

EVAPORATION OF PETROLEUM HYDROCARBON PESTICIDES
UNDER CONTROLLED AND FIELD CONDITIONS

CONTRACT No. A1-037-32
CALIFORNIA AIR RESOURCES BOARD
FINAL REPORT
APRIL, 1983

JAMES E. WOODROW
JAMES N. SEIBER
YONG-HWA KIM

DEPARTMENT OF ENVIRONMENTAL TOXICOLOGY
UNIVERSITY OF CALIFORNIA
DAVIS, CALIFORNIA 95616

TP
696.8
W66

ABSTRACT

The evaporation of Beacon selective and non-selective Chevron weed oils was studied under both laboratory and field conditions. The Beacon oil (mean vapor pressure ~ 1.5 mm Hg at 30°C) and the Chevron oil (mean vapor pressure ~ 0.3 mm Hg at 30°C) exhibited laboratory evaporative half-lives of 53 min and 24 hrs, respectively, for $8-10$ mg/cm² on an inert Teflon[®] surface ($23 \pm 1^{\circ}\text{C}$; no wind). These times were reduced to 9-16 min for Beacon oil and 5.5 hrs for Chevron oil under a slight breeze (~ 0.43 m/sec). Furthermore, 50% evaporation time decreased with decrease in starting surface concentration (mg/cm²). When surface applied at $6-7$ mg/cm² to moist soil in a field test plot, 50% of the Beacon oil vaporized in about 51 min ($10-20^{\circ}\text{C}$). Half of the Chevron oil on dry soil in an alfalfa field vaporized in 12-13 hrs ($20-40^{\circ}\text{C}$) for an initial deposit of ~ 0.2 mg/cm². On glass plates and paper filters in the same field, average 50% loss times for the same oil deposit were 6-10 min and 14-21 min, respectively. Evaporation from glass plates was used to model evaporation from the alfalfa field since oil residue levels on foliage samples were essentially the same as those on glass for the same post-spray times. Despite the multicomponent nature of these oils, measured evaporation rates correlated well with results of a mathematical simulation which took into account the rates of application and component vapor pressures. That simple evaporation was the only significant loss route under the conditions studied was confirmed for both oils by capillary GLC analysis of air samples collected by XAD-4 polystyrene adsorbent above and near the treated fields.

TABLE OF CONTENTS

| | <u>Page</u> |
|------------------------------------------------------------------------------------------------------|-------------|
| Abstract | i |
| List of Figures | iii |
| List of Tables | v |
| Acknowledgments | viii |
| I. Introduction | 1 |
| II. Experimental Procedures | 1 |
| A. Laboratory | 1 |
| B. Field | 2 |
| 1. Beacon Oil | 2 |
| 2. Chevron Oil | 4 |
| 3. Analytical Methodology | 10 |
| III. Results and Discussion | 14 |
| A. Laboratory | 14 |
| B. Field | 18 |
| 1. Beacon Oil | 18 |
| 2. Chevron Oil | 21 |
| C. Emission Estimation Methodology | 37 |
| IV. Conclusions | 38 |
| V. References | 40 |
| Appendix A. Simulated Evaporation of Beacon and Chevron Weed Oils. | 41 |
| Appendix B. Estimation of Loss of Leffingwell Uni-Par and Ortho- K-Ready Mix from Citrus Foliage. | 57 |
| Appendix C. XAD-4 Polymeric Adsorbent Air Sampling of Beacon and Chevron Weed Oils. | 68 |

LIST OF FIGURES

| <u>Figure No.</u> | | <u>Page</u> |
|-------------------|-------------------------------------------------------------------------------------------------------------------------------|-------------|
| 1 | Schematic Representation of Beacon Oil Test Plot, U.C. Davis, July 22, 1982. | 3 |
| 2 | Multiple Cartridge Air Sampler. | 5 |
| 3 | Schematic Representation of Chevron Oil-Treated Alfalfa Field, Helm, CA, Aug. 18-20, 1982. | 8 |
| 4 | Gas Chromatograms of Beacon Carrot Oil (A) and Hydrocarbon References (B). | 42 |
| 5 | Calculated Evaporation of Beacon Oil from an Inert Surface. | 47 |
| 6 | Calculated Evaporation of Beacon Oil from Inert Surface Using Oil Component Properties (A) and Average Properties (B). | 48 |
| 7 | Calculated Evaporation of Chevron Oil from Inert Surface Using Oil Component Properties (A) and Average Properties (B). | 49 |
| 8 | Evaporation of Beacon Oil from Soil--Field. | 51 |
| 9 | Evaporation of Chevron Oil from Glass--Field. | 52 |
| 10 | Evaporation of Chevron Oil from Paper--Field. | 53 |
| 11 | Capillary Gas Chromatogram of Leffingwell Uni-Par. | 58 |
| 12 | Capillary Gas Chromatogram of Ortho-K-Ready Mix, Light Medium. | 59 |
| 13 | Calculated Evaporation of Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (UKRM) from Citrus Leaves. | 66 |

| <u>Figure No.</u> | | <u>Page</u> |
|-------------------|------------------------------------------------------------------------------------------------------------------------|-------------|
| 14 | Schematic Representation of Laboratory Apparatus for Determining Trapping of Weed Oil Vapors by XAD-4 Adsorbent. | 69 |
| 15 | Adsorption of Beacon and Chevron Weed Oils by XAD-4 Adsorbent. | 71 |

LIST OF TABLES

| <u>Table No.</u> | | <u>Page</u> |
|------------------|------------------------------------------------------------------------------------------------------------------------------|-------------|
| 1 | Temperature and Relative Humidity Profiles for the Beacon oil Test Plot. U.C. Davis, July 22, 1982. | 6 |
| 2 | Cup Anemometer Wind Speed 61 cm Above Ground for Beacon oil Test Plot. U.C. Davis, July 22, 1982. | 7 |
| 3 | Temperature of Exposed Soil Surface in the Chevron Oil Alfalfa Field, Helm, CA, August 19-20, 1982. | 11 |
| 4 | Air Temperature and Relative Humidity Profiles for the Chevron Oil Alfalfa Field. Helm, CA, August 18-20, 1982. | 12 |
| 5 | Cup Anemometer Wind Speed for the Chevron Oil Alfalfa Field. Helm, CA, August 18-20, 1982. | 13 |
| 6 | Evaporation of Beacon and Chevron Oils from Inert Surfaces with no Air Flow, Laboratory Tests. | 15 |
| 7 | Effect of Surface Concentration on the Evaporation of Beacon Oil from an Inert Surface, no Air Flow, Laboratory Tests. | 16 |
| 8 | Evaporation of Beacon and Chevron Oils from Inert Surfaces Under Slight Wind Conditions, Laboratory Tests. | 17 |
| 9 | Evaporation of Beacon Oil from Two Surfaces Sprayed with 150 μ m VMD Droplets, Slight Wind Conditions, Laboratory Tests. | 19 |
| 10 | Evaporation of Beacon Oil from Yolo Sandy Loam, Field Test Plot, U.C. Davis, July 22, 1982. | 20 |

| <u>Table No.</u> | | <u>Page</u> |
|------------------|------------------------------------------------------------------------------------------------------------------------------|-------------|
| 11 | Vapor Density of Beacon Oil Above the Treated Field Plot. U.C. Davis, July 22, 1982. | 22 |
| 12 | Composition of Beacon Oil in Air Above Treated Field Plot. U.C. Davis, July 22, 1982. | 23 |
| 13 | Chevron Oil Residues on Soil Screens in Alfalfa Field. Helm, CA, August 18-20, 1982. | 24 |
| 14 | Chevron Oil Residues on Glass in Alfalfa Field. Helm, CA, August 18-20, 1982. | 26 |
| 15 | Chevron Oil Residues on Filter Paper in Alfalfa Field. Helm, CA, August 18-20, 1982. | 28 |
| 16 | Chevron Oil Residues on Three Surfaces in Plot No. 3. Helm, CA, August 18-20, 1982. | 32 |
| 17 | Flux of Chevron Oil Residues from Treated Alfalfa Field. Helm, CA, August 18-20, 1982. | 33 |
| 18 | Chevron Oil Concentration in Air in an Alfalfa Field Environment--High Volume Samplers. Helm, CA, August 18-20, 1982. | 35 |
| 19 | Chevron Oil Concentration in Air in an Alfalfa Field Environment--Multiple Cartridge Samplers. Helm, CA, August 18-20, 1982. | 36 |
| 20 | The Component and Weighted Average Properties of Beacon and Chevron Oil Standards. | 43 |
| 21 | Component Vaporization of Beacon and Chevron Oil Standards at 30°C. | 46 |
| 22 | Deposition of Chevron Oil During Application. | 55 |

| <u>Table No.</u> | | <u>Page</u> |
|------------------|---------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 23 | Mole Fractions of Individual Hydrocarbons in Leffingwell Uni-Par(LU) and Ortho-K-Ready Mix(OKRM). | 60 |
| 24 | Hydrocarbon Vapor Pressures (C_{14} - C_{26}) and Partial Pressures for Leffingwell Uni-Par (LU) and Ortho-K- Ready Mix (OKRM). | 62 |
| 25 | Vaporization Rates(F_i) and Rate Constants (k_i) for Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (OKRM). | 63 |
| 26 | Calculated Evaporation of Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (OKRM) from Citrus Leaf Surface. | 65 |
| 27 | Field and Calculated Vapor Densities for Beacon and Chevron Weed Oils. | 74 |

ACKNOWLEDGMENTS

The authors wish to thank Mr. Eric Fujita and Mr. Howard Linnard of ARB for fruitful discussions and helpful suggestions and criticisms during the course of this study. We also wish to acknowledge the help of Mr. Bob Sheesley of the U.C. Cooperative Extension who did much to implement some of our field tests, and provided liaison with a cooperating grower who kindly granted us access to his ranch property for some of our field tests. In addition, the technical and field assistance of Mr. Michael Majewski and Mr. Michael McChesney was greatly appreciated.

This report was submitted in fulfillment of ARB Contract No. A1-037-32 by the Department of Environmental Toxicology, University of California, Davis, under the sponsorship of the California Air Resources Board whose financial support we gratefully acknowledge.

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

INTRODUCTION

Vapors of petroleum hydrocarbon pesticides (PHP) may enter the atmosphere during spraying and by post-application evaporation from soil and plant surfaces. Their extensive use in California as dormant sprays and herbicides (weed killers), the level of use (yearly average of 9×10^6 kg for 1979-81), and vapor pressures commonly greater than 10^{-2} mm Hg at ambient temperatures suggest that PHP may contribute significantly to the hydrocarbon emissions in some agricultural areas of the state. However, emissions measurements and their correlation with physico-chemical properties and environmental conditions have been done primarily for the synthetic pesticides of toxicological interest; very little information is available on the more heavily used PHP.

This report summarizes the results of a study to determine the rate of evaporation of selective and non-selective weed oils under typical use conditions. Included are laboratory and field measurements of relative volatility of these oils from inert, soil, and foliage substrates and laboratory measurements of vapor pressures of the oil mixtures. Air sampling and analysis techniques were developed for determining oil concentration in air and these techniques were used to obtain representative air samples in and near agricultural treatment sites.

EXPERIMENTAL PROCEDURES

A. Laboratory

Beacon selective weed oil #5 (Beacon Oil Co., Hanford, CA) was applied to weighed Teflon® and soil surfaces by spraying at field rates (467.4 - 934.9

L/ha) with droplet diameters of 150 μ m VMD generated by a glass TLC sprayer. Droplet diameter was determined using a Particle Size Measuring System, Inc., Model 11-C laser sizing device. Immediately after spraying, the treated surfaces were weighed and placed in a 4 cm dia. Teflon® cylinder, and filtered air was allowed to flow over the surface for one hour at 1 LPM (0.013 m/sec) to a vapor trap consisting of a 50 ml bed of 20-50 mesh XAD-4 polystyrene macroreticular resin (Rohm and Haas, Philadelphia, PA); temperature and relative humidity were determined using a hygromograph. The Beacon oil and non-selective Chevron weed oil (Chevron, Richmond, CA) were applied to weighed Teflon® and polyethylene surfaces (8.1-10.5 mg/cm²) using a glass pipette and the samples were weighed at time intervals from 0.5 hr to 7.4 hrs post-application under static wind conditions. In addition, Beacon oil was applied to Teflon® surfaces at three rates (30.15, 16.22 and 9.27 mg/cm²) and the samples were weighed 0.5, 1.0, 1.5 and 2.0 hrs post-application under static wind conditions. Also, polyethylene surfaces treated separately with Beacon and Chevron oil (8.9-10.5 mg/cm²) were weighed, subjected to an air flow of 40 LPM (~0.43 m/sec), and weighed again at intervals from 0.5 to 7.3 hrs post-treatment.

B. Field

1. Beacon Oil. A plot 9.14 m square (83.6 m²) located at the University of California, Davis, was divided into quarter sections and into each section was placed a glass plate covered with 14 glass microscope slides (19.0 cm² each). A fifth set of glass slides was placed at the center of the plot (Figure 1). Using a flour sifter, finely ground Yolo sandy loam soil was dusted over each set of slides, followed by a light application of distilled water using a mister. At 0610 on July 22, 1982, the plot was treated with

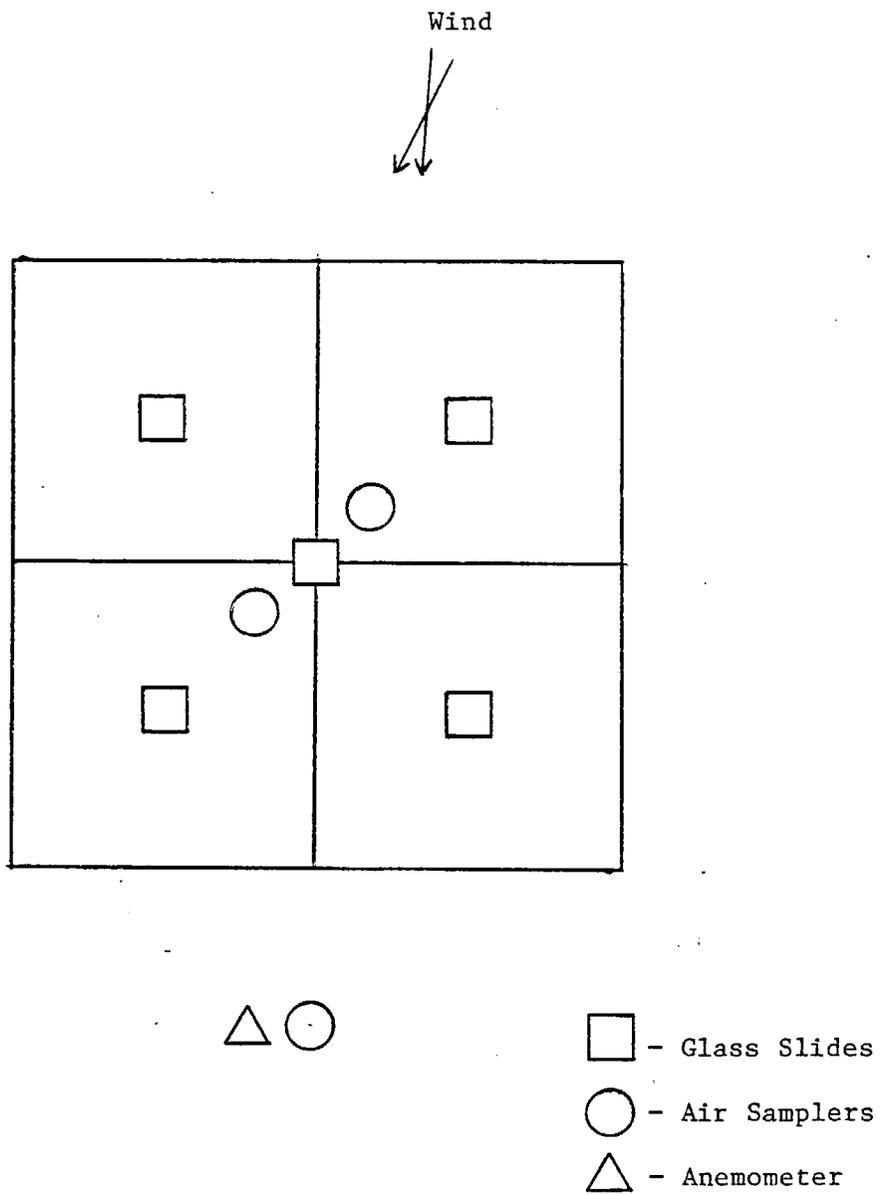


Figure 1. SCHEMATIC REPRESENTATION OF BEACON OIL TEST PLOT.

6.92 L neat Beacon oil using a carbon dioxide-pressurized backpack sprayer. The application consisted of six passes over the plot requiring about 10.23 sec per pass (61.4 sec total); each pass laid down a swath 1.52 m wide. After application, one slide was removed from each placement (5 slides per sample) for each sampling period.

