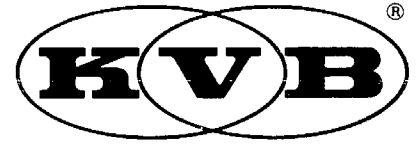


**DEVELOPMENT OF EMISSION  
FACTORS FOR REACTIVE  
HYDROCARBONS USED IN  
PESTICIDE FORMULATIONS**



KVB13 5809-1256

**EXECUTIVE REPORT**

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**CONTRACT NO.  
A8-124-31**

**PREPARED FOR:  
CALIFORNIA AIR RESOURCES BOARD  
SACRAMENTO, CALIFORNIA**

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JULY 1981**

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KVB 13-5809-1256

### ACKNOWLEDGEMENTS

KVB wishes to acknowledge the contributions in various forms made by others to this program. Dr. Walt Farmer of the Department of Soil and Environmental Sciences at University of California Riverside acted as an academic sponsor of the program and gave generously of his opinions and suggestions. He was joined in that role by Dr. Bill Spencer of the U.S. Department of Agriculture, who is also a professor at UCR. Field work done at the University of California South Coast Field Station near El Toro was under the friendly aegis of the supervisor there, Dr. Randy Keim. We also wish to thank his foreman, Ray Leonard, who oversaw the tillage and culture of our test crops. The cooperation of pesticide manufacturers in supplying generous samples of their products and pertinent technical data is appreciated. We wish to acknowledge the interest of Chevron Research Co. and Chevron Chemical Co., whose representatives met with the project staff on several occasions for the exchange of information and ideas. Thanks are also due to Dr. Steve Leung, President of Eureka Laboratories, Sacramento, in assisting the program in the selection of candidate pesticides. Finally, we wish to express our appreciation to the ARB Project Officer Mr. Eric Fujita for his patience and understanding during a program he entered late and that due to its nature, encountered a plethora of setbacks and problems.

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.

## EXECUTIVE SUMMARY

### 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 dodecyl-benzenesulfonic 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.

## SUMMARY AND CONCLUSIONS

### Summary of Results

#### 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:

<u>Brand or Generic Name</u>	<u>Pesticide Category</u>
<u>Non-synthetics:</u>	
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
<u>Synthetics:</u>	
Dacthal	Preemergence Herbicide
Methomyl	Insecticide
Molinate	Selective Herbicide
Toxaphene	Insecticide
Kelthane	Miticide
DEF-6	Defoliant
<u>Reference:</u>	
Dodecane	--

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. RELATIVE EVAPORATION RATES OF THE MORE VOLATILE CANDIDATE MATERIALS

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

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<u>Test Material</u>	<u>Time Required To Evaporate 20%</u>
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.

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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.

#### Task III - Field Emission Measurements--

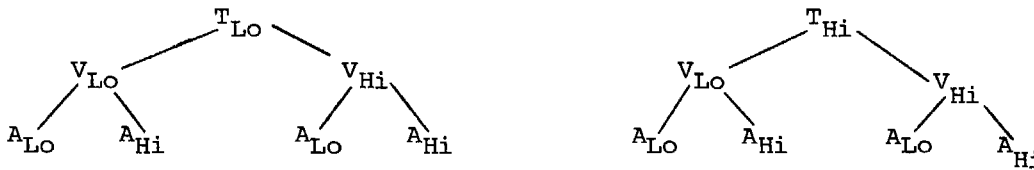
Acquisition of a field site resulted in access permission being granted for space use at the University of California South Coast Field Station (UCSCFS) near the El Toro U.S. Marine Corps Air Station (MCAS-El Toro). A large field test chamber was built. This basically consists of a Tedlar-skinned rectangular 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:

<u>Crop</u>	<u>Pesticide</u>
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 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 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.

#### Task IV - Estimation of Evaporation from Drifted Pesticide--

A review of the literature was made to ascertain typical drift fall-out 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 aerosols (<10  $\mu\text{m}$  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).

#### 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.

#### Conclusions

##### 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  $1 \times 10^{-5}$  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.

##### 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.

##### 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.

## RECOMMENDATIONS

### 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.

### 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.