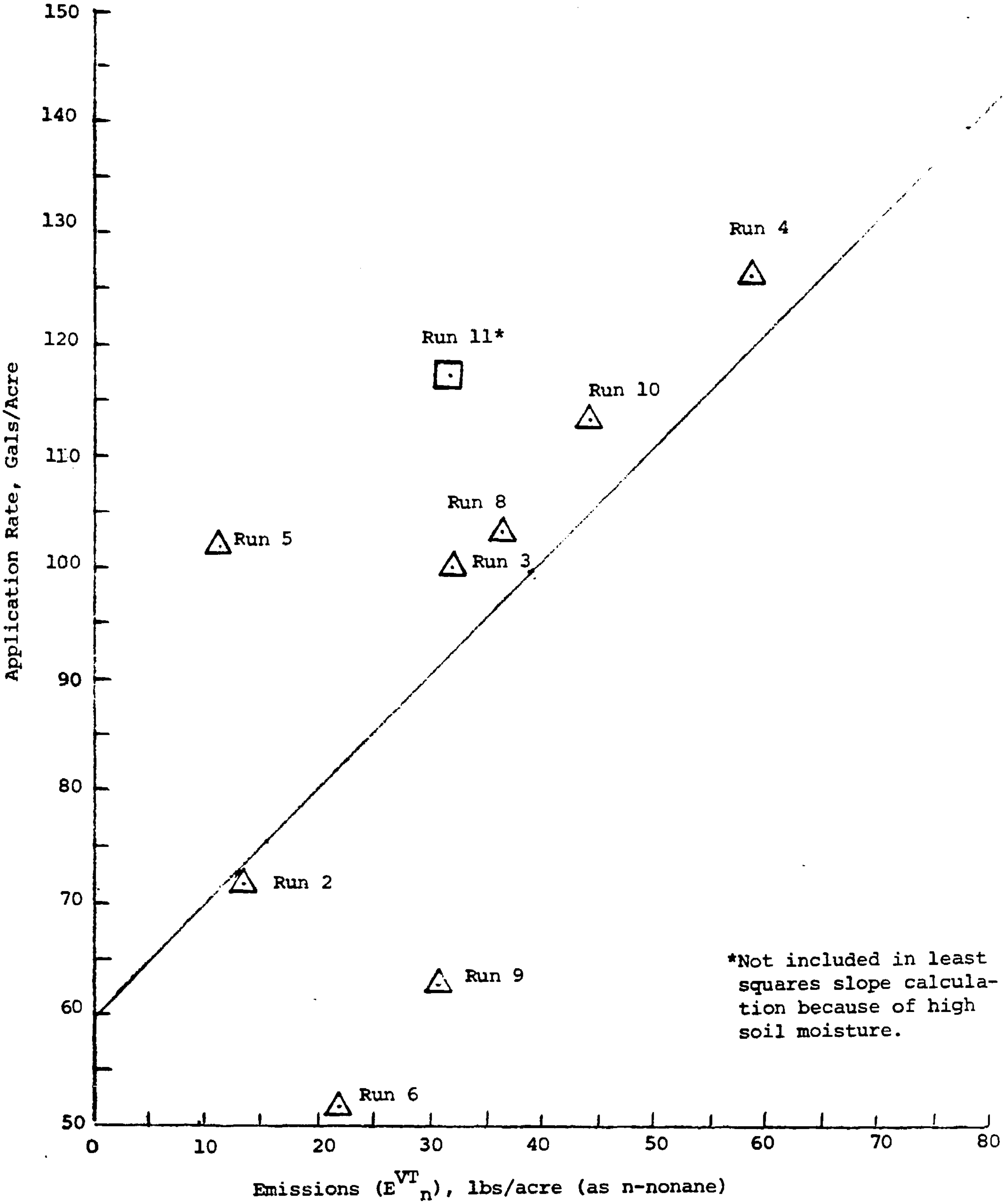

Figure A-16. Correlation of temperature and wind normalized carrot oil emissions with respect to application rate.