Immediately after application, air samplers were placed near the center of the plot (Figure 1). These consisted of two high volume air samplers, each connected to three sampling cartridges (Figure 2). Duplicate cartridges, filled with 50 ml 20-50 mesh XAD-4 resin, were placed at 30.48, 60.96, and 106.68 cm above the plot. Air sampling was begun 13, 38, and 156 min post-application with run times of 18, 49, and 59 min, respectively. Average flow rate for each cartridge was 56.45 LPM. High volume samplers, filled with 200 ml XAD-4 each, were placed 2.13 m and 7.92 m from the approximate downwind and upwind edges, respectively (Figure 1). The downwind sampler (height \approx 30.48 cm) was operated for 62 min beginning 19 min post-application; the upwind, background sampler was operated for 60 min beginning 20 min post-application. Average flow rate for both samplers was 0.74 m³/min.

Temperature and relative humidity were determined using a hygrothermograph (Table 1) and wind speed was measured 61 cm above ground using a three cup totalizing anemometer (Table 2).

2. Chevron Oil. A 32.4 ha field planted in seed alfalfa, located near Helm, CA, was divided into quadrants and one subplot ~6 m square was established in each quadrant (Figure 3). A control plot was established in an adjacent untreated alfalfa field. Prior to application, each plot contained three sets of metal soil screens (19.4 cm² each) previously dipped in a mud slurry and air dried, 14 screens per set on glass plates, 10 glass petri

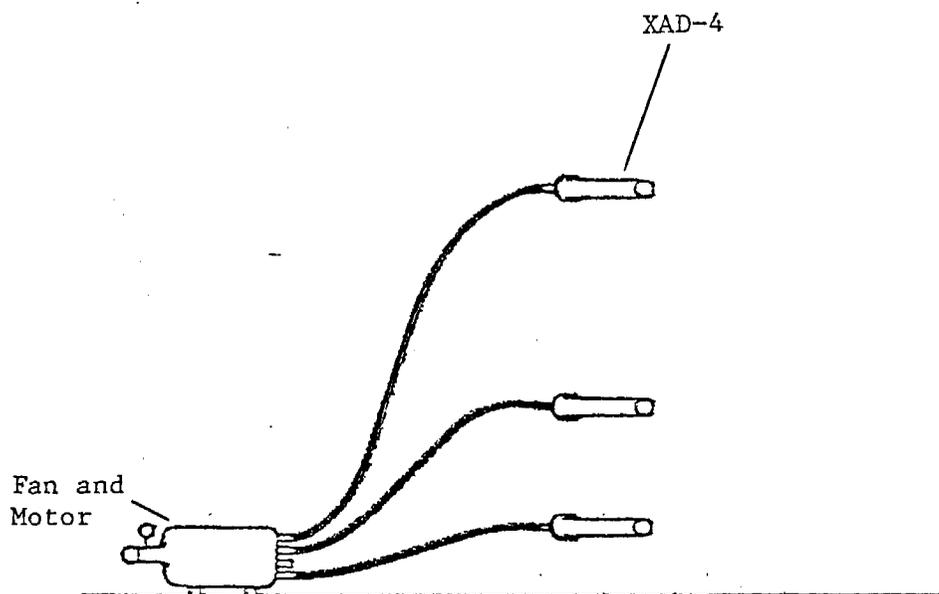


Figure 2. Multiple Cartridge Air Sampler.

Table 1. Temperature and Relative Humidity Profiles for the Beacon Oil Test Plot. U.C. Davis, July 22, 1982.

| <u>Time</u> | <u>Temperature, °C</u> | <u>% Relative Humidity</u> |
|-------------|------------------------|----------------------------|
| 0600 | 10.0 | 100 |
| 0700 | 12.0 | 100 |
| 0800 | 14.1 | 100 |
| 0830 | 16.0 | 98.9 |
| 0900 | 20.5 | 75 |
| 1000 | 24.5 | 56 |
| 1100 | 28.5 | 47.8 |
| 1200 | 30.5 | 38.9 |
| 1300 | 32.5 | 35.8 |
| 1400 | 34.7 | 26.9 |
| 1500 | 36.5 | 23.3 |
| 1600 | 38.5 | 20 |
| 1700 | 39.5 | 18.9 |
| 1800 | 37.0 | 19.4 |

Table 2. Cup Anemometer Wind Speed 61 cm Above Ground for Beacon Oil Test
Plot. U.C. Davis, July 22, 1982.

| <u>Time Interval</u> | <u>Average Wind Speed, m/sec</u> |
|----------------------|--------------------------------------|
| 0600 - 0830 | 0.46 |
| 0830 - 1021 | 0.85 |
| 1021 - 1220 | 0.66 |
| 1220 - 1416 | 0.75 |
| 1416 - 1608 | 0.88 |
| 1608 - 1738 | 1.16 |

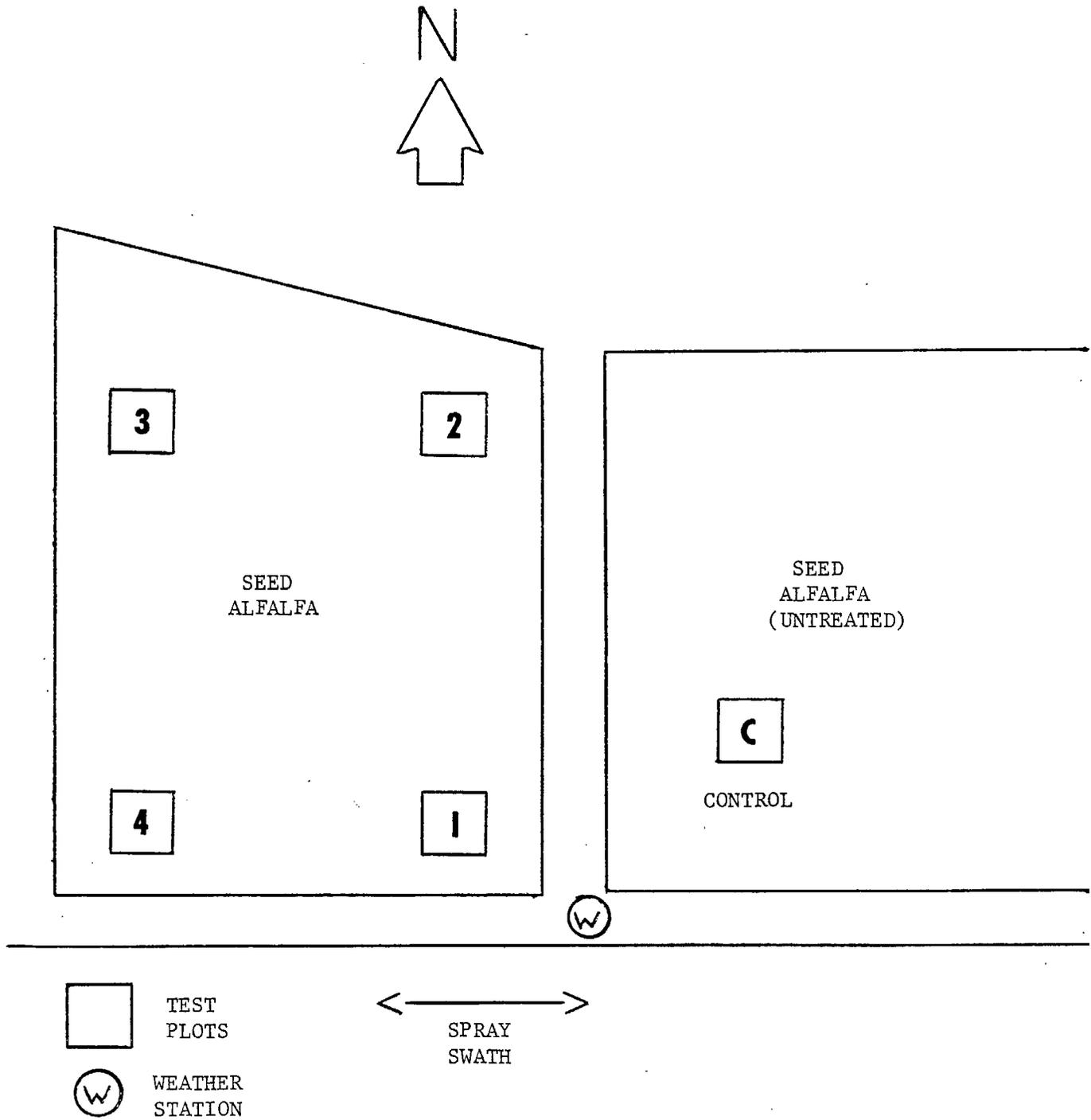


Figure 3. SCHEMATIC REPRESENTATION OF CHEVRON WEED OIL-TREATED ALFALFA FIELD.

dishes (73.14 cm² each), and one paper filter disc marked for division into eight equal sections (56.55 cm² per section). The field was treated twice by Ag-Cat spray plane equipped with #46 disc nozzles on August 18 (1010-1052) and 20 (0938-1035), 1982, with 47 L Chevron oil with emulsifier in 47 L water/ha. The plane applied material at ca 1.2 m from the crop canopy. Included in the spray mix was 2.5-5.0 L/ha 30% dinitro (2-sec-butyl-4,6-dinitrophenol). During application, high volume air samplers, charged with 200 ml XAD-4, were operated downwind at distances up to ~400 m (Aug 18) and 48 m (Aug 20). Average flow rate was 0.74 m³/min.

Immediately after each application, air samplers were placed in plot no. 1 (Figure 3). These consisted of two high volume air samplers, each connected to three sampling cartridges (Figure 2). Duplicate cartridges, filled with 50 ml 20-50 mesh XAD-4 adsorbent, were placed at about 49, 113, and 184 cm above the plot; average flow per cartridge was 33 LPM (27-45 LPM). A high volume sampler, filled with 200 ml XAD-4, was placed 76-95 cm above the plot; average flow was 0.74 m³/min. Air samples were taken at intervals up to 29 hrs after the first application and up to 4 hrs after the second application.

One soil screen sample (three screens), one petri dish (solvent rinse), and one section of the filter paper disc were taken from each plot during each sampling interval up to 32 hrs after the first application and up to 4 hrs after the second application. In addition, one alfalfa foliage sample (10 stems plus leaves) was taken from each plot along with the other samples. All samples, including air, were placed in sealed containers to which ethyl acetate solvent had been added and immediately stored in styrofoam chests filled with dry ice for transport to Davis, where they were stored at -20°C until analyzed.

Soil surface temperature was measured using a thermocouple with digital read-out (Table 3). Air temperature and relative humidity (Table 4) were measured using a hygrothermograph located at the weather station (Figure 3). Wind speed was measured using a three cup totalizing anemometer placed 61-122 cm (Aug 18) and 44-89 cm (Aug 20) above the plot containing the air samplers and at about 195 cm height using a recording anemometer at the weather station (Figure 3; Table 5).

C. Analytical Methodology

The soil slides/screens and XAD-4 air samples in ethyl acetate were shaken for 1 hr, using a rotary shaker, decanted, filtered, and rinsed. The filter paper and alfalfa plant samples were removed from the solvent and rinsed; the extracts were analyzed without further treatment, as were the petri dish rinses.

Analysis was accomplished by gas chromatography using a Varian Model 1700 gas chromatograph equipped with a 30 m × 0.25 mm (ID) fused silica capillary column coated with SE-54 (J & W Scientific, Inc., Rancho Cordova, CA) and a flame ionization detector (FID); the FID and injection port temperatures were each 250°C. The column was temperature programmed from 50°C to final temperatures of 170°C (Beacon oil) and 250°C (Chevron oil) at 4°C/min, and then immediately cooled to the starting temperature for the next injection. The FID response was recorded using a Hewlett-Packard Model 3390A reporting integrator programmed to give total area plus four subareas (Beacon oil) and seven subareas (Chevron oil) of equal time. Carrier and make-up gas (N₂) flows were ~1 and 20 ml/min, respectively; air and hydrogen flows were ~285 and 13 ml/min, respectively.

Table 3. Temperature of Exposed Soil Surface in the Chevron Oil Alfalfa Field, Helm, CA, August 19-20, 1982.

| <u>Time</u> | <u>Temperature, °C</u> | |
|-------------|------------------------|------------------|
| | <u>August 19</u> | <u>August 20</u> |
| 1006 | 40 | - |
| 1044 | 41 | - |
| 1130 | 43 | - |
| 1141 | - | 45 |
| 1143 | - | 49 |
| 1210 | 49 | - |
| 1230 | 51 | - |
| 1242 | - | 58 |
| 1302 | 57 | - |
| 1316 | - | 60 |
| 1336 | 60 | - |
| 1351 | - | 59 |
| 1424 | 61 | - |
| 1502 | 60 | - |
| 1526 | 48 (cloudy) | - |
| 1603 | 52 | - |

Table 4. Air Temperature and Relative Humidity Profiles for the Chevron Oil
Alfalfa Field, Helm, CA, August 18-20, 1982.

| <u>Date</u> | <u>Time</u> | <u>Temperature, °C</u> | <u>% Relative Humidity</u> |
|-------------|-------------|------------------------|----------------------------|
| 8/18 | 0835 | 26.0 | 54 |
| | 1035 | 32.5 | 31.5 |
| | 1235 | 37.0 | 28 |
| | 1435 | 41.0 | 26 |
| | 1635 | 40.5 | 25 |
| | 1835 | 37.5 | 25 |
| 8/19 | 0950 | 27.0 | 49.5 |
| | 1150 | 28.0 | 40.5 |
| | 1350 | 34.5 | 30 |
| | 1550 | 34.8 | 28 |
| | 1750 | 36.0 | 27 |
| 8/20 | 0725 | 21.0 | 69.5 |
| | 0925 | 26.5 | 49.5 |
| | 1125 | 32.0 | 32.5 |
| | 1325 | 35.5 | 28 |
| | 1525 | 39.0 | 26 |

Table 5. Cup Anemometer Wind Speed for the Chevron Oil Alfalfa Field, Helm, CA, August 18-20, 1982.

| <u>Date</u> | <u>Time</u> | <u>Average</u> | | <u>Average</u> | |
|-------------|-------------|---------------------------|-------------|----------------------------|--|
| | | <u>Wind Speed, m/s</u> | | <u>Wind Speed, m/s</u> | |
| | | <u>Alfalfa</u> | | <u>Weather</u> | |
| | | <u>Field (Height, cm)</u> | <u>Time</u> | <u>Station^a</u> | |
| 8/18 | 1153-1419 | 1.14 (122) | 0812-0852 | 1.01 | |
| | 1421-1608 | 0.91 (76) | 0852-1309 | 1.04 | |
| | 1609-1718 | 1.48 (61) | 1309-1625 | 1.37 | |
| | 1719-1820 | 1.42 (61) | 1625-1821 | 2.31 | |
| | | | 1821-1848 | 2.43 | |
| 8/19 | 0948-1043 | 1.87 (76) | 0944-1039 | 3.16 | |
| | 1043-1143 | 1.69 (76) | 1039-1217 | 2.74 | |
| | 1144-1259 | 1.84 (76) | 1217-1340 | 3.25 | |
| | 1300-1354 | 1.96 (76) | 1340-1515 | 2.82 | |
| | 1354-1501 | 1.80 (76) | 1515-1635 | 3.37 | |
| | 1501-1601 | 2.08 (76) | 1635-1641 | 2.19 | |
| | 1601-1617 | 2.10 (76) | | | |
| 8/20 | 1123-1159 | 3.17 (89) | 0722-0842 | 3.20 | |
| | 1159-1239 | 2.12 (89) | 0842-1018 | 2.79 | |
| | 1239-1330 | 2.01 (89) | 1018-1145 | 3.08 | |
| | 1348-1432 | 1.84 (44) | 1145-1314 | 3.03 | |
| | | | 1314-1441 | 3.08 | |
| | | | 1441-1502 | 2.55 | |

^aHeight maintained at 195 cm.

RESULTS AND DISCUSSION

A. Laboratory

Beacon selective weed oil is commonly applied to fields containing young carrots (three frond stage) for weed control while non-selective Chevron weed oil is a broad-spectrum herbicide commonly applied to alfalfa as a seed harvest aid. The selectivity of the Beacon oil, as compared to the Chevron oil, is due in part to its low content of aromatic compounds and to the presence of highly volatile aliphatics. GC-MS analysis of the two oils indicated that Beacon oil is comprised primarily of aliphatics (C_9-C_{12}) and Chevron oil contains substituted benzene and naphthalene, as well as some aliphatics (C_9-C_{19}).

The evaporation rates for the two oils in the laboratory are compared in Table 6. For comparable amounts of the oils applied to inert surfaces (Teflon®, polyethylene) under static wind conditions, 50% disappearance occurred in ~0.88 hr and ~24 hrs for Beacon and Chevron oil, respectively. Moreover, time for 50% disappearance decreased with decreasing starting surface concentration (mg/cm^2) for Beacon oil (Table 7), in agreement with the observations of Que Hee and Sutherland (1974) for single component herbicides. In the presence of a slight breeze (~0.43 m/sec), the time required for 50% loss was decreased dramatically to 0.15-0.26 hr for Beacon oil and ~5.5 hrs for Chevron oil (Table 8). The application rates (mg/cm^2) used for Beacon oil in the laboratory were comparable to the rates used under actual field conditions; while the laboratory amounts of Chevron oil correspond to some field uses, certain other field applications (seed alfalfa) will lead to much lower residues and, thus, to shorter times for significant loss (Que Hee and Sutherland, 1974).

Table 6. Evaporation of Beacon and Chevron Oils from Inert Surfaces with No Air Flow, Laboratory Tests.

| <u>Time, Hr</u> | <u>Temp., °C</u> | <u>Percent Remaining</u> | |
|-----------------|------------------|---------------------------|----------------------------|
| | | <u>Beacon^a</u> | <u>Chevron^b</u> |
| 0.5 | 22.6 | 68.1 | - |
| | 22.8 | 57.8 | - |
| 1.0 | 23.0 | 45.3 | - |
| | 22.8 | 39.2 | - |
| 2.0 | 23.2 | 30.3 | 93.2 |
| | 23.4 | 30.4 | - |
| 4.0 | 23.7 | - | 88.1 |
| 7.4 | 24.5 | - | 80.1 |

^a8.1-9.4 mg/cm²; 50% loss: 0.88 hr

^b10.3-10.5 mg/cm²; 50% loss: 24 hr

Table 7. Effect of Surface Concentration on the Evaporation of Beacon Oil from an Inert Surface, No Air Flow, Laboratory Tests.

| Time, hr | Percent Remaining ^a | | |
|----------|--------------------------------|---------------------------|--------------------------|
| | 30.15 mg/cm ^{2b} | 16.22 mg/cm ^{2c} | 9.27 mg/cm ^{2d} |
| 0.5 | 84.8 | 77.9 | 68.1 |
| 1.0 | 74.8 | 63.8 | 45.3 |
| 1.5 | 66.0 | 52.4 | - |
| 2.0 | 56.9 | 43.6 | 30.3 |

^aT = 23°C

^b50% loss: 2.5 hrs

^c50% loss: 1.6 hrs

^d50% loss: 0.96 hrs

Table 8. Evaporation of Beacon and Chevron Oils from Inert Surface, Under Slight Wind Conditions, Laboratory Tests.

| Time, hr | Temp., °C | Percent Remaining ^a | |
|----------|-----------|--------------------------------|----------------------|
| | | Beacon | Chevron ^d |
| 0.50 | 22.8 | 26.1 ^b | - |
| 0.63 | 25.8 | 5.0 ^c | - |
| 2.00 | 23.2 | - | 73.4 |
| 4.00 | 23.8 | - | 62.0 |
| 7.30 | 24.6 | - | 47.5 |

^aWind Speed ~0.43 m/s

^b9.4 mg/cm²; 50% loss: 0.26 hr

^c8.9 mg/cm²; 50% loss: 0.15 hr

^d10.4-10.5 mg/cm²; 50% loss: 5.5 hr

Loss of Beacon oil from Teflon® and soil surfaces, and subsequent trapping of the vapor by XAD-4 adsorbent, under very slight air movement (~0.01 m/sec) is summarized in Table 9. Application was done by spraying the surfaces with droplets of 150 µm VMD, comparable to sizes generated under field conditions. The results for Teflon® were similar to those observed in a previous experiment (Table 6); however, loss from soil was somewhat greater, in agreement with the results of Roberts (1981), because of the inherently greater surface area for finely-divided soil. Furthermore, evaporative loss based on GC analysis compared well with evaporative loss determined by weighing the deposits. This result is important because the field samples were to be analyzed by GC only.

B. Field

1. Beacon oil. Evaporation of Beacon oil from the soil-coated slides is shown in Table 10, which includes both observed and calculated amounts of oil (mg/cm²) for each sampling period. The calculated amounts were derived from a computer fit of observed data to an exponential expression; the resulting first-order rate constant and half-life were 0.0137 min⁻¹ and 50.6 min, respectively. These results compare well with those observed in the laboratory for both soil (50% loss: 30-60 min) and plastic (50% loss: 52 min)(Tables 6 and 9) surfaces despite the significant temperature change (Table 1) and measurable wind in the field (Table 2). Contributing to the appreciable volatility of the oil in the field was the high soil moisture content, a condition which commonly exists in carrot fields during application. Extrapolation of the field data to time = 0 gave an initial oil deposit of 6.62 mg/cm² which is equivalent to 827.5 L/ha (typical field rate is 467.4-934.9 L/ha). The flux (mg/cm²/hr) was derived from the calculated

Table 9. Evaporation of Beacon Oil from Two Surfaces Sprayed with 150 μm VMD Droplets, Slight Wind Conditions, Laboratory Tests.

| Surface | Temp., $^{\circ}\text{C}$ | Initial Deposit, mg/cm^2 ^a | Percent Remaining ^b | | Percent Evaporated ^b | |
|---------------------|---------------------------|-------------------------------------------------------|--------------------------------|------|---------------------------------|------|
| | | | Wt. | GC | Wt. | GC |
| Teflon [®] | 23.0 | 5.0 | 38.2 | 33.7 | 61.8 | 51.7 |
| | 22.5 | 7.3 | 51.2 | 43.4 | 48.8 | 42.6 |
| Soil ^c | 22.0 | 8.0 | 30.3 | 36.6 | 69.7 | 57.8 |
| | 22.5 | 5.3 | 27.7 | - | 72.3 | 68.1 |

^aHeld in air stream flowing at 1.0 LPM (0.01 m/s) for 1 hour.

^bWt. = by weight; GC = by gas chromatography.

^cYolo Sandy Loam.

Table 10. Evaporation of Beacon Oil from Yolo Sandy Loam, Field Test Plot,
UC Davis, July 22, 1982.

| <u>Time, min^a</u> | <u>Surface Conc., mg/cm²</u> | | <u>Flux, mg/cm²/hr^c</u> |
|------------------------------|---------------------------------------------|--------------------------|---------------------------------------------------|
| | <u>obs.</u> | <u>calc.^b</u> | |
| 1.02 | 6.42 | 6.53 | 5.29 |
| 16.20 | 4.86 | 5.30 | 4.86 |
| 31.20 | 4.92 | 4.32 | 3.92 |
| 49.20 | 4.08 | 3.37 | 3.17 |
| 64.80 | 4.00 | 2.72 | 2.50 |
| 154.80 | 0.34 | 0.79 | 1.29 |
| 274.80 | - | 0.15 | 0.32 |
| 394.80 | 0.04 | 0.03 | 0.06 |

^aPost-application

^bCalculated from: $\ln (\text{mg/cm}^2) = 1.8898 - 0.0137 (\text{min})$

where the rate constant = 0.0137 min^{-1} and

50% loss = 50.6 min

^cDerived from calculated surface concentration

dissipation of the oil; flux for each sampling period was determined using as the initial oil deposit that remaining at the end of the previous period.

Theoretical calculations using vapor pressures and heats of vaporization of hydrocarbon standards (APPENDIX A) gave 50% evaporation times that ranged from 62 min (10°C) to 32 min (20°C) for an initial deposit of 6.62 mg/cm². Since most of the oil vaporized within three hours after application, during which time the temperature rose from 10°C to 20°C (Table 1), the calculated estimates agree well with observation.

Concentration of Beacon oil in air above the treated plot is shown in Table 11. Decrease in observed concentration with height partly reflected the effect of vapor density and oil composition on the collection efficiency of the air samplers. The composition in air changed both with time and height (Table 12) such that the early and lower samples were enriched in the more volatile components and the later and upper samples were enriched in the less volatile components relative to an oil standard. Using the GC-derived oil composition and vapor pressures (from C₉-C₁₂ hydrocarbon reference pressures, APPENDICES A and C), adjustments were made to the observed air concentrations to compensate for collection efficiency. The resulting high air residues and the vapor concentration at the off-site downwind air sampler (observed = 108 mg/m³; adjusted = 177 mg/m³) fit with the observed rapid dissipation of the oil from the soil-coated slides.

2. Chevron oil. The evaporation of this oil from soil, glass, and filter paper surfaces for each plot is summarized in Tables 13 to 15. On glass and filter paper, oil evaporation followed inverse-time relationships, while evaporation from soil exhibited an exponential decay. Extrapolation of the soil data to time = 0 for all four of the test plots gave initial deposits of 0.11-0.18 mg/cm² and 0.22 mg/cm² for the August 18 and 20 applications,

Table 11. Vapor Density of Beacon Oil Above the Treated Field Plot, UC
Davis, July 22, 1982.

| Time, hr ^a | | Concentration, mg/m ³ | | |
|-----------------------|----------------|----------------------------------|-----------------------|------------------------|
| | | 30.48 cm ^b | 60.96 cm ^b | 106.68 cm ^b |
| 0.22 | 0 ^c | 231.48 | 83.46 | 25.43 |
| | A ^d | 231.79 | 160.48 | 92.18 |
| 0.63 | 0 | 31.74 | 12.98 | 4.10 |
| | A | 95.13 | 56.44 | 25.30 |
| 2.60 | 0 | 10.96 | 6.63 | 3.76 |
| | A | 29.54 | 20.02 | 12.51 |

^aPost-application.

^bHeight above plot.

^cObserved concentration.

^dAdjusted concentration (taking collection efficiency into account).

Table 12. Composition of Beacon Oil in Air Above Treated Field Plot, UC Davis, July 22, 1982.

| Time, hr ^b | Height, cm | Oil Mole Fraction ^a | | | |
|-----------------------|------------|--------------------------------|------|------|------|
| | | 1 | 2 | 3 | 4 |
| 0.22 | 30.48 | 0.33 | 0.42 | 0.18 | 0.07 |
| | 60.96 | 0.23 | 0.42 | 0.24 | 0.11 |
| | 106.68 | 0.24 | 0.51 | 0.21 | 0.04 |
| 0.63 | 30.48 | 0.09 | 0.32 | 0.39 | 0.20 |
| | 60.96 | 0.06 | 0.30 | 0.44 | 0.20 |
| | 106.68 | - | 0.34 | 0.52 | 0.14 |
| 2.60 | 30.48 | 0.03 | 0.29 | 0.42 | 0.26 |
| | 60.96 | - | 0.30 | 0.58 | 0.12 |
| | 106.68 | - | 0.34 | 0.66 | - |
| Standard | - | 0.13 | 0.27 | 0.24 | 0.36 |

^aRelative amounts of GC chromatographic subareas (1-4) derived from reference hydrocarbons (Figure 4).

^bPost-application.

Table 13. Chevron Oil Residues on Soil Screens in Alfalfa Field, Helm, CA,
August 18-20, 1982.

| <u>Application Date</u> | <u>Plot No.^a</u> | <u>Time Post Spray, hr</u> | <u>Oil Conc., mg/cm²</u> |
|-------------------------|-----------------------------|--------------------------------|-------------------------------------|
| 8/18 | 1 | 0.23 | 0.119 |
| | | 1.80 | 0.080 |
| | | 3.37 | 0.082 |
| | | 4.94 | 0.112 |
| | | 6.55 | 0.100 |
| | | 19.38 | 0.027 |
| | | 25.33 | 0.023 |
| | | 31.30 | 0.030 |
| | 2 | 0.39 | 0.144 |
| | | 1.99 | 0.166 |
| | | 3.72 | 0.132 |
| | | 5.45 | 0.117 |
| | | 6.78 | 0.139 |
| | | 19.56 | 0.032 |
| | | 25.73 | 0.038 |
| | 3 | 0.82 | 0.152 |
| | | 2.39 | 0.154 |
| | | 3.96 | 0.101 |
| | | 5.53 | 0.153 |
| | | 7.15 | 0.125 |
| | | 19.83 | 0.064 |
| | | 25.82 | 0.051 |
| | 31.62 | 0.040 | |

| | | | |
|------|----------------|-------|-------|
| | 4 | 0.94 | 0.199 |
| | | 2.42 | 0.131 |
| | | 4.19 | 0.181 |
| | | 5.64 | 0.124 |
| | | 7.15 | 0.074 |
| | | 20.12 | 0.064 |
| | | 26.05 | 0.046 |
| | | 31.88 | 0.018 |
| 8/20 | 1 ^b | 0.20 | 0.250 |
| | | 1.52 | 0.357 |
| | | 3.42 | 0.316 |
| | 2 | 1.83 | 0.199 |
| | | 3.62 | 0.206 |
| | 3 | 2.05 | 0.154 |
| | | 3.83 | 0.191 |
| | 4 | 0.78 | 0.206 |
| | | | 0.177 |
| | | 2.17 | 0.113 |
| | | | 0.145 |
| | | 4.00 | 0.226 |
| | | | 0.095 |

^aPlot 1: $\text{Ln (mg/cm}^2) = -2.20331 - 0.05297 \text{ (hrs post spray)}$

Plot 2: $\text{Ln (mg/cm}^2) = -1.75869 - 0.06722 \text{ (hrs post spray)}$

Plot 3: $\text{Ln (mg/cm}^2) = -1.83202 - 0.04426 \text{ (hrs post spray)}$

Plot 4: $\text{Ln (mg/cm}^2) = -1.71443 - 0.06272 \text{ (hrs post spray)}$

^bAll points combined: $\text{Ln (mg/cm}^2) = -1.5291 - 0.05466 \text{ (hrs post spray)}$

Table 14. Chevron Oil Residues on Glass in Alfalfa Field, Helm, CA,
August 18-20, 1982.

| <u>Application Date</u> | <u>Plot No.^a</u> | <u>Time Post Spray, hrs</u> | <u>Conc., mg/cm²</u> |
|-------------------------|-----------------------------|---------------------------------|---------------------------------|
| 8/18 | 1 | 1.67 | 1.203×10^{-3} |
| | | 6.58 | 3.514×10^{-4} |
| | | 19.40 | 1.115×10^{-4} |
| | | 25.38 | 5.993×10^{-5} |
| | | 31.17 | 3.654×10^{-5} |
| | 2 | 0.39 | 2.19×10^{-2} |
| | | 2.03 | 1.792×10^{-3} |
| | | 3.73 | 1.883×10^{-3} |
| | | 6.80 | 5.196×10^{-4} |
| | | 19.62 | 8.586×10^{-5} |
| | 3 | 0.70 | 4.163×10^{-2} |
| | | 2.25 | 1.805×10^{-3} |
| | | 4.02 | 3.854×10^{-3} |
| | | 7.02 | 1.805×10^{-3} |
| | | 19.87 | 5.682×10^{-4} |
| 25.87 | | 1.223×10^{-4} | |
| 31.75 | | 1.805×10^{-4} | |
| 8/20 | 1 ^b | 0.10 | 4.810×10^{-2} |
| | | 1.55 | 5.615×10^{-3} |
| | | 3.32 | 1.825×10^{-3} |
| | 2 | 0.28 | 1.167×10^{-2} |
| | | 1.75 | 1.795×10^{-3} |
| | | 3.53 | 1.600×10^{-4} |

| | | |
|---|------|------------------------|
| 3 | 0.50 | 5.329×10^{-2} |
| | 1.97 | 8.320×10^{-3} |
| | 3.75 | 2.375×10^{-3} |
| 4 | 0.70 | 8.028×10^{-3} |
| | 2.15 | 1.368×10^{-3} |
| | 3.97 | 7.219×10^{-4} |

^aPlot 1: $(\text{mg}/\text{cm}^2) = -2.0491 \times 10^{-6} + 2.02883 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 2: $(\text{mg}/\text{cm}^2) = -9.92538 \times 10^{-4} + 8.83993 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 3: $(\text{mg}/\text{cm}^2) = -2.88271 \times 10^{-3} + 2.94143 \times 10^{-2}/(\text{hrs Post Spray})$.

^bPlot 1: $(\text{mg}/\text{cm}^2) = 1.4932 \times 10^{-3} + 4.66503 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 2: $(\text{mg}/\text{cm}^2) = -4.96234 \times 10^{-4} + 3.41378 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 3: $(\text{mg}/\text{cm}^2) = -6.08259 \times 10^{-3} + 2.96401 \times 10^{-2}/(\text{hrs Post Spray})$.

Plot 4: $(\text{mg}/\text{cm}^2) = -1.09913 \times 10^{-3} + 6.07074 \times 10^{-3}/(\text{hrs Post Spray})$.

Table 15. Chevron Oil Residue on Filter Paper in Alfalfa Field, Helm, CA
August 18-20, 1982.

| <u>Application Date</u> | <u>Plot No.^a</u> | <u>Time Post Spray, hrs</u> | <u>Conc., mg/cm²</u> |
|-------------------------|-----------------------------|---------------------------------|---------------------------------|
| 8/18 | 1 | 0.13 | 1.937×10^{-2} |
| | | 1.78 | 4.918×10^{-3} |
| | | 3.48 | 8.030×10^{-3} |
| | | 6.62 | 3.922×10^{-3} |
| | | 19.42 | 1.339×10^{-3} |
| | | 25.42 | 3.165×10^{-4} |
| | | 31.18 | 6.598×10^{-4} |
| | 2 | 0.43 | 5.618×10^{-3} |
| | | 2.05 | 1.354×10^{-3} |
| | | 3.77 | 1.494×10^{-3} |
| | | 6.82 | 1.418×10^{-3} |
| | | 19.65 | 8.061×10^{-4} |
| | | 25.65 | 3.678×10^{-4} |
| | | 31.50 | 5.680×10^{-4} |
| | 3 | 0.73 | 0.1085 |
| | | 4.05 | 1.844×10^{-2} |
| | | 7.05 | 1.424×10^{-2} |
| | | 19.90 | 1.109×10^{-2} |
| | | 25.92 | 6.271×10^{-3} |
| | | 31.77 | 5.098×10^{-3} |
| 8/20 | 1b | 0.12 | 2.988×10^{-2} |
| | | 1.58 | 6.825×10^{-3} |
| | | 3.33 | 4.743×10^{-3} |

| | | |
|---|------|------------------------|
| 2 | 0.32 | 4.575×10^{-2} |
| | 1.78 | 1.096×10^{-2} |
| | 3.55 | 6.727×10^{-3} |
| 3 | 0.53 | 0.143 |
| | 1.98 | 2.241×10^{-2} |
| | 3.77 | 1.156×10^{-2} |
| 4 | 0.72 | 1.562×10^{-2} |
| | 2.18 | 7.059×10^{-3} |
| | 3.98 | 6.536×10^{-3} |

^aPlot 1: $(\text{mg}/\text{cm}^2) = 2.74966 \times 10^{-3} + 2.19063 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 2: $(\text{mg}/\text{cm}^2) = 6.40221 \times 10^{-4} + 2.13468 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 3: $(\text{mg}/\text{cm}^2) = 3.364 \times 10^{-3} + 7.63482 \times 10^{-2}/(\text{hrs Post Spray})$.

^bPlot 1: $(\text{mg}/\text{cm}^2) = 4.34193 \times 10^{-3} + 3.0671 \times 10^{-3}/(\text{hrs Post Spray})$.

Plot 2: $(\text{mg}/\text{cm}^2) = 3.06962 \times 10^{-3} + 1.36651 \times 10^{-2}/(\text{hrs Post Spray})$.

Plot 3: $(\text{mg}/\text{cm}^2) = -1.46435 \times 10^{-2} + 8.30612 \times 10^{-2}/(\text{hrs Post Spray})$.

Plot 4: $(\text{mg}/\text{cm}^2) = 3.89025 \times 10^{-3} + 8.3608 \times 10^{-3}/(\text{hrs Post Spray})$.

respectively. The August 20 soil data for all plots were combined since there was substantial scatter in the data points for each plot. Average 50% loss times were 12.53 hrs and 12.68 hrs for the August 18 and 20 applications to soil, respectively. Evaporation was unexpectedly slow, given the initial deposits and high soil temperatures (Table 3). The dry condition of the soil (adsorption) was no doubt partly responsible for this behavior. These initial deposits were confirmed using a modified form of an expression published elsewhere (Eureka, 1980) which allows one to calculate the amount of material deposited if vapor pressure and temperature are known (APPENDIX A). The modification involved using mole fraction and vapor pressure for each subarea of the oil GC chromatogram. Given the application rate supplied to us by the spray plane pilot in this study (0.41 mg/cm^2), the calculated amounts deposited were 0.16 mg/cm^2 and 0.22 mg/cm^2 for the August 18 and 20 applications, respectively. It should be noted, however, that the spray plane had not been specially calibrated for this study.

Using the initial deposits from the soil data in the inverse-time relationships exhibited by the oil on glass (Table 14) and paper (Table 15) gave times for 50% loss that fell in the range 2-21 min ($\bar{X} = 10 \text{ min}$) (Aug 18) and 2-16 min ($\bar{X} = 6 \text{ min}$) (Aug 20) for glass, and 2-40 min ($\bar{X} = 14 \text{ min}$) (Aug 18) and 2-60 min ($\bar{X} = 21 \text{ min}$) (Aug 20) for paper. Theoretical calculations using vapor pressures and heats of vaporization of hydrocarbon standards on inert surfaces (APPENDIX A) gave 50% loss times ranging from 11 min (20°C) down to 0.9 min (60°C) for an initial deposit of 0.15 mg/cm^2 , comparable to the data for glass. These observed and calculated 50% loss times are considerably less than those observed in the laboratory (Table 6). The difference is primarily due to the $\sim 100\times$ greater concentrations (mg/cm^2) used in the laboratory.

Loss of Chevron oil from plant surfaces, as well as from glass and filter paper, is summarized in Table 16 for one of the test plots. Due to a lengthy analysis, only a representative sample of the plant data is included in this report. As can be seen, the early residue levels on glass and plant surfaces compare well for both applications, while residues on paper were somewhat greater. Since the behavior of the oil on plant and glass surfaces was essentially the same, oil flux ($\text{mg}/\text{cm}^2/\text{hr}$) for the alfalfa field was estimated using the data on glass (Table 17). The tabulated values were derived from the calculated dissipation of the oil; flux for each time interval was determined using as the initial oil deposit that remaining at the end of the previous interval.

Concentration of the Chevron oil in field air is summarized in Tables 18 and 19 for both applications. These tabulated values are observed concentrations and they were not adjusted for collection efficiency of the air samplers (APPENDIX C). Residue levels in air reflected the substantial volatility of the oil in the field environment. Levels near the field during the August 18 application exceeded $1 \text{ mg}/\text{m}^3$, while farther downwind ($\sim 400 \text{ m}$) concentration decreased to only about $0.5 \text{ mg}/\text{m}^3$. During the August 20 application, residue levels of the drift were considerably greater, but this was due in part to the more optimum location of the samplers in relation to the prevailing wind. Furthermore, an ambient sample taken $\sim 8 \text{ km N.}$ of the field contained some oil residue ($0.02 \text{ mg}/\text{m}^3$) indicating widespread movement of the oil. It should be noted that several seed alfalfa fields in the vicinity of the test field were treated prior to and during this study. A sample taken 8 m downwind over one hour after application indicated substantial vaporization and drift from the field; its residue level was comparable to that in a sample taken simultaneously in the field at the same

Table 16. Chevron Oil Residues on Three Surfaces in Plot No. 3, Helm, CA,
August 18-20, 1982.

| Application Date | Time Post Spray, hr | Concentration, mg/cm ² | | |
|------------------|---------------------|-----------------------------------|------------------------|------------------------|
| | | Foliage | Glass ^a | Paper ^a |
| 8/18 | 0.65 | 1.232×10^{-2} | 4.237×10^{-2} | 0.121 |
| | 3.93 | 6.422×10^{-3} | 4.602×10^{-3} | 2.279×10^{-2} |
| | 25.75 | 5.216×10^{-3} | - | 6.329×10^{-3} |
| 8/20 | 0.40 | 2.114×10^{-2} | 6.802×10^{-2} | 0.193 |
| | 1.87 | 1.045×10^{-2} | 9.768×10^{-3} | 2.977×10^{-2} |
| | 3.68 | 1.055×10^{-2} | 1.972×10^{-3} | 7.927×10^{-3} |

^aCalculated values using inverse-time relationships (Tables 14 and 15).

Table 17. Flux of Chevron Oil Residues from Treated Alfalfa Field, Helm, CA,
August 18-20, 1982.

| <u>Application Date</u> | <u>Plot No.^a</u> | <u>Time Post Spray, hr</u> | <u>Oil Deposit, mg/cm²</u> | <u>Oil Flux, mg/cm²/hr</u> |
|-------------------------|-----------------------------|----------------------------|---------------------------------------|---------------------------------------|
| 8/18 | 1 | 0.05 | 4.057×10^{-2} | 1.396 |
| | | 0.20 | 1.014×10^{-2} | 0.203 |
| | | 0.80 | 2.534×10^{-3} | 0.013 |
| | | 3.20 | 6.320×10^{-4} | 7.925×10^{-4} |
| | | 12.80 | 1.564×10^{-4} | 4.954×10^{-5} |
| | 2 | 0.10 | 8.741×10^{-2} | 0.849 |
| | | 0.40 | 2.111×10^{-2} | 0.221 |
| | | 1.60 | 4.532×10^{-3} | 0.014 |
| | | 6.40 | 3.887×10^{-4} | 8.632×10^{-4} |
| | 3 | 0.50 | 5.595×10^{-2} | 0.208 |
| | | 1.00 | 2.653×10^{-2} | 0.059 |
| | | 2.00 | 1.182×10^{-2} | 0.015 |
| | | 4.00 | 4.471×10^{-3} | 3.647×10^{-3} |
| | | 8.00 | 7.941×10^{-4} | 9.192×10^{-4} |
| | 8/20 | 1 ^b | 0.05 | 9.479×10^{-2} |
| 0.20 | | | 2.482×10^{-2} | 0.466 |
| 0.80 | | | 7.324×10^{-3} | 0.029 |
| 3.20 | | | 2.951×10^{-3} | 1.822×10^{-3} |
| 12.80 | | | 1.858×10^{-3} | 1.138×10^{-4} |
| 2 | | 0.05 | 6.778×10^{-2} | 3.044 |
| | | 0.20 | 1.657×10^{-2} | 0.341 |
| | | 0.80 | 3.771×10^{-3} | 0.021 |
| | | 3.20 | 5.706×10^{-4} | 1.334×10^{-3} |

| | | | |
|---|------|------------------------|------------------------|
| | 6.40 | 3.717×10^{-5} | 1.667×10^{-4} |
| 3 | 0.20 | 0.142 | 0.390 |
| | 0.40 | 6.802×10^{-2} | 0.370 |
| | 0.80 | 3.097×10^{-2} | 0.093 |
| | 1.60 | 1.244×10^{-2} | 0.023 |
| | 3.20 | 3.180×10^{-3} | 5.788×10^{-3} |
| 4 | 0.05 | 0.120 | 2.000 |
| | 0.15 | 3.937×10^{-2} | 0.806 |
| | 0.45 | 1.239×10^{-2} | 0.090 |
| | 1.35 | 3.398×10^{-3} | 0.010 |
| | 4.05 | 3.998×10^{-4} | 1.110×10^{-3} |

^aPlot 1: $C_0 = 0.1104 \text{ mg/cm}^2$

Plot 2: $C_0 = 0.1723 \text{ mg/cm}^2$

Plot 3: $C_0 = 0.1601 \text{ mg/cm}^2$

^b $C_0 = 0.22 \text{ mg/cm}^2$ used for all plots.

Table 18. Chevron Oil Concentration in Air in an Alfalfa Field Environment--
High Volume Samplers, Helm, CA, August 18-20, 1982.

| <u>Application Date</u> | <u>Time, hr^a</u> | <u>Downwind Distance (D) or Height (H)^b</u> | <u>Air Conc., mg/m³</u> |
|-------------------------|-----------------------------|--------------------------------------------------------|------------------------------------|
| 8/18 | Spray | 8m (D) | 1.479 |
| | Spray | 48m (D) | 0.373 |
| | Spray | 402m (D) | 0.562 |
| | 1.76 | 8m (D) | 0.641 |
| | 1.58 | 76cm (H) | 0.650 |
| | 3.05 | 76cm (H) | 0.153 |
| | 4.62 | 76cm (H) | 0.111 |
| | 28.48 | 76cm (H) | 0.052 |
| | Ambient/Pre-Spray | 8Km N. of Field | 0.020 |
| | 8/20 | Spray | 17m (D) |
| Spray | | 48m (D) | 7.979 |
| 1.17 | | 95cm (H) | 1.009 |
| 2.48 | | 95cm (H) | 0.317 |

^aTimes are after application, except when noted otherwise.

^bDownwind (D) and ambient samplers were 76-95cm above the ground. Samplers at specified height (H) were located in Plot No. 1 (Figure 3).

Table 19. Chevron Oil Concentration in Air in an Alfalfa Field Environment--
Multiple Cartridge Samplers, Helm, CA, August 18-20, 1982.

| Application | Time Post Spray, hr | Air Concentration, mg/m ³ | | |
|-------------|------------------------|--------------------------------------|-----------------------|-----------------------|
| | | 48.90cm ^a | 113.35cm ^a | 183.83cm ^a |
| 8/18 | 1.59 | 0.398 | 0.291 | 0.250 |
| | 3.05 | 0.176 | 0.083 | 0.045 |
| | 4.64 | 0.114 | 0.091 | 0.078 |
| | 6.96 | 0.198 | 0.132 | 0.114 |
| | 23.88 | 0.248 | 0.198 | 0.155 |
| | 26.16 | 0.113 | 0.107 | 0.090 |
| | 28.48 | 0.054 | 0.058 | 0.050 |
| 8/20 | 1.15 | 0.788 | 0.499 | 0.395 |
| | 2.48 | 0.214 | 0.170 | 0.148 |
| | 3.58 | 0.130 | 0.119 | 0.113 |

^aHeight above Plot No. 1.

height. Average oil flux was estimated using a concentration profile given by the multiple cartridge samplers (plot no. 1), average wind speed, and the method of Wilson et al. (1982). For the period 0.98-2.18 hrs post-application (August 18), the average flux calculated using air sample data only was $<9 \times 10^{-3}$ mg/cm²/hr, compared to the range 0.85 - 4.2×10^{-3} mg/cm²/hr given by the loss of oil from glass in the same plot (Table 17). Loss of oil from glass averaged over the entire field gave an average flux of $\sim 6 \times 10^{-3}$ mg/cm²/hr for the same time period.

C. Emission Estimation Methodology

The emissions methodology discussed in the Eureka report (1980) uses average properties of the oil mixtures to estimate evaporative loss. It is assumed that these average properties do not change during the course of evaporation. Furthermore, evaporation of the oil mixtures is treated as a first-order process. The approach described in detail in APPENDIX A of this report assumes independent evaporation of each oil component, as related to component vapor pressure and surface concentration (mg/cm²). Implied in this is that first-order evaporation occurs only for each component of the mixture rather than for the mixture itself and that average properties of the mixture will change with time. Since the most volatile and least volatile components of the oils have vapor pressures greater and less than the average vapor pressures, use of average properties will lead to under-estimation of loss early in the course of evaporation and over-estimation of loss at later times.

By comparing evaporation rates measured in the field with calculated rates, it was concluded that the approach described in APPENDIX A best describes evaporation of the oil mixtures. Moreover, this approach is particularly useful for describing evaporation during short time intervals

(~mins) post-application. Also, this approach can easily incorporate the effects of temperature and amount of applied oil on evaporation rate; the effect of wind speed can also be incorporated once the relationship between evaporation rate and wind speed is determined. The methodology discussed in the Eureka report (1980) can only give average behavior over broader time intervals and cannot reflect moment-to-moment changes in micro-meteorological conditions, as can the method presented in this report.

CONCLUSIONS

Evaporation of Beacon and Chevron oils depended not only upon their vapor pressures, but also upon their surface concentrations (wt/area), with all other conditions constant (wind speed, temperature). This was clearly shown for Beacon oil in the laboratory where a threefold increase in concentration resulted in about a threefold increase in 50% evaporation time. Comparable amounts of Chevron oil gave loss times that were ~20× those for Beacon oil, due to difference in vapor pressures, while in the field, where Chevron oil concentrations were about 40× less than those for Beacon oil, Chevron oil loss times were about 1/5th those for Beacon oil. Residue levels in field air, as well as theoretical calculations derived from the properties of hydrocarbon standards (APPENDIX A), tended to substantiate these loss rates.

Beacon oil is commonly applied at night under conditions of cool temperatures and no wind. A ground rig is used with nozzles ~15 cm above the ground. This leads to momentarily high soil residues for optimum weed control in carrot fields. However, the high moisture content of the soil (application is generally made 1-2 days after irrigation) and its high sand content would promote substantial post-application evaporation, as was observed in this study. Chevron oil is applied by air during daylight hours under warm summer

temperatures ($>30^{\circ}\text{C}$) and some wind (up to ~ 4.5 m/sec). These conditions would promote significant loss of the material, as was indicated in this study by high oil residues in the downwind air samplers. Also, based on the vapor pressure of the material and the prevailing temperature during application, calculated losses (APPENDIX A) indicated that only 38-53% of the applied material impacted the field, assuming that the oil was applied at the rate stated by the spray plane pilot. The matter of drift losses during application should be studied separately, using an experimental design which includes a calibrated spray plane.

Most of the applied oils became airborne within a day after application. For Beacon oil, the field data convincingly show that about 95% of the residue evaporated in 3 hrs after application. For Chevron oil, about 46% (average of the two applications) apparently became airborne as drift during application, and 50% of the surface residue evaporated within 30 min after application. Furthermore, our analysis of vapor samples taken above the treated fields and downwind from them showed that no detectable decomposition of oil constituents occurred in the time-frame of our studies, reinforcing the conclusion that loss of surface oil was totally due to evaporation.

Comparison of the two approaches to the simulation of oil evaporation, discussed in APPENDIX A of this report and the Eureka report (1980), led to the conclusion that the former best describes the behavior of oil mixtures since it accounts for oil component evaporation and changing oil composition. It can also incorporate the effects of temperature, amount of applied oil, and wind speed on oil evaporation rate. The approach detailed in the Eureka report (1980) can only give average behavior and is unsuitable for describing evaporation during short time intervals after application.

REFERENCES

- Eureka Laboratories, Inc. April, 1980. Air Pollution Emissions Associated with Nonsynthetic Hydrocarbon Applications for Pesticidal Purposes in California, Vol. II. Final Report to the California Air Resources Board.
- Que Hee, S.S.; and Sutherland, R.G. 1974. Weed Sci. 22, 313.
- Roberts, R.M. July, 1981. Development of Emission Factors for Reactive Hydrocarbons used in Pesticide Formulations. Final report to the California Air Resources Board.
- Wilson, J.D.; Thurtell, G.W.; Kidd, G.E.; and Beauchamp, E.G. 1982. Atmos. Environ. 16, 1861.

APPENDIX A

Simulated Evaporation of Beacon and Chevron Weed Oils

The method for estimating evaporation presented in this report works from the assumptions that (1) the components of an oil mixture vaporize independently of each other and (2) the evaporation of each component in a mixture follows first-order kinetics. While the first assumption may not be necessarily true and is difficult to assess, the second assumption has been shown to be true if evaporation is kinetically controlled (i.e., dynamic evaporation into an infinite reservoir) (Que Hee and Sutherland, 1974).

