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FINAL REPORT

AIR POLLUTION EMISSIONS ASSOCIATED  
WITH NONSYNTHETIC HYDROCARBON APPLICATIONS FOR  
PESTICIDAL PURPOSES IN CALIFORNIA

VOLUME II

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The California Air Resources Board

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## ABSTRACT

This report presents the results of analysis of the use pattern of 1977 estimated nonsynthetic hydrocarbons used for pesticidal purposes in California. Alternative measures and their associated impacts that can lead to a use reduction of the nonsynthetics are also presented. The entire analysis in this report is based on estimated oil use obtained by questionnaire surveys and 1977 California Pesticide Use Report.

The total estimated consumption of nonsynthetic hydrocarbons for pesticidal purpose in 1977 in California was 225.2 million pounds. Of this quantity, 96.5% was applied in pure oil form (formulation 10), and 3.5% as minor ingredients (nonformulation 10). The formulation 10 products were applied in four categories: general weed control (53.9%), agricultural use (27.5%), wood preservation (11.8%), and miscellaneous uses (3.3%). The general weed control use overlaps with the second and fourth categories. The miscellaneous uses of oil pesticides include home and garden, industrial, manufacturing, residential pest control, etc.

The top 17 commodities that had 500,000 pounds or more of oil pesticide applied were studied with regard to oil use pattern, related pest problems and alternative measures capable of reducing oil use. The total possible quantity of oil that could be saved and the associated hydrocarbon emission reduction are estimated. Recommendations are made on the most feasible alternative measures for reducing oil use based on energy, economic and air quality impact assessments.

Each of the alternative measures are evaluated for their impacts on air quality, energy use, and cost. All alternatives can achieve a reduction of hydrocarbon emissions as shown below.

<u>Alternative</u>	<u>Estimated Oil Use Reduction (in 1000 lbs.)</u>	<u>Potential Emission Reduction tons/TPD<sup>a</sup></u>	<u>Potential % Reduction in Total Oil Use</u>
<u>Synthetic Pesticides</u>			
Insecticide	11,063.4	4,949/13.6	5.1
Herbicide	111,127.0	52,630/144.2	51.1
Application Method	4,023.2-5,275.7	1,813-2,202/5.0-6.0	1.9-2.4
<u>IPM (Integrated Pest Management)</u>	4,573.9-9,147.6	2,047-4,096/5.6-11.2	2.1-4.2

<sup>a</sup>TPD = Tons per day.

The alternatives will also result in reduced energy consumption. The estimated annual energy use reductions were 55,307 barrels of crude oil equivalent for alternative application methods, 63,793-143,399 barrels for IPM practices and 1,875,370 barrels for synthetic pesticide. The energy consumption resulting from conventional oil application was 1,899,365 barrels of crude oil equivalent.

Cost analysis of different alternatives provided a somewhat different impact pattern. The costs of synthetic pesticides and their application are higher for citrus and lower for deciduous tree crops when compared to the costs of oil insecticide use. In vegetable crops the cost of synthetic herbicidal treatment is about three times lower than the cost for control with

weed oil. For school district and weed control unclassified, the synthetic herbicidal treatment cost is higher than for oil use. In three citrus crops, costs for IPM-oil practice and non-IPM oil use are similar while costs for IPM-synthetic practice are higher. These costs, however, are the cost per treatment year. With IPM, treatment may not be required for each year. For the long term consideration, the cost for IPM will be reduced and become very competitive with conventional oil application. The use of low volume spray can result in oil use reduction and thus in cost savings.

Based on the impacts assessment of the different alternatives summarized earlier, the following conclusions are made with consideration given to hydrocarbon emission reduction, cost and energy use in descending priority of importance.

- (1) Synthetic insecticides and herbicides are available as substitutes for all but three of the crops considered in this report. These materials are, in general, more toxic than the oil pesticides. Investigations of the relative health impacts is beyond the scope of this study. The cost of synthetic herbicides, on the other hand, varies depending on the particular applications, but in general are comparable to the costs of nonsynthetics.

- (2) Oil use reduction can be achieved in part by increasing the use of low volume and new sprayer techniques for some of the oil application on deciduous and citrus tree crops.
- (3) IPM procedures may or may not result in immediate oil use and cost reductions. In the long term consideration, oil use and cost reduction can be achieved.

## TABLE OF CONTENTS

	<u>Page</u>
Abstract	iii
List of Tables	xiv
List of Figures	xx
Abbreviations and Symbols	xxi
Acknowledgements	xxii
1.0 Conclusions	1
2.0 Recommendations	5
3.0 Introduction	7
3.1 Project Objectives	7
3.2 Scope	8
3.3 References	11
4.0 Background Information	12
4.1 1977 Air Quality in California	12
4.2 Use of Oil as Pesticides	14
4.2.1 Historical Development and Types of Oil	14
4.2.2 Types of Oil and Oil Specifications	16
4.2.3 Refining of Oil	19
4.2.4 Chemical and Physical Characteristics of Petroleum Oil Pesticides	22
4.2.5 Use of Petroleum Oil Pesticides and Mechanism of Toxicity Action	26
4.2.5.1 Insecticides	26
4.2.5.2 Herbicides	30
4.2.5.3 Fungicides and Other Pesticides	32

	<u>Page</u>	
4.4	References	36
5.0	Application and Use Pattern Inventories	38
5.1	Introduction	38
5.2	Application and Use Pattern Inventories	38
	Methodology	
5.2.1	Overview	38
5.2.2	Inventory Approaches	40
	5.2.2.1 Pesticide Use Report	41
	5.2.2.2 Questionnaire Surveys	41
	5.2.2.3 Interview Surveys	47
5.2.3	Method of Calculating Application	
	Inventory	48
5.3	Application and Use Pattern Inventories	55
5.3.1	General Summary	58
5.3.2	Application Inventory	61
	5.3.2.1 Temporal Application Patterns	61
	5.3.2.2 Spatial Distribution	73
5.3.3	Use Patterns	75
	5.3.3.1 Agricultural Use	81
	5.3.3.2 Non-Agricultural Use	84
	5.3.3.3 General Weed Control	85
5.4	Conclusions and Recommendations	96
5.5	References	103
6.0	Emission Inventory	104
6.1	Introduction	104
6.2	Emission Estimation Methodology	105

	<u>Page</u>
6.2.1 Pesticide Vaporization	105
6.2.1.1 Methodologies	105
6.2.1.2 Emission During Pesticide Application	113
6.2.1.3 Sorption and Sequestration of Pesticide	115
6.2.1.4 Degradation of Pesticides	116
6.2.2 General Emission Methodology	118
6.2.3 Emission Calculation for Wood Preservatives	128
6.2.3.1 Introduction	128
6.2.3.2 Emissions Estimation	130
6.3 Emission Inventory	131
6.4 Conclusions and Recommendations	144
6.5 References	149
7.0 Alternatives to Pesticide Oil Use	154
7.1 Introduction	154
7.2 Oil Treatment	157
7.2.1 Introduction	157
7.2.2 Pest Problems	157
7.2.2.1 Insect and Mite Pests of Citrus	157
7.2.2.2 Insect and Mite Pests of Deciduous Tree Crops	158
7.2.2.3 Weed Pests of Alfalfa and Carrots	160
7.2.2.4 Weed Pests of Orchards, Vineyards and Non-Crop Areas	160

	<u>Page</u>
7.2.3 Recommended Oil Treatments and Current Practices	161
7.2.3.1 Recommended Oil Treatments - Agricultural Crops	162
7.2.3.2 Recommended Oil Treatments - Orchards, Vineyards and Non-Crop Areas	165
7.2.3.3 Pesticide Oil Use in Non- Agricultural Practice	167
7.2.4 Discussion and Recommendations	171
7.2.4.1 Citrus	171
7.2.4.2 Dormant Season Control of Deciduous Fruit Trees	172
7.2.4.3 Foliar Sprays	174
7.2.4.4 Row and Field Crops	174
7.3 Pesticide Application Techniques	176
7.3.1 Introduction	176
7.3.2 Pesticide Application Methods and Equipment	176
7.3.2.1 Ground Application	177
7.3.2.2 Aerial Application	179
7.3.3 Potential Wastes and Losses in Pesticide Application	180
7.3.3.1 Potential Pesticide Wastes	181
7.3.3.2 Potential Pesticide Losses	186
7.3.4 Quantifying Wastes and Losses	191

	<u>Page</u>
7.3.4.1 Current Pesticide Application Practices in California	192
7.3.4.2 Overuse Waste	195
7.3.4.3 Drift Losses	198
7.3.4.4 Potential Use Reduction	201
7.3.5 Conclusion and Recommendations	203
7.4 Synthetic Pesticides	204
7.4.1 Introduction	204
7.4.2 Synthetic Alternatives	205
7.4.3 Summary, Discussion and Recommendations	213
7.5 Other Alternatives	216
7.5.1 Introduction	216
7.5.2 Integrated Pest Management	217
7.5.2.1 Introduction	217
7.5.2.2 IPM in Citrus	217
7.5.2.3 IPM in Pears	218
7.5.2.4 IPM in Other Deciduous Fruit Trees	219
7.5.2.5 IPM in Field and Row Crops	219
7.5.2.6 IPM for Weed Control in Orchards, Vineyards and Non-Crop Areas	219
7.5.2.7 Summary and Recommendations	220
7.5.3 Biological Control	220

	<u>Page</u>
7.5.3.1 Introduction	220
7.5.3.2 Biological Control in Citrus	221
7.5.3.3 Biological Control in Pears	222
7.5.3.4 Biological Control in Other Deciduous Fruit Trees	222
7.5.3.5 Biological Control in Field and Row Crops	222
7.5.4 Cultural Practices	223
7.5.4.1 Introduction	223
7.5.4.2 Cultural Practices in Deciduous Fruit Trees	223
7.5.4.3 Cultural Practices in Field and Row Crops	223
7.5.5 Mechanical Control and Flaming	224
7.5.5.1 Mechanical Control in Field and Row Crops	225
7.5.5.2 Mechanical Control of Weeds in Orchards, Vineyards and Non-Crop Areas	225
7.5.5.3 Flaming	225
7.5.6 Summary and Conclusions	226
7.6 Summary of Alternatives to Oil Use	227
7.6.1 Citrus Crops	227
7.6.2 Deciduous Fruit Trees	227
7.6.3 Alfalfa	229
7.6.4 Carrots	230

	<u>Page</u>
7.6.5 Orchards, Vineyards and Non-Crop Areas	230
7.6.6 Promising Alternatives	230
7.6.7 Conclusions and Recommendations	231
7.7 References	235
8.0 Impact Potential of Pesticides	240
8.1 Introduction	240
8.2 Health Impact Assessment	240
8.3 Energy Use Assessment	242
8.3.1 Introduction	242
8.3.2 Estimation Approach for Energy Use	242
8.3.3 Energy Use Evaluation	247
8.4 Economic Impact Assessment	250
8.4.1 Introduction	250
8.4.2 Evaluation Approach	250
8.4.3 Impact Evaluation	254
8.5 Air Quality Impact Assessment	259
8.5.1 Evaluation Approach	259
8.5.2 Impact Evaluation	262
8.6 Conclusion and Recommendations	268
8.6.1 Summary	268
8.6.2 Conclusions and Recommendations	270
8.7 References	276

## LIST OF TABLES

		<u>Page</u>
4-1	Products Derived from Crude Petroleum	20
4-2	Physical Characteristics of Nonsynthetic Hydrocarbon Pesticide Chemicals	27
5-1	Summary Table of Questionnaire Surveys Sent and Received	42
5-2	Estimated Creosote Use in California During 1977 Based on Questionnaire Survey Responses	54
5-3	Summary of Survey Results	56
5-4	1977 Estimated Oil Pesticide Use in California by Source	57
5-5	Total Nonsynthetic Hydrocarbon Pesticide Application in California in 1977	59
5-6	Formulation 10 Pesticide Oil Application by Chemical in California in 1977	62
5-7	Statewide Monthly Applications Distribution of Formulation 10 Pesticide Oils in 1977 by Type (1000 Pounds)	69
5-8	Statewide Monthly Applications of Formulation 10 Pesticide Types on the Top 17 Commodities in 1977 (1000 Pounds)	70
5-9	Statewide Monthly Application for Selected Formulation 10 Chemicals in 1977 (1000 Pounds)	74
5-10	1977 Oil Pesticide Consumed by the Top 13 Counties in California	76

		<u>Page</u>
5-11	1977 Distribution of NSHC Pesticides by County in California	77
5-12	Use Patterns of Formulation 10 Nonsynthetic Hydrocarbons of All Oil Pesticide Types by Users in California in 1977	82
5-13	Twelve Main Commodities for Which Over One Million Pounds of Oil was Used in California in 1977	83
5-14	List of Pesticide Uses and Their Definitions (in California)	86
5-15	Herbicide Oil Use Reported in Survey of Growers	89
5-16	Estimated General Distribution of Oil in Weed Control Unclassified Category	92
5-17	Estimated Distribution of Oil in Weed Oil Unclassified by Use and County in 1977	93
5-18	Comparison of Surveyed Weed Oil Product Sales in California in 1977 and Estimated Usage	97
6-1	Reported Pesticide Losses During Application	114
6-2	Physical Characteristics of Nonsynthetic Hydrocarbon Pesticide Chemicals	127
6-3	Estimated Hydrocarbon Emissions Associated with Creosote and Creosote Petroleum Treatment and Use in California During 1977	132

	<u>Page</u>	
6-4	1977 Monthly Total Organic Gas (TOG) Emissions from Formulation 10 Oil Pesticide Applications Shown as a Percentage of Annual Total in California	134
6-5	Summary of Monthly Emission Distribution of Formulation 10 Chemicals Applied in California in 1977	136
6-6	Summary of Monthly Emission Distribution of Formulation 10 Oil Pesticide Applied in California in 1977	137
6-7	Summary of Monthly Emission Distribution of Formulation 10 Oil Pesticides Applied in Each of the 58 California Counties in 1977	138
6-8	Summary of Monthly Emission Distribution of Formulation 10 Oil Pesticides Applied in Each of the Top 17 California Counties in 1977 (1000 lbs.)	141
6-9	1977 Summary of Monthly Emission Distribution from Formulation 10 Pesticide Application in 13 Top Counties in California by Use and Type	143
6-10	Emission Sources of Major Oil Pesticide Applications by Uses, Types and Commodities in 3 California Counties in 1977	145
7-1	Pests of Selected Deciduous Fruit Trees Against Which NSHC Spray Oils are Used as Insecticides	159

	<u>Page</u>	
7-2	Recommended Oil and Fortified Oil Treatments for Control of Insects and Mites of Citrus Crops	163
7-3	Recommended Oil and Fortified Oil Treatments for Control of Insects and Mites in Deciduous Fruit Tree Crops	164
7-4	Recommended Oil and Fortified Oil Treatments for Weed Control in Field and Row Crops	166
7-5	Recommended Oil and Fortified Oil Treatments for Control of Weeds in Fruit and Nut Crops and Non-Crop Areas	168
7-6	Synthetic Pesticides Used in Vector Control	170
7-7	Likelihood of Pesticide Drift During Agricultural Crop Treatment with Different Methods of Application	190
7-8	Summary of Application Methods and Percentage of Practice Used for Each Crop in California	194
7-9	Weighted Average of Recommended Application Rates for 10 Tree Crops in California, 1977	196
7-10	Overapplication of Reported Nonsynthetic Pesticide for Agricultural Use on 14 Crops in California in 1977	197
7-11	Summary of Application Method, Spray Volume and Estimated Drift Loss for 14 Crops	199
7-12	Estimated Drift Loss During Oil Applications on High Use Commodities in 1977	200

	<u>Page</u>
7-13 Recommended Synthetic Pesticide Treatments for Control of Insects and Mites in Citrus	206
7-14 Recommended Synthetic Pesticide Treatments for Insect and Mite Control in Almond, Apricot, Peach, Nectarine, Plum, Prune and Pear Trees	207
7-15 Recommended Synthetic Pesticide Treatments for Selected Field and Row Crops	208
7-16 Recommended Treatments for Selected Synthetic Herbicides on Fruit and Nut Crops and Non- Crop Areas	209
7-17 Estimated Potential Reduction in F-10 Oil Use by Alternative Control Methods	232
8-1 Acute Toxicity Rating	243
8-2 Energy Inputs for Selected Pesticides	246
8-3 Summary of Energy Use of Saving Resulting from Use of Alternatives to Pesticide Oil	248
8-4 Summary of Application Costs	253
8-5 A Summary of Annual Treatment Costs with Nonsynthetic and Synthetic Pesticides	255
8-6 Annual Costs for Two IPM Programs	256
8-7 Cost and Oil Use Reduction Due to Use of Low Volume Application Methods	257
8-8 Estimated Cost of Emission Reduction by Different Alternatives	261
8-9 Summary of Emission Reductions from Different Alternatives in Three California Counties by Calendar Quarter	265

	<u>Page</u>
8-10 Summary of Estimated Emission Reduction as a Percentage of 1976 TOG Stationary Source Emissions from Different Alternatives in Three California Counties	266
8-11 A Summary of Comparative Impacts Among Alternative Pest Control Methods for 16 Commodities	269

## LIST OF FIGURES

	<u>Page</u>	
4-1	Classification Status for Oxidant	13
4-2	Typical Distillation Ranges of Various Oils	24
5-1	Application Inventory Overview	39
5-2	Monthly Application of Pure Oil Pesticides in California in 1977 with Non-Acreage, Acreage and Creosote Distribution	63
5-3	Monthly Applications of Formulation 10 Petroleum Oil Pesticides Used in California in 1977	65
5-4	Monthly Distribution of Application for Major Pesticide Oil Uses in California, 1977	66
6-1	Loss of Spray Oil From Leaves of Fruit Trees	111
6-2	Flow Diagram for Emission Estimation	120
6-3	Emissions of Total Organic Gas (TOG) Resulting from Formulation 10 Oil Pesticide Use in California in 1977	133

## ABBREVIATIONS AND SYMBOLS

ai	active ingredient
A.P.I.	American Petroleum Institute
CARB	California Air Resources Board
DNBP	dinoseb
F-10	formulation 10
HV	high volume spray
IGR	insect growth regulator
IPM	integrated pest management
Kcal	kilocalorie
LC <sub>50</sub>	lethal dose at which 50% mortality occurs
LPG	liquid petroleum gas
LV	low volume spray
NF-10	non-formulation 10
NR	narrow range
NSHC	nonsynthetic hydrocarbon or oil pesticide
Penta	pentachlorophenol
PUR	Pesticide Use Report
®	registered
TC	total coverage
TOG	total organic gas
TPD	tons per day
U.C.	University of California
ULV	ultra low volume spray
U.R.	unsulfonated residue
μ	micron = 10 <sup>-6</sup> meter
WP	wettable powder

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## 1.0 CONCLUSIONS

The following conclusions are based on the interpretation of data presented in this report.

- (1) The total estimated consumption of oil pesticide in California in 1977 was 225.2 million pounds. Of this quantity, 217.3 million pounds (96.5%) was applied in pure oil form (formulation 10), and 7.9 million pounds (3.5%) as minor ingredients (non-formulation 10). The formulation 10 products were applied in four categories: general weed control (53.9%), agricultural use (27.5%), wood preservation (11.8%), and miscellaneous uses (3.3%). The total organic gas (TOG) emissions from formulation 10 oil pesticide use was 91,010 tons or 249.3 tons per day (TPD) and about 41 percent of this emission took place in June through October. When compared to CARB's 1976 Statewide Emission Inventory, the 1977 oil pesticide emissions would account for 10.3 percent of the TOG emissions from all stationary sources. In some counties, however, this source of emissions accounts for more than half of all stationary source emissions. (e.g. San Joaquin County - 55%; Monterey County - 64%)

The major emission peaks during the year were in April through June and then a relatively high monthly emission rate was maintained through September. The months of relatively high emissions correspond best to both

the high ambient levels of TOG in some areas in the state and a high frequency of oxidant standard violations. It appears that pesticide oil applications during the summer and fall months could contribute significantly to oxidant problems in some areas.

- (2) A reduction in the use of pesticide oil with a resultant emission reduction can be achieved by synthetic pesticide substitution, using more efficient application methods and by adopting IPM practices. The emission reduction achievable by synthetic pesticide substitution was 157.8 TPD or 63.3 percent of the annual total oil emission, and the reduction achievable by new application methods and IPM procedures was 5.0-6.0 TPD (1.9-2.4 percent of the total emission from oil use) and 6-11 TPD (2.1-4.2) percent of the total emission from oil use) respectively.
- (3) Alternative measures examined would result in a reduction in energy use. The reduction was 55,307 barrels of crude oil equivalent for using more efficient application methods, 63,793-143,399 barrels for IPM practices, and 1,875,370 barrels for synthetic pesticides. The energy consumption of conventional oil application was equivalent to 1,899,365 barrels of crude oil equivalent.
- (4) In comparing the cost of alternatives with conventional oil applications, the cost of materials and application labor in using synthetic insecticides and most herbi-

cides were generally lower. With IPM practices, during the treatment year, costs on a per acre basis are higher than costs for non-IPM oil use. Since a high level of treatment is not required each year with IPM, costs for IPM practice could be lower in the long run. Considerable savings would result in changing to more efficient application methods. The average costs per acre and the relative cost effectiveness of emission reduction on a per ton basis realized in each of the alternatives for those commodities considered in this study, are presented below. Relative cost effectiveness is defined in this report as cost above or below the cost of oil use.

<u>Alternative</u>	<u>Potential Emission Reduction tons/TPD<sup>a</sup></u>	<u>Average Relative Cost Effectiveness<sup>b</sup> (\$/ton of Emission Reduced)</u>
<u>Synthetic Pesticides</u>		
Insecticides	4,949/13.6	-1,054
Herbicides	52,630/144.2	143
<u>IPM</u>		
Oil	2,047/5.6	673
Synthetic	4,096/11.2	1,032
Application Methods	1,813-2,202/5.0-6.0	-568

<sup>a</sup>TPD = Tons per day.

<sup>b</sup> - sign denotes a savings.

- (6) Based on the possible impact that each alternative may have on energy use, costs and air quality, the following alternatives are recommended for consideration to implement in order to reduce oil use.

- . Use of more efficient application methods
- . Adoption of IPM procedures
- . Synthetic herbicide substitution

## 2.0 RECOMMENDATIONS

- (1) Three alternative measures are recommended for implementation to the extent possible for the reduction of hydrocarbon emission from oil pesticide use. These alternatives are synthetic herbicide substitution, adoption of IPM procedures and use of more efficient application methods.

The use of weed oil for non-crop areas and for those field crops considered in this report could be phased out with synthetic herbicide substitutions. There is some question, however, on the availability of a real substitute for stoddard solvent as herbicide for carrots. With the current increases in price of petroleum products and energy considerations, the use of weed oil may be gradually phased out voluntarily by the end-users themselves.

IPM procedures are available for some tree fruits which include grapefruits, lemons, oranges, and pears.

Reduction in oil use and costs could be achieved by using low volume spray and tower sprayers.