Combining equations (3) and (4) the total measurable* emissions (E_m) from a carrot oil application should then become:

$$E_m = (0.14A - 57.60)[(\bar{V} - V_{lim})0.05 + 1]e^f \qquad (5)$$

Where L_{lim} is 0.9 mph and T_r is 292°K. The other terms were defined previously.

The above relationship states that at the reference point conditions [0.9 mph wind and 292°K (66°F) average temperature], no emissions will be detected at applications below 57 gal/acre (recommended minimum is 50 gal/acre; 100 gal/acre is recommended maximum). At maximum application rate, temperature (80°F - if we wish to avoid any extrapolation) and wind speed (5.0 mph again, no extrapolation), we calculate a release of 78.6 lbs/acre of hydrocarbons (as n-nonane). The range beyond the test conditions observed that the expression can be applied is unknown. It was considered advisable, however, to designate the lower wind speed as a limit rather than just a reference point since evaporation rates decrease rapidly as wind speeds approach zero.

Again the caveat should be remembered, that the above derivation is based on measurable emissions. That is, emissions that could be discerned from background under the test arrangement employed. There is no question but that unmeasured hydrocarbons were released, the quantities of which can only be dimensioned by more sensitive test techniques. Therefore, these results should not be used for emission factor purposes until further research results are available.

A final comment goes to the results obtained in the Run No. 11 where the soil moisture was increased (see Table A-7) from an average of 5.4 percent (measured in the first 5 tests) to 15.0 percent (17.1 percent initially, finishing at 12.8 percent after the ventilated test). The results of this test were excluded in the derivation of the Figure A-16 because of this

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*Above background using continuous THC monitor.

rendered variation. It will be seen in that figure, however, that the plot for Run No. 11 (the "wet" test) correlates reasonably well with the "drier" runs and is even superior in that respect to Run No. 5. Thus the results of this single test are inconclusive and cannot be said to support the findings of others working with synthetic pesticides. Willis, for example, found that dieldrin vaporized from moist soils at rates two to three times what was observed on dry plots (Ref. A-9). Similarly, Gray and Weierich found that the loss of EPTC from wet soil was twice as great as from dry (Ref. A-7). Spencer and Cliath published data (Ref. A-10) for vapor densities of trifluralin at two soil concentrations (8.4 and 72 µg/g) over a soil moisture range from zero to 24%. The concentration of trifluralin in the vapor zone over the soil increased by 90% and 40% for the two respective dosages, when the soil moisture was increased from 5.4% to 15.0%. As pointed out in the beginning of this paragraph, that is the moisture difference prevailing between the average of the several "normal" and the one "wet" test conducted with carrot oil on this program.

APPENDIX A

REFERENCES

A- 1. S. K. Leung, et al., "Air Pollution Emissions Associated with Non-synthetic Hydrocarbon Application for Pesticidal Purposes in California," Eureka Laboratories Final Report No. 80-E-107 to the California Air Resources Board on Contract No. A7-173-30, April 1980.

A- 2. S. K. Leung, et al., "Air Pollution Emissions Associated with Pesticide Applications in Fresno County," Eureka Laboratories Final Report No. 77-E-02 to the California Air Resources Board on Contract No. ARB A7-047-30, December 1978.

A- 3. California Air Resources Board, "Characterization of Non-synthetic Hydrocarbon Pesticides by Gas Chromatography/Mass Spectrometry (GC/MS)," Report on Project No. RS-05-LNP by Organic Analysis Section, Haagen-Smit Laboratory Division, June 1980.

A- 4. J. A. Lipe, "The Role of Ethylene in Fruit Dehiscence and Young Fruit Abscission of Cotton, Pecan and Okra," Dissertation Abstracts International, Vol. 32/10-B, p. 5651, 1971.

A- 5. P. W. Morgan, et al., "Ethylene Production by the Cotton Flower, Rule and Regulation," Proc. 8th Int. Conf. Plant Growth Subst., p. 1062, Tokyo, Japan 1974.

A- 6. W. A. Dietz, "Response Factors for Gas Chromatographic Aanlysis," J. Gas Chromatography, 68 (Feb. 67).

A- 7. R. A. Gray and A. J. Weierich, "Factors Affecting the Vapor Loss of EPTC from Soils," Weeds, <u>13</u>, 141 (1965).

A- 8. R. Grover, et al., "Droplet and Vapor Drift from Butyl Ester and Dimethylamine Salt of 2,4-D," Weed Sci., <u>20</u>, 320 (1972).

A- 9. G. H. Willis, et al., "Volatilization of Dieldrin from Fallout Soils as Affected by Different Water Regimes," J. Environ. Quality, <u>1</u>, 193 (1972).

A-10. W. F. Spencer and M. M. Cliath, "Factors Affecting Vapor Loss of Trifluralin from Soil," J. Agr. Food Chem., <u>22</u> (6), 987 (1974).

APPENDIX B

CALCULATIONS FOR ESTIMATING HYDROCARBON LEVELS IN THE FIELD EMISSIONS MEASUREMENT APPARATUS

As stated in Appendix A of this report (Subsection A-5.5), hydrocarbon emissions were not detected when a weed oil (ARCO Weed Killer "A" Lite) was applied in the spray chamber. Because vapor pressure data had just been published (Ref. 1), calculations were done to determine what THC levels might be expected under the conditions of the tests if all assumptions taken proved valid. The approach used was reviewed and corrected by W. F. Spencer* of the USDA's Science and Education Administration, then professor at U.C. Riverside. These calculations follow.

CASE 1 - CALCULATIONS BASED ON EUREKA LABORATORIES DATA

(See Note at end of this Appendix)

According to Leung (Ref. 6, p. 288) the typical non-selective weed oil has a vapor pressure of 8.5 x 10^{-4} Torr and average molecular weight of 275. To estimate evaporation rate, Hartley's equation is applied:

$$-\frac{dm}{dt} = \frac{ET_j}{(1-RH)} \cdot \frac{p_i\ (M_i)^{1/2}}{p_w\ (M_w)^{1/2}} \qquad (1)$$

where $-\frac{dm}{dt}$ = pesticide evaporation rate, lbs/acre-hr.

ET_j = Evapotranspiration rate, lbs water/acre-hr.

R.H. = Relative humidity

p = Vapor pressure, consistent units

M = Molecular weight; i = pesticide; w = water

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*Private communication to author, January 18, 1980.

The conditions assumed for the calculations are as follows:

temperature = 30°C (86°F)
relative humidity = 50%
Et_j = 8381 lbs water/acre-hr.

The evapotransporation rate (ET_j) was suggested as a reasonable value by Dr. Spencer for the calculation. The value was extracted from the National Oceanic and Atmospheric Administration "Climatological Data for California." It represents the maximum of the range of evaporation rates (0.17 to 0.37 in. standard pan) for Chula Vista in September of 1979. The climatology is similar to that prevailing at the UCSCFS and the time of year coincided with the first field test effort.

The first step was to convert the Eureka Labs vapor pressure value from 20° to 30°C. This was done using the Clapeyron equation, viz.

$$\log \frac{p_2}{p_1} = \frac{\Delta H_v}{2.303\ R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2)$$

The heat of vaporization (ΔH_v) was assumed to be 17,000 cal/g-mole. This was based on a C_{21} aromatic hydrocarbon, such as picene (3,4-benzochrysene; B.Pt. = 518°C; M.W. = 278.4), which should roughly fit the characteristics involved. Applying equation (2), we would estimate the weed oil vapor pressure as follows:

$$\log p_2 = \log 8.5 + 10^{-4} \times \frac{18{,}000}{2.303 \times 1.99} \left(\frac{1}{293} - \frac{1}{303}\right)$$

$$p_2 = 2.3 \times 10^{-3} \text{ Torr}$$

When this value and the other conditions itemized above are entered into equation (1), we have a weed oil evaporation rate as follows:

$$-\frac{dm}{dt} = \frac{8381}{(1-0.5)} \bullet \frac{2.3 \times 10^{-3} (275)^{1/2}}{32\ (18)^{1/2}}$$

$$-\frac{dm}{dt} = 4.7 \text{ lb/acre-hr.}$$

This outcome can be related to the field test chamber where these conditions pertain:

Test Area = 140 sq. ft. (3.2×10^{-3} acre)

Air Throughput @ 5 mph (100 sq. ft. cross sec.)

= 44,000 acfm
= 1246 m^3/min

The volume of THC in cc's per m^3 air or ppm of THC can be expressed as:

$$cc_{THC}/m^3_{air} = \frac{n/min\ RT/p}{1246} \tag{3}$$

$$= \frac{g/min \times 82.05 \times 303}{1 \times 1246 \times 275}$$

$$= 0.0725 \times g/min.$$

Evaporation rate is 4.7 lb/acre-hr. or 0.113 g/min. in the chamber (3.2×10^{-3} acre x 4.7 lbs x 453.6/60 min). Thus, the concentration of THC leaving the rig would be:

0.0725 x 0.113 x 1000 = 8.2 ppb

This level would clearly not be detectable using the test configuration described.

CASE 2 - CALCULATIONS BASED ON ARCO WEED OIL SPECIFICATIONS

ARCO literature covering its ARCO Weed Killer "A" Lite furnishes a typical boiling range from 225°C (IBP) to 315°C (90% distilled). This is about represented by the boiling points of naphthalene (218°C) and anthracene (340°C). These compounds have vapor pressures of 1.0 Torr at 52.6°C and 145.0°C, respectively and ΔH_v's of 12,311 and 16,823 cal/g-mole, respectively. Adjusting to 30°C, using the Clapeyron equation (Eq. 2), we estimate vapor pressures of 0.241 and 4.7×10^{-2} for naphthlene and authracene, respectively. These values, of course, are much higher than those reported by Leung (Ref. 1) as typical for the generic classification of non-selective weed oils.

When the above vapor pressures are run through the calculations employed in Case 1, we estimate evaporation rates ranging from 77.4 (anthracene) to 336.8 (naphthalene) lbs/acre-hr. In the field test rig, at the conditions previously specified, this should produce THC levels in the exhaust of 0.59 ppm and 0.14 ppm for the naphthalene and anthracene ends, respectively, assuming the presence of an evaporable film. If we assume that the weed oil is a perfect binary mixture, which of course it is not, having equimolar concentrations of the two aromatics, then the THC readout would be the average of the above two numbers, or 0.36 ppm.

While this estimated value is decidedly below background (air pollution level at the site), the pesticide should be monitorable if, perhaps, with marginal accuracy.

CASE 3 - CALCULATIONS BASED ON TASK II LABORATORY RESULTS

Although direct comparisons between the Task II and Task III evaporation rate test results were not intended, rough correlations were expected. In the present situation, it was desirable to attempt the comparison because of the disparity in the results of the Case 1 and 2 calculations. These disagreed by a factor of 45 but both calculations depended on volatility factors that might not necessarily be appropriate to the weed oil actually tested. In Case 1 a vapor pressure from the Eureka report (Ref. 1) was used that can only be associated with the generic classification in which the ARCO product belongs. In Case 2, ARCO boiling range data were used and these were described as only being "typical" of the product. In the course of the Task I effort, considerable advice was received from pesticide suppliers as to the variability of some of the classifications of non-synthetic pesticides. In attempting to predict THC levels in the field test chamber from results obtained in the laboratory wind tunnel, one at least knows that the material used in both systems was the same.

In the tests run on the ARCO weed oil with soil in the evaporation pan, about 6 percent of the oil was lost in the first hour of exposure. This was at 2.5 mph wind speed and a temperature of 76°F. Assuming a direct dependence on vapor pressure and neglecting any influence of wind speed, the loss would be about 9 percent at 86°F (vapor pressures about double every 10°C).

At an application rate of 25 gals per acre, the amount put down in the field test chamber would be:

$$7.4 \text{ lbs/gal} \times 25 \text{ gals} \times 140 \text{ sq.ft.}/43{,}560$$

or 0.59 lbs. According to the law for perfect gases, the vapor equivalent to 1 lb. of pesticide at 86°F would be:

$$\frac{1.0 \times 0.729 \times 546}{1.0 \times MW} \quad \text{cu.ft.}$$

or 398/MW cu.ft. The air volume passing through the chamber at 5.0 mph is 5.28×10^6 cu.ft./hr. Therefore, the average THC concentration in the exhaust during the first hour of evaporation would be roughly:

$$\frac{0.59 \times 0.09 \times 398 \times 10^9/MW}{5.28 \times 10^6} \quad \text{ppb}$$

If the average MW is 275 (Case 1), the average THC concentration 14.5 ppb. If MW is 153 (Case 2), the concentration calculates out at 26.1 ppb. Taking the average of these two numbers, and there is no particular logic to defend so doing, we have a value (20.3 ppb) that is reasonably close to the Case 1 result (8.2 ppb).

Note: In their review of these calculations, the ARB stated:

> "The typical vapor pressure and average molecular weight for nonselective weed oil used in the Case 1 calculation in [this] Appendix... is incorrect [as reported by Eureka Laboratories in Ref. 1]. According to the chemical analysis of the test materials by the Haagen-Smit Laboratory [Ref. A-3, which was not available when the above calculations were made], the values cited are not average but are attributable to the most nonvolatile components. Based on the analysis, the average vapor pressure and molecular weight of nonselective weed oils are 4×10^{-2} mm Hg @ 30°C and 177, respectively. Using these values in Hartley's equation, the results agree reasonably well with the results of Case 2."

APPENDIX C

COST ESTIMATES FOR CONDUCTING FIELD TESTS OF PESTICIDE APPLICATION TECHNIQUES SUGGESTING EMISSIONS REDUCTION

Rough costs are developed here for conducting field tests that would determine the benefits of using application techniques that would reduce hydrocarbon emissions. The preliminary test plan considered here would involve the following evaluations:

- FMC Law Electrostatic sprayer* vs. conventional nozzles.
- Low pressure, deflector type (KGF) nozzles vs. conventional nozzles.
- Adjuvant doped vs. undoped pesticide using optimum nozzle configuration and air sheer.

This testing scope can be expanded or reduced, of course, but was selected as a reasonable costing basis. Three tests would be performed on each system for a total of nine tests. Conditions would be sought that would be as close as possible for each of the three sets of comparative tests.

The basic testing approach would be to apply a weed oil on some weed-free row crop, such as asparagus. The vegetation would be used as a weed substitute which, being cultivated rather than wild growth, would have a more uniform ground distribution.

Monitoring the emissions of each test would involve both the drift and vapor following the wind. The sampling train would consist of an isokinetic cascade impactor followed by a solid sorbent trap (XAD-2 or equivalent) mounted in a Battelle extractor fitting. The impactor would be removed after the drift process was complete. The solid sorbent would be exposed until several cubic meters of air had been passed.

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*As of this reporting, this device is still in development and testing at FMC. A commercial version is assumed to be available for this study.

The field chamber would be modified so that lower wind speeds could be reproducibly maintained. The wind screens would be discarded and the open end would be modified with a covering that would dampen external wind disturbances. Lower fan speeds would also then be possible. Otherwise, operation of the chamber would be essentially as described in this report.

Costs for conducting the described tests are based on an assumed start up date of 1 March 1981 with field testing beginning in early July, completing by the end of August.

ESTIMATED COSTS FOR TEST PROGRAM

Labor		Burdened Cost, $
Management & Reporting	-	24,700
Field Rig Modification & Shakedown	-	5,500
Field Tests (9 weeks)	-	9,700
Clerical Support	-	1,100
Laboratory		
	-	9,700
Materials		
	-	6,000
Rental Equipment		
		4,000
TOTAL	-	$60,700