Since it was difficult and inconvenient to determine each component of the Beacon and Chevron oil mixtures, gas chromatograms (GC) of these oils were divided into four areas (Beacon) and seven areas (Chevron) using a programmed electronic integrator. The retention times spanned by each area were adjusted to include at least one hydrocarbon reference, preferably near the center of each area (Figure 4). By dividing the relative percent for each area, given by the integrator, by the molecular weights of the hydrocarbon references and summing the resulting "moles," mole fraction for each area was derived (Table 20). Using this procedure, weighted average molecular weights and vapor pressures were determined for Beacon oil (153.79; 1.5 mm Hg at 30°C) and for Chevron oil (188.43; 0.3 mm. Hg at 30°C).

The vaporization rate of each hydrocarbon reference was determined from the relationship first proposed by Hartley (1969)

$$F_1 = \frac{P_1 (M_1)^{1/2}}{P_2 (M_2)^{1/2}} \cdot F_2$$

where P = vapor pressure, M = molecular weight, 1 = hydrocarbon reference, 2 =

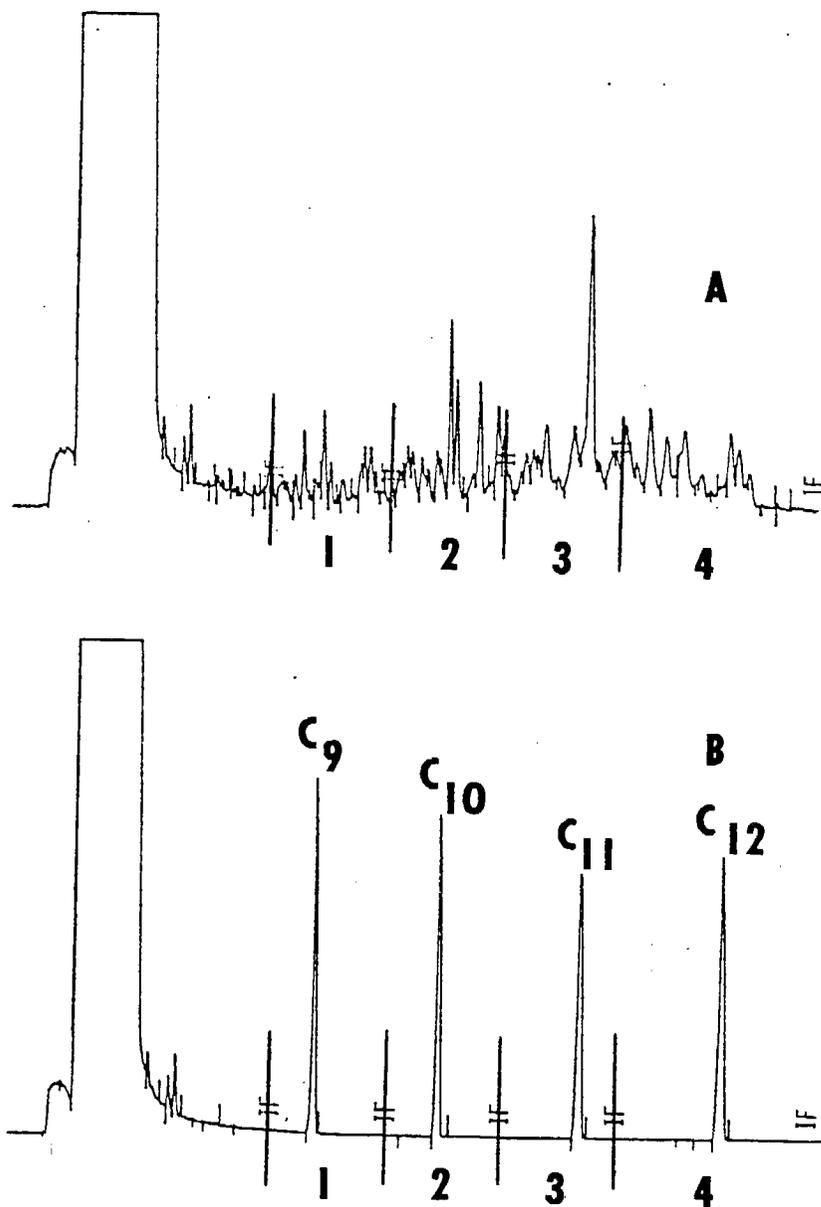


Figure 4. GAS CHROMATOGRAMS OF BEACON CARROT OIL (A) AND HYDROCARBON REFERENCES (B).

Table 20. The Component and Weighted Average Properties of Beacon and Chevron Oil Standards.

| G.C. Area # | Reference C # | Reference MW | Mole Fraction | MW | Vapor Press (30°C), mm Hg | Partial Press (30°C), mm Hg |
|---------------------|---------------|--------------|-----------------|---------------|---------------------------|------------------------------------------|
| <u>Beacon Oil:</u> | | | | | | |
| 1 | 9 | 128.26 | 0.131 | 16.802 | 6.1920 | 0.8112 |
| 2 | 10 | 142.29 | 0.274 | 38.987 | 1.8257 | 0.5002 |
| 3 | 11 | 156.31 | 0.239 | 37.358 | 0.5721 | 0.1367 |
| 4 | 12 | 170.34 | 0.356 | <u>60.641</u> | 0.1796 | <u>0.0639</u> |
| | | | $M = 153.788^a$ | | $P = 1.5120^b$ | |
| <u>Chevron Oil:</u> | | | | | | |
| 1 | 9-10 | 135.28 | 0.053 | 7.170 | 3.5805 | 0.1898 |
| 2 | 11 | 156.31 | 0.148 | 23.134 | 0.5721 | 0.0847 |
| 3 | 12-13 | 177.36 | 0.340 | 60.302 | 0.0916 | 0.0311 |
| 4 | 14 | 198.39 | 0.278 | 55.152 | 0.0160 | 4.448×10^{-3} |
| 5 | 16 | 226.45 | 0.134 | 30.344 | 1.25×10^{-3} | 1.674×10^{-4} |
| 6 | 18 | 254.50 | 0.040 | 10.180 | 1.145×10^{-4} | 4.580×10^{-6} |
| 7 | 19 | 268.53 | 0.008 | <u>2.148</u> | 2.95×10^{-5} | <u>2.360×10^{-7}</u> |
| | | | $M = 188.430^a$ | | $P = 0.3102^b$ | |

^aM = Weighted average molecular weight.

^bP = Weighted average vapor pressure.

standard, and $F_2 = 1.458 \times 10^{-5}$ mg/cm²/hr for dieldrin standard at 303°K (Spencer et al., 1973). The effective vapor pressure corresponding to the given vaporization rate and the molecular weight for dieldrin are 1.6×10^{-6} mm.Hg (303°K) and 380.93. Vapor pressure (P) for each hydrocarbon reference was determined from the Antoine equation

$$\ln P = A - \frac{B}{(T+C)}$$

where the constants A, B, and C are taken from Reid et al. (1977) and T = °K (Table 20). The first-order rate constant, k_i , for the vaporization of each hydrocarbon reference was calculated using the expression

$$k_i = F_i/a_i$$

where $a_i = \bar{X}_i A_0$ (\bar{X}_i = GC area mole fraction; A_0 = amount of oil mixture). From this, the fraction (A_t/A_0) of total oil remaining at any time t is

$$A_t/A_0 = \sum \bar{X}_i \exp(-k_i t)$$

where $\bar{X}_i \exp(-k_i t)$ is the fraction remaining of each GC area. Furthermore, the rate constant at any other temperature can be computed using the expression

$$k_i' = k_i \exp - \frac{\Delta H_i}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

where k_i' is the new rate constant at the new temperature T_2 , and ΔH_i and R are the hydrocarbon heat of vaporization and the gas law constant (1.99 cal/°K mole). Also, the rate constant at any other total amount of oil can be

obtained from

$$k_i'' = k_i (A_1/A_2)$$

where k_i'' is the new rate constant at the new oil amount, A_2 . So in summary,

$$A_t/A_0 = \sum \bar{X}_i \left\{ \exp-t \left[k_i(r) \exp- \frac{\Delta H_i}{R} \left(\frac{T_1-T_2}{T_1 T_2} \right) \right] \right\}$$

where $r = A_1/A_2$. Table 21 lists vaporization rate, rate constant, and heat of vaporization for Beacon and Chevron oil GC areas.

While $\bar{X}_i \exp(-k_i t)$ is first-order, the sum, $\sum \bar{X}_i \exp(-k_i t)$, is not. This is illustrated in Figure 5 for four hydrocarbon references (C_9-C_{12}) used to represent the Beacon oil mixture. The evaporation of each hydrocarbon reference is a first-order process, represented by the straight lines of the Log-linear plots in Figure 5. The resultant curve, which represents the observed evaporation of the bulk oil, shows a rapid decline near time = 0, due to loss of the more volatile components, and it approaches the evaporation rate of the least volatile components.

This behavior implies that properties of the bulk mixture (average molecular weight and vapor pressure) will change with time. However, the emissions methodology discussed in the Eureka report (1980) uses average properties of the oil mixtures to estimate evaporative loss. It is assumed that these average properties do not change during the course of evaporation. Furthermore, evaporation of the oil mixtures is treated as a first-order process. By using average vapor pressures and molecular weights in the Hartley equation (1969), evaporation curves for Beacon and Chevron oils can be derived for isothermal conditions (Figures 6 and 7). Since the most volatile and least volatile components of the oils have vapor pressures

Table 21. Component Vaporization of Beacon and Chevron Oil Standards at 30°C.

| GC Area # | Vaporization Rate (F), mg/cm ² /hr | Vaporization Rate ^a Const. (K), hr ⁻¹ | Heat of Vaporization (ΔH), Cal/mole |
|---------------------|-----------------------------------------------|-------------------------------------------------------------|-------------------------------------|
| <u>Beacon Oil:</u> | | | |
| 1 | 32.741 | 37.78 | 10456.9 |
| 2 | 10.170 | 5.61 | 10912.0 |
| 3 | 3.340 | 2.11 | 11481.7 |
| 4 | 1.095 | 0.46 | 11857.7 |
| <u>Chevron Oil:</u> | | | |
| 1 | 19.444 | 2446.93 | 10684.4 |
| 2 | 3.340 | 150.50 | 11481.7 |
| 3 | 0.5696 | 11.17 | 12424.5 |
| 4 | 0.1049 | 2.52 | 13750.0 |
| 5 | 8.78×10^{-3} | 0.44 | 15405.5 |
| 6 | 8.53×10^{-4} | 0.14 | 15447.0 |
| 7 | 2.26×10^{-4} | 0.188 | 16497.3 |

^aInitial amount of oil = 6.62 mg/cm² for Beacon oil and 0.15 mg/cm² for Chevron oil.

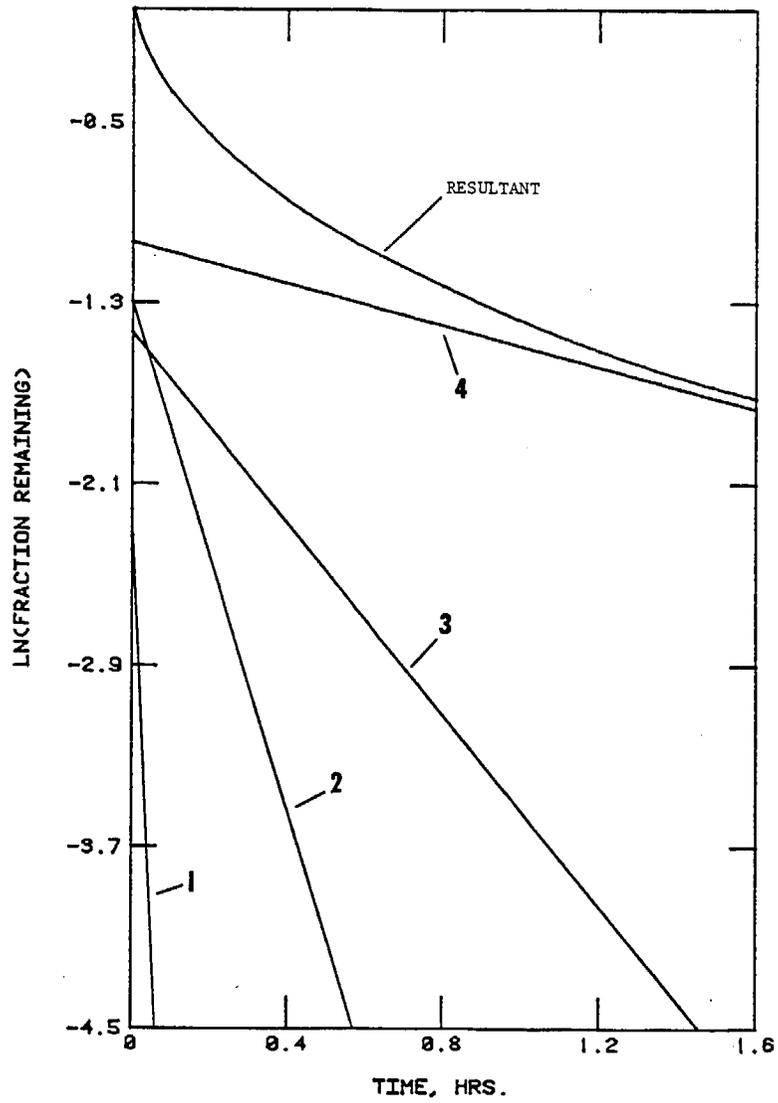


Figure 5. CALCULATED EVAPORATION OF BEACON OIL FROM AN INERT SURFACE. NO'S 1-4 REPRESENT GC SUBAREAS.

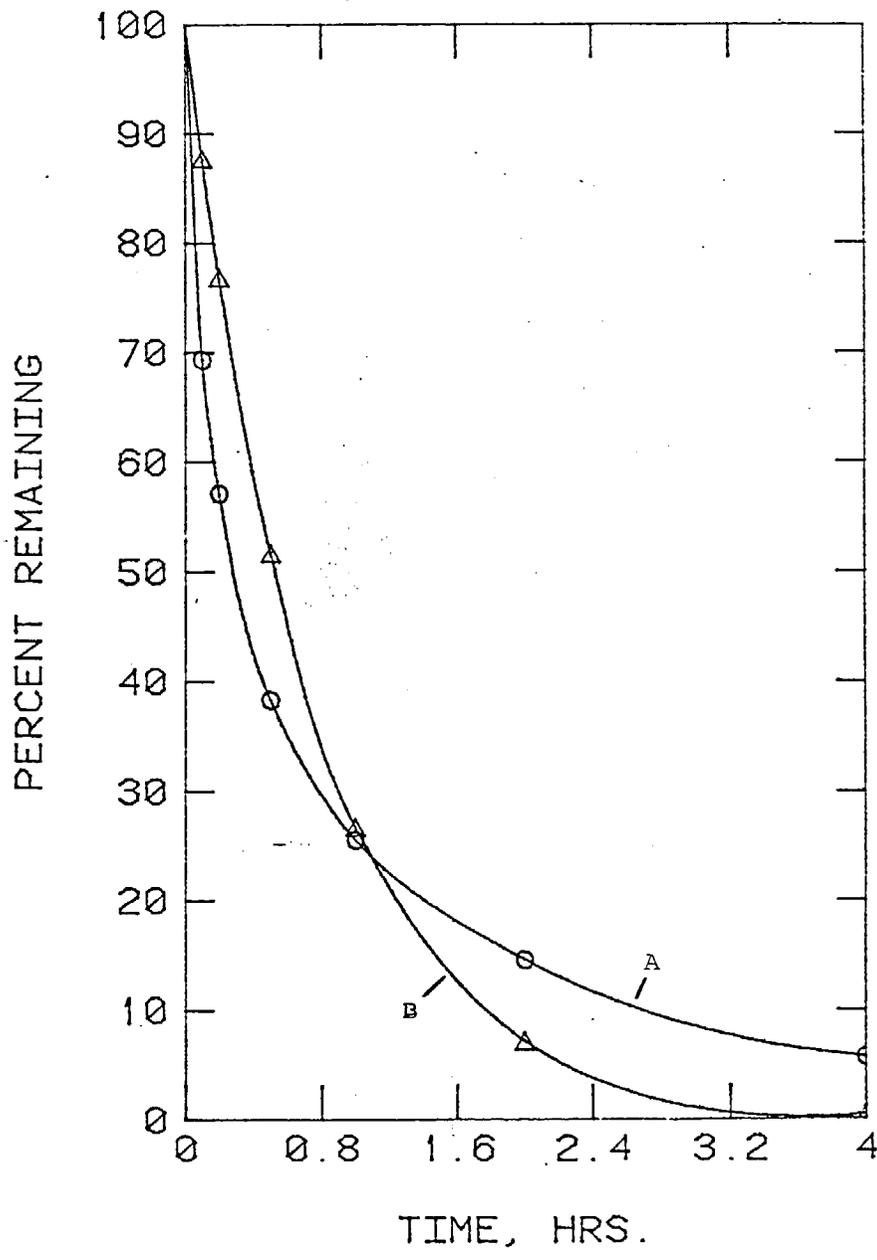


Figure 6. CALCULATED EVAPORATION OF BEACON OIL FROM INERT SURFACE USING OIL COMPONENT PROPERTIES (A) AND AVERAGE PROPERTIES(B).

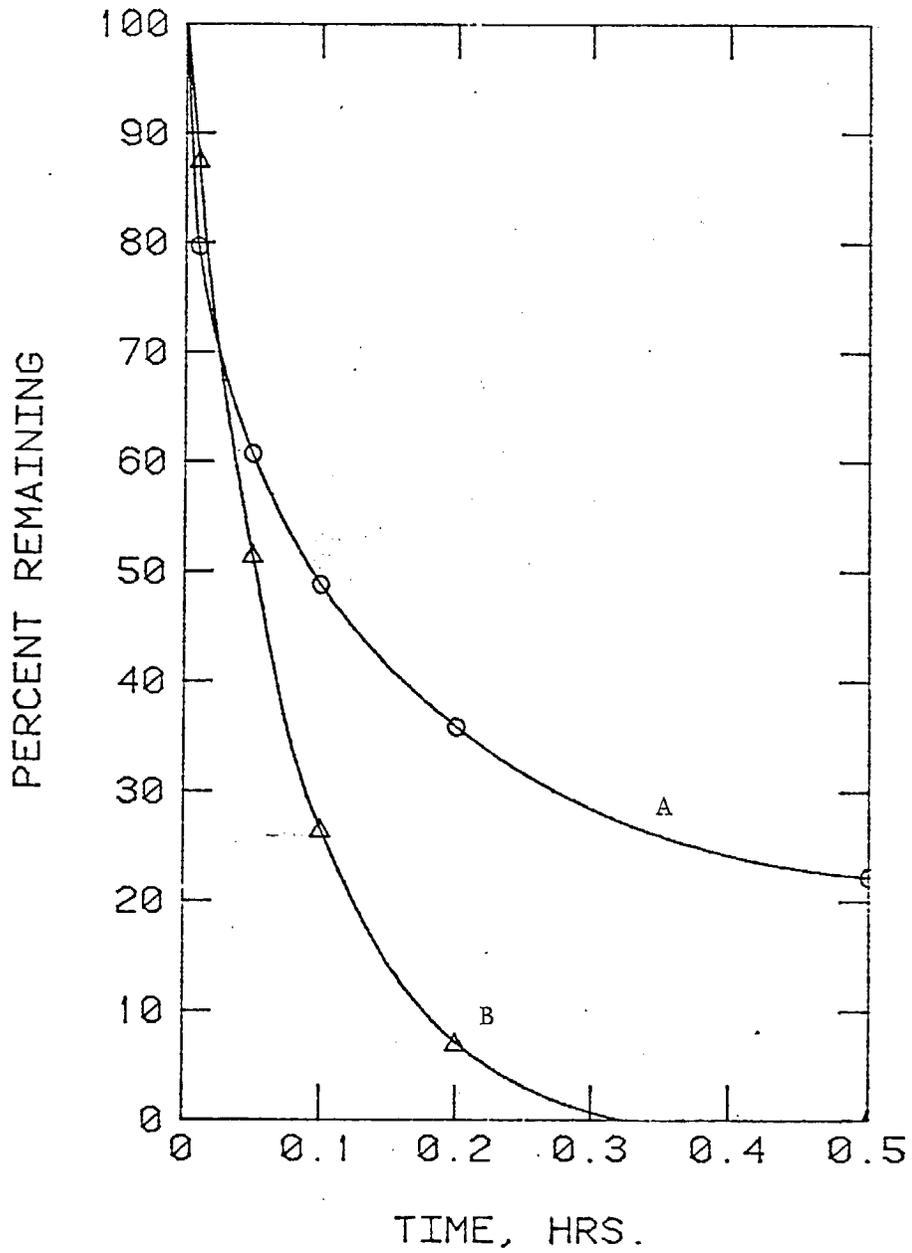


Figure 7. CALCULATED EVAPORATION OF CHEVRON OIL FROM INERT SURFACE USING OIL COMPONENT PROPERTIES (A) AND AVERAGE PROPERTIES (B).

greater and less than the average vapor pressures, use of average properties will lead to under-estimation of loss early in the course of evaporation and over-estimation of loss at later times. This behavior is also clearly shown for the two oils under field conditions where the temperature changed with time. The observed time for 50% loss of Beacon oil from soil was about 51 min (Figure 8); use of component properties gave a 50% loss time of about 65 min; use of average properties gave a 50% loss time of about 97 min, almost twice the observed time. For Chevron oil, observed times for 50% loss from glass (Figure 9) and paper (Figure 10) were 6-10 min and 14-21 min, respectively. Calculated 50% loss time derived from component properties was 9 min, while average properties gave a 50% loss time of about 2-4 min.

The Eureka report (1980) gave an equation for computing the amount of a single material deposited during application if the vapor pressure of the material and temperature are known:

$$A_2 = A_1 \{1 - [(4.625)(\log P + 7)(0.0024T^2)(0.01)]\} .$$

A_2 is the amount deposited after loss during application, A_1 is the application rate, P is the vapor pressure at 20°C, and T (°C) is the average temperature during application. This expression is easily modified to fit the weed oil mixtures using component properties,

$$A_2 = A_1 \sum \bar{x}_i \{1 - [(4.625)(\log P_i + 7)(0.0024T^2)(0.01)]\},$$

where \bar{x}_i and P_i are the mole fraction and vapor pressure of each GC area. Applying this expression to the two Chevron oil applications gave calculated deposited residues of 0.16 mg/cm² (Aug 18) and 0.22 mg/cm² (Aug 20) which

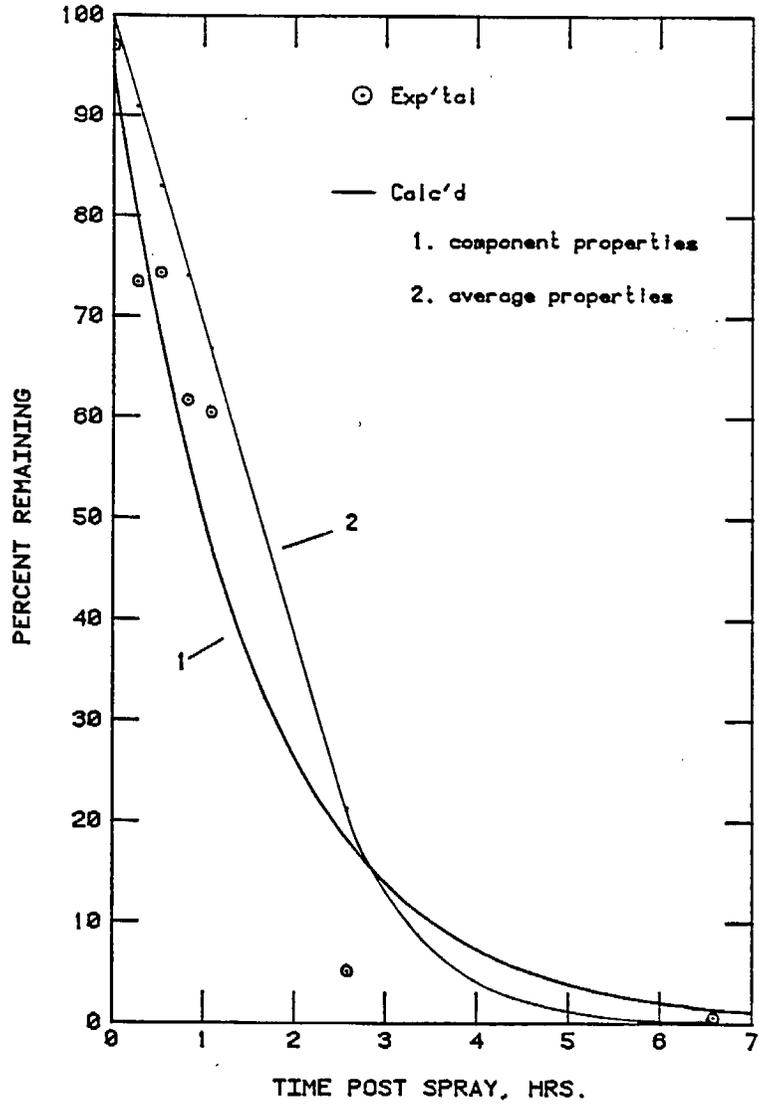


Figure 8. EVAPORATION OF BEACON OIL FROM SOIL--FIELD

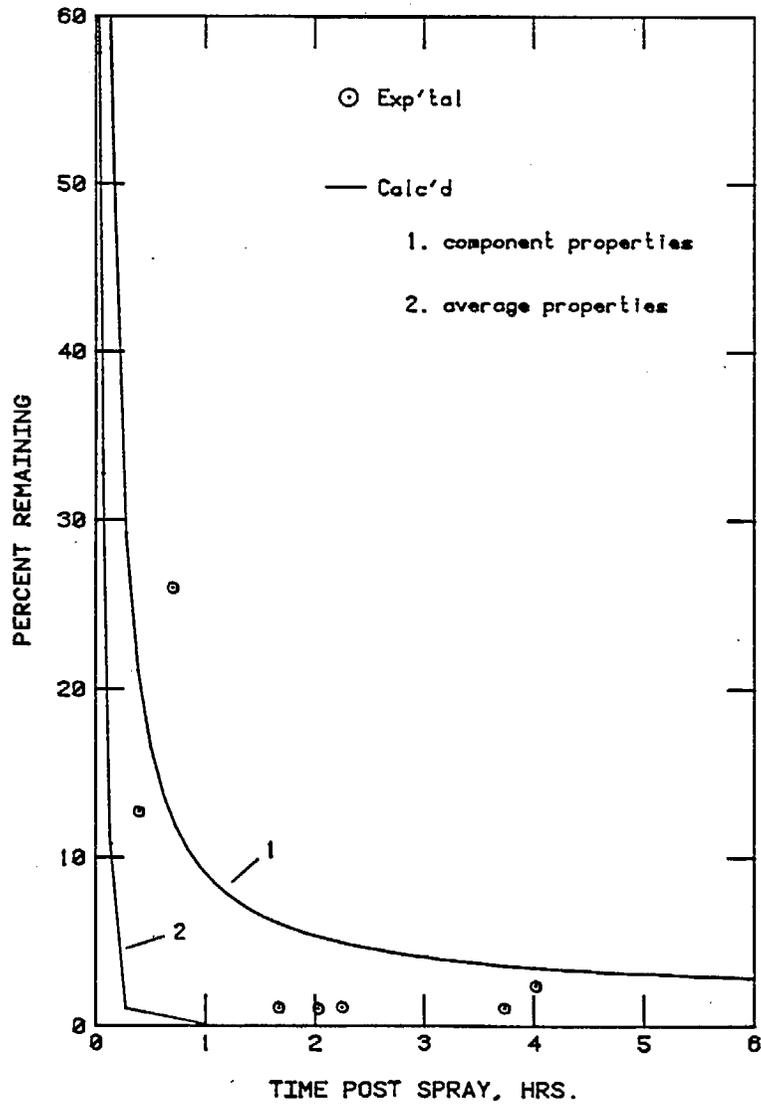


Figure 9. EVAPORATION OF CHEVRON OIL FROM GLASS--FIELD

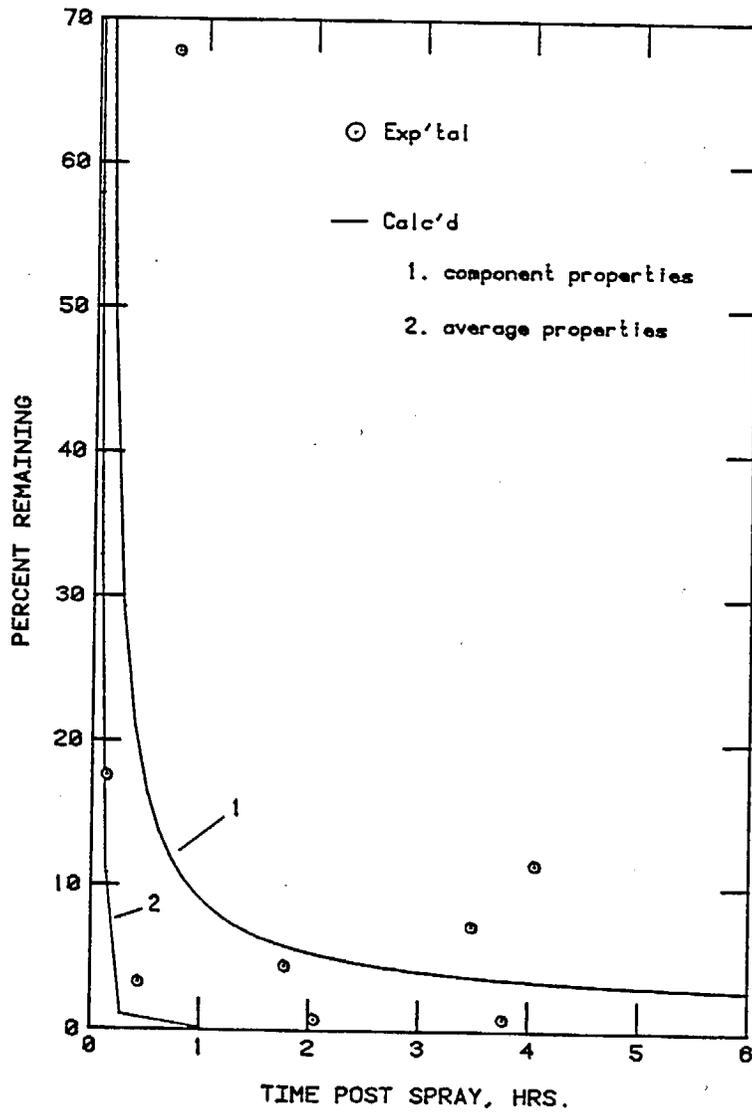


Figure 10. EVAPORATION OF CHEVRON OIL FROM PAPER--FIELD

agree well with observed values (Table 22). However, by using average molecular weight and vapor pressure in the Eureka (1980) expression, calculated deposited residues were 0.11 mg/cm² (Aug 18) and 0.18 mg/cm² (Aug 20).

Table 22. Deposition of Chevron Oil During Application.

| GC Area # | Mole Fraction | Vapor Press., mm Hg ^a | Fraction Deposited, A_2/A_1 ^b | |
|-----------|---------------|-------------------------------------|--------------------------------------------|---------------------|
| | | | 32.5°C ^c | 28.5°C ^d |
| 1 | 0.053 | 1.9557 | 0.0077 | 0.0182 |
| 2 | 0.148 | 0.2987 | 0.0355 | 0.0614 |
| 3 | 0.340 | 0.0453 | 0.1145 | 0.1666 |
| 4 | 0.278 | 0.0073 | 0.1196 | 0.1562 |
| 5 | 0.134 | 5.22×10^{-4} | 0.0753 | 0.0888 |
| 6 | 0.040 | 4.78×10^{-5} | 0.0275 | 0.0304 |
| 7 | 0.008 | 1.16×10^{-5} | <u>0.0058</u> | <u>0.0063</u> |
| | | | $\Sigma = 0.3859$ | 0.5279 |

^aT = 20°C

^b $A_1 = 0.411 \text{ mg/cm}^2$

^cAug 18 application. $A_2 = 0.16 \text{ mg/cm}^2$ (observed = 0.11-0.18 mg/cm²; ave = 0.15 mg/cm²).

^dAug 20 application. $A_2 = 0.22 \text{ mg/cm}^2$ (observed = 0.22 mg/cm²).

REFERENCES

- Eureka Laboratories, Inc. April, 1980. Vol II. Final Report to the California Air Resources Board.
- Hartley, G.S. Adv. Chem. Series. 1969. 86, 115.
- Que Hee, S.J.; Sutherland, R.G. 1974. Weed Sci. 22, 313.
- Reid, R.C.; Prausnitz, J.M.; and Sherwood, T.K. 1977. The Properties of Gases and Liquids, 3rd ed. McGraw-Hill: New York.
- Spencer, W.F.; Farmer, W.J.; and Cliath, M.M. 1973. Res. Rev. 49, 1.

APPENDIX B

Estimation of Loss of Leffingwell Uni-Par and Ortho-K-Ready Mix From Citrus Foliage

Two commercial petroleum hydrocarbon pesticides were chosen to estimate loss from citrus foliage. The pesticides were Leffingwell Uni-Par (LU), a narrow boiling range oil for fruit trees, and Ortho-K-Ready Mix Light Medium (OKRM), an insecticide oil. Assumptions that were made in the loss estimates are as follows: (1) Applied material is evenly distributed over the leaf surface area; (2) the leaf surface is inert (no absorption) and there is no chemical degradation of the hydrocarbon mixtures; (3) static wind conditions prevail; (4) hydrocarbon distribution of applied material is the same as the bulk mixture; (5) material components evaporate independently; and (6) component evaporation is first-order.

Using the approach of Eggertsen et al. (1980), gas chromatograms of the formulations were divided into areas approximately by carbon number (Figures 11 and 12), with each area centered about its particular carbon number. Each area was cut out and weighed on an analytical balance, each weight was divided by the molecular weight of the appropriate normal hydrocarbon, the resulting relative mole numbers were summed, and the mole fraction for each hydrocarbon area was determined (Table 23). From the mole fraction and molecular weight of each hydrocarbon, average molecular weights for the formulations were calculated. For LU and OKRM, molecular weights were 300.18 and 267.72, respectively.

Vapor pressures of the normal alkanes C_{14} - C_{26} were determined from the Antoine equation

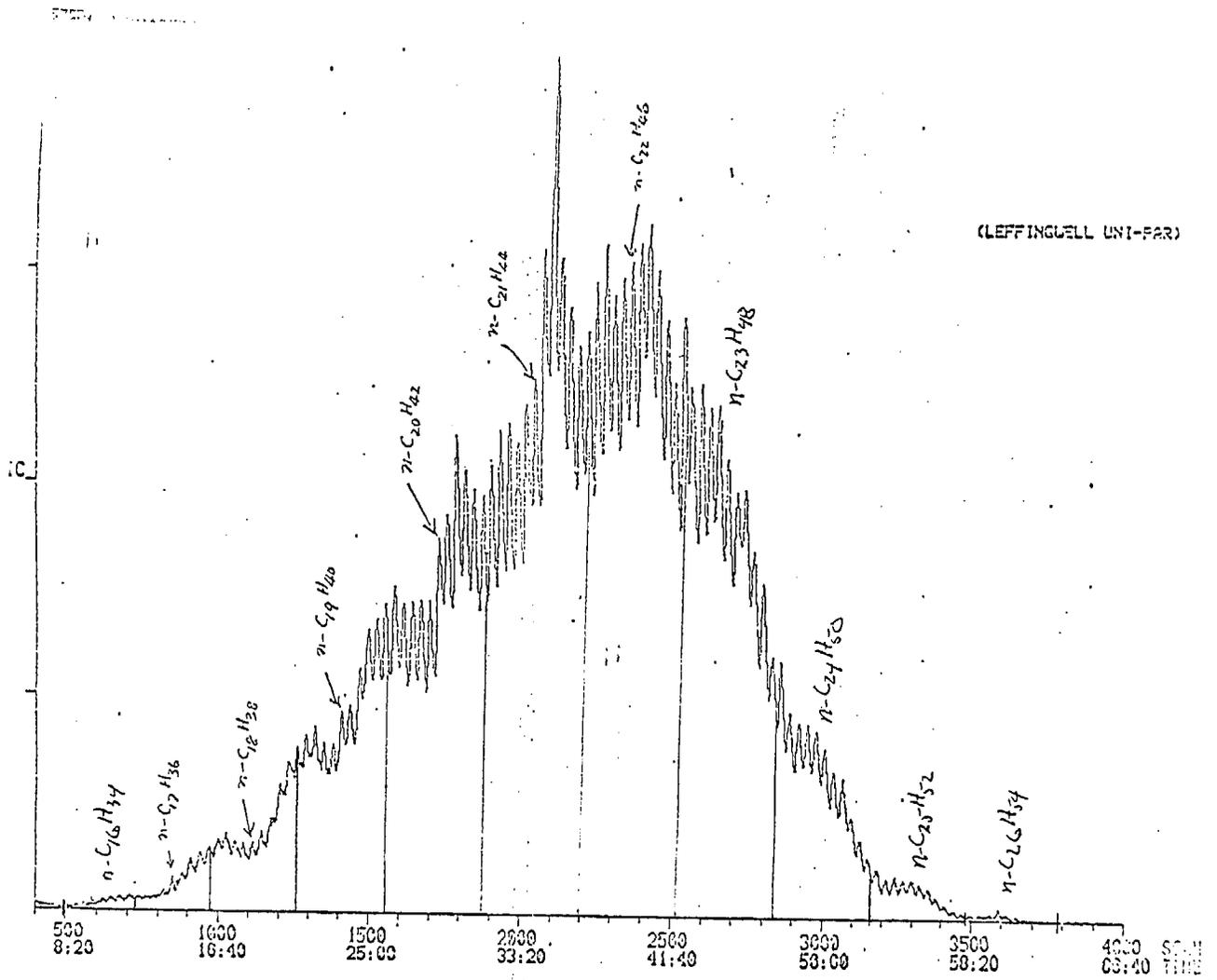


Figure 11. CAPILLARY GAS CHROMATOGRAM OF LEFFINGWELL UNI-PAR.

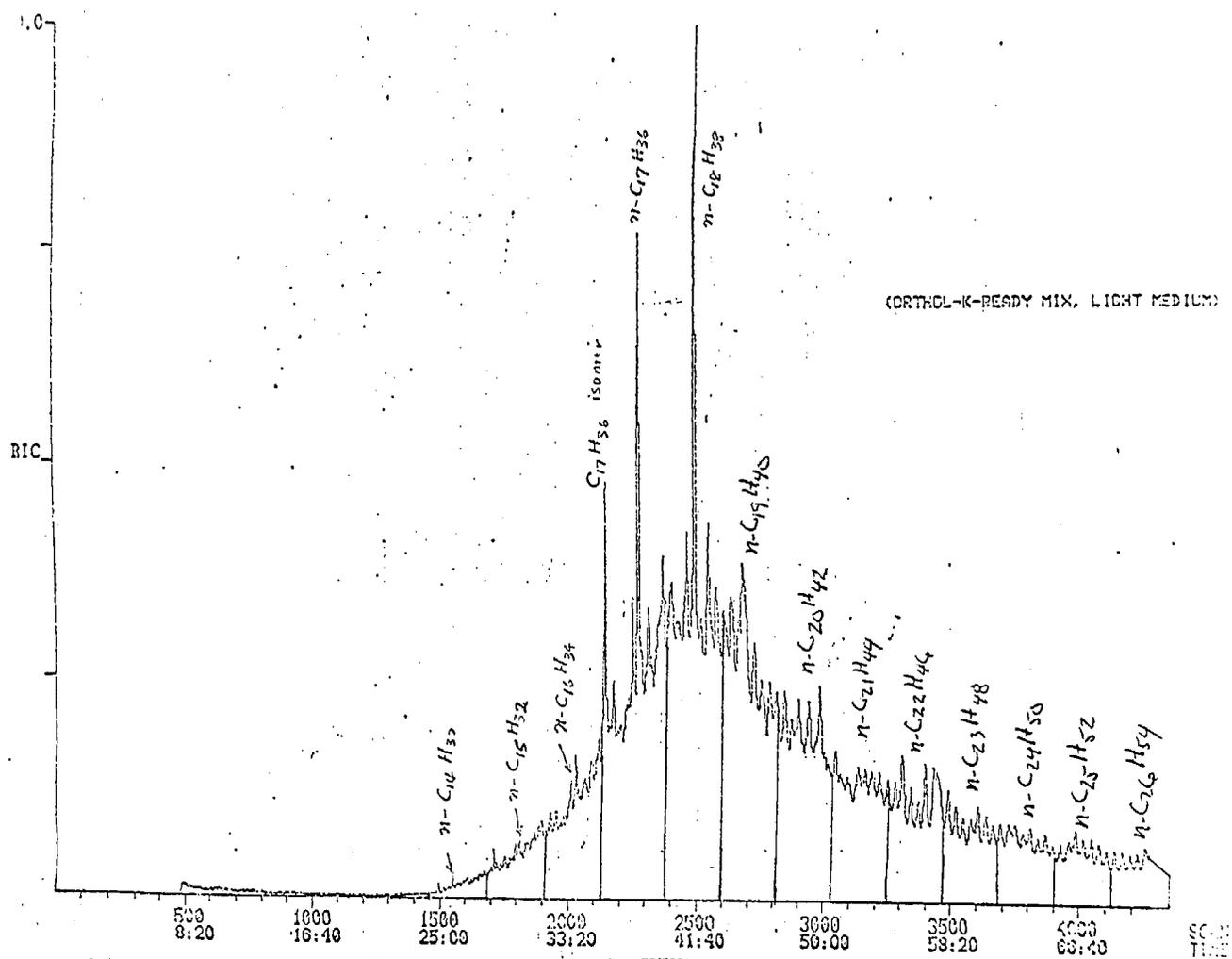


Figure 12. CAPILLARY GAS CHROMATOGRAM OF ORTHO-K-READY MIX, LIGHT MEDIUM.

Table 23. Mole Fractions of Individual Hydrocarbons in Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (OKRM).

| Hydrocarbon | M _g /mole | LU | | | OKRM | | |
|---------------------------------|----------------------|--------|---------------|---------------|--------|---------------|---------------|
| | | Wt, mg | Wt/M | Mole Frac. | Wt, mg | Wt/M | Mole Frac. |
| C ₁₄ H ₃₀ | 198.39 | - | - | - | 3.3 | 0.0166 | 0.0132 |
| C ₁₅ H ₃₂ | 212.42 | - | - | - | 10.0 | 0.0471 | 0.0374 |
| C ₁₆ H ₃₄ | 226.45 | 2.8 | 0.0124 | 0.0044 | 22.2 | 0.0980 | 0.0778 |
| C ₁₇ H ₃₆ | 240.48 | 9.8 | 0.0408 | 0.0144 | 60.1 | 0.2499 | 0.1984 |
| C ₁₈ H ₃₈ | 254.50 | 26.7 | 0.1049 | 0.0370 | 64.8 | 0.2546 | 0.2021 |
| C ₁₉ H ₄₀ | 268.53 | 71.0 | 0.2644 | 0.0933 | 49.0 | 0.1825 | 0.1448 |
| C ₂₀ H ₄₂ | 282.56 | 125.6 | 0.4445 | 0.1569 | 32.1 | 0.1136 | 0.0902 |
| C ₂₁ H ₄₄ | 296.58 | 184.7 | 0.6228 | 0.2199 | 24.2 | 0.0816 | 0.0648 |
| C ₂₂ H ₄₆ | 310.61 | 213.6 | 0.6877 | 0.2428 | 21.5 | 0.0692 | 0.0549 |
| C ₂₃ H ₄₈ | 324.64 | 148.9 | 0.4587 | 0.1619 | 16.0 | 0.0493 | 0.0391 |
| C ₂₄ H ₅₀ | 338.66 | 53.6 | 0.1583 | 0.0559 | 13.7 | 0.0404 | 0.0321 |
| C ₂₅ H ₅₂ | 352.69 | 11.0 | 0.0312 | 0.0110 | 11.1 | 0.0315 | 0.0250 |
| C ₂₆ H ₅₄ | 366.72 | 2.6 | <u>0.0071</u> | 0.0025 | 9.3 | <u>0.0254</u> | 0.0201 |
| | | Σ = | 2.8328 | | | Σ = | 1.2597 |

$$\ln P = A - \frac{B}{(T+C)}$$

where the constants A, B, and C were taken from Reid et al. (1977) and T = °K (Table 24). These constants were available only for the hydrocarbons up through C₂₀. Vapor pressures (P) for C₁₀-C₂₀ (30°C) were correlated (r² = 0.94) with carbon number (#) through the expression

$$P = A' \exp B' (\#).$$

The latter was used to compute vapor pressures for hydrocarbons C₂₁-C₂₆. From the data in Table 24, computed average vapor pressures for LU and OKRM were 1.94 × 10⁻⁵ mm Hg and 5.86 × 10⁻⁴ mm Hg, respectively.

The vaporization rate (F) of each hydrocarbon in the formulations was determined from the relationship first proposed by Hartley (1969)

$$F_1 = \frac{P_1 (M_1^{1/2})}{P_2 (M_2^{1/2})} \cdot F_2$$

where P = vapor pressure (mm Hg), M = molecular weight, 1 = unknown, 2 = reference, and F₂ = 0.035 Kg/ha/day for dieldrin at 30°C (Spencer et al., 1973; Table 25). Vapor pressure and molecular weight for dieldrin are 1.6 × 10⁻⁶ mm Hg (30°C) and 380.93. Vaporization rates were converted to units related to a single tree (Kg/tree/day) by taking into account the total average leaf surface area (5 × 10⁶ cm²/tree).

The first-order rate constant (k_i, Table 25) for the vaporization of each hydrocarbon was determined using the expression

$$k_i = F_i / \bar{X}_i A_0$$

Table 24. Hydrocarbon Vapor Pressures (C₁₄-C₂₆) and Partial Pressures for Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (OKRM).

| Reference Carbon # | Vapor Pressure (30°C), mm Hg | Partial Pressure (30°C), mm Hg | |
|-----------------------|---------------------------------|-----------------------------------|------------------------|
| | | LU | OKRM |
| 14 | 1.60×10^{-2} | - | 2.11×10^{-4} |
| 15 | 4.60×10^{-3} | - | 1.72×10^{-4} |
| 16 | 1.25×10^{-3} | 5.50×10^{-6} | 9.72×10^{-5} |
| 17 | 3.93×10^{-4} | 5.66×10^{-6} | 7.80×10^{-5} |
| 18 | 1.14×10^{-4} | 4.22×10^{-6} | 2.30×10^{-5} |
| 19 | 2.95×10^{-5} | 2.75×10^{-6} | 4.27×10^{-6} |
| 20 | 4.00×10^{-6} | 6.28×10^{-7} | 3.61×10^{-7} |
| 21 | 2.10×10^{-6} | 4.62×10^{-7} | 1.36×10^{-7} |
| 22 | 6.00×10^{-7} | 1.46×10^{-7} | 3.29×10^{-8} |
| 23 | 2.00×10^{-7} | 3.24×10^{-8} | 7.82×10^{-9} |
| 24 | 4.62×10^{-8} | 2.58×10^{-9} | 1.48×10^{-9} |
| 25 | 1.31×10^{-8} | 1.44×10^{-10} | 3.28×10^{-10} |
| 26 | 3.70×10^{-9} | 9.25×10^{-12} | 7.44×10^{-11} |
| | | P = | |
| | | 1.94×10^{-5} | 5.86×10^{-4} |

Table 25. Vaporization Rates (F_i) and Rate Constants (K_i) for Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (OKRM).

| Reference Carbon # | Vaporization Rate (F_i), Kg/tree/day | Heat of Vaporization (ΔH), Cal/mole | Vaporization Rate Constant (K_i), day ⁻¹ ^a | |
|-----------------------|------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------------------------|-----------------------|
| | | | LU | OKRM |
| 14 | 12.63 | 13750.0 | - | 956.82 |
| 15 | 3.76 | 14635.9 | - | 100.53 |
| 16 | 1.05 | 15405.5 | 238.64 | 13.50 |
| 17 | 0.342 | 15608.5 | 23.75 | 1.72 |
| 18 | 0.102 | 15447.0 | 2.76 | 0.505 |
| 19 | 0.027 | 16497.3 | 0.289 | 0.186 |
| 20 | 3.77×10^{-3} | 17028.2 | 0.024 | 0.042 |
| 21 | 2.03×10^{-3} | 17702.2 | 9.23×10^{-3} | 0.031 |
| 22 | 5.93×10^{-4} | 18315.4 | 2.44×10^{-3} | 1.08×10^{-2} |
| 23 | 2.02×10^{-4} | 19082.1 | 1.25×10^{-3} | 5.17×10^{-3} |
| 24 | 4.76×10^{-5} | 19642.5 | 8.52×10^{-4} | 1.48×10^{-3} |
| 25 | 1.38×10^{-5} | 20815.9 | 1.25×10^{-3} | 5.52×10^{-4} |
| 26 | 3.97×10^{-6} | 21605.7 | 1.59×10^{-3} | 1.98×10^{-4} |

^a Kg/tree application rate

where F_i = hydrocarbon vaporization rate (Kg/tree/day), \bar{X}_i = hydrocarbon mole fraction, and A_0 = oil application (Kg/tree). From k_i , it was then possible to compute fraction remaining of each hydrocarbon in the initial deposit at any time t using

$$\bar{X}_i \exp(-k_i t),$$

and the fraction of total oil remaining (A_t/A_0) using

$$A_t/A_0 = \sum \bar{X}_i \exp(-k_i t).$$

From APPENDIX A, the latter expression can be expanded to

$$A_t/A_0 = \sum \bar{X}_i \left\{ \exp-t \left[k_i(r) \exp- \frac{\Delta H_i}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right) \right] \right\}$$

to allow for changes in temperature and different application rates. Heats of vaporization (ΔH_i) for the hydrocarbons are listed in Table 25.

The evaporation rates for LU and OKRM are listed in Table 26 and illustrated in Figure 13. The calculations were based on an application rate of 1 kg/tree, which is comparable to actual field rates. Over 70% of LU is represented by the hydrocarbons C_{20} - C_{23} (max at C_{22}), while over 70% of OKRM is represented by hydrocarbons C_{16} - C_{20} (max. at C_{18}). This difference in composition is reflected in the much greater evaporation rate for OKRM (~46 hrs. for 50% loss compared to >1,000 hrs. for LU).

Table 26. Calculated Evaporation of Leffingwell Uni-Par (LU) and Ortho-K-Ready Mix (OKRM) from Citrus Leaf Surface.

| <u>Time, hrs</u> | <u>Percent Remaining^a</u> | |
|------------------|--------------------------------------|-------------------------|
| | <u>LU^b</u> | <u>OKRM^c</u> |
| 1 | 98.11 | 89.67 |
| 4 | 96.24 | 80.85 |
| 16 | 92.94 | 65.71 |
| 32 | 90.65 | 55.36 |
| 64 | 87.69 | 45.20 |

^a1 Kg/tree application rate.

^b50% loss: >1,000 hrs.

^c50% loss: ~46 hrs.

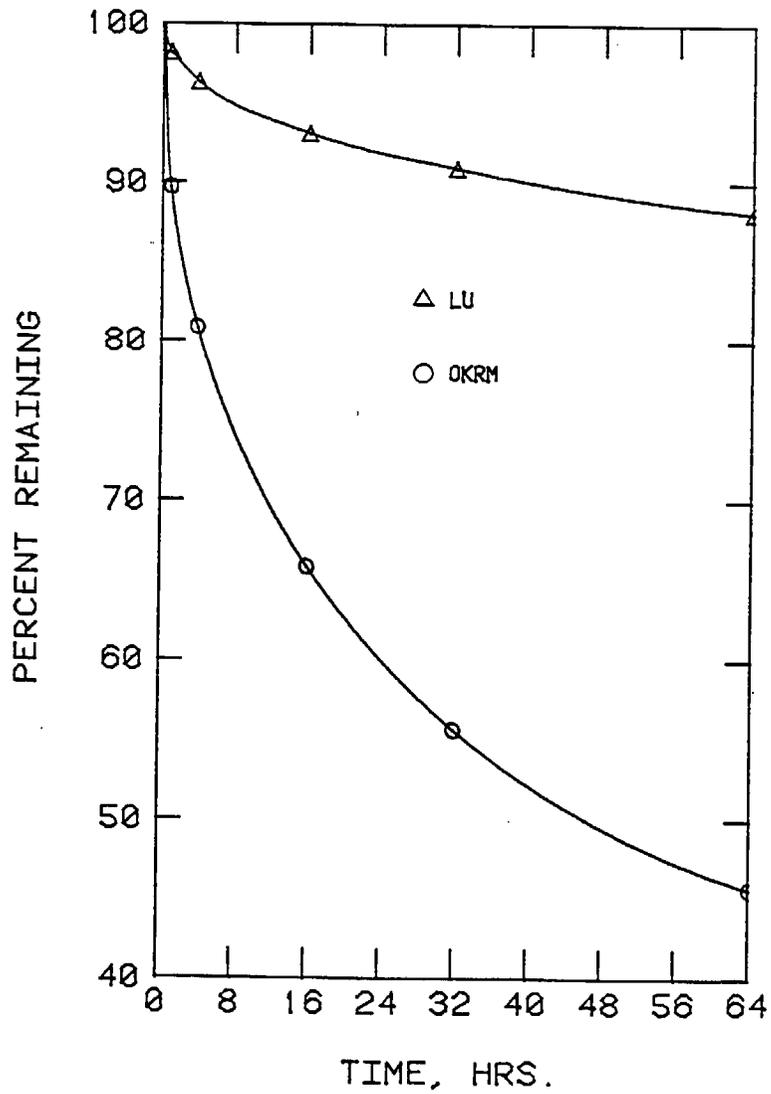


Figure 13. CALCULATED EVAPORATION OF LEFFINGWELL UNI-PAR (LU) AND ORTHO-K-READY MIX (OKRM) FROM CITRUS FOLIAGE.

REFERENCES

- Eggertsen, F.T.; Nygard, N.R.; and Nickoley, L.D. 1980. *Anal. Chem.* 52, 2069.
- Hartley, G.S. 1969. *Adv. Chem. Series* 86, 115.
- Reid, R.C.; Prausnitz, J.M.; and Sherwood, T.K. 1977. *The Properties of Gases and Liquids*, 3rd ed. McGraw-Hill: New York.
- Spencer, W.F.; Farmer, W.J.; and Cliath, M.M. 1973. *Res. Rev.* 49, 1.

APPENDIX C

XAD-4 Polymeric Adsorbent Air Sampling of Beacon and Chevron Weed Oils

Trapping of Beacon and Chevron weed oils by XAD-4 polystyrene macroreticular adsorbent was determined using the apparatus illustrated in Figure 14. It consisted of a glass tube 30 cm × 2.6 cm (ID) with a side arm 3 cm × 1.2 cm (ID); to the tube was attached a Teflon® column section 12 cm × 4 cm (ID) fitted with a 4.3 cm dia. 100 mesh stainless steel screen for holding the adsorbent (30 ml for Beacon oil and 50 ml for Chevron oil). To the side arm of the glass tube was attached a polyethylene vial 5.5 cm × 1.5 cm dia. containing a weighed amount of weed oil. The column containing the adsorbent was connected to a vacuum source, a rotameter flow meter was connected to the intake, and incoming air (~30 LPM) was purified by filtration through a bed of XAD-4 adsorbent. After a prescribed period of time (<1 hr up to ~50 hrs), air flow was stopped, the vial containing the oil was weighed, and the XAD-4 adsorbent was extracted with excess ethyl acetate for 1 hr using a table-top rotary shaker. High vapor densities (short run times) were achieved by diverting a fraction of air stream through the vial over the surface of the oil. To achieve low vapor densities (long run times), the oil was contained in a smaller vial, 2.5 cm × 1.2 cm dia. with a 0.4 cm dia. opening, placed inside the larger vial.

Dubin (1947 and 1949) and Jonas and Rehrmann (1972 and 1973), from their work with activated carbons, determined that adsorption of a chemical vapor is related to its vapor density (equilibrium vapor pressure) through the expression

$$\ln W_e = \ln W_o - k[RTL \ln(P_o/P)]^2.$$

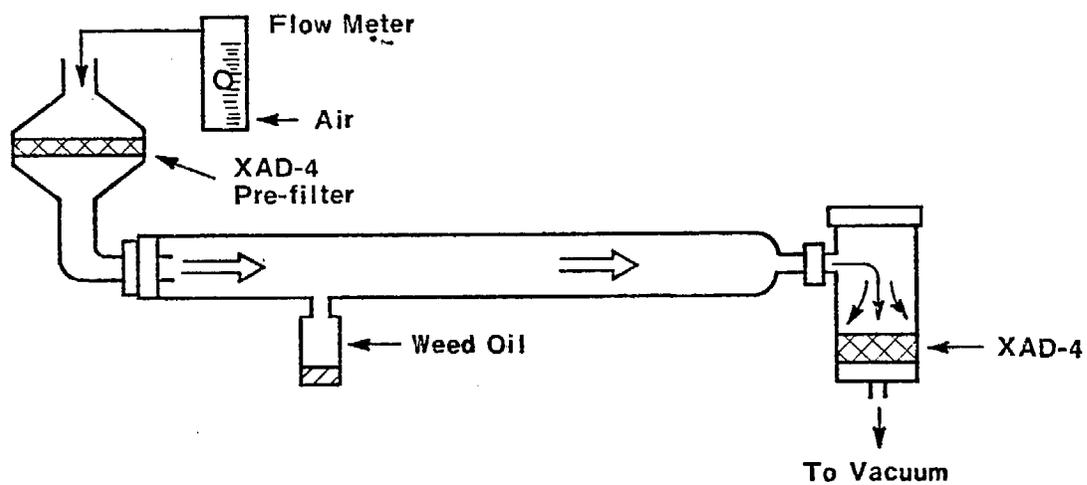


Figure 14. SCHEMATIC REPRESENTATION OF LABORATORY APPARATUS FOR DETERMINING TRAPPING OF WEED OIL VAPORS BY XAD-4 ADSORBENT.

W_e and W_0 are the amount (g/g) of condensed vapor (adsorbate) and the maximum capacity (g/g), respectively; k is a constant related to the structure of the adsorbent $(\text{cal/mole})^{-2}$; $RT \ln P_0/P$ is the adsorption potential (cal/mole), where P_0 is the saturated vapor pressure of the condensed adsorbate at T and P is the equilibrium pressure of the adsorbate vapor at T . P is determined from the vapor density using the ideal gas law:

$$P = \frac{n}{V}RT.$$

Adsorption potential is defined by Jonas and Rehrmann (1972) as the change in free energy during the reversible isothermal transfer of a mole of the adsorbate from bulk liquid to an infinitely large amount of adsorbent. Jonas and Rehrmann (1973) demonstrated that the above adsorption relationship held for both equilibrium and kinetic (flow) conditions.

The adsorption relationship was used to relate the laboratory adsorption data for Beacon and Chevron oils to their field data in an attempt to determine actual field vapor densities. An added consideration was that, for a given amount of oil, changing vapor composition will affect adsorption by changing the vapor pressure, P , in the adsorption potential term. Using the oil component method described in APPENDIX A, vapor composition and component partial pressures were determined from gas chromatograms of the oils extracted from the XAD-4 adsorbent. In the laboratory apparatus, oil vapor density, determined from vial weights and measured air volumes, was related to adsorption potential derived from XAD-4 extracts. Figure 15 shows this relationship for the weed oils and for a single compound, 1,2,3-trimethylbenzene. By taking into consideration the effect of changing weed oil vapor composition on adsorption by XAD-4, the weed oil plots had slopes essentially the same as that for 1,2,3-trimethylbenzene.

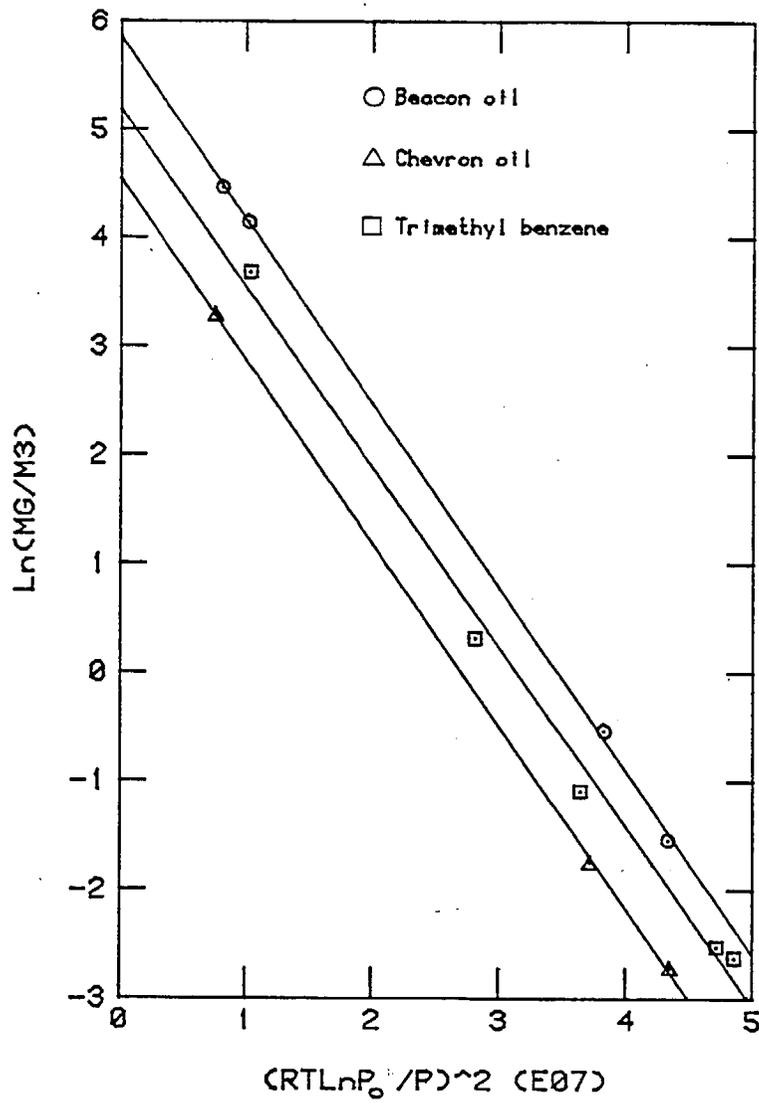


Figure 15. ADSORPTION OF BEACON AND CHEVRON WEED OILS BY XAD-4 ADSORBENT.

The regression equations for the weed oils (Figure 15) are as follows:

Beacon oil -

$$\ln(\text{mg}/\text{m}^3) = 5.8519 - 1.6908 \times 10^{-7} [\text{RTLn}(P_o/P)]^2$$

Chevron oil -

$$\ln(\text{mg}/\text{m}^3) = 4.5428 - 1.6809 \times 10^{-7} [\text{RTLn}(P_o/P)]^2.$$

The amounts of oil trapped by XAD-4 under field conditions and the composition of the trapped oil were used in the regression equations to compute vapor density in the field. Table 27 summarizes some of the results for the Beacon and Chevron oils. While the results for Beacon oil show a decrease in collection efficiency with height and time, as would be expected, the results for Chevron oil do not show as clear-cut a trend. This can be attributed to significant contribution of the adsorbent and non oil-related background constituents to the total gas chromatographic response of the Chevron oil extracts. This was a problem since the Chevron oil samples had to be dramatically reduced in volume for analysis due to the low vapor densities in the field. There was no way to subtract background contributions. This was not a significant problem with Beacon oil, however, because of its much greater application rate (>40x) and average vapor pressure (5x that of Chevron oil at 30°C) which gave much greater vapor densities in the field.

The air sampling method described here is a special case for very volatile compounds and their mixtures. For compounds with much lower vapor pressures (<~10⁻³ mm Hg), the effect of vapor density on air sampler collection efficiency becomes negligible. Much of the air sampling work to date using XAD-4 adsorbent has been with the synthetic pesticides whose vapor pressures commonly fall in the range 10⁻⁴ - 10⁻⁷ mm Hg at ambient

temperatures. With these compounds, determination of air sampler collection efficiency simply involved vaporizing the compounds into the air sampler intake from deposits upstream and determination of the amount of material trapped by the XAD-4 adsorbent and the amount of material remaining in the upstream deposit. Percent collection efficiency (%CE) is the ratio of material trapped by the adsorbent (W_a) to the material that vaporized into the air sampler intake (W_v):

$$\%CE = (W_a/W_v) \times 100.$$

For a more complete discussion of collection efficiency, see Woodrow and Seiber (1978) and Seiber et al. (1980).

Table 27 Field and Calculated Vapor Densities for Beacon and Chevron Weed Oils.

| <u>Time, hrs^a</u> | <u>Height, cm</u> | <u>Vapor Density, mg/m³</u> | | <u>% C.E.^b</u> |
|---------------------------------|--------------------|----------------------------------------|--------------|---------------------------|
| | | <u>Field</u> | <u>Calc.</u> | |
| <u>Beacon Oil:</u> | | | | |
| 0.22-0.52 | 30.48 | 231.48 | 231.79 | 99.87 |
| | 60.96 | 83.46 | 160.48 | 52.01 |
| | 106.68 | 25.43 | 92.18 | 27.59 |
| 0.63-1.45 | 30.48 | 31.74 | 95.13 | 33.36 |
| | 60.96 | 12.98 | 56.44 | 23.00 |
| | 106.68 | 4.10 | 25.30 | 16.20 |
| 2.60-3.58 | 30.48 | 10.96 | 29.54 | 37.11 |
| | 60.96 | 6.63 | 20.02 | 33.12 |
| | 106.68 | 3.76 | 12.51 | 30.05 |
| 0.33-1.37 | 30.48 ^c | 107.88 | 176.78 | 61.02 |
| <u>Chevron oil^d:</u> | | | | |
| 1.00-2.18 | 8/18 48.90 | 0.3982 | 0.4460 | 89.28 |
| | 113.35 | 0.2910 | 0.3122 | 93.21 |
| | 183.83 | 0.2498 | 0.2667 | 93.66 |
| 2.52-3.58 | 48.90 | 0.1758 | 0.1116 | 157.53 |
| | 113.35 | 0.0830 | 0.0433 | 191.68 |
| | 183.83 | 0.0453 | 0.0184 | 246.20 |
| 4.10-5.17 | 48.90 | 0.1136 | 0.0515 | 220.58 |
| | 113.35 | 0.0907 | 0.0396 | 229.04 |
| | 183.83 | 0.0784 | 0.0328 | 239.02 |
| 0.63-1.67 | 8/20 48.90 | 0.7877 | 1.2402 | 63.51 |
| | 113.35 | 0.4988 | 0.7925 | 62.94 |

| | | | | |
|-----------|--------|--------|--------|--------|
| | 183.83 | 0.3954 | 0.6419 | 61.60 |
| 2.03-2.93 | 48.90 | 0.2144 | 0.2290 | 93.62 |
| | 113.35 | 0.1705 | 0.1921 | 88.76 |
| | 183.83 | 0.1476 | 0.1620 | 91.11 |
| 3.20-3.95 | 48.90 | 0.1296 | 0.1006 | 128.83 |
| | 113.35 | 0.1189 | 0.0971 | 122.45 |
| | 183.83 | 0.1126 | 0.0931 | 120.94 |

^aPost application.

^bPercent collection efficiency relative to trapping under laboratory conditions.

^cDownwind HiVol Sampler.

^dPartial listing. See Table 19 for complete listing.

REFERENCES

Dubinina, M.M.; Zaverina, E.D.; and Radushkevich, L.V. 1947. Zhur. Fiz. Kim. 21, 1351.

_____ ; and Zaverina, E.D. 1949. Zhur. Fiz. Kim. 23, 1129.

Jonas, L.A. and Rehrmann, J.A. 1972. Carbon. 10, 657.

_____ and Rehrmann, J.A. 1973. Carbon. 11, 59.

Seiber, J.N.; Ferreira, G.A.; Hermann, B; and Woodrow, J.E. 1980. In: Pesticide Analytical Methodology, Harvey, Jr., J; and Zweig, G. (Eds.). ACS Symposium Series #136, pg 177.

Woodrow, J.E. and Seiber, J.N. 1978. Anal. Chem. 50, 1229.