- (2) Implementation of the recommended alternatives can be accomplished either by voluntary program or enforcement procedures. Economic feasibility should be one of the prime considerations in taking any implementation steps.

- (3) IPM procedure development is an existing function of the University of California and the California Department of Food and Agriculture (CDFA). With the current interest of the Air Resources Board on air pollution emissions from pesticide use, research fundings should be pooled and efforts coordinated between relevant institutions and agencies.
- (4) Air pollution emissions may not be a current primary concern of the regulatory function of the CDFA, and if this is the case, the air pollution concern should be integrated into the overall pest management consideration.
- (5) The current emission inventory was based primarily on survey sales and use data. A study of this design has some limitations with regard to assuring the accuracy and representativeness of data. Data generated by this approach should be validated by source reconciliation field studies. Validation should include intensive survey of end-users in the studied areas. Such an effort is especially important in better defining the pesticide uses in what are now included in the category of weed control unclassified.

### 3.0 INTRODUCTION

Air pollution is usually viewed as associated with sources such as motor vehicles, power plants, incinerators, and with industrial processes such as chemical manufacturing, iron and steel production, and cement production. Despite the fact that pesticides have the potential for contaminating the air, until recently agricultural processes have not been ordinarily considered as contributing to the pollution burden of the atmosphere in the same manner as some of the familiar pollutants such as sulfur oxides, nitrogen oxides, and carbon monoxide. In two studies,<sup>1,2</sup> preliminary findings indicate that pesticide applications for agricultural purposes may be found to be one of the major potential contributors to atmospheric hydrocarbons in some rural areas in California. Nonsynthetic hydrocarbons (NSHC) used as herbicides and insecticides appear to be by far the greatest contributors to this air pollution problem. To date, there has been no detailed county-by-county inventory made of hydrocarbon emissions associated with the agricultural use of NSHCs in California. In addition, the use patterns of these NSHCs in different counties have not been analyzed.

#### 3.1 Project Objectives

The primary objective of this project is to identify the use patterns of NSHCs in California and recommend possible alternative substitutes for the NSHC pesticides. In achieving this objective, a 1977 application and emission inventory associated

with the pesticidal usages of NSHCs in California was conducted. Specifically, this project seeks to:

1. Identify the use patterns of NSHCs in pesticidal applications including applications for agricultural, home and garden, and other non-agricultural uses,
2. Recommend possible alternative pest control methods as substitutes for NSHC applications with the primary purpose of reducing NSHC uses,
3. Inventory the hydrocarbon emissions associated with NSHC applications as herbicides and insecticides, and
4. Establish a general methodology(ies) for an emission inventory of NSHCs used for pesticidal purposes.

### 3.2 Scope

This entire report consists of three volumes. The body of the report is presented in Volume II, while the executive summary and appendices are presented in Volumes I and III respectively.

The body of the report in Volume II is presented in four parts. The first part is primarily concerned with data collection. The second part presents the emission inventory while concomitantly delineating the use patterns of NSHC pesticides. The third part identifies possible alternative methods which may lead to a reduction in NSHC applications. The last part provides an environmental, economic, public health and energy impact assessment of the alternative pest control methods.

The data collection effort in the first part involved primarily unreported NSHC pesticide use data. The reported data that were used in this report were obtained from the Pesticide Use Report (PUR) through the data bank of the Food Protection and Toxicology Center at U.C. Davis. The unreported data were obtained by questionnaire surveys, telephone surveys and personal and telephone interviews of pesticide manufacturers, dealers, farm advisors, county agriculture commissioners, end-users such as farmers, railroad companies, utilities, and governmental agencies. Appropriate statistics from the literature were also used.

The emission inventory was conducted in two steps. The initial step was to estimate the total annual pesticide applications. The second step was to calculate the emissions resulting from such applications on soil surfaces, leaves or water surfaces based upon vapor pressure, molecular weight, relative humidity and temperature, etc. At the same time, the 1977 use patterns of NSHC pesticides in California were also identified.

The alternative pest control methods considered in this report included chemical methods, cultural control, biological control, integrated pest management (IPM) and application methods. Application methods were included here not as a substitute for NSHCs but as means to reduce use of NSHCs.

Impact assessment of the various alternative control methods were considered in the last part of this report. Considerations in this part included the possible impacts of different alternative control methods on public health, energy use,

economics and air quality. Based on these impact assessments, recommendations were made with regard to the use of NSHCs for pesticidal purposes.

### 3.3 References

1. Wiens, F.J. 1977. Reactive Organic Gas Emissions from Pesticide Use in California. Staff Report, California Air Resources Board.
2. Leung, S., R. Johnson, T. Ling, C.S. Liu, R. Peter, W. Reed, T. Tanton A. Wong. 1978. Air Pollution Emissions Associated with Pesticide Applications in Fresno County. Final Report No. 77-E-02 prepared by Eureka Laboratories, Inc. for the California Air Resources Board.

## 4.0 BACKGROUND INFORMATION

### 4.1 1977 Air Quality in California

Air quality problems in California are both significant and far-ranging. In order to carry out the Clean Air Act requirements (Sec. 107-d-1), the California Air Resources Board (CARB) submitted designations of attainment/nonattainment areas for the state of California to the Environmental Protection Agency (EPA). The submittal dated December 2, 1977 indicates which areas of the state conformed to (attainment) or violated (nonattainment) national ambient air quality standards, and which were unclassified due to a lack of valid air quality data. From this submittal, it is evident that the most serious and widespread problem is the violation of the national ambient standard for oxidant (8 pphm).<sup>\*</sup> However, the EPA has since modified this standard to 12 pphm while the state implementation plan and the control strategies in other states are still based on the 8 pphm standard. Figure 4-1 shows that most California counties were classified as nonattainment for oxidant while the remaining counties were unclassified in 1977. Areas in which levels are high enough to be of concern are the South Coast Basin, San Diego County, the San Francisco Bay Area, the San Joaquin Valley, and the Sacramento Valley. Even though there were no counties classified as attainment, some unclassified counties could probably have been designated as attainment if valid data were available.

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<sup>\*</sup>Parts per hundred million.

# CLASSIFICATION STATUS FOR OXIDANT

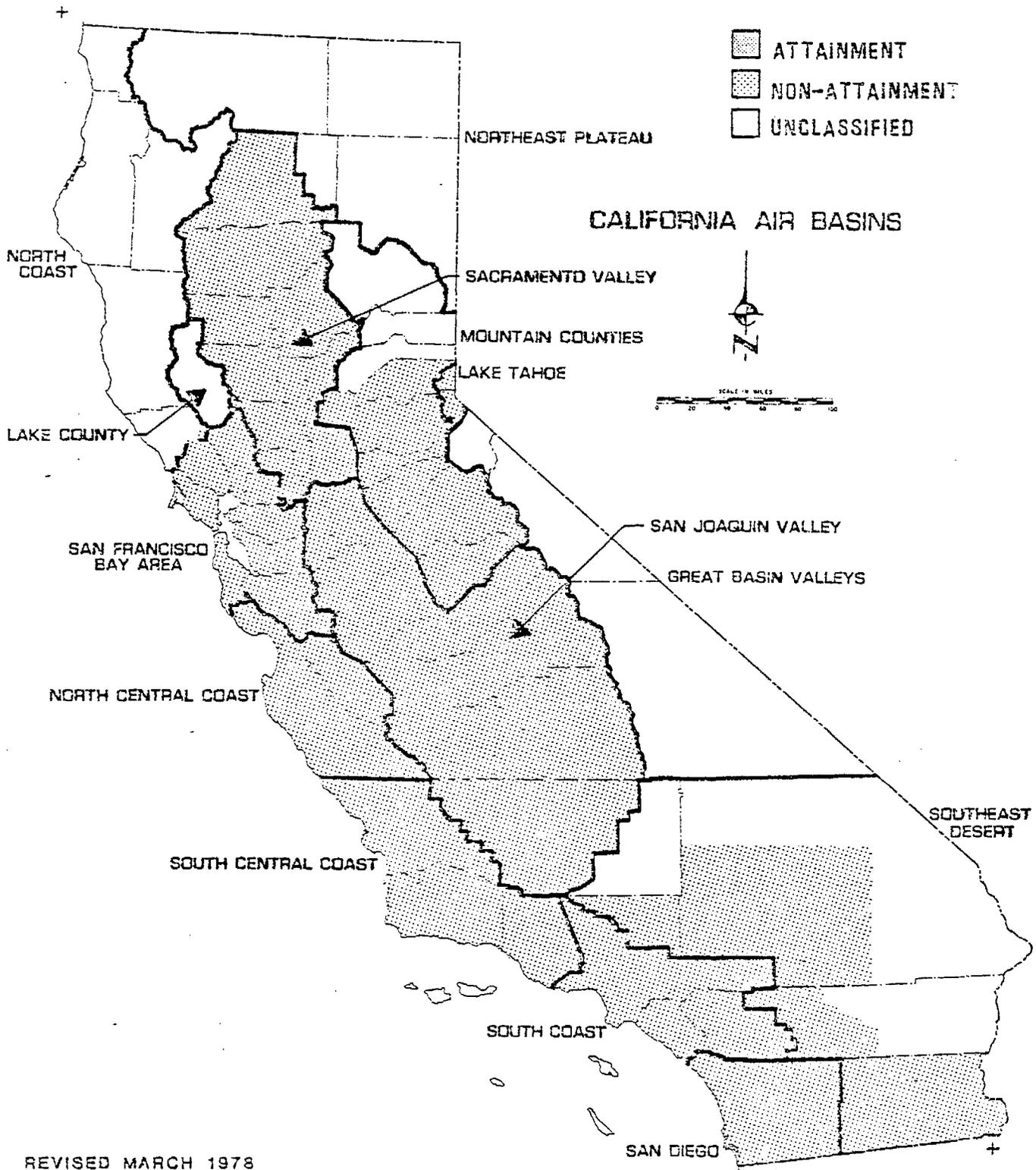


Figure 4-1. Classification Status for Oxidant

Presently, in many parts of the state, control strategies are being developed which are designed to achieve the national ambient standard for oxidant. These control strategies involve the reduction of emissions of oxides of nitrogen and of reactive hydrocarbons which are the precursors of photochemical oxidant. These strategies are being developed by local planning agencies and air pollution control districts as part of the State Implementation Plan (SIP). Most of the agricultural counties in the state, including those in the Central Valley, recognize the significant contribution of pesticide applications to hydrocarbon emissions. The control strategies for achieving the oxidant standards in these areas include the use of Integrated Pest Management to reduce organic pesticide applications. It is expected that the SIP will be finalized and submitted to the EPA for approval some time in the near future.

#### 4.2 Use of Oil as Pesticides

##### 4.2.1 Historical Development and Types of Oil

The use of petroleum oil as an insecticide was referred to in the literature as early as 1787,<sup>1</sup> and kerosene was used against scale insects on orange trees around 1865.<sup>2</sup> A crude oil emulsion was used by Smith<sup>3</sup> as a summer and dormant fruit tree spray in 1897. However, there was damage to plants from the unrefined oil especially with variations in the oil obtained. Experiments with various oil fractions showed that oil in the

light lubricating class was most suitable as a tree spray;<sup>4</sup> however, various fractions continued to be used by growers. In the 1930's, oils refined by the sulfuric acid process lowered the unsaturated hydrocarbon content of spray oil so that in many places it could be sprayed at any time of the year without apparent damage to trees.<sup>5</sup> Later improvements in refining of oil were made based on experiments which showed how to select those characteristics of oil which were needed to kill insects while avoiding the characteristics which damage plants.<sup>6</sup>

There is no clear history of petroleum oil use as a herbicide prior to this century. Undoubtedly growers used various kinds of oils as available to kill weeds. Gray<sup>7</sup> in 1919 noted that petroleum distillates killed plants better if they were not refined with sulfuric acid.

According to Gray and DeOng<sup>8</sup> the sulfonation test which measures unsaturated hydrocarbons was the most reliable indication of phytotoxicity. Experiments by Crafts and Reiber,<sup>9</sup> Havis et al.<sup>10</sup> and others in the 1950's showed that aromatics were the compounds most toxic to plants. Various low cost oil fractions such as kerosene, diesel oil and the tailings from solvent extraction processes were used for weed control before and since proprietary products specifically for weed control were marketed.<sup>11</sup> The products marketed as weed oils are made to specifications while other products such as diesel oil may have a decreasing content of aromatics due to improved refining methods.

#### 4.2.2 Types of Oil and Oil Specifications

Petroleum oil is a mixture of a large number of organic compounds which are predominantly hydrocarbons, and there are variations in the constituents present in crude petroleum oil obtained from different regions.<sup>12</sup> In the United States the crude oils are classified as paraffinic-base, asphaltic-base and mixed-base depending on the content of paraffin or asphalt.<sup>5</sup> The finished oils refined from the different crude oils differ depending on the source. For example, pesticide spray oils produced from the highly asphaltic California crude are higher in naphthenic hydrocarbons than are those produced from crudes of the Eastern U.S.<sup>13</sup>

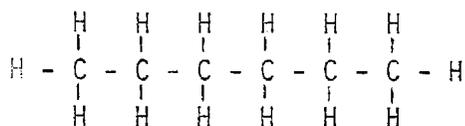
There are some 2,000 petroleum products in the U.S. market, including about 25 kinds of distillates, 100 kinds of white oils and 300 kinds of solvents.<sup>14</sup> This list does not include compounds such as plastics and fertilizer which are made by chemical modifications but only those separated from the variety of molecular structures in crude oil.

Other systems of classifications for the hydrocarbon chemicals in petroleum have been used, but in the system most commonly used in relation to pesticide oils, these chemicals have been divided into four broad groups: (1) paraffins, (2) naphthenes, (3) aromatics and (4) unsaturates.<sup>5</sup> The term hydrocarbon designates molecules composed solely of hydrogen and carbon atoms. These groups are briefly described.

Paraffins are saturated hydrocarbons. They have single

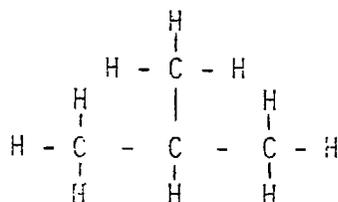
valence bonds between carbon atoms and the maximum number of hydrogens are bonded to the carbon. The paraffins may be straight-chained or branched-chain molecules as illustrated:

Straight-chain



n-hexane

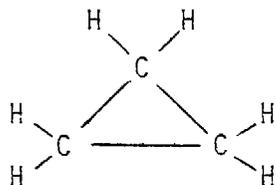
Branched-chain



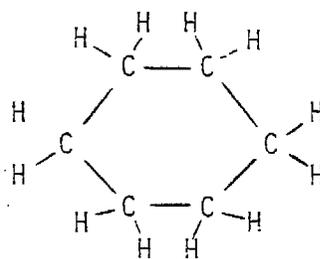
iso-butane

Chemically, paraffins are relatively inert. At ordinary temperatures they resist the action of most acids and bases, and they are only slowly oxidized by bromine, chlorine and iodine and in the presence of air.

Naphthenes are saturated ring structures which may be single ring or multiple ring in higher boiling point fractions. Examples of naphthenes are:



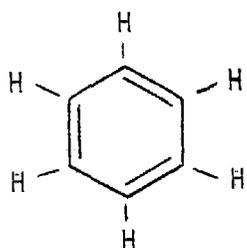
Cyclopropane



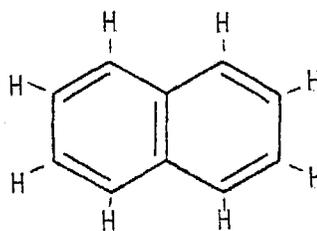
Cyclohexane

Chemically, naphthenes are similar to paraffins, but physical properties may differ. For example, at the same molecular weight, the naphthene oil has a higher viscosity than the paraffin.<sup>15</sup>

Aromatics are ring hydrocarbons with double bonds. They are unsaturated compounds which are usually composed of benzene or its derivative. Two or more rings may be bonded together in different configurations. Some examples of aromatics are:



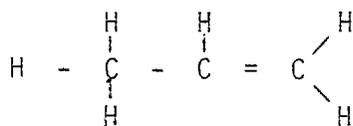
Benzene



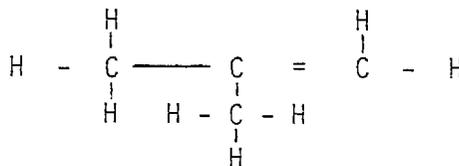
Napthalene

Aromatic compounds are more reactive chemically than saturated molecules and they can be removed from oil by acid treatment. Aromatics usually have a higher boiling temperature than saturated molecules of similar weight.

Unsaturates. Unsaturated hydrocarbons (deficient in hydrogen) have double or triple valence bonds between carbon atoms, and there may be one or more such bonds in each molecule. Some examples of straight-chain and branched-chain unsaturated hydrocarbons (also called olefins) are:



Propylene



Isobutylene

Unsaturated hydrocarbons are the reactive components of oil, whether open chain or aromatic. They are easily oxidized, react with acid and have some tendency to polymerize. They are also the main components of oils which cause phytotoxicity.

There are also other sulfur and oxygen containing constituents in petroleum but these occur mainly in the higher boiling point fractions which would not be found in pesticidal oils.

#### 4.2.3 Refining of Oil

Crude petroleum is separated by distillation into various fractions of different boiling points. The distilled fractions are usually purified further by solvent extraction, chemical treatment or other means.<sup>5</sup>

Pesticide oils come from the range of light and intermediate distillates among the range of products shown in Table 4-1 which are distilled and refined from crude petroleum.

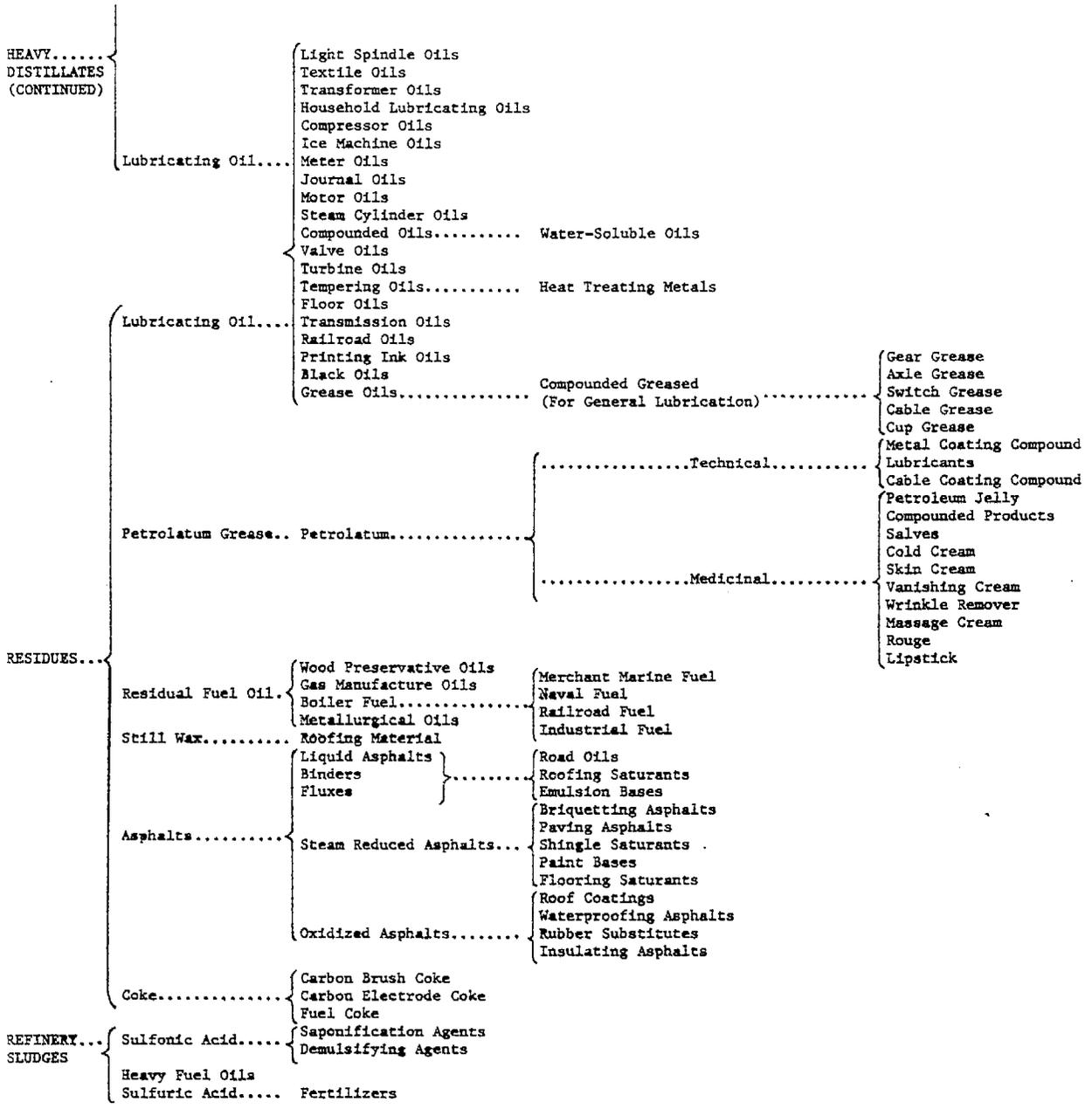
Weed oils may be produced from the highly aromatic residues extracted from other purification processes or they may be distilled and blended to meet the required specifications.

Tree spray oil for application to foliage has stringent purification requirements for pesticide oils. Tree spray oil

TABLE 4-1

Products Derived from Crude Petroleum<sup>14</sup>

HYDROCARBON GASES	Liquefied Gases....	Metal Cutting Gas		
		Illumination Gas		
	Petroleum Ether....	Laboratory Ether		
		Motor Priming Ether		
	Alcohols.....	Isopropyl.....	Solvents	
		Secondary Butyl	Acetone	
		Secondary Amyl		
	Other Synthetics..	Secondary Hexyl	Lacquer Solvents	
		Benzene.....	Chemicals, Explosives, Pharmaceuticals	
		Toluene.....	Explosives, Toluidine, Saccharin	
Xylene.....		Explosives, Dyes		
Naphthalene.....		Dyes, Perfumes		
Gas Black.....	Anthracene.....	Dyes		
	Resins.....	Lacquers, Varnishes, Paints		
Fuel Gas	Rubber Tires	Gas Machine Gasoline.....	Domestic Illumination Naphtha	
	Light Naphthas....	Inks	Pentane.....	Candlepower Standardization Nap.
Paints		Hexane.....	Laboratory Naphtha	
LIGHT..... DISTILLATES	Naphthas.....	Light Naphthas.....	Chemical Solvents.....	Drug Extraction Solvent
		Intermediate Naphthas....	Aviation Gasoline	
	Refined Oils.....	Motor Gasoline	Commercial Solvents.....	Rubber Solvent
		Blending Naphtha		Fatty Oil Solvent (Extraction)
	Naphthas.....	Varnishmakers & Painters Naphtha		Lacquer Diluents
		Dyers & Cleaners Naphtha		
	Refined Oils.....	Turpentine Substitutes		
		Soaps		
	INTERMEDIATE DISTILLATES	Gas Oil.....	Kerosene.....	Lamp Fuel
			Signal Oil.....	Stove Fuel
Absorber Oil.....		Mineral Seal Oil.....	Motor Fuel	
		Carburation Oils	Railroad Signal Oil	
Gas Oil.....		Metallurgical Fuels	Lighthouse Oil	
		Cracking Stock	Coach & Ship Illuminants	
Absorber Oil.....		Household Heating Fuels	Gas Absorption Oils	
		Light Industrial Fuels		
Absorber Oil.....		Diesel Fuel Oils		
		Gasoline Recovery Oil		
Absorber Oil.....	Benzol Recovery Oil	.....Technical.....	Emulsified Spray Oil	
	White Oils.....	.....Medicinal.....	Bakers Machinery Oil	
HEAVY..... DISTILLATES	Technical Heavy Oil	Saturating Oils.....	Wool Oils	
		Emulsifying Oils.....	Twine Oils	
	Wax.....	Electrical Oils.....	Cutting Oils	
		Flotation Oils.....	Transformer Oils	
	Wax.....	Candymakers Wax	Switch Oils	
		Candle Wax	Metal Recovery Oils	
	Wax.....	Laundry Wax.....	Detergent Wax	
		Sealing Wax	Iron Wax	
	Wax.....	Etchers Wax	Cardboard Wax	
		Saturating Wax.....	Match Wax	
Wax.....	Chewing Gum Wax	Paper Wax		
	Medicinal Wax			
Wax.....	Insulation Wax			
	Canning Wax			



is refined by solvent extraction to remove aromatics and by hydrogenation to further lower the concentration of unsaturates.<sup>6,16</sup> Special narrow-distillation-range fractions are made for some spray oils, e.g. NR-415, NR-440, in order to increase insecticidal efficiency and reduce phytotoxicity.

#### 4.2.4 Chemical and Physical Characteristics of Petroleum Oil Pesticides

The compositions of petroleum oil pesticides are very complex, and oils of exactly the same composition cannot be made each time the oil is produced. It was found necessary, therefore, to specify limits for certain chemical and physical characteristics of oils according to the intended use. The main characteristics and importance of the measurements are described as follows:<sup>17</sup>

(a) Density (or specific gravity). The density of petroleum is measured in "API degrees", this is the minimum temperature for the appearance of the cloud point for aniline and oil in a one to one mixture. API degrees may be converted to grams/ml by the following formula:

$$\text{Density (g/ml)} = \frac{141.5}{131.5 + \text{API degrees}}$$

The density of pesticide oil increases from paraffins to naphthenes to aromatics and is important as one of the criteria used in determining the content of aromatics and naphthenics.<sup>18</sup>

(b) Distillation Range. The distillation range is the range of temperatures over which the component oils of the product will boil or distill. Selection of the right distillation range is the primary method used to obtain the most appropriate oils for the pest control problem. Use of the right range is particularly important with foliage spray oils. As shown in Figure 4-2, oils which distill at less than 370°F (at 10 mm Hg) are ineffective for pest control and those which distill above 460°F are efficient miticides but also cause increased plant damage. Only oils distilled in the range of 370° to 460°F are efficient foliage sprays.<sup>19,20</sup>

Temperatures are usually reported for 10%, 50% and 90% distillation. Distillation of spray oil is usually done at 10 mm Hg pressure in order to avoid cracking or breaking apart of oil molecules at temperatures above 750 F.<sup>21</sup>

(c) Unulfonated Residue (UR). This is the percentage of an oil which does not react with sulfuric acid in a standard test. It is a measure of the content of reactive components which are primarily unsaturated molecules such as aromatics and olefins.<sup>6</sup> The UR indicates the extent to which a pesticide oil may be safely used on plants. UR's range from 15% for weed oils to 85% for dormant oil and 92-96% for foliar oils.

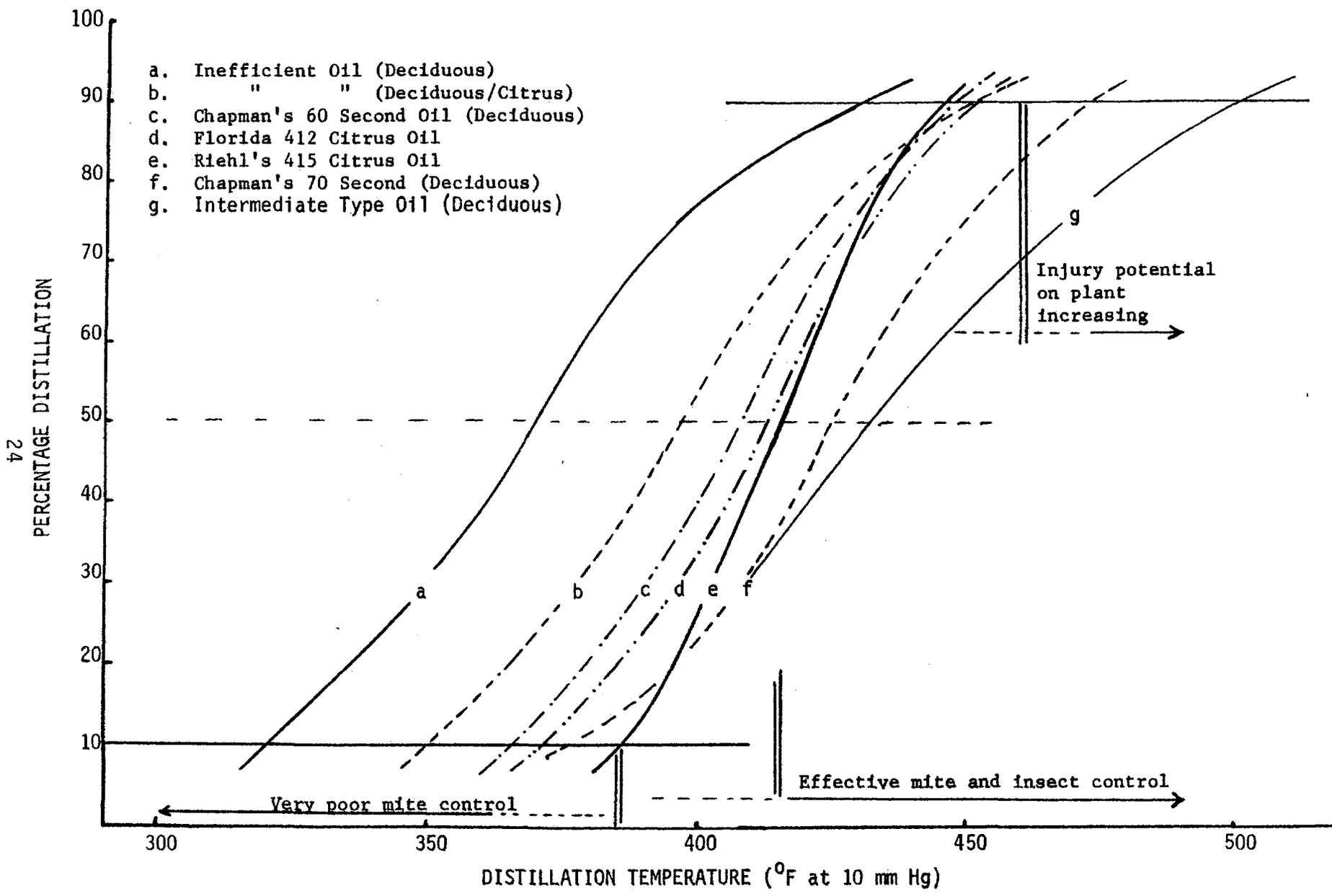


Figure 4-2. Typical Distillation Ranges of Various Oils

(d) Viscosity. Viscosity is a measure of the internal resistance to flow of a fluid. Viscosity of pesticide oils is measured with a Saybolt Viscosimeter and reported in seconds Saybolt Universal (SSU), the time it takes for 60 ml of fluid to flow through a capillary.<sup>5</sup>

Viscosity is closely related to distillation range and molecular weight for oils from similar origin. For pesticide oils, generally viscosity is of some importance in that oils are generally applied with a sprayer, and oils should not be so viscous as not to spread easily to cover surfaces of plants or insects.

Spray oils have SSU viscosities of 57 to 140 seconds.

(e) Volatility and Vapor Pressure. Volatility is directly related to the vapor pressure of a substance. Vapor pressure has been measured for very few petroleum hydrocarbons in the molecular weight range of pesticide oils.<sup>22</sup> Volatility is easily measured<sup>5</sup> but is not routinely reported.

The volatility of oil must be appropriate to the purpose for which it is used. Selective weed oil applied to carrots must not remain so long that it is present when carrots are harvested. Spray oils for insect and mite control are ineffective if they are too light because they evaporate too quickly.

(f) Aromatic Content. The content of aromatic hydrocarbons in pesticide oil is primarily responsible for their phytotoxic action. General contact weed killers should have a high aromatic content (50-100%) and spray oils should be low in aromatics if they are to contact foliage.

A list of physical and chemical characteristics of petroleum oil pesticides classified according to chemical types is shown in Table 4-2.

#### 4.2.5 Use of Petroleum Oil Pesticides and Mechanism of Toxicity Action

##### 4.2.5.1 Insecticides

In insect control petroleums, oils may be used in the following three ways:

- a. They may be used as adhesives in the formulation of sprays and dusts -- when used in this manner, the inherent toxicity of oil is not of primary interest;
- b. They may be used as solvents which serve as carriers for toxicants such as rotenone, pyrethrin, and diazinon -- "fly spray" is an example of this type; and
- c. They may be used as the principal toxic agent as in the case of horticultural sprays.

Apparently 80 to 90 percent of petroleum oil pesticide used is of the third type.<sup>23,24</sup> The literature indicates that oils have been tested against a wide variety of pests. In some

TABLE 4-2

## Physical Characteristics of Nonsynthetic Hydrocarbon Pesticide Chemicals

Chemicals (DFA Designation)	Percentage <sup>a</sup> used in pesticide types (%)	Major application	Aromatic <sup>b</sup> contents & % of class III reactivity (%)	Mean boiling <sup>b</sup> point (°F)	Range of <sup>b</sup> distillation (°F)	Vapor <sup>c</sup> pressure (mmHg at 20°C)	Viscosity (SSU-second)	Unulfonated residue (UR %)	Density <sup>b</sup> (gm/ml)	Molecular <sup>b</sup> weight
Aromatic Petroleum Solvent	100% (Herb)	Aquatic Weed	>90%	279	8	6.5	-	-	0.875	110
Mineral Oil	100% (Ins)	Fruit & nut oil spray	10%	690	51	$7.4 \times 10^{-6}$	70-90	90-95	0.866	327
Petroleum Oil Unclassified	98.3% (Ins)	Fruit & nut oil spray	5%	680	90	$2.89 \times 10^{-5}$	37-134	85-95	0.874	307
Petroleum Distillate	100% (Ins)	Mosquito larvicide	8%	571	133	$9.11 \times 10^{-4}$	46.61	85-95	0.889	253
Petroleum Hydrocarbon Nonselective	100% (Herb)	General contact herbicide & defoliant	65%	569	250	$9.54 \times 10^{-4}$	31-41	-	0.94	160
Selective		Carrots & other vegetables	10%	350	82	0.546		-	0.81	124

<sup>a</sup>Based on PUR 1977<sup>b</sup>From manufacturers' data<sup>c</sup>Calculated values from boiling points (Maxwell and Bonnell, 1957)

cases, it is the egg stage against which oils are effective and in other cases, it is the adult or juvenile insects. However, the oil-susceptible species fall into rather distinct biological groups. For example, oil is effective in the control of many scale insects in the family Coccidae -- which are soft scale insects such as San Jose Scale and armoured scale insects of the family Diaspididae such as California Red Scale. Also, many mites in the order Acarina, like the citrus red mite are controlled effectively by oil.<sup>5</sup>

Mode of Action of Oils as Insecticides. Although petroleum oils have for a long time been used as insecticides, the manner in which they produce toxic effects is not fully understood. Relatively little work has been directed at this seemingly important point. Undoubtedly, our meager knowledge on this has hampered the development of more effective hydrocarbons.

Oils are used effectively against both the egg stage and hatched form of insects. However, the sensitivity varies not only among different species but also among life stages of the same species. For instance, eggs of the pear psylla are not highly susceptible to oil sprays while the hatched forms are readily killed by these sprays.

Theories on the mode of action of ovicides suggested by Hoskins<sup>25</sup> and Martin<sup>26</sup> are summarized as follows: The oil may prevent the normal exchange of gases through the outer casing of the egg, or may harden the outer casing so as to prevent hatching. The oil may interfere with the water balance of the egg, or may soften or dissolve the outer casing of the

egg. Through interference with the normal development of the embryo, the oil may penetrate the egg and interfere with enzyme or hormone activity, or the oil may come in contact with the emerging insect and exert its toxic effect upon the delicate integument.

Considering these possibilities, it seems reasonable that the mechanism of killing might vary with the different species or that several modes of action might operate simultaneously or at different stages in the development of the embryo. Many experiments have been done and most of the observations strongly suggest that oil exerts its lethal effect through a mechanical interference with the normal gaseous exchange mechanism. This physical mechanism rather than chemical seems to be further borne out by the fact that less reactive paraffin oils show even greater ovicidal efficiency than do the more reactive unsaturated oils.

The mode of action involved in the toxic effect of oils on adult forms is no better understood than in the case of ovicides. Several theories which have been advanced are summarized by Shepard<sup>27</sup> as follows: Oil blocks the spiracles resulting in suffocation of the insects. Oil penetrates the tissue in the liquid phase and kills by "corroding" them -- by breaking down the tissue structure. Volatile components of the oil are toxic and act as fumigants.

Again, it is more likely that several modes operate simultaneously and that other modes of action are also involved.

In general, it would appear that the chemically-active, unsaturated oils might exert a toxic effect by virtue of their chemical structure, and the highly refined saturated and inactive oils would appear to exert their toxic effect chiefly through their physical characteristics, but such is not the case.

#### 4.2.5.2 Herbicides

Oil toxicity. Oils vary considerably in their toxicity to plants. As with most herbicides, the basic causes of herbicidal action are only partially delineated although the effects are much better understood.

Oils wet plant surfaces readily and tend to spread as a thin film. The oil may rapidly penetrate the cuticle especially if it is thin. Once oil reaches the inside of the leaf, it solubilizes the lipids of the cell membranes; cell sap leaks into the intercellular spaces, and the cell begins to collapse. Plants sprayed with oil usually first show a darkening of the youngest leaf tip presumably as a result of the cell sap leakage into intercellular spaces. This gives the plant a water-soaked appearance. There is a loss of turgor and a dropping of stems and leaves, and the plants may have an odor of macerated tissue of new-mown hay.<sup>3</sup>

The injurious action of oil to plants was found to be largely due to the aromatics and unsaturates present in the oil.<sup>8</sup> Such injury may be of an acute type with a quick

burning of the leaves due to oils of a low boiling fraction or a chronic effect that develops slowly as a yellowing of the foliage due to the oils of the high boiling fraction. Part of the injury is due to the formation of organic acids through the slow oxidation of the thin films of oil on or within the leaf.

The phytotoxicity of oil is related to its viscosity and surface tension. Light oils have lower viscosities and surface tensions and they enter plant tissue more readily than heavy oils. The hydrocarbons with boiling points between 280°F and 510°F are generally more toxic to plants than those with higher or lower boiling points.<sup>8</sup> The excessively high rate of evaporation of the low boiling point oils and the high viscosity of high boiling point oils probably account for their lower toxicities.

Herbicidal Uses. Oils used in the field of chemical weed control function as toxicants, solvents, film agents, and carriers. In view of some very effective synthetic compounds now used as toxicants, the toxicity of the oils themselves is somewhat less important than it once was. Oils used as solvents and carriers have the property of aiding in the contact, spreading, and penetration of pesticides.<sup>28</sup>

There are two general types of weed-killer pesticide: selective and nonselective. The former destroys the weed but does not affect the crop; the latter kills all types of plants. The nonselective herbicides are used annually in treating

rights-of-way and along roadside fences and ditches where weeds are a fire hazard. For these purposes, a wide variety of petroleum oils are used which are primarily light aromatic oils registered as weed oils. These nonselective weed oils cause acute toxicity; also used are heavy oils, such as diesel and fuel oils which cause chronic toxicity. Quite often, the oils are fortified with other chemical toxicants to increase their phytotoxicity.

Preemergence sprays are used with many crops after the seeds have been planted but before they have started to grow and the ground surface is covered with small weeds which are vulnerable to light petroleum distillates ranging from mineral spirits to diesel fuel. Stoddard solvent and other light distillates are used as selective petroleum herbicides with certain crops where the weeds can be killed without leaving a petroleum flavor in the crops. Crops treated in this manner include beets, berries, carrots, celery, cotton, flax, grapes, onion, parsnips, and soy beans. Some orchard crops are also treated with selective oils. A common petroleum oil widely used in this kind of service has a distillation range of around 300° to 400°F, API gravity of 40° to 44°F, flash point above 100°F, and aromatic content of 14 to 15 percent.

#### 4.2.5.3 Fungicides and Other Pesticides

Although oils have mainly been used as insecticides and herbicides, the value of petroleum oils as fungicides has also been realized. The oil is applied to banana and other crops

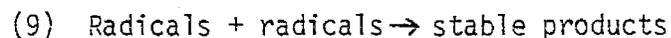
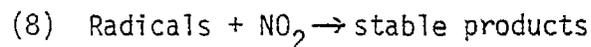
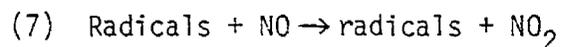
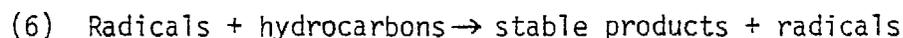
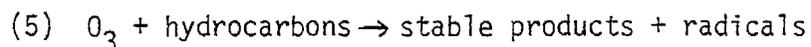
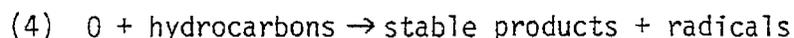
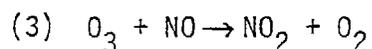
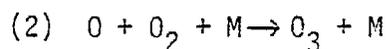
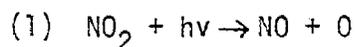
in the form of a fine mist by sprayer or by aircraft to control Sizatoka disease and others. White mineral oil has been found effective in preventing the growth of suckers on tobacco plants.<sup>28,29</sup>

Oils may serve as adjuvants in formulations involving 2,4-D, 2,4,5-T, DNBP compounds, trichloroacetates, and others.

Many halogenated hydrocarbons -- chloropicrin, ethylene dichloride, etc. have proven highly effective against nematodes. However, pure oil alone has hardly been used as a nematocide. Nevertheless, petroleum oils are used as parasiticides with applications on livestock.

#### 4.3 Photochemical Reactions of NSHC Pesticides in the Atmosphere

Photochemical "smog" or oxidants are formed when sufficient quantities of hydrocarbons and oxides of nitrogen in the atmosphere are exposed to sunlight ( $h\nu$ ). The reactions which produce these oxidants (primarily ozone) are complex and only partially understood. However, they can be summarized in the following highly generalized scheme.<sup>30</sup>



Reactions 1 through 3 represent those reactions which occur in the atmosphere with little or no hydrocarbons present.  $\text{NO}_2$ , when irradiated with ultraviolet light, disassociate to NO and a single oxygen atom. The single atom of oxygen is highly unstable, and will rapidly combine with  $\text{O}_2$  in the presence of another molecule to form  $\text{O}_3$ , or ozone. Ozone, in turn, reacts with NO to produce  $\text{NO}_2$  and an oxygen molecule. This series of reactions is self-limiting and allows for relatively little ozone accumulation. However, the introduction of reactive hydrocarbons to the atmospheric "mixture" results in the formation of radicals (reactions 4 through 7), which in turn oxidize the NO (reaction 7) to  $\text{NO}_2$ . This action breaks the self-limiting cycle of reactions 1 through 3 and allows more ozone to build up in the atmosphere. More specifically, the radicals oxidize the NO molecules formed in reaction 1 before the ozone can do so, thus "preserving" the  $\text{O}_3$  molecules. Reaction 3 becomes much more insignificant as a consequence. It is important to note that the ozone produced in this process is the result of the action of ultraviolet light in sunshine upon  $\text{NO}_2$  in the atmosphere. Reactive hydrocarbons do not enhance this action but only permit the ambient concentration of ozone to increase.

Reactions 4 and 5 gradually convert the hydrocarbons to stable (nonreactive) products and radicals, and reactions 6, 8 and 9 convert the radicals to stable products. Thus, oxidant formation is limited by the relative concentrations

of hydrocarbons (HC) and oxides of nitrogen (NO). If  $[\text{NO}_x] \gg [\text{HC}]$ , the hydrocarbon is expended before NO is converted to  $\text{NO}_2$ . With a significant quantity of NO remaining, reaction 3 prevents  $\text{O}_3$  buildup. If  $[\text{NO}_x] \ll [\text{HC}]$ , all NO is rapidly converted to  $\text{NO}_2$  (reaction 7), with a great deal of HC still remaining. The reaction of ozone and atomic oxygen (reactions 4 and 5) with the HC also prevents  $\text{O}_3$  buildup. However, there is a broad range of relative HC and  $\text{NO}_x$  concentrations between these extremes which permits  $\text{O}_3$  levels in the ambient air to become excessive.

With ample quantities of both hydrocarbons and oxides of nitrogen in many areas in California (mostly from combustion sources, such as automobiles), ozone production will be further enhanced by additional hydrocarbon emissions in most instances. This is certainly true of emissions of hydrocarbons resulting from the application of NSHC pesticides. The reactivity of these emitted hydrocarbons varies, but the bulk of them are either moderately or highly reactive in terms of the rates at which they foster ozone formation. Understandingly, the control of these emissions is of concern to those involved in the study or control of air pollution in California.

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## 5.0 APPLICATION AND USE PATTERN INVENTORIES

### 5.1 Introduction

This section summarizes the application distribution and use patterns of nonsynthetic hydrocarbon (NSHC) pesticides in California during 1977. The data presented in this report are based on data obtained from a number of surveys of end-users, farm advisors, pesticide dealers and manufacturers, and from the PUR data base of the Environmental Toxicology Library at U.C. Davis. The data in this report include reported and unreported applications by growers and by commercial applicators for agricultural and non-agricultural uses. These uses are described in detail in the latter part of this section.

The presentation of this section is organized in three parts. The first part is concerned with the application and use pattern inventories methodology. The second part deals with the temporal and spatial distributions of the applications. The last part describes the use patterns of the nonsynthetic hydrocarbon pesticides in California during 1977.

### 5.2 Application and Use Pattern Inventories Methodology

#### 5.2.1 Overview

An overview of the application inventory is presented in Figure 5-1. The manufacturers of NSHC pesticides and the dealers who are registered with the CDFA to sell pesticides were surveyed by questionnaire to determine the types, quantities

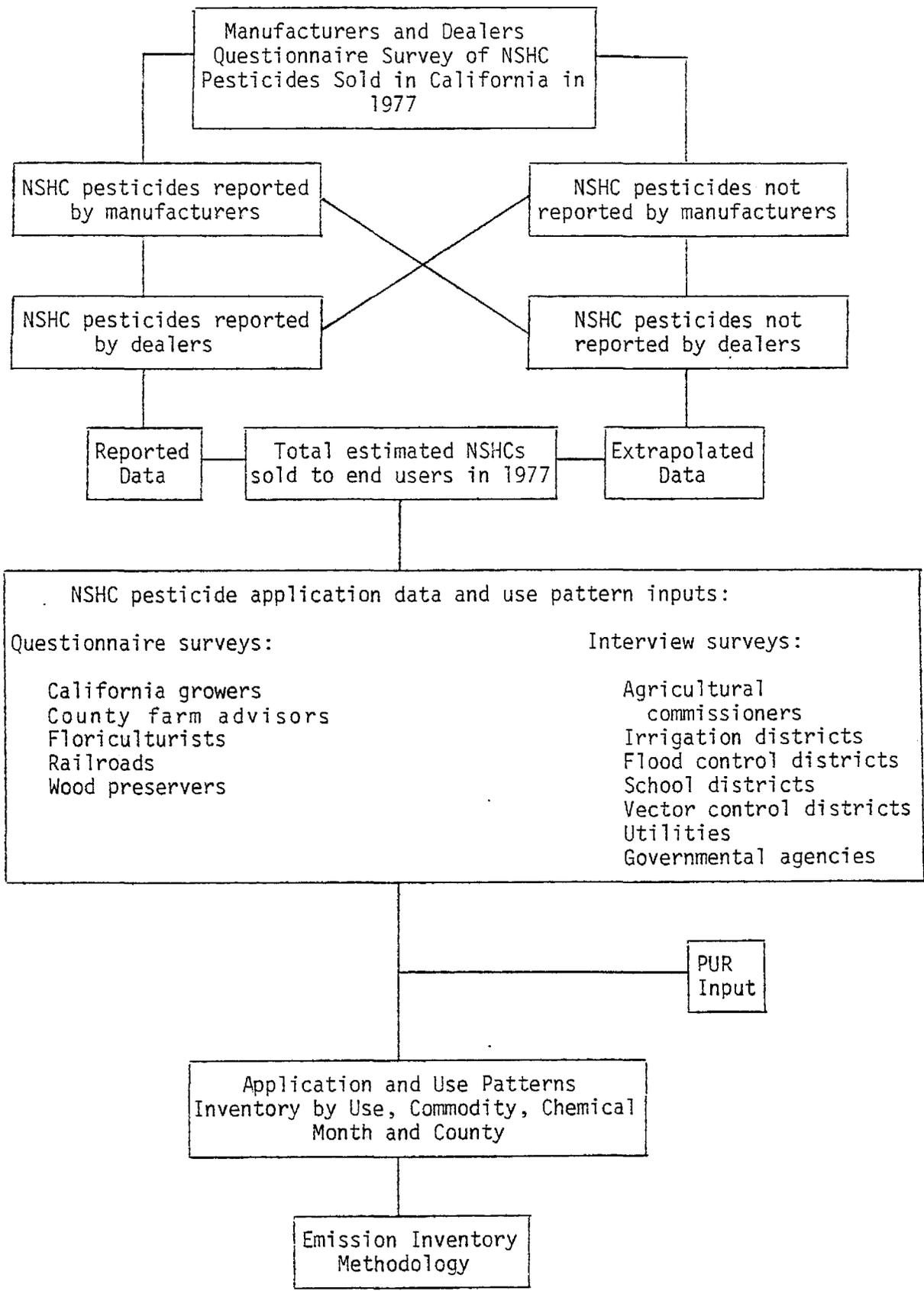


Figure 5-1. Application Inventory Overview

and locations of the NSHC pesticides sold in California during 1977.

To determine the application and use pattern of the NSHC pesticidal oils sold in California during 1977, questionnaire surveys were sent to: California growers, county farm advisors, floriculturists, railroads and wood preservers, and interview surveys were conducted with: agricultural commissioners, irrigation districts, flood control districts, school districts, vector control districts, utilities and several governmental agencies. These inputs were supplemented with the PUR data which provided a partial basis for the distribution of application, by commodity, month and county. At this point, after completing an application inventory, the emission inventory methodology was applied as described in Chapter 6.

#### 5.2.2 Inventory Approaches

A statewide inventory of NSHC pesticidal oils required knowledge of how much oil was used on what commodities, during which months and in what areas of the state. A survey of the manufacturers and dealers was designed to provide the data from which to extrapolate the quantities of NSHCs sold to all the end-users in 1977. Questionnaire and interview surveys of different end-users and agricultural advisors, together with PUR data, provided data for the determinations of use patterns and application distribution.

#### 5.2.2.1 Pesticide Use Report

The PUR data obtained from the Environmental Toxicology Library at U.C. Davis was used as the general framework for the application and use pattern inventories. However, the PUR data for each commodity had to be carefully evaluated because only the NSHC pesticidal oils applied by licensed pest control operators are required to be reported to the CDFA and hence are included in the PUR. Grower applied NSHC pesticidal oils are not required to be reported; therefore, the PUR does not accurately describe the application pattern in each county. For example, of all the pear growers in California who use a dormant spray, only those areas sprayed by pest control operators will appear in the PUR as having received a dormant spray. Therefore, it is necessary to determine by other means what the actual application pattern was for at least the most oil intensive commodities. This was accomplished by the use of questionnaire and interview surveys.

#### 5.2.2.2 Questionnaire Surveys

All questionnaire surveys were mailed out with explanatory cover letters and postage paid return envelopes. Copies of each questionnaire and cover letter are in Appendix A.2.1.1 of this report. A summary of all the questionnaire surveys is detailed in Table 5-1. A brief discussion of each survey follows:

Manufacturer Survey. A computer printout was obtained

TABLE 5-1

Summary Table of Questionnaire  
Surveys Sent and Received

NSHC Survey	# Sent	Positive Reply		Negative Reply		% Total Response
			%		%	
Manufacturers listed in Master Label File	47	18	38	4	9	47
Manufacturers not listed in Master Label File	25	0		11	44	44
Dealers	1083	148	14	134	12	26
Railroads	22	6	27	9	41	68
Wood preservers	24	6	25	10	42	67
Floriculture	966	35	4	79	8	12
Farm Advisors	103	18	17	14	14	31
Growers (subsample)	742	42	6	37	5	11
Growers	5776	164	3	280	5	8
Combined Growers Survey	6518	206	3	315	5	8

from the Environmental Toxicology Library at U.C. Davis which provided a list of names and addresses of all the manufacturers whose NSHC pesticides were sold in California during 1977. The printout listed 47 manufacturers and the 135 products they sold in 1977. To ascertain that the list of 47 manufacturers was a complete list, a random sample of 25 California oil companies was also surveyed to determine if they manufactured any NSHC pesticidal oil products. All responses from those of the 25 oil companies that responded to the survey reported that no NSHC pesticides were manufactured. The manufacturers survey requested use pattern literature, quantities of products sold during 1977 as well as physical and chemical properties of products so that emissions could be determined.

Dealer survey. All 1,062 pesticide dealers licensed by the CDFA for the year 1977 were surveyed to determine the quantities of NSHC pesticide oils sold in each county during 1977. Additionally, the dealers were asked to describe the intended use of the oils as well as the approximate percent of the oils sold directly to users rather than to other distributors. In Table 5-1, the number of dealer surveys reported as sent out is 1,083 because one of the major weed oil dealers duplicated our survey and sent it out to an additional 21 dealers who were not on the original mailing list but responded to the survey.

Grower Survey. The CDFA reported that California had 65,000 farms in 1977, so it was decided that 10 percent of

the growers would be surveyed. A mailing list of California growers was obtained from Dun and Bradstreet Marketing Services and used for the survey. The mailing list sample consisted of producers actually engaged in growing operations according to the Standard Industrial Classification (SIC) numbers supplied with the list. The mailing list included farms in every county except one which has only 4 farms recorded in the 1974 U.S. Census of Agriculture. A sample of appropriate size was selected by computer through random selections from the list.

Some tests for the reliability of the list indicated a fairly close correspondence between the list and the total number of farms in the state. When the percentage in the list for the number of employees per farm, for 5 groups ranging from 0 to 99 employees per farm, was compared with similar figures for all farms in California according to statistics from the CDFA, the correlation coefficient for the comparison was 0.949. The correlation coefficient was 0.931 for the comparison of the number of farms in each county shown in the sample list and the number recorded in the U.S. Census of Agriculture, 1974, the latest year available.

The survey was conducted in two parts. The first part consisted of a random subsample of 742 growers out of the total 6,518 growers that were eventually surveyed. The subsample was initiated to determine what kind of response could be expected from the survey and cover letter before the entire survey was mailed out. As a result of the subsample responses,

the cover letter was rewritten and some low response questions were clarified along with some of the sample information provided on the questionnaire.

The farmer survey was designed to solicit information concerning: the pesticide oil product used, the manufacturer's name, the specific use of the product, the target pest, the commodity being treated, gallons of product used per application, the acreage or units treated, the months when applied and the method and cost of application.

Floriculture Survey. California floriculture growers were also surveyed to determine if they used any NSHC pesticidal oils. The CDFA reported that there were 941 floriculturists in California in 1977, each with gross sales of over \$10,000.<sup>1</sup> The floriculture mailing list obtained from Dun and Bradstreet Marketing Services contained 966 names; therefore, it is assumed that most, if not all, of the California floriculture companies were surveyed. The floriculture questionnaire requested essentially the same information as the growers with only a few changes.

Farm Advisor Survey. The farm advisor questionnaire survey was initiated due to a low grower response. It was hoped that the farm advisors would be able to provide NSHC pesticidal oil use information for each county for the crop of their specialty. County farm advisors seemed to be the individuals who would have the greatest familiarity with crops in their areas of specialization with regard to recommended

practice and to what farmers are actually doing.

The accuracy of oil use estimates made by farm advisors cannot be verified. Generally no other source is available for unreported oil use on the crop considered. Most farm advisor estimates used in this report are based on crop acreage and an estimate of the percentage receiving a particular type of oil treatment. Usage often varies from one county to another. For example, carrots in Kern County received an estimated 80 gallons of weed oil per acre,<sup>2</sup> and for San Bernardino County it was stated that no oil was used but only synthetic herbicides.<sup>3</sup> Although application estimates by farm advisors have a degree of uncertainty, they are based on recorded crop acreages and some knowledge of usage in each county.

The questionnaire sent to farm advisors requested detailed oil use information on the 16 most oil intensive crops: lemon, orange, almond, peach, prune, pear, plum, grapefruit, nectarine, olive, apricot, carrot, alfalfa, clover, celery and onion. According to the 1977 PUR, these crops received 89 percent of the total reported formulation 10 oil applied in California.

The University of California Extension Service farm advisors for the 16 crops were surveyed in each county, and a total of 103 questionnaires were mailed out.

Wood Preserver Survey. A list of 24 companies selling wood preservatives or performing wood preserving in California was developed from the California telephone directories and the 1977 California Manufacturers Register. These companies

were surveyed to determine the amounts and types of creosote that were used or sold for wood preserving in 1977. The wood preserving companies were also requested to provide a description of the items treated, the treatment rates in lbs./ft.<sup>4</sup>, the month of the treatment and the manufacturer or distributor of the creosote.

Railroad Survey. The 22 railroads operating in California were surveyed to determine the types and amounts of weed oils and creosotes used in 1977 for right-of-way maintenance and wood preserving. They were also requested to provide information including a description of the items treated, treatment rates, month of treatment and the manufacturers or distributors of the creosote and weed oils used.

#### 5.2.2.3 Interview Surveys

Interview surveys were used to contact the numerous agencies throughout the state to determine the application inventory and use pattern of any NSHC pesticide oils they may have used in 1977. Most of the interviews were conducted by telephone, but some of the interviews were conducted in person. Some of the agencies interviewed in selected counties were: agricultural commissioners, irrigation districts, flood control districts, and vector control districts. Interview surveys were also conducted with representatives of four electric utilities and one telephone company which provide service to 97 and 79 percent of the California population respectively. Additionally, telephone interview surveys were conducted with

a random sample of 5.8 percent of 1,110 school districts in California to provide an application inventory and use pattern data base that could be used to extrapolate the NSHC pesticidal oil used by the 7,471 schools in California.

Manufacturers who did not respond to the questionnaire survey were contacted by telephone. Of the 30 manufacturers contacted, two major manufacturers responded, and the remaining did not provide any data. Of the two responding manufacturers, input from one manufacturer was included in the manufacturers' total sale figure. The sale statistic from the second manufacturer ( $\approx 6.2$  million pounds), was not considered in the manufacturers' total figure due to late input.

### 5.2.3 Method of Calculating Application Inventory

The pesticide application inventory was conducted according to the format of the CDFA classification system for pesticide use types, chemicals and commodities. The weed oil for which a specific use could not be specified and the oil use estimates based on the school district survey were placed under general weed control, a new use category not included in the CDFA classification. The weed oil under this use category for which the specific commodities treated are not definitely known are placed together as a commodity designated weed control unclassified.

The total quantities of pesticide oil of various types sold in the state were estimated on the basis of survey results.

The distribution of oil applications to different types of usage was based first on the PUR<sup>4</sup> for oil sold as insecticide or herbicide. Quantities of oil for some applications reported in the PUR were modified on the basis of applications estimated in surveys for the same commodities. The distribution of oil used as wood preservative was made on the basis of surveys and inputs from local Air Pollution Control Districts.

Pesticide oils are purchased by some of the smaller pesticide manufacturers from larger producers and are sold to pesticide dealers. The total of the sales by all manufacturers of pesticide oils is therefore vulnerable to double counting. In order to avoid the double counting, manufacturers and dealers were requested to provide names and transaction volumes of their customers and suppliers, respectively, in their survey responses.

The manufacturer survey, including both questionnaires and interviews, provided basic types of information. First, the survey provided descriptions of the physical and chemical properties of the pesticide oils sold. This information was used in determining the emissions inventory as described in Section 6.0. Second, the survey results indicated the total quantity of pesticide oils sold by 18 of the total 47 manufacturers listed in the Master Label File. Third, the estimate of the ratio of spray oils (i.e. insecticides) to weed oils used throughout the state (1:4) was provided. Finally, the survey results were used to estimate a major part of the distribution of oil usage among the 58 counties in the state.

The total amount of pesticide oil sold in the state had to be estimated by extrapolation since none of the surveys provided a complete accounting for this figure. This total could be extrapolated from either the sales reported in the manufacturer survey or the dealer survey. A larger quantity of oil sales was reported by manufacturers than by dealers (Table 5-3) but the number of manufacturers reporting such sales was much smaller (17 to 148) than the dealers' responses. A statistical calculation of confidence intervals indicates the dealer survey data set is a much better predictor of total sales than the manufacturer survey data set. The 95% confidence intervals are  $\pm 35\%$  of the mean quantity sold per dealer and  $\pm 105\%$  of the mean quantity sold per manufacturer.

The extrapolation of total oil sales was performed by dividing the total amount of oil reported sold by the dealers,  $46.19 \times 10^6$  lbs., by 0.26, the proportion of the total number of dealers who responded. The resulting figure is  $177.7 \times 10^6$  lbs. This figure for the total formulation 10 oil use in California receives some support from PUR data. Those products registered by the 18 manufacturers who reported their sales in the manufacturer survey accounted for 83 percent of the total formulation 10 product use reported in the 1977 PUR. Note that the total  $141.2 \times 10^6$  lbs. of oil sold by the 18 responding manufacturers is 79 percent of the total estimated formulation 10 use of  $177.7 \times 10^6$  lbs. in this report. If the sale of  $6.2 \times 10^6$  lbs. from the late responding manufacturer is also considered, the responding manufacturers' total would

be  $147.4 \times 10^6$  lbs. or 83 percent of the total estimated oil use. Considering the possible sales by those manufacturers who did not respond, the total estimated oil use of  $177.7 \times 10^6$  appears to be rather conservative.

The grower/farmer survey yielded too low a response (8%) to allow extrapolation to total oils used. However, the data obtained in this survey were useful in estimating the use of diesel and miscellaneous oils, and the monthly distribution of weed oil applications. Miscellaneous oils reported used included gasoline, kerosene, motor oil, used motor oil, road oil, and others. The responses also indicated that the use ratio of miscellaneous oils to general weed oils was approximately 1:10. This ratio was used to estimate the quantity of diesel and miscellaneous oils applied where this figure was not present in the survey. The monthly distribution of applications for oil in weed control unclassified was based on the weed oil use reported in the farmer survey.

Because of the low grower survey response, over 100 farm advisors were contacted by phone or by mail. As was mentioned in Section 5.2.2.2, the farm advisors were questioned as to oil use in their counties on the 16 most oil intensive crops. The relevant data in the PUR were modified to account for the input from the farm advisor survey. This survey accounted for  $52.3 \times 10^6$  lbs. of oil application. Of this quantity,  $24.8 \times 10^6$  lbs. was spray oil and  $27.5 \times 10^6$  lbs. was weed oil. Table A.2-1 lists the farm advisors estimates of applications

to crops in each county. The vector control agency and school district surveys provided information on the geographical distribution of oil applications by these organizations and the types of oils applied - spray oils, weed oils and miscellaneous oils. The total applications reported were  $7.5 \times 10^6$  lbs., of which  $2.5 \times 10^6$  lbs. were diesel and miscellaneous oils. A more complete breakdown of survey results is shown in Table 5-3.

Commodities in the PUR not modified by substitution of farm advisor, school district or vector control figures accounted for  $12.7 \times 10^6$  lbs.

The survey of floricultural businesses produced both low application figures and a low response (11%) - too low for extrapolation. The reported application for 1977 was only  $0.026 \times 10^6$  lbs.

The survey of railroads and wood preservers yielded a high response, about 68%. The survey results indicate that poles, piling, railroad ties, and lumber are the primary wood products receiving creosote or creosote-petroleum mixture. In California, these wood products are primarily Douglas fir and Ponderosa pine products. The creosote used for wood preservation purpose is low-residue creosote.<sup>4</sup>

From the wood preserver study results and the American Wood Preservers' Association (AWPA) wood preservation statistics for 1977,<sup>5</sup> it was determined that there were four treatment plants in California that treated with creosote or creosote solutions during 1977. Two of these plants responded

to the survey and provided data. Use pattern information for the third treatment plant was obtained from data provided by the local APCD. Creosote use for the fourth treatment plant was estimated by linear regression. The total number of cubic feet of pressure treatment cylinder space at each plant (taken from the wood preserving statistics) and the amount of creosote that was used by each of the three known treatment plants were used as the ordinates for the regression. The unknown creosote usage ordinate for the fourth plant was then computed. This estimation was based on the assumption that all the treatment plants pressure treated wood in amounts proportionate to their pressure treatment cylinder capacity.

All but two of the railroads responding to the survey reported that the creosoted wood products used in 1977 were purchased from treatment plants in California; therefore, only the creosoted wood products reported by the one railroad as purchased out of the state but used in California and the other railroad that reported treating their own ties were added to the inventory.

The quantity of creosote sold in California during 1977 and reported by wholesalers that responded to the questionnaire survey was also included in the inventory. The treatment plants and wholesalers were not identified to avoid disclosure of information from an individual company. Table 5-2 details the estimated use of creosote in California during 1977 based on questionnaire survey responses.

TABLE 5-2

Estimated Creosote Use in California During 1977 Based  
on Questionnaire Survey Responses

	Products treated	Pounds of creosote and creosote solution used or sold
Wood Preserving Plants	poles, piling ties, lumber	12,768,100 <sup>a+b</sup>
Railroad	cross ties	12,824,200 <sup>a</sup>
Wholesale Distributors	unknown	<u>963,800<sup>a</sup></u>
Total		26,556,100

a reported

b estimated

A summary of all the survey results and extrapolated estimates are shown in Table 5-3.

With the sum of all the above information, total oil application figures were calculated. First, the total extrapolated dealer-supplied pesticide oil figure of  $177.7 \times 10^6$  lbs. was used. Of this total value,  $70.4 \times 10^6$  lbs., can actually be broken down to crop type or other use as shown in Table 5-4. The remaining  $107.2 \times 10^6$  lbs. was classified for purposes of this study as "weed control unclassified". Based upon the grower survey, it was determined that the ratio of miscellaneous and diesel oils to weed oils used was about 1:10. Thus, a total miscellaneous oil application figure of  $10.6 \times 10^6$  lbs. was calculated. The addition of non-formulation 10 oils (from the PUR), miscellaneous oils used by school districts and for vector control, and wood preservative oils rounds out the list, as shown in Table 5-4.

### 5.3 Application and Use Pattern Inventories

The terms application inventory and use pattern inventory are synonymous to many. For the purpose of this study, application inventory deals with the quantities of pesticide applied in relation to time and space temporally and spatially, and use pattern inventory deals with the quantity of pesticide applied in a specific type of use. The application inventory will provide the data base for emission inventory calculations. The use pattern inventory will serve as an indicator of where

TABLE 5-3

## Summary of Survey Results

Surveys	Questionnaire Response		Total Oil of Responding Survey (10 <sup>3</sup> lbs.)				Extrapolated Total Oils Used (10 <sup>6</sup> lbs.)				Remarks	
	% of Total Response <sup>a</sup>	% of Positive Response <sup>a</sup>	Spray Oil (Ins.)	Weed Oil (Herb.)	Other	Total (10 <sup>3</sup> lbs.)	Spray Oil (Ins.)	Weed Oil (Herb.)	Other	Total (10 <sup>6</sup> lbs.)		
Manufacturers	45	36	26,780	111,930	2,430	141,140	-	-	-	-	177.65	% of response is too small for extrapolation.
Dealers	26	14	12,966	33,224	-	46,190	-	-	-			
Growers	8	3	2,240	2,587	230	5,057	-	-	-			
Floriculturists	12	4	1.42	22.56	2.5	26.48	-	-	-	-	-	% of response is too small for extrapolation.
Wood Preservatives	67	25							26.55	26.55		A combination of two surveys.
Railroads	68	27										
Farm Advisors	31	17	24,816	27,458		52,274						Conducted additional follow-up telephone survey of 22 counties.
School Districts <sup>b</sup>	91	55	44.1	132.8	63.6	240.5	0.050	2.325	1.127	3.50		Based on telephone survey response of districts chosen at random. Extrapolation by straight multiplication of response.
Vector Control			2,776	275	1,402	4,453				4.45		Based on 1977 oil application reported by state vector control agencies.

a. Refers to percent of the number of questionnaires sent out.

b. Based on a random sampling of 5.8 percent of the 1,110 school districts in California.

TABLE 5-4

## 1977 Estimated Oil Pesticide Use in California by Source

Source	Quantity of Oil (10 <sup>6</sup> lbs.)
Farm Advisors	52.3
PUR, Other	12.8
School Districts, pesticide oils	2.4
Vector Control, pesticide oils	3.0
Weed Control Unclassified, pesticide oils	<u>107.2</u>
Subtotal	177.7 <sup>a</sup>
School Districts, diesel oil	1.1
Vector Control, diesel oil	1.4
Weed Control Unclassified, diesel and miscellaneous oil <sup>b</sup>	<u>10.6</u>
Subtotal	13.1 <sup>c</sup>
PUR, Non-Formulation 10 oil	7.8
Wood Preservers	<u>26.6</u>
Subtotal	34.4
GRAND TOTAL	225.2

a. Estimated from dealers' survey data.

b. Miscellaneous oils include gasoline, kerosene, diesel, motor oil, used motor oil, road oil, and others.

c. Estimated from survey and 10% of weed oil use.

control strategies should be formulated.

### 5.3.1 General Summary

Table 5-5 is an overall summary of nonsynthetic hydrocarbon pesticide application in California in 1977. From this table it is evident that the vast majority, (96.5%) of all oils applied were formulation 10, or "pure oils", including diesel and miscellaneous oil. Only a very small portion, 3.5%, was oil present in non-formulation 10 pesticides as minor active ingredients. Of the pure oil application, most were in the "general use" (includes weed control unclassified) category. As was explained in Section 5.2.3, the weed control unclassified is comprised of those pure oil applications which could not be assigned to any specific use category, nor be accounted for by the PUR or farm advisors. Nevertheless, the use of this quantity of oils is substantiated by both the dealer and manufacturer surveys.

After the general use oils, formulation 10 acreage applications are the next largest category - 29.7% of all oils applied. This category contains 95% of formulation 10 oils, other than wood preservatives, to which a specific use could be assigned as a result of the farm advisor survey and the use of PUR data. Of the 66.8 million pounds of oil applied in this category, most (61.8 million pounds) were for agricultural purposes.

Wood preservatives also make up a significant fraction of

TABLE 5-5

Total Nonsynthetic Hydrocarbon  
Pesticide Application in California  
in 1977

Type	Pounds (10 <sup>6</sup> lbs.)	Acreage (10 <sup>6</sup> acre)	Percentage (%)
Pure Oil (Formulation 10)			
-A-	66.8	1.1	29.7
-0-			
(General use)	124.0		55.1
Creosote (Wood preservative)	26.6		<u>11.8</u>
Subtotal	217.4		96.5%
Minor Active Ingredients (Non-Formulation 10)			
-A-	6.1	5.0	2.7
-0-	1.7		<u>0.8</u>
Subtotal	7.8		3.5%
GRAND TOTAL	225.2		100%

A = acreage application

0 = non-acreage application

the total oil applications (11.8%). These preservatives consisted entirely of creosote, with which fence posts, railroad ties and other wooden structural components are treated to prevent rot and insect damage.

The non-formulation 10 oil application figures are based upon the PUR. Most of these oils (about 80%) were acreage applications.

The chemical classification of NSHC pesticides used in this report is the classification followed by the CDFA and used in the PUR where NSHC oils are classed as aromatic petroleum solvents, mineral oil, petroleum distillates, petroleum hydrocarbons and petroleum oil unclassified. Two additional categories, creosote and diesel and miscellaneous oils, were added to account for such oils reported by wood preservers, school districts, vector control districts and farmers. Miscellaneous oils included such products as gasoline, kerosene, motor oil and road oil.

Oils which fall under one chemical type in the CDFA classification are almost all registered for one type of use. For example, nearly all general contact and selective herbicides are registered as petroleum hydrocarbons. Reported usage of petroleum hydrocarbons not registered as herbicides were less than one-thousandth percent of total herbicide use in the 1977 PUR.

Estimated quantities of oil were placed in the application inventory in the appropriate usage category and received the

chemical designation according to the major chemical usage in that category. These chemical and usage categories are shown in Table 6-2.

Table 5-6 shows the breakdown of the 1977 pesticide oil application by chemical. The majority of these oils, about two-thirds, were classified as petroleum hydrocarbons. Unclassified petroleum oils (12%) and creosote (12%) were also large categories. These chemical classifications were used to develop the emission inventory, described in Section 6.0.

### 5.3.2 Application Inventory

#### 5.3.2.1 Temporal Application Patterns

The distribution of pesticide oil applications over time is particularly important for assessing potential air quality impacts. Hydrocarbon emissions resulting from these applications can contribute to ozone formation during California's "smog season," which includes the summer and fall months, July, August and September in particular.

Figure 5-2 is a summary of total nonsynthetic pesticide oil (formulation 10) applications in California in 1977, broken down by acreage (-A-) and non-acreage (-O-) applications and creosote wood preservatives. The figure shows a major peak in April, with smaller peaks in January, June, August and November. Of these, the August peak is of greatest concern, although applications remain relatively high throughout spring and summer. The April peak is too early in the year to present

TABLE 5-6

Formulation 10 Pesticide Oil Applications  
By Chemical in California in 1977

Chemicals	Pounds (10 <sup>6</sup> lbs.)	Percentage (%)
Aromatic Petroleum Solvent	0.83	0.4
Mineral Oil	2.41	1.1
Petroleum Distillates	3.04	1.4
Petroleum Hydrocarbons	144.27	66.4
Petroleum Oil Unclassified	27.13	12.5
Diesel & Creosote Petroleum	13.15	6.0
Creosote	<u>26.55</u>	<u>12.2</u>
TOTAL	217.38	100

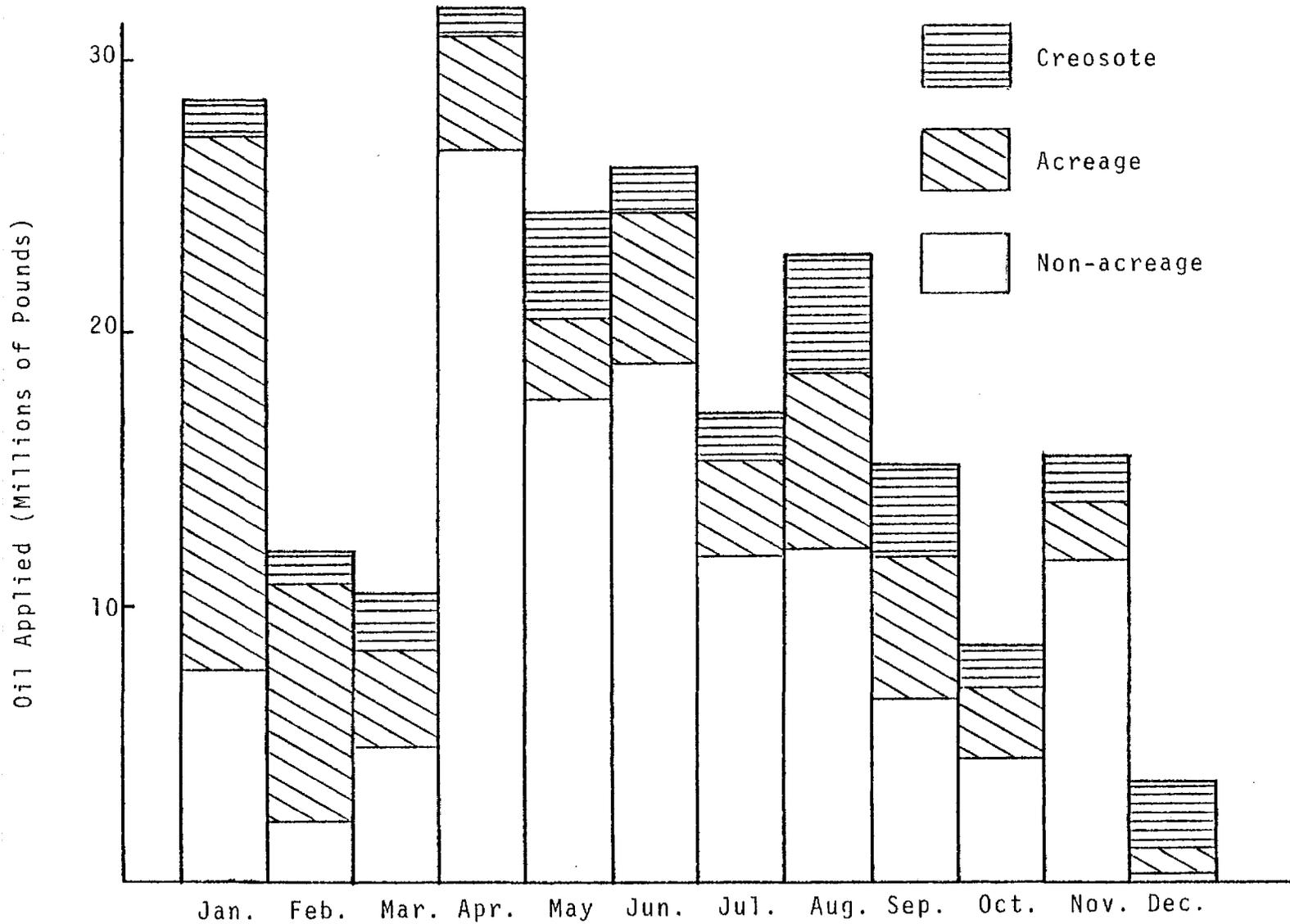


Figure 5-2. Monthly Application of Pure Oil Pesticides in California in 1977 with Non-Acreage, Acreage and Creosote Distribution

a great air quality problem in most parts of the state, and November is too late in the year. Another pattern appears in this annual distribution of applications: except for the winter months of December, January and February, the nonacreage applications exceeded the acreage application, generally by a wide margin. This is reflective of the large weed control unclassified use classification, which is placed in the nonacreage category. Figure 5-3 reflects the large amount of general weed control applications. This figure is a plot of the use of formulation 10 pesticides throughout the year. While the use of insecticides is relatively low and constant, the use of herbicides is much greater for all seasons except December, and the overall proportion of herbicide use is very high. Herbicide use is also almost solely responsible for the pesticide oil use peaks mentioned earlier.

The uses which have major influences on the total application in some part of the year are alfalfa, deciduous fruit trees, citrus fruits and weed control unclassified. The monthly distributions of each of these is shown in Figure 5-4.

The major use of herbicidal oil during winter months was for the dormant season control of weeds in alfalfa. An oil treatment was applied in summer months for defoliation of the alfalfa seed crop. Oil was used on dormant alfalfa primarily in the Sacramento and San Joaquin Valleys. Defoliant was applied mostly in the Sacramento and San Joaquin Valleys and in Imperial County.

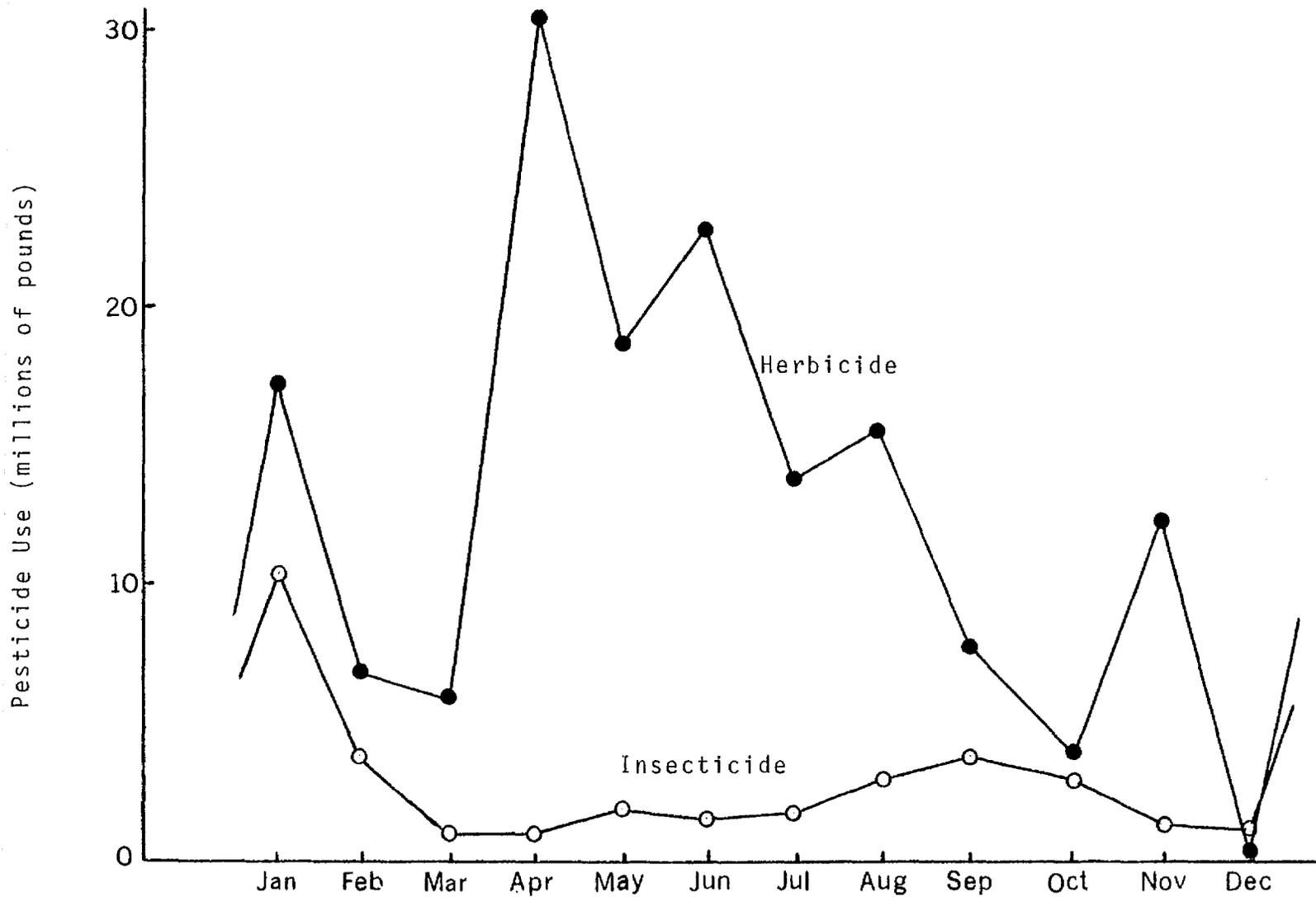


Figure 5-3. Monthly Applications of Formulation 10 Petroleum Oil Pesticides Used in California in 1977

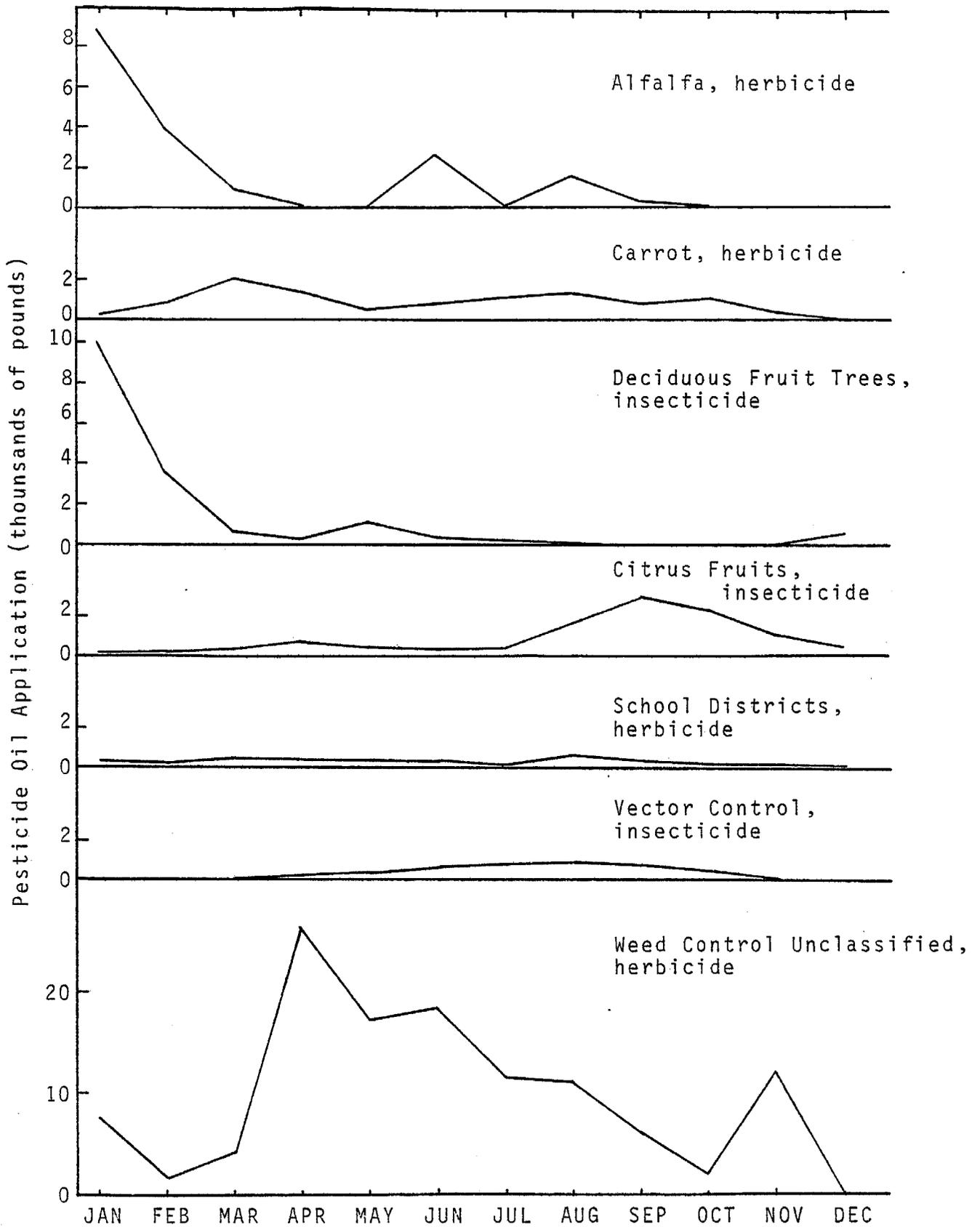


Figure 5-4. Monthly Distribution of Application for Major Pesticide Oil Uses in California, 1977. - Note the difference in scale for Weed Control Unclassified. 66

Oil use on the carrot crop was distributed into three broad peaks which extend throughout most of the year (Figure 5-4). Most of the carrot oil is applied to multiple crop cycles grown each year primarily in Imperial, Monterey and Kern Counties.

Almost all of the insecticide oil applied in January and February (95%) was for dormant season control in deciduous fruit trees. These applications are predominate in the Sacramento and San Joaquin Valleys but considerable amounts of oil are also used in center coast counties.

A considerable amount (6.6 million pounds) of insecticidal spray oil was applied to citrus crops (Figure 5-4) in the months of August through October, with relatively little applied at other times. Most of the citrus application of oil was in the south coast and southern interior citrus growing regions.

Oil applications by school districts and vector control agencies did not contribute in a major way to the overall pattern of pesticide oil use in the state (Figure 5-4). These uses were low in winter and reached a maximum level in August for both agencies. The applications were also widely distributed geographically, although somewhat larger quantities were used for vector control in the Sacramento and San Joaquin Valleys.

Oil applications under Weed Control Unclassified account for the largest portion of pesticide oil use in California and have the greatest influence on the temporal use pattern.

Herbicide oil applications are made according to the need for the control of weeds. In accord with the pattern shown in Figure 5-4, the largest amount is used in spring when the weather is warm and there is a plentiful supply of water. The need for weed control decreases as weeds are brought under control and the supply of water decreases during the later months of summer.

The distribution of oil under Weed Control Unclassified to individual crops or other uses is not known. Some estimates of this distribution within larger use categories are considered in Section 5.3.3.3.

Table 5-7 gives a more detailed numerical breakdown of formulation 10 pesticide application throughout the year and by type. Once again, it is apparent that herbicide applications comprise the bulk of all formulation 10 applications (excluding creosote). Insecticides make up a much smaller fraction, and the use of the remaining types of oils is almost insignificant.

Table 5-8 shows the types of formulation 10 oils applied to the 18 main crops, in terms of the quantities of oils applied, in California in 1977. As was pointed out in Section 5.3.2, alfalfa receives more pesticide oil applications than any other crops, followed closely by carrots, lemons, almonds, oranges pears, school districts and vector control which also receive large oil applications. In addition, this table indicates that certain crops receive a very large proportion of a specific

TABLE 5-7

Statewide Monthly Applications Distribution of  
Formulation 10 Pesticide Oils in 1977 by Type (1000 Pounds)

Pesticide Type	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
Adjuvants -A-	2	10	4	10	28	17	2	20	21	10	3	1	128
Herbicides -A-	9,345	4,622	2,362	3,035	1,161	1,519	2,068	2,272	1,148	1,516	840	48	29,936
-O-	7,762	1,956	4,584	26,787	17,713	18,935	11,713	11,802	6,762	2,733	11,804	247	122,798
Insecticides -A-	10,231	3,694	974	1,126	1,783	1,298	1,370	2,572	3,706	2,716	1,188	1,021	31,679
-O-	62	32	16	55	40	103	255	476	58	65	32	16	1,210
Fungicide & Insecticide -A-	0	0	0	0	0	0	0	0	0	2	0	4	6
Herbicide & Insecticide -A-	1	2	4	29	47	44	50	40	39	77	47	5	385
Defoliant -A-	96	203	11	0	0	2,584	0	1,448	270	0	0	0	4,612
-O-	0	34	0	0	0	1	7	6	1	7	0	0	56
Wood Preservative -O-	1,328	1,328	1,859	797	3,717	1,593	1,859	4,514	3,452	1,859	1,593	2,655	26,554
TOTAL	28,827	11,881	9,814	31,839	24,489	26,094	17,324	23,150	15,457	8,985	15,507	3,997	217,364

TABLE 5-8

Statewide Monthly Applications of Formulation 10 Pesticide Types on  
the Top 17 Commodities in 1977 (1000 Pounds)<sup>a, b</sup>

Commodity	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
Alfalfa													
Herbicide	8,695	3,634	74	0	0	0	0	59	11	0	0	0	12,473
Defoliant	96	203	11	0	0	2,584	0	1,405	270	0	0	0	4,570
Carrot													
Herbicide	290	903	2,073	1,419	560	903	1,188	1,423	828	1,100	411	0	11,099
Adjuvant	0	1	1	1	1	0	1	2	0	0	0	0	7
Almonds													
Herbicide	0	0	0	0	2	0	0	0	0	0	0	0	2
Insecticide	5,811	1,610	68	104	142	59	25	0	0	0	71	267	8,157
Fungicide & Insecticide	0	0	0	0	0	0	0	0	0	0	0	4	4
Avocado													
Herbicide	0	0	0	620	0	0	310	0	0	310	0	0	1,240
Insecticide	0	0	0	0	0	0	0	0	0	1	0	0	1
Apricot													
Insecticide	381	213	0	19	23	0	0	0	0	0	0	1	638
Nectarines													
Insecticide	590	164	0	0	0	3	0	0	5	0	0	66	830
Peach													
Herbicide	124	49	2	0	0	13	0	0	0	0	0	98	285
Insecticide	1,665	575	0	3	5	6	5	0	0	0	46	121	2,426
Herbicide & Insecticide	1	0	0	0	0	0	0	0	0	0	0	1	1

TABLE 5-8 (cont'd)

Commodity Pesticide Type	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
Pear Insecticide	885	369	26	56	729	63	55	13	0	90	4	17	2,308
Plum Insecticide	492	301	0	0	5	0	0	0	2	11	3	11	824
Prune Insecticide	148	192	500	16	61	76	3	2	0	0	0	0	996
Citrus <sup>c</sup> Herbicide	259	55	124	927	551	548	347	288	69	66	409	7	3,650
Insecticide	7	0	1	4	1	0	0	5	25	0	1	0	46
Grapefruit Insecticide	0	1	0	4	1	0	0	76	119	201	91	9	502
Herbicide & Insecticide	0	0	0	0	0	0	0	0	1	0	4	0	5
Lemon Insecticide	49	130	260	467	394	386	336	836	1,606	961	568	352	6,344
Herbicide & Insecticide	0	0	0	28	47	38	50	36	1	9	3	0	211
Orange Insecticide	3	24	36	263	56	6	50	683	1,114	1,002	326	50	3,615
Fungicide & Insecticide	0	0	0	0	0	0	0	0	0	2	0	0	2
Herbicide & Insecticide	0	0	0	0	0	6	0	4	37	68	40	5	161
Adjuvant	0	0	0	0	0	0	0	0	0	1	0	0	1

TABLE 5-8 (cont'd)

Commodity Pesticide Type	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
School District Herbicide	219	177	427	481	426	280	102	548	336	237	184	32	3,452
Insecticide	0	0	1	1	0	0	33	1	17	0	0	0	50
Vector Control Herbicide	6	3	7	15	6	16	92	74	85	38	17	2	359
Insecticide	9	13	43	172	291	608	777	907	752	425	57	23	4,074
Weed Control Unclassified Herbicide	7,545	1,754	4,090	26,191	17,191	18,507	11,435	10,987	6,290	2,232	11,479	211	117,913
TOTAL	27,275	10,371	7,744	30,791	20,492	24,102	14,809	17,349	11,568	6,754	13,714	1,276	186,245

- 72
- More than half a million pounds of pesticide oil was applied to each of the 17 commodities.
  - Due to rounding off numbers to nearest integers, the sum of monthly values may not equal the annual total which is the sum of values before rounding off.
  - The herbicide application to individual citrus crops was not reported.

pesticide oil type. For example, alfalfa, carrot and school districts receive herbicide and defoliant type oils almost exclusively. On the other hand, almond, grapefruit and other fruit tree crops receive insecticide type oil applications, and little reported application of herbicides. Oil applications for vector control, however, show a fairly even distribution of insecticide and herbicide oils. The nature of the crop clearly dictates what oil types will be used.

Finally, Table 5-9 provides a breakdown of pesticide oil applications by chemical, like Table 5-5, only with distribution by month. Petroleum hydrocarbons are the largest classification for every month of the year, often by a wide margin, except for the month of December.

#### 5.3.2.2 Spatial Distribution

The spatial, or geographical, distribution of pesticide oil applications is also very important. In those areas where particularly high ozone concentrations occur, hydrocarbon emissions are of special concern.

The geographical distribution of oil use was obtained from the surveys or other sources used for NSHC application data. To obtain the estimated spatial distribution for weed control unclassified applications, all designated applications of weed oil from the PUR, farm advisors, school districts, and vector control districts were added together in each county. The oil use under weed control unclassified was distributed in each

TABLE 5-9

Statewide Monthly Applications for Selected Formulation 10  
Chemicals in 1977 (1000 Pounds)

Chemical	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTAL
Mineral Oil	849	247	42	56	106	150	109	267	193	261	98	27	2,405
Petroleum Hydrocarbon	16,702	6,103	6,285	29,350	17,494	20,255	12,353	12,554	6,810	3,697	12,379	288	144,270
Aromatic Petroleum Solvents	290	243	2	13	17	64	33	92	68	6	0	0	828
Petroleum Distillates	2	7	14	93	130	424	697	939	450	250	28	6	3,040
Petroleum Oil Unclassified	9,526	3,716	938	974	1,514	642	636	1,668	2,882	2,383	1,255	995	27,129
Diesel & Miscellaneous Oil	131	236	673	556	1,512	2,968	1,648	3,116	1,602	528	154	25	13,149
Creosote	1,328	1,328	1,859	796	3,717	1,593	1,859	4,514	3,452	1,859	1,593	2,655	26,553
TOTAL	28,828	11,880	9,813	31,838	24,490	26,096	17,335	23,150	15,457	8,984	15,507	3,996	217,375

county in proportion to the county total of weed oil applications from these other sources.

Table 5-10 shows those 13 counties with pesticide oil applications of about five million pounds or more. As described in Section 4.1, all of these counties are designated as ozone nonattainment areas. Of these, those located in the San Joaquin Valley and South Coast Air Basin have the greatest ozone problems. Most of the counties listed are located in one of these basins. This table also shows the commodities which accounted for the greatest pesticide oil applications in each county. General weed control accounted for the greatest amount of oils applied in every county. The second major commodity in most of the counties was an agricultural crop. Los Angeles County was an exception with school districts being the number two commodity.

Table 5-11 presents an overall summary of pesticide oil applications in each of the 58 counties. The applications in each county are divided into formulation 10 (acreage and non-acreage), non-formulation 10 and creosote. Total pesticide oil applications range from 33.3 million pounds (14.8% of the state total) in San Joaquin County, to about 4,000 pounds in Alpine County. Pure oil application accounts for the majority of all pesticide oil applications in most counties although in a few counties creosote applications comprise the major oil type applied.

### 5.3.3 Use Patterns

TABLE 5-10

1977 Oil Pesticide Consumed By the Top 13  
Counties in California

County	Total Oil Used (10 <sup>6</sup> lbs.)	Use Reported in PUR (10 <sup>6</sup> lbs.)	Main Commodities Receiving Pesticide Oil
San Joaquin	33.25	2.43	w.c.u. <sup>a</sup> alfalfa, almond, vector control
Monterey	29.63	5.11	w.c.u. carrots, celery
Tulare	19.44	0.80	w.c.u. citrus, plum, nectarine, olives
Kern	16.32	1.38	w.c.u. carrots, almond vector control, alfalfa
Fresno	14.51	0.97	w.c.u. alfalfa, peach, plum, almond, vector control
Sacramento	13.85	0.48	w.c.u. alfalfa, pear, vector control, clover
Stanislaus	10.49	1.48	w.c.u. almond, alfalfa vector control, peach
Imperial	10.14	1.85	w.c.u. carrots, alfalfa sorghum
Ventura	8.57	5.71	w.c.u. lemon, orange, flood control
Merced	8.36	1.93	w.c.u. alfalfa, almond peach, vector control
Los Angeles	7.95	0.70	w.c.u. school districts, vector control, agencies
Madera	6.54	0.71	w.c.u. alfalfa, almond, irrigation districts, vector control
San Bernardino	4.81	1.41	w.c.u. orange, lemon, school districts
Subtotal (10 <sup>6</sup> lbs.)	183.86 (81.64%)	24.96 (80.0%)	
Statewide Total	225.2 (100%)	31.2 (100%)	

a - w.c.u. = Weed Control Unclassified.

TABLE 5-11

## 1977 Distribution of NSHC Pesticides By County in California

County	Pure Oil Applications (1000 lbs.)			Non- Formulation 10 Application (PUR) (1000 lbs.)	Creosote- Petroleum (Wood Preservation) (1000 lbs.)	Total Oil Application (1000 lbs.)	Percent of California Total
	Acreage -A- (1000 acres)	Non-Acreage -0-	Total Poundage				
Alameda	32.6 (0.6)	831.7	864.3	31.5	722.3	1,618.1	0.7
Alpine	0.3 (0)	3.8	4.1	0	0	4.1	-
Amador	0 (0)	22.2	22.2	61	61	144.2	0.1
Butte	385.8 (15.0)	118.7	504.5	52.2	483.3	1,040	0.5
Calaveras	41.6 (0.2)	185.4	227	2.9	74	303.9	0.1
Colusa	79.2 (2.5)	25.1	104.3	49.5	260	413.8	0.2
Contra Costa	10.3 (0.8)	467.3	477.6	27.6	590	1,095.2	0.5
Del Norte	0 (0)	19.3	19.3	1.9	0	21.2	-
El Dorado	52.2 (1.4)	71.4	123.6	1.1	112	236.7	0.1
Fresno	4,513.2 (92.1)	9,395.2	13,908.4	1,155.0	446	15,509.4	6.9
Glenn	161.8 (6.6)	89.0	250.8	67	220	537.8	0.2
Humboldt	0.5 (0.2)	140.7	141.2	2.2	295	438.4	0.2
Imperial	2,499 (15.2)	5,972	8,471	928.8	741	10,140.8	4.5

TABLE 5-11 (continued)

County	Pure Oil Applications (1000 lbs.)			Non- Formulation 10 Application (PUR) (1000 lbs.)	Creosote- Petroleum (Wood Preservation) (1000 lbs.)	Total Oil Application (1000 lbs.)	Percent of California Total
	Acreage -A- (1000 acres)	Non-Acreage -O-	Total Poundage				
Inyo	21.6 (0.1)	34.7	56.3	1.4	221	278.7	0.1
Kern	5,385.9 (146)	9,020.2	14,406.1	404	1,508	16,318.1	7.2
Kings	2,013.9 (35.9)	88.1	2,102	411	239	2,752	1.2
Lake	46 (2)	41.1	87.1	13	0	100.1	-
Lassen	-	44.4	44.4	1.1	815	860.5	0.4
Los Angeles	331.5 (21)	4,017.8	4,349.3	119.3	3,482	7,950.6	3.5
Madera	2,091.9 (34.6)	4,046.9	6,138.8	185	220	6,543.8	2.9
Marin	6.9 (0)	216.2	223.1	3.8	112	338.9	0.2
Mariposa	-	20.4	20.4	0.5	0	20.9	-
Mendocino	0 (0)	90.0	90	27.4	406	523.4	0.2
Merced	3,259.4 (70)	4,431.2	7,690.6	222	446	8,358.6	3.7
Modoc	-	29.7	29.7	3.4	629	662.1	0.3
Mono	11.4 (0.2)	17.3	28.7	0	0	28.7	-
Monterey	6,058 (31.8)	22,488.8	28,546.8	492.3	589.5	628.6	13.2
Napa	3.7 (0.2)	100.4	104.1	8	152	264.1	0.1

TABLE 5-11 (continued)

County	Pure Oil Applications (1000 lbs.)			Non- Formulation 10 Application (PUR) (1000 lbs.)	Creosote- Petroleum (Wood Preservation) (1000 lbs.)	Total Oil Application (1000 lbs.)	Percent of California Total
	Acreage -A- (1000 acres)	Non-Acreage -O-	Total Poundage				
Nevada	-	38.6	38.6	1.5	74	114.1	-
Orange	192.9 (4.5)	1,695.2	1,888.1	42.5	667	2,597.6	1.2
Placer	8.4 (0.1)	116.6	125	4.0	446	575	0.3
Plumas	-	23.2	23.2	1.1	446	470.3	0.2
Riverside	1,441 (22)	452.9	1,893.9	441.9	1,038	3,373.8	1.5
Sacramento	4,401.6 (54.5)	8,711.7	13,113.3	70.4	667	13,850.7	6.1
San Benito	25.9 (1.2)	87.7	113.6	52.4	130	296	0.1
San Bernardino	1,624 (10.7)	720.8	2,344.8	18.4	2,443	4,806.2	2.1
San Diego	524.2 (13.8)	1,158.8	1,683	86.8	741	2,510.8	1.1
San Francisco	-	202.7	202.7	9.9	43	255.6	0.1
San Joaquin	8,583.9 (139.1)	23,333.9	31,917.8	556.8	778	33,252.6	14.8
San Luis Obispo	447 (2.4)	1,734.7	2,181.7	36.3	221	2,439	1.1
San Mateo	4 (0.3)	402.3	406.3	18.8	204	629.1	0.3
Santa Barbara	2,656.7 (14.1)	265.8	2,922.5	72.5	521	3,516	1.6
Santa Clara	90 (4.5)	963.9	1,053.9	61	372	1,486.9	0.7

TABLE 5-11 (continued)

County	Pure Oil Applications (1000 lbs.)			Non- Formulation 10 Application (PUR) (1000 lbs.)	Creosote- Petroleum (Wood Preservation) (1000 lbs.)	Total Oil Application (1000 lbs.)	Percent of California Total
	Acreage -A- (1000 acres)	Non-Acreage -O-	Total Poundage				
Santa Cruz	61.0 (1.5)	221.9	282.9	363.5	220	866.4	0.4
Shasta	189 (14)	148.1	337.1	16.4	295	648.5	0.3
Sierra	-	18.1	18.1	0.2	37	55.3	-
Siskiyou	2.2 (0.2)	98.0	100.2	2.7	629	731.9	0.3
Solano	850.0 (13.0)	1,602.4	2,452.4	140.2	372	2,964.6	1.3
Sonoma	1.6 (0.1)	243.2	244.8	162	258	664.8	0.3
Stanislaus	3,493.2 (90.2)	6,061.9	9,555.1	379	555	10,489.1	4.7
Sutter	324 (12)	58.7	382.7	90	183	655.7	0.3
Tehama	114 (6)	94.3	208.3	16.8	183	408.1	0.2
Trinity	-	41.5	41.5	0.3	37	78.8	-
Tulare	6,021.6 (111.8)	12,032.3	18,053.9	431	961	19,445.9	8.6
Tuolumne	-	28.4	28.4	2	96	126.4	0.1
Ventura	6,515 (50)	1,264.5	7,779.5	229.6	557	8,566.1	3.8
Yolo	1,521.9 (128.6)	167.6	1,689.5	249.6	372	2,311.1	1
Yuba	657.4 (18.2)	63.9	721.3	25.5	183	929.8	0.4
Grand Total (x10 <sup>6</sup> lbs./acre)	66.76 (1.1)	124.08	190.8	7.8	26.6	225.2	100%

### 5.3.3.1 Agricultural Use

Use pattern data were obtained from the NSHC application inventory which was prepared according to procedures described in Section 5-2. Table 5-12 shows the uses of pure oil pesticides in California in 1977, exclusive of wood preservatives. General weed control is the largest single use category at 64% of total pure oil applications. Although much of the general weed control applications were undoubtedly for agricultural purposes, it was not possible to verify this. The general weed control category in relation to agriculture is considered again in Section 5.3.3.3. Applications readily classified as agricultural comprised 32% of the total pure oil applications. If oil in weed control unclassified is added to this the total would be 94% agricultural.

Table 5-13 shows the 12 main commodities for which over one million pounds of oil was used in California in 1977. After weed control unclassified and wood preservation, agricultural applications account for nearly all pesticide oil use. Over one million pounds of oil was applied to each of the following crops: alfalfa, carrot, lemon, almond, orange, pear, peach, and avocado. Among these crops, the greatest quantity of oil was applied to alfalfa, 17.0 million pounds. Carrots received nearly as great a quantity of oil applications at 11.1 million pounds. A further breakdown of the types of oils applied (i.e. insecticides, defoliants, etc.) is

TABLE 5-12

Use Patterns of Formulation 10 Nonsynthetic Hydrocarbons of All  
Oil Pesticide Types By Users in California in 1977<sup>a</sup>

( ) Indicates acreage to which pesticides were applied.  
(-A- acreage, -0- nonacreage; units in 1,000 lbs. and 1,000 acres)

Type Use	Herbicide		Insecticide		Fungicide & Insecticide		Herbicide & Insecticide		Defoliant		Adjuvants		Total		Total Pounds Applied	Percent (%)
	-A-	-0-	-A-	-0-	-A-	-0-	-A-	-0-	-A-	-0-	-A-	-0-	-A-	-0-		
Agriculture	29,575 (148)	829	26,129 (484)	217	6 (0)	-	386	-	4,612 (58)	57			60,708 (520)	1,103	61,811	32
Home & Garden	-	3.6	719 (13)	43									719 (13)	46.6	765.6	0.4
Industrial			-	7									-	7	7	-
Manufacturing			-	0.2									-	0.2	0.2	-
Non-Crop	359 (244)	705	4,074 (298)	835									4,433 (542)	1,540	5,973	3.1
Spreader Sticker	1 (0.4)	-	756 (21)	4							138 0 (37)		895 (58.4)	4	899	0.5
General Weed Control	-	121,260											-	121,260	121,260	64
Total (Acreage & Non- Acreage)	29,935 (392)	122,798	31,678 (816)	1,106	6 (0)	-	386	-	4,612 (58)	57	138 0 (37)		66,755 (1,133)	123,961	190,716	100%
Total Pounds	152,733		32,784		6		386		4,669		138		190,716		190,716	100%
Percentage (%)	80.1%		17.2%		-		0.2%		2.4%		0.1%		100%		100%	100%

a. Excluding 26.6 million pounds of creosote for wood preservation purpose.

TABLE 5-13

Twelve Main Commodities For Which Over  
One Million Pounds of Oil was  
Used in California in 1977

Commodities	Poundage (10 <sup>6</sup> lbs.)	Percentage (%)
Weed Control Unclassified	117.91	54.24
Wood Preservation	26.55	12.21
Alfalfa	17.04	7.84
Carrots	11.11	5.11
Almond	8.16	3.75
Lemon	6.55	3.01
Vector Control	4.43	2.04
Orange	3.78	1.74
School District	3.50	1.61
Peach	2.71	1.25
Pear	2.43	1.12
Avocado	1.24	0.57
TOTAL	205.41	94.49
Statewide Total Pure Oils Used	217.37	100%

presented in Table 5-7 to 5-8.

#### 5.3.3.2 Non-Agricultural Use

Other than general weed control, which undoubtedly includes both agricultural and non-agricultural uses, the non-agricultural uses of pure oils are rather limited. At 26.6 million pounds, the use of creosote for wood preservation accounts for most of the non-agricultural applications. From Table 5-12, only 7.6 million pounds of pure oils were applied in other uses. These uses included home and garden, industrial, manufacturing, non-crop and spreader-sticker.

Non-crop, at 6.0 million pounds, was the largest use category in this latter group. This use category includes pesticide oil applications to non-agricultural areas such as rights-of-way, ditch banks, non-crop land, etc. Some of the end-users in this category are governmental agencies such as school districts and flood control districts.

The home and garden category, an important indicator of non-commercial consumption, shows only a 0.4 percent of the total pure oil applied. In an on-site store survey for home and garden pesticide products in Sacramento, California, Leung et al. observed that about 15% of the 100 on-the-shelf items were formulation 10 products.<sup>6</sup>

The pesticide oil applications in all the other non-agricultural use categories were minor, with less than one million pounds in each category. Definitions of these use

categories are tabulated in Table 5-14.

#### 5.3.3.3 General Weed Control

Tables 5-4 to 5-8 indicate that 121 million pounds of oil were used for general weed control. This is more than twice the amount used in any other category. The major part of the estimated oil used in this category is based on figures for the amount of weed oil produced and sold by dealers in 1977, as described in Section 5.2.3.

Although the quantity of weed oil sold is large, no definite pattern of use has emerged for a large part of the estimated usage which has been placed in the category of weed control unclassified. In attempts to define the pattern of weed oil use, the following potential users, distributors and specialists were contacted:

- Farmers and Growers
- Public School Districts
- Public Utilities
- Railroads
- Irrigation Districts
- Caltrans
- Local Military Installations
- Flood Control Districts
- Wood Preservative Industry
- Vector Control Districts
- County Farm Advisors

TABLE 5-14

List of Pesticide Uses and Their  
Definitions (in California)

Use	Remarks
Agricultural	Used on crops and agricultural areas.
Home Garden	Used by consumer on noncommercial crops and ornamentals in home garden.
Household	Used in the home or on human beings.
Industrial	Used in industrial areas such as factories, processing plants, structural treatments in schools, restaurants, and similar institutions.
Residential	Pest control by professional operators only.
Structural	Used on buildings, boats, and other structures. Usually in paints, and wood preservatives, and for termite control.
Noncrop	Used in nonagricultural areas such as rights-of-way, railroads, noncrop land, ditch banks, etc.
Turf	Used on turf only.
Nursery	Used in nurseries and/or greenhouses on ornamentals and/or fruit trees.
Spreader Sticker	Used to obtain better adhesion to target surfaces.
Soil Fumigation	Used for preplanting or postplanting treatment of fallow land or noncrop land.
Agricultural Commissioner	Used by county agricultural commissioners. Usually rodenticides.
General Weed Control	Used for general weed control purposes which are not specified in the above uses.

County Agricultural Commissioners  
Pesticide Manufacturers and Dealers  
University Weed Control Specialists

The usage of some weed oil was accounted for on the basis of information from the above contacts including School Districts, Flood Control Districts and Vector Control Districts. After this information was incorporated into the use pattern estimates, there remained some 118 million pounds of weed oil for which the use is still somewhat uncertain.

Some organizations, public utilities, railroads, Caltrans, and military installations, indicated that they used little or no pesticide oil in 1977, but that they are using other forms of weed control. The other forms of weed control used were primarily mechanical methods and synthetic pesticides.

Weed control specialists were not aware of wide spread use of weed oil in quantities sufficient to account for the total oil use, nor were they able to estimate the average use per farm. The total of estimates from farm advisors for use of weed oil on crop and on non-crop use fall far short of the amount of weed oil sold. In fact, some farm advisors indicated weed oil was used, for example, on fruit and nut crops, but declined to estimate the quantity.

There is some evidence that most of the weed oil use has been agricultural. This is primarily from the dealers who sell weed oil. In the mailed questionnaire survey of dealers, the 148 who reported pesticide oil sales reported

more than 99 percent of weed oil was sold for agricultural and less than one percent for other purposes. Thirteen pesticide oil dealers were later contacted by telephone specifically for the purpose of learning where weed oil was sold. All of these dealers reported selling primarily to agribusinesses.

The most appropriate source of information on the use of oil in agriculture is the farmers and growers who used the oil. Unfortunately, from among the growers surveyed by mailed questionnaires, only 78 responses reporting use of weed oil were received which showed the quantity of oil applied. We have considered this number too small to be used as a basis for estimating the total quantity of weed oil used or the use pattern. However, the use of weed oil in these 78 reports is highly informative in helping to substantiate the total weed oil use in agriculture and in giving an indication of the general pattern of weed oil use by growers.

The pattern of herbicidal oil use reported by responding growers is shown in Table 5-15. About one-third of the total was used on field crops which is a category fairly well reported from other sources, e.g. farm advisor estimates and the PUR. More than half of the oil was used on fruit and nut crops which are poorly reported from other sources. Reports from other sources were available for only four of these crops, each reported in only one county. Fifteen percent of the oil was for non-crop uses which are almost entirely unreported

TABLE 5-15

## Herbicide Oil Use Reported in Survey of Growers

Use	Weed Oil		Diesel & Misc. Oil	
	Amount Used (Pounds)	Percent	Amount Used (Pounds)	Percent
<u>Field Crops</u>				
Alfalfa	726,039			
Carrot	22,050			
Clover	53,539			
Celery	12,285			
Corn	8,802			
Lettuce	15,600			
Subtotal	838,315	35.9		
<u>Fruit and Nut Crops</u>				
Avocado	69,436		14,568	
Citrus	136,305		6,693	
Grape	327,600		19,203	
Grapefruit	146		-	
Fruit trees	4,680		630	
Lemon	44,021		-	
Orange	15,902		945	
Olive	46,046		-	
Peach	156		4,116	
Pear	-		945	
Plum	15,912		4,116	
Nectarine	-		4,116	
Strawberry	780		-	
Almond	446,043		14,175	
Pistachio	163,800		14,175	
Walnut	1,040		-	
Subtotal	1,271,867	54.5	83,682	33.0
<u>Non-Crop</u>				
Ditches and roadsides	195,070		94,059	
Around build- ings	1,170		-	
Yards	2,535		-	
Fence lines	4,033		-	
Irrigation ditches	234		-	
Non-crop, other	19,964		75,967	
Subtotal	223,006	9.6	170,026	67.0
TOTAL	2,333,188	100	253,708	100

from other sources.

The data of Table 5-15 show that farmers did apply herbicidal oil to at least 16 fruit and nut crops and for various non-crop purposes. Unfortunately, the number of farmers reporting applications averaged only 2.6 for each fruit and nut crop. The number is too small to permit use of the distribution pattern for extrapolation to statewide application estimates for specific crops.

If the oil placed in weed control unclassified is considered to consist of agricultural applications with all reported and estimated agricultural applications distributed into three general areas of usage according to the percentage in each found in the grower survey, the 118 million pounds in this category would be distributed as shown in Table 5-16. When it is distributed in this way, the 14.9 million pounds for non-crop use in the second column appears unrealistically low. This is not an unexpected result from a survey with low response. Oil applications to crops such as alfalfa and citrus are relatively easy to record and report. The applications generally are larger and standardized with regard to rate and application time. By contrast, most non-crop applications are not applied to known acreages. They are applied according to need and often to small areas. The applications are more difficult to record and report so that the response to surveys would be less. From the qualitative responses in the farmer survey in which the weed oil use was

stated but not the quantity, more than three times as many applications were reported for non-crop as for crop use. The number of non-crop responses is increased by about 50 percent if these qualitative responses are counted. On this basis it is estimated that the non-crop total in Table 5-16 should be 1.5 times as large as shown in the second column. The third column of Table 5-16 is an estimate of the statewide distribution of oil into the three usage groups based on the acreage reported for each county for field crops and field and nut crops by the California Crop and Livestock Reporting Service. The acreage used included only those crops for which oil is registered as a herbicide and excluded carrot and alfalfa which are adequately covered elsewhere. An estimate of 19% ( $12.6\% \times 1.5$  in Table 5-16) of the weed control unclassified oil in each county was used for non-crop purposes, and the remaining quantity from the application inventory was applied in proportion to the field crop and fruit and nut crop acreages in each county. The non-crop use statistics were derived from farmer data survey as noted above. The estimated applications into the three usage groups is shown for each county in Table 5-17. The total for non-crop is greater than 19% because every county does not have fruit and nut and field crops.

Slightly more than 10 percent of those who responded to the grower survey reported use of weed oil, and the average quantity reported is 29,000 pounds per farm in 1977. If the

TABLE 5-16

Estimated General Distribution of Oil  
in Weed Control Unclassified Category

Use	Quantity Shown in Application Inventory (1000 lbs.)	Weed Control Unclassified Distribution by Farmer Survey <sup>a</sup> (1000 lbs.) (%)	Weed Control Unclassified Estimated Distribution (1000 lbs.) (%)
Field Crop	29,131	23,785 (20.2)	24,255 (20.6)
Fruit and Nut Crops	4,995	79,267 (67.2)	70,500 (59.8)
Non-Crop	<u>659</u>	<u>14,859 (12.6)</u>	<u>23,146 (19.6)</u>
TOTAL	34,785	117,913 (100)	117,913 (100)

- a. The total quantity of weed oil under these categories shown in the application inventory (34,785,000 lbs.) was added to the 107 million pounds of weed oil under Weed Control Unclassified. The total was distributed in proportion to weed oil use in Table 5-15, then the quantities shown in the application inventory were subtracted and 10 percent was added for estimated diesel and misc. oil use.

TABLE 5-17

Estimated Distribution of Oil in Weed Oil  
Unclassified by Use and County in 1977

County	Field Crops (Pounds)	Fruit & Nut Crops (Pounds)	Non-Crop (Pounds)	Total (Pounds)
Alameda	172,147	328,350	119,698	620,195
Alpine	-	-	2,940	2,940
Amador	-	12,576	3,612	16,188
Butte	-	69,756	20,020	89,776
Calaveras	-	-	-	-
Colusa	1,304	14,139	3,693	19,136
Contra Costa	68,775	214,876	67,837	351,488
Del Norte	-	-	134,718	134,718
El Dorado	-	42,342	12,152	54,494
Fresno	542,778	6,922,225	1,785,311	9,250,514
Glenn	1,125	57,896	14,115	73,136
Humboldt	36,895	49,809	20,736	107,440
Imperial	3,879,924	914,386	1,146,595	5,940,905
Inyo	-	20,582	5,907	26,489
Kern	259,183	6,949,211	1,723,941	8,932,335
Kings	1,882	52,751	13,068	67,711
Lake	-	-	2,991	2,991
Lassen	13,891	-	19,990	33,881
Los Angeles	716,473	1,452,799	518,798	2,688,070
Madera	7,664	2,966,425	711,275	3,685,364
Marin	-	130,065	37,329	167,394
Mariposa	-	12,340	3,542	15,882
Mendocino	37	54,599	13,067	67,703
Merced	269,195	3,061,719	796,613	4,127,527
Modoc	9,053	-	13,027	22,080
Mono	-	-	13,246	13,246
Monterey	10,933,340	7,168,618	4,329,217	22,431,175
Napa	-	60,264	17,306	77,570
Nevada	-	22,887	6,568	29,455
Orange	343,509	693,382	247,980	1,284,871
Placer	-	71,387	20,488	91,875
Plumas	-	13,746	3,945	17,691
Riverside	28,590	210,468	57,172	296,230

TABLE 5-17 (cont'd)

County	Field Crops (Pounds)	Fruit & Nut Crops (Pounds)	Non-Crop (Pounds)	Total (Pounds)
Sacramento	1,788,842	5,107,477	1,649,305	8,545,642
San Benito	19,658	44,807	15,417	79,882
San Bernardino	3,869	435,919	105,179	544,967
San Diego	59,820	633,216	165,745	858,781
San Francisco	-	-	198,377	198,377
San Joaquin	3,139,752	15,507,904	4,459,725	23,107,381
San Louis Obispo	406,660	970,031	329,246	1,705,937
San Mateo	213,522	22,504	56,447	292,473
Santa Barbara	58,864	65,993	29,860	154,717
Santa Clara	229,383	351,715	138,974	720,072
Santa Cruz	64,161	90,490	36,986	191,637
Shasta	-	92,796	26,632	119,428
Sierra	-	-	13,252	13,252
Siskiyou	30,680	-	44,150	74,830
Solano	208,791	1,006,880	290,737	1,506,408
Sonoma	148	147,206	35,241	182,595
Stanislaus	463,344	4,039,752	1,076,948	5,580,044
Sutter	8,027	27,662	8,535	44,224
Tehema	79	61,438	14,712	76,229
Trinity	-	-	26,537	26,537
Tulare	98,926	9,565,264	2,311,262	11,975,452
Tuolumne	-	17,128	4,916	22,044
Ventura	164,712	618,282	187,259	970,253
Yolo	30,970	24,883	13,358	69,211
Yuba	598	37,145	10,832	48,575
TOTAL	24,276,581	70,569,574	23,174,839	118,020,994 <sup>a</sup>

a - Due to rounding-off errors in computer calculations, this total differs slightly from that shown for Weed Control Unclassified in other tables.

farms comprising those in the survey responses are considered representative of all 65,000 farms in California, then the total weed oil use extrapolated from 10 percent of the farms would be 194.4 million pounds in 1977. This is more than the total estimated use of 145.6 million pounds in the state.

Some additional information on the unreported uses of weed oils in California was obtained from the distribution of sales of various oil products reported in the survey of pesticide dealers. The reported sales of the various products in each county were grouped according to the registered uses of the products. The reported quantity sold for each use category was compared with the usage of these products reported in the PUR for the respective counties and commodities plus usage estimated from other sources such as farm advisors.

In the comparison of reported sales with usage shown in Table 5-18, reported sales of some types of oil exceed estimated usage by more than 10 million pounds. Most of this excess of sales over estimated usage is in the area of fruit crops which concurs with the large amount of usage in this category noted in the survey of growers. Other categories in which sales exceed usage are aquatic weeds, residential pest control, and vegetable crops. In each of these, the number of counties in which sales are reported is small and they may not be representative of other counties. The three groups of products for which estimated usage exceeds reported sales include the products registered for field crops such

as alfalfa and carrot for which reports of usage are most complete.

The data presented in Table 5-18 clearly demonstrate that a large quantity of oil registered for uses such as fruit crops was sold in California in 1977 although no quantitative record of the usage is available. In consideration of this data, the following points should be borne in mind:

- . The quantity of weed oil reported by the dealers is estimated to be about one-fourth of the total amount sold in 1977.
- . Some of the registered uses are shown in more than one of the registration groups.
- . There were other products sold in the state which were not reported in the dealer survey.
- . Oils registered for field crops and fruit crops are also registered for non-crop use which among farmers is largely unreported.

#### 5.4 Conclusion and Recommendation

The total estimated consumption of nonsynthetic hydrocarbons for pesticidal purpose in 1977 in California was 225.2 million pounds. Of this quantity, 96.5% was applied in pure oil form (formulation 10), and 3.5% as minor ingredients (non-formulation 10). The formulation 10 products were applied in four categories: general weed control (55.7%), agricultural use (28.4%), wood preservation (12.2%), and

TABLE 5-18

Comparison of Surveyed Weed Oil Product Sales  
in California in 1977 and Estimated Usage

County	Group 1 Oil Products Registered Uses: Alfalfa, Clover Potato, Non- Crop Areas		Group 2 Oil Products Registered Uses: Carrot, Celery, Parsnip		Group 3 Oil Products Registered Uses: Orchard Floors, Nut Crops, Other Crops, Non-Crop Areas		Group 4 Oil Products Registered Uses: (Defoliant) Alfalfa, Clover, Potato, Cotton, Sorghum		Group 5 Oil Products Registered Uses: Aquatic Weeds, No crops		Group 6 Oil Products Registered Uses: Residential Pest Control		Group 7 Oil Products Registered Uses: Beet, Carrot, Lettuce, Celery, Onion, Anise, Berries	
	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)	Reported Sales (Pounds)	Sales Less Esti- mated Usage (Pounds)
Alameda													7,800	7,800
Butte	104,887	102,926			139,464	139,384								
Calusa	78,663	74,654			187,863	187,863								
Glenn					5,460	3,563								
Fresno	956,280	-1,760,808	95,200	95,200	613,564	587,675								
Imperial	3,657,997	3,335,359	556,746	-1,178,311	2,591,355	2,583,057	314,340	-215,959						
Kern	2,475,119	535,120	1,555,378	947,022	299,130	299,130								
Kings	1,895,400	778,384			192,013	192,013								
Lassen					4,290	4,290								
Los Angeles	138,918	535,120	574,495		458,812	450,097								
Madera	49,257	-1,473,426			519,823	240,265			8,760	8,760				
Modoc														
Merced	404,843	-764,175			5,884,835	5,846,571								
Monterey			17,925	-4,238,918							75,124	75,124		
Orange	904,220	778,384			271,253	271,253								
Riverside	61,737	61,737			15,600	15,600								
Sacramento	707,945	-1,870,943												
San Bernardino									60,626	60,626				
San Joaquin	865,769	-5,358,402		-5,811,542	379,454	379,454			50,187	50,187				
San Diego					126,649	126,649								
Santa Clara					140,400	136,190							14,820	14,820
Santa Cruz					234,000	223,486					3,503	3,503		
Solano					67,805	66,145								
San Mateo													780	730
Stanislaus	437,596	237,521			539,206	457,311								
Sutter	32,526	32,526												
Tehama	53,040	38,851			15,506	15,506								
Tulare	47,736	46,314			1,943,994	1,707,426					6,143	4,721		
Ventura	655,535	57,848												
Yolo	138,918	52,268	57,848		76,463	69,209								
Reported Sales Total	13,666,386		2,857,592		14,706,939		314,340		119,573		84,770		23,100	
Total Sales Less Usage		-4,560,742		-10,186,549		14,002,139		-215,959		119,573		83,348		23,400

miscellaneous uses (3.7%). The last three categories involve application of oil pesticides to specific uses, while information is insufficient for specific use designation for a major part of the first category. The general weed control use overlaps with the second and fourth categories. The miscellaneous uses of oil pesticides include home and garden, industrial, manufacturing, residential pest control, etc.

The use patterns of pesticide oils in California in 1977 are reflected in the temporal and spatial distributions of the pesticide oils. The majority of the oil was applied during the spring and summer months, and most of the oils applied at this time were herbicides. The counties in which most of the pesticide oil was applied are located in nonattainment areas for ozone. Additionally, most of these counties are located in air basins which have the state's most serious ambient ozone problems. Studying use patterns of pure oil pesticides is important for air quality planners attempting to determine the significant sources of air quality problems and the most effective means of reducing emissions. Not only does total pesticide oil use vary widely among the 58 counties and throughout the year, but major commodities and pesticide oil types also vary significantly. Air quality planning must take this latter fact into account in forming control strategies.

The data reported in this application inventory were based in part on a number of estimates and assumptions, as discussed earlier. These estimates were derived in two steps.

The initial step was to arrive at a statewide total oil pesticide consumption. The second step was to make a detailed breakdown of oil pesticide application by county and by use.

The 1977 statewide oil pesticide consumption estimate was 225.2 million pounds. The oil pesticides include 177.7 million pounds of formulation 10 products, 26.6 million pounds of creosote, 13.1 million pounds of miscellaneous oil (e.g. diesel oil, road oil, etc.) and 7.8 million pounds of non-formulation 10 oil. The formulation 10 figure of 177.7 million pounds was extrapolated from the dealers' survey responses. This figure is considered to be conservative when it is compared to the reported sale of 141.4 million pounds by 47% of the oil pesticide manufacturers in California. The implication that a smaller amount of oil was sold by the remaining 53% of the 47 manufacturers is supported by the 1977 PUR data on product sales. Further credence is lent to this figure since it was extrapolated from 282 dealers' responses (26%), a rather significant statistic. The data on creosote applications are well supported numbers. The creosote data were derived from wood preservers' inputs and calculations based on the number of cross ties treated in the total railroad track mileage in every county in California. The data on non-formulation 10 oil and miscellaneous oil applications represent the best available data to date. The non-formulation 10 data were obtained from the 1977 PUR,<sup>4</sup> which excluded the improper, unrecorded and unreported pesticide applications.

The non-formulation 10 oil pesticides are usually applied as a minor ingredient in synthetic products. There is no information available as to the quantity of unreported synthetic pesticide applied in California. The miscellaneous oil use was extrapolated from a low farmer survey response (8%). It is felt that data reported here for non-formulation 10 and miscellaneous oil uses are conservative estimates. The estimate for these two categories is less than 10 percent of the total applied oil pesticide.

The task of breaking down application estimates by county and by use was more difficult than estimating total quantities. The distribution of oil pesticide use was based primarily on the 1977 PUR along with specific information from county farm advisors for specific crops in individual counties. Some of the distributions in smaller use categories may deviate considerably from actual use but quantities involved have less influence on the total distribution.

Patterns based on surveys were used for oil used in wood preservation, school districts and vector control. The first two include data from a significant number of respondents and the last includes data for all of the oil applied by vector control agencies. The data are probably the most accurate among all categories.

There are some uncertainties about the specific uses of general weed oil. The use pattern estimates reported here are based on the grower survey response, the school district

and vector control surveys and the sale of weed oil products registered for various uses as reported by dealers. None of these give an accurate picture of use for all of the weed oil applied, but the estimates represent the best obtainable from the available data.

In summary, the data reported are reasonable. This study relied upon several assumptions, and, at the same time, it represents a major effort in developing an inventory of pesticide use where applications are mostly unreported. More importantly, its findings include a large quantity of pesticides which have never been reported previously.

Several areas that deserve further consideration are recommended. First, the use of pesticides in home and garden applications should be investigated more thoroughly. Although the relative amount of oil pesticide use in this sector is rather small, the quantity of synthetic pesticide use may be significant.

Secondly, effort should be extended toward defining the unreported synthetic pesticide use. At present, there is no requirement for farmers or non-commercial applicators to report the use of unrestricted synthetic pesticide applications. Such information is important for hydrocarbon emission inventory especially for those counties classified as nonattainment areas for ozone.

For use in estimating hydrocarbon emissions from pesticides, manufacturers of pesticide oils should be required to report to state agencies on an annual basis the quantity of various types of oil sold by them in California. An alternative approach is to require the manufacturer to submit annual sales records by pesticide formulation type to the state. This information can be pooled together as a statewide statistics, and thus avoid revealing confidential sales information.

## 5.5 References

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## 6.0 EMISSION INVENTORY

### 6.1 Introduction

Two of the primary objectives of this project were to establish a methodology for estimating pesticide emissions, and based on that methodology to conduct an inventory of emissions associated with nonsynthetic hydrocarbon pesticide applications in California for the calendar year 1977. In meeting the first objective, experimental and theoretical data were obtained from the literature to establish a general emission estimation methodology. In meeting the second objective, application data secured from surveys and interviews of farmers, pesticide manufacturers and dealers, farmer advisors, floricultural businesses, utilities, railroads, and wood preservers were used. Based on the survey data, emissions were calculated.

The emission estimation methodology was based on the pesticide evaporation equation proposed by Hartley.<sup>1</sup> Hartley's equation was modified to include considerations of emissions during pesticide applications, sorption and sequestration of pesticide, and pesticide degradation. The methodology allows for emission estimation from carry-over of residual pesticide from applications of previous month(s). Depending on weather variables, the resulting emissions range from about 85 percent to 95 percent of the applied pesticides. This methodology was not applicable to creosote used as wood preservatives. A simple emission factor was used to estimate creosote emissions.

The 1977 total emissions resulting from formulation 10

nonsynthetic hydrocarbon pesticide applications in California amounts to 182 million pounds or 249 TPD. In some counties, pesticide use is a major source of hydrocarbon emissions. Depending on the seasonal use patterns, pesticide applications may have potential significant impacts on air quality in some nonattainment areas.

The following sections summarize the methodology used to estimate emissions, the assumptions and input data, and the 1977 inventory of emissions resulting from formulation 10 nonsynthetic pesticide applications in California. Appropriate discussions of the implications of these emissions on air quality are also made.

## 6.2 Emission Estimation Methodology

### 6.2.1 Pesticide Vaporization

#### 6.2.1.1 Methodologies

The subject of pesticide vaporization was reviewed extensively by Spencer et al.<sup>2</sup> and by Spencer and Cliath.<sup>3,4</sup> Other reviews covering different aspects of pesticide volatilization were made by Wheatley,<sup>5</sup> Plimmer<sup>6</sup> and Taylor.<sup>7</sup>

Most of the work on pesticide vaporization has been concerned with the various factors which influence the evaporation rate, e.g. temperature and soil moisture. The models which have been proposed for predicting vaporization rates include one for estimating loss from surface deposits.<sup>1</sup> A number of other models have been proposed which depend on calculation of the rate of movement

to the surface for pesticides mixed in soil or dissolved in bodies of water.<sup>8,9,10</sup>

The present discussion of pesticide vaporization will be concerned with those particular aspects of pesticide vaporization which affect the rate of evaporation loss of petroleum oil. Since oil pesticides are applied as surface deposits and are not normally mixed with soil nor dissolved appreciably in water, only the model proposed by Hartley<sup>1</sup> for surface deposits is applicable.

The rate of evaporation of a chemical is related to its vapor pressure (P) and the rate of diffusion of vapor away from the evaporating surface.<sup>1</sup> This diffusion of mass away from the evaporating surface is proportional to the vapor density times the diffusion coefficient of the vaporizing substance. Since the diffusion coefficient is inversely proportional to the square root of the molecular weight (M) and the vapor density is proportional to P x M the rate of evaporation loss will be proportional to  $P(M^{1/2})$ .<sup>1</sup> Hartley<sup>1</sup> proposed the following equation to predict the rate of evaporation of compound 1 based on the known rate for a model compound 2:

$$E_1 = E_2 \frac{P_1(M_1^{1/2})}{P_2(M_2^{1/2})} \quad (\text{Eq. 6-1})$$

where: E = evaporation rate

P = vapor pressure

M = molecular weight

and 1 and 2 are subscripts designating compounds

with unknown and known evaporation rates respectively.

If the model compound is water, the water evaporation rate in the equation must be modified to account for the affect of relative humidity (R.H.):

$$E_p = \frac{E_w}{(1-R.H.)} \times \frac{P_i (M_i^{1/2})}{P_w (M_w^{1/2})} \quad (\text{Eq. 6-2})$$

where:  $E_p$  = the evaporation rate of compound  $i$  per unit area; and

$E_w$  = the evaporation rate of water per unit area

The water evaporation rate,  $E_w$ , for Equation 6-2 can be obtained by one of the methods developed for estimating evapotranspiration (ET), the combined loss of water from evaporation and transpiration of plants on vegetated land.<sup>11</sup> Some of the methods which are applicable under a wide range of conditions are the following:

- (1) Empirical methods. These relate meteorological factors to measured ET from individual crop surfaces. The most well-known use the Thornthwaite<sup>12</sup> and the Blaney-Criddle<sup>13</sup> formulas. The latter requires a separate crop factor for each month and is the most widely used on semi-arid lands of the western U.S.
- (2) Energy-balance calculations. In these methods ET is estimated as a function of available radiant energy. The approach was found appropriate for use in a wide range of climates.<sup>14,15</sup> Some methods are based solely on weather and radiation data.<sup>16</sup>
- (3) Use of evaporimeters. Evaporimeters are: a) open water pans or b) porous surface atmometers.

The water lost from the evaporimeter is correlated experimentally with water lost by evapotranspiration from water, soil or crop surfaces.<sup>17</sup> The ratio of evaporation from a pan to evapotranspiration from a crop needs to be determined for each growing stage of the crop and for areas with similar weather if the values are to be reasonably accurate.<sup>17</sup>

The evaporimeter method is used in this report for estimation of water evaporation rates to be used in Equation 6-2. Monthly water evaporation and other climatological data are reported for many points in California by the Environmental Data Service.<sup>18</sup>

Water evaporation from evaporimeter pans is not the same as evaporation from crop lands of various kinds, nor even the same as evaporation from large bodies of water. The pan evaporation must be modified by a coefficient experimentally determined for each surface.<sup>17,18</sup> This coefficient has been reported to vary between 0.75 and 1.15 for a variety of mature crops.<sup>17</sup> The mid-value of 0.95 was taken as representative of the average condition and used for calculating evapotranspiration from vegetated land. An additional factor of 0.77 was applied to the pan evaporation to account for the difference which has been observed when pan measurements were made outside the vegetated surface area.<sup>20</sup> Therefore, the value of ET will be designated  $E_A$  and for vegetated surface  $E_A = 0.95E_{\text{pan}} \times 0.77 = 0.73E_{\text{pan}}$ .

A separate value of  $E_A$  was used for calculation of emission from soil since evaporation of water is generally lower from soil than vegetated surfaces. The pan to soil evaporation ratio varies

greatly depending on the amount of drying that has occurred after watering. A pan ratio of 0.40 has been found for soil kept moist enough to maintain seedling growth and this value was used in the calculation.<sup>19,20</sup>

The average coefficient for evaporation from water surface in relation to Class "A" pans is 0.70.<sup>22</sup> This coefficient was used in calculation of emissions from water surfaces.

The acreage was considered to be vegetated land if an insecticide, fungicide or defoliant was applied since such treatments are applied to mature or maturing crops and, therefore, the surface is vegetated. Herbicides are applied to soil or to immature weed growth, therefore, the treatment surface was considered to be soil if an herbicide was applied. The treated water surfaces are those to which aquatic insecticides or herbicides were applied.

Time-dependent changes in vaporization rate. The rate of evaporative loss from applied pesticide would be constant from a complete, unbroken surface layer. The rate of loss would decrease if the surface exposed to the air is decreased through evaporation.

Laboratory experiments<sup>23,24</sup> have shown that evaporation of pesticide from finely divided particles or from very thin layers follows first order kinetics which can be described by the equation:

$$2.303 \log \frac{a}{a-x} = kt \quad (\text{Eq. 6-3})$$

where:  $a$  is the initial amount of chemical,  
 $k$  is the rate constant and  
 $a-x$  is the amount of chemical remaining at time  $t$ .  
Thus, the rate of loss is proportional to the amount remaining.  
First order volatility loss has been demonstrated for several  
5-triazines<sup>24</sup> and a number of organochlorine insecticides<sup>25</sup>  
evaporated from glass or metal surfaces.

Volatility losses from soil applied pesticides may follow  
a similar pattern of first order kinetics under constant envi-  
ronmental conditions.<sup>2,6</sup> Many soil-applied pesticides are  
strongly adsorbed to soil particles especially if they are dry.  
Higher soil water content can displace the pesticides from the  
adsorption sites leading to a much higher rate of evaporation.<sup>1,26</sup>  
Evaporation of pesticides from leaves of plants is also rapid  
immediately after application and decreases with time. This  
kind of evaporative loss was observed by Taylor et al.<sup>27</sup>  
following application of heptachlor and dieldrin to orchard  
grass. The rate of loss for these compounds was proportional to  
the residue remaining for about 10 days and then continued at  
a much lower rate.

Figure 6-1 shows examples of the relationship between time  
and the oil residue remaining on and in fruit trees after appli-  
cations of light and light-medium foliar spray oil in the field.  
In these examples the rate of loss is greater than first-order  
for about one week and approximately first-order for some time  
thereafter. The actual percentages of initial deposit reported  
by Rohrbaugh<sup>28</sup> may be in error, since his first measurement was

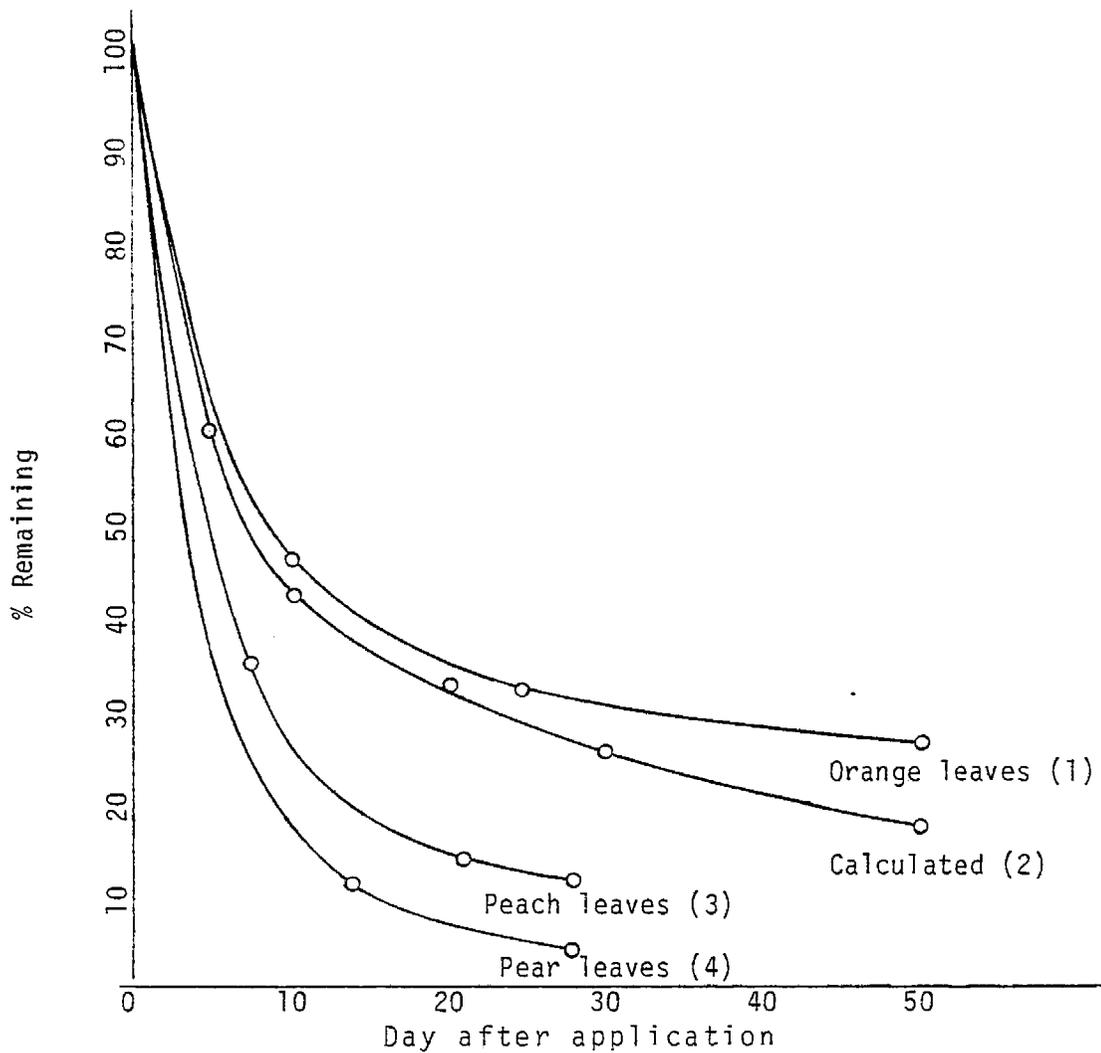


Figure 6-1. Loss of Spray Oil From Leaves of Fruit Trees.

Pesticide applications were in July or August.

1) Oil: Volck light spray oil. Source:Rohrbaugh, 1934.

2) Oil: Petroleum oil, unclassified. Source:Calculation, based on conditions in Madera County. Assumed application, July, 1977.

3) & 4) Oil: Light-medium summer spray oil. Source:John Dibble and Clarence S. Davis, 1967 (unpublished).

made after detached leaves became dried in the laboratory. He did find however, that residues of spray oil remained in citrus leaves at least 12 months after the time of application.

Heavier spray oils evaporate at a considerably slower rate than light and light-medium oils. On the basis of residue measurements, Allison (reported by Ebeling<sup>29</sup>) estimated that eighty percent of a light-medium oil applied to citrus trees in the fall at 1.75 percent solution can be expected to leave the foliage in 17 to 25 days. A medium oil will require about 40 to 45 days for 80 percent and a heavy oil 4 to 5 months.

No experimental evidence has been found on the kinetics of NSHC evaporation from soil or water but it would presumably be similar to the kinetics noted above for synthetic organic pesticides.<sup>2,6,24,27</sup>

In this report, emission rates from oil pesticides are assumed to follow first-order kinetics, except in the case of oil applied to vegetation. Since the experimental evidence cited above (Figure 6-1) shows that evaporation of pesticide oil from fruit tree foliage is initially faster than predicted from the first-order equation, the method of estimation for emission from vegetation was modified in order to more nearly match the experimental loss curves shown in Figure 6-1. Curve 2 of Figure 6-1 is a loss curve calculated by the modified method which is described in Section 6.2.2.

The observed rates of oil loss shown in Figure 6-1 are more rapid than would be calculated by Hartley's equation (Eq. 6-1). A high evaporation rate of this kind probably occurs from vegetation because the surface area of leaves is usually

several acres on a crop covering one acre of ground surface. This difference in area should be compensated by using the comparison of pesticide loss with water loss as in Equation 6-2, but apparently the compensation is not adequate in some instances.

#### 6.2.1.2 Emission During Pesticide Application

Pesticides in most cases are applied as sprays and in almost every instance the amount which can be measured on the target surface is less than the amount applied.<sup>30</sup> Some of the quantity lost is carried away in particulate form as spray drift and some as vaporized chemical. Wheatly estimates that not more than 5 percent of conventionally applied ground sprays are lost from the target area as drift,<sup>4,31</sup> though it is difficult to assess the proportionate amounts in drift and vapor, and no reports of actual measurements have been found. The losses reported during application vary with the pesticide, the mode of application and the conditions of applications.

No models or procedures have been found in the literature for estimation of pesticide loss during application. The estimation of evaporative loss of NSHC pesticides will be based on the data of reported application losses shown in Table 6-1 using the same method followed in a previous report.<sup>32</sup>

The data in Table 6-1 indicate an average of 18.5 percent of applied pesticide with average vapor pressure of about  $10^{-3}$  mm Hg was lost during application when the temperature was 68.8°F (20.4°C). The application loss in these data appears to be approximately linearly related to the log of the vapor pressure of the pesticides,

TABLE 6-1

## Reported Pesticide Losses During Application

Pesticide	Vapor Pressure (mm Hg)	Application Temperature (°F)	Percent Loss During Application	Reference
Disulfoton	$1.8 \times 10^{-7}$ (20°C)	70	18	33
Phorate	$8.4 \times 10^{-4}$ (20°C)	70	0	33
Zinophos	$3 \times 10^{-3}$ (30°C)	71	46	34
Dyfonate	$2.1 \times 10^{-4}$ (25°C)	61	12.6	34
Dimethoate	$8.6 \times 10^{-6}$ (25°C)	<u>72</u>	<u>16</u>	35
Average	$8.12 \times 10^{-4}$	68.8	18.5	

with negligible loss for vapor pressure less than  $10^{-7}$  mm Hg. A similar relationship was observed for herbicide evaporation from metal planchets.<sup>24</sup> From other evaporation data, it was estimated that the rate of pesticide evaporation is approximately proportional to the square of the temperature within the range of about 5° to 30°C.<sup>36,37,38</sup> By incorporating these relationships, the following equations were obtained for estimation of emission during pesticide application:

$$A_1 - A_2 = \text{Emission during application} \quad (\text{Eq. 6-4})$$

$$A_2 = A_1 \left[ 1 - \left\{ (4.625)(\log P_i + 7)(0.0024 T^2)(0.01) \right\} \right] \quad (\text{Eq. 6-5})$$

where:  $A_1$  = the amount of pesticide applied

$A_2$  = the amount of pesticide deposited on soil  
or other surface after application loss

$P_i$  = the vapor pressure in mm Hg of pesticide  $i$   
at 20°C

$T$  = application temperature in °C (average  
monthly temperature used), and 4.625 and  
0.0024 are constants obtained by solution of  
the equation using the empirical data.

The calculated values for application loss will be treated as emissions in this calculation since the proportions of drift and evaporation are not known.

#### 6.2.1.3 Sorption and Sequestration of Pesticide

After pesticides are sprayed on foliage or soil surfaces,

a considerable portion of the deposited pesticide enters the atmosphere over a period of time in the form of vapor.<sup>6,28</sup> Some portion of the pesticide on leaves will enter the leaf and may remain there for a year or more, some will be washed off onto the ground. Some of the pesticide which reaches the soil is firmly bound to soil particles, especially to dry soil. A part of the pesticide will be carried to lower levels in the soil.

Pesticide binding by soil or other materials is generally considered a reversible process.<sup>39,40</sup> The actual removal of pesticide from the sequestering sites may require long periods of time and there is some recognition of the concept that a portion of the bound pesticide may be unavailable to processes which lead to degradation or removal.<sup>41</sup>

There are models designed to estimate the loss of pesticide from sites or pools having different rates of loss,<sup>41</sup> but there is not sufficient data available to apply these models to highly variable regional applications of pesticides such as that involved in NSHC applications in California.

Since it is recognized in this report that some portion of applied NSHC pesticide can be unavailable for evaporation for an indefinite time, it will be estimated that 2 percent of deposited pesticides are bound. The magnitude of such loss is uncertain and this estimate is based on an assumption that loss by sequestration is small.

#### 6.2.1.4 Degradation of Pesticides

Applied pesticides are degraded in the environment by a variety of mechanisms. Among the known mechanisms are chemical, photochemical, and biological degradation.

Pesticide oil degradation has not been specifically studied although there are numerous reports of petroleum oil degradation in soil and water.<sup>42,43,44</sup> Most of this petroleum oil degradation has been attributed to the action of micro-organisms.

The chemical conversions involved in pesticide degradation do not necessarily reduce the quantity of hydrocarbon compounds which may be subject to vaporization and atmospheric reactions. If a molecule is split in two, there may be two molecules with the same total mass as before. The volatility of degradation products may also be higher or lower than the original chemical. The ultimate products of biodegradation of organic pesticides are carbon dioxide and water, but studies do not show most pesticides degraded to that point. There is very little reported on the degradation products of NSHC in soil.<sup>41,42,44</sup>

Quantitatively, soil degradation of pesticides has mainly been interpreted using first order reaction kinetics. Burschel and Freed,<sup>45</sup> for example, studied the decomposition rate of three herbicides in soil and concluded the rate of degradation followed first order kinetics which is true for most microbiological processes. Some others have found the pesticide degradation rate to be more complicated and influenced by environmental factors such as soil moisture and temperature.<sup>42,43</sup>

In one investigation, Raymond et al.<sup>42</sup> studied the loss of five petroleum oil fractions worked into the soil of field plots.

The oils included used crankcase oil, crude oil and fuel oil. After one year the average reductions ranged from 48.5 to 90 percent. No estimate of evaporation was made though the expected evaporation would be small for oil mixed into the soil.

No established procedures or models have been found which may be applied to calculation of the degradation losses of pesticide oils applied to crop or non-crop surfaces. Therefore, in the present report the rate of degradation of deposited NSHC pesticide will be estimated to be 4 percent per month for the oil available at the start of the month. This degradation loss rate is based on the average monthly degradation rate in the study by Raymond et al.<sup>42</sup>

#### 6.2.2 General Emission Methodology

The method for estimating emissions from applied NSHC pesticides is that used by Leung et al.<sup>31</sup> with some modifications. This method depends primarily on the model developed by Hartley for pesticide volatilization from surface deposits. The basic emission rate is calculated from Equation 6-2 which is derived from physical principles. After the initial rate is established from Equation 6-2, the emission is considered to follow a time-course through each month which is first order or a summation of 2 first order time-courses.

The factors which were discussed in Section 6.2.1 and which need to be considered in pesticide emission estimation are:

- . Emission during pesticide application
- . Sorption and sequestering of pesticide

- . Degradation of pesticide
- . Emission from deposited pesticide
  - a) Emission surface, i.e. soil, vegetated land, water
  - b) Time-dependent change in emission rate

A flow diagram of the emission estimation methodology is shown in Figure 6-2. Details of the steps in the calculations are explained in the following pages.

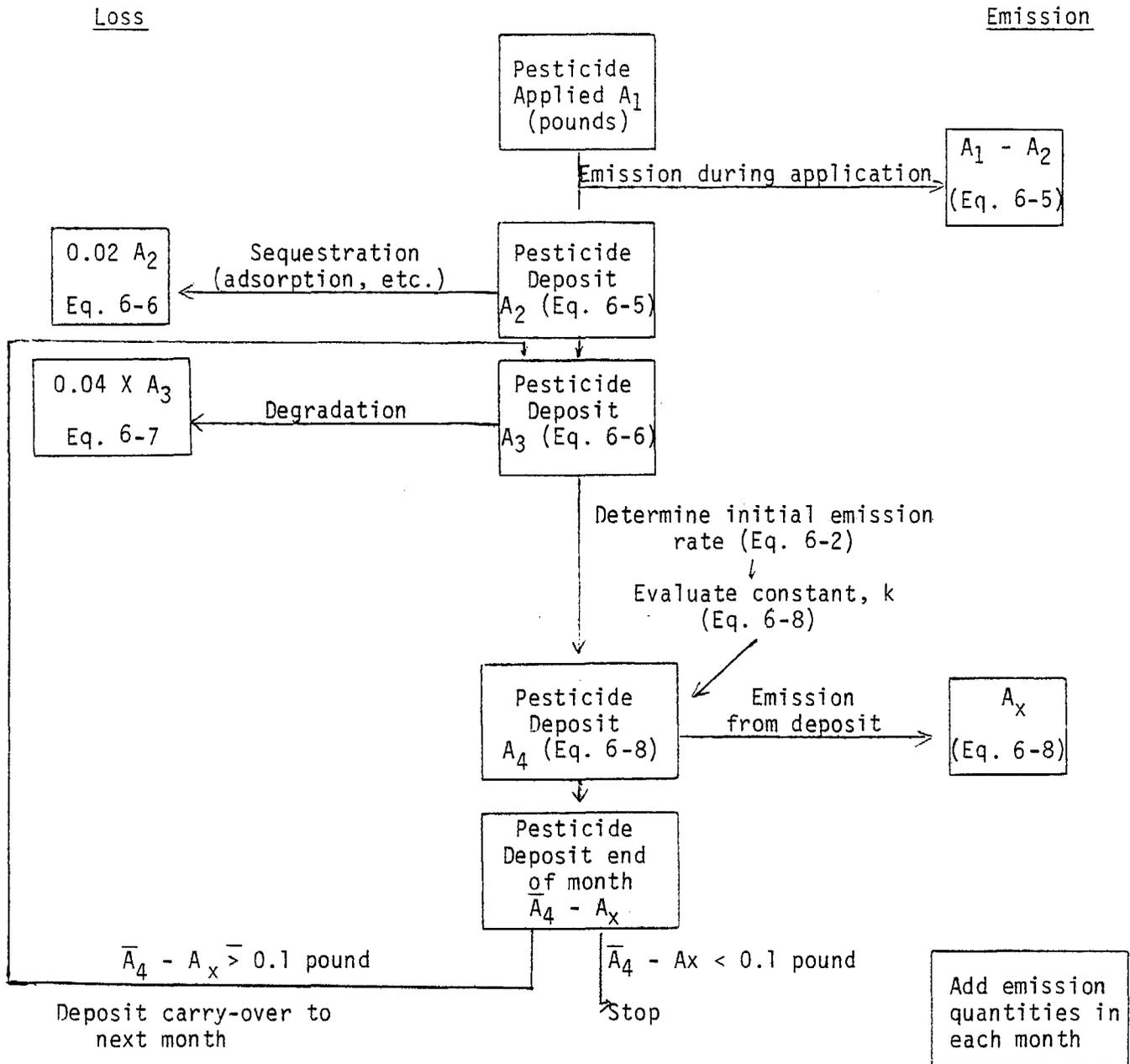
The estimation of hydrocarbon emissions from a NSHC pesticide applied to acreage was determined by the method which follows. The pesticide application in pounds per acre for each month was obtained from the application inventory.

1. Calculation of emission during application. The emission during application is the amount which evaporates from the pesticide spray before it is deposited on the target surface. This quantity is calculated through use of Equation 6-5 which makes adjustments for variations in the temperature during application and for differences in the volatility of the pesticide.

$$A_2 = A_1 \left\{ 1 - \left[ (4.625)(\log P_i + 7)(0.0024 T^2)(0.01) \right] \right\} \quad (\text{Eq. 6-5})$$

- where:  $A_2$  = the quantity of pesticide  $i$  deposited after emission loss during application
- $A_1$  = the quantity (pounds) of pesticide  $i$  applied
- $P_i$  = the vapor pressure of pesticide  $i$  at 20°C
- $T$  = average temperature (°C) during the month application occurs
- $A_1 - A_2$  = the quantity (pounds) of emission during application

Figure 6-2. Flow Diagram for Emission Estimation



The letters  $A_1$  to  $A_4$  and  $A_x$  refer to quantities in equations (Eq.) indicated in the text.

The quantity of emission from the application is added later to the total emission. The amount of pesticide deposited ( $A_2$ ) is used in the next step of the calculation.

2. Calculation of pesticide loss by sequestration (adsorption and other). It is assumed that the amount of pesticide removed by irreversible sequestration equals 2 percent of the amount deposited. Therefore:

$$A_3 = (1-l)A_2 \quad (\text{Eq. 6-6})$$

where:  $l$  = the loss coefficient for sequestration,  
evaluated here at 0.02

$A_2$  = the quantity of pesticide deposited on the  
surface

$A_3$  = the quantity remaining after loss by sequestration.

The estimated amount of pesticide lost by degradation is calculated from  $A_3$ .

3. Calculation of the pesticide loss by degradation. Loss by degradation is calculated from  $A_3$  in the month the pesticide was applied and, in subsequent months, from the quantity of pesticide left from the previous month. Degradation loss is obtained from the following equation:

$$A_4 = (1-l')A_3 \quad (\text{Eq. 6-7})$$

where:  $l'$  = the loss coefficient for degradation evaluated  
at 0.04 per month

$A_3$  = the pesticide remaining after loss by sequestration

$A_4$  = the pesticide quantity remaining and capable of evaporation in any month.

The quantity  $A_4$  is used in step (5) after determination of the initial emission rate.

4. Calculation of the pesticide emission rate. The emission rate ( $E_p$ ) is determined for each pesticide as an estimate of the evaporation rate which takes into account the vapor pressure and molecular weight of the pesticide and also those environmental conditions during the month which influence the water evaporation rate. The emission rate is calculated by use of Equation 6-8 as follows:

$$E_p = \frac{E_A}{1-R.H.} \times \frac{P_i (M_i)^{\frac{1}{2}}}{P_w (M_w)^{\frac{1}{2}}} \quad (\text{Eq. 6-2})$$

where:  $E_p$  = the maximum, initial emission rate of compound  $i$  per acre

$E_A$  = the adjusted water evaporation rate per acre

$E$  = the quantity of water evaporation per acre calculated from pan evaporation

R.H. = relative humidity

$P_i$  = vapor pressure of compound  $i$  at cited temperature

$P_w$  = vapor pressure of water at temperature cited for  $P_i$

$M_i$  = molecular weight of compound  $i$

$M_w$  = molecular weight of water

$E_p$  is calculated for each month that there is pesticide available for evaporation.  $E_A$  is equal to 0.73  $E$ , 0.04  $E$  and 0.70  $E$  for

applications to vegetated land, soil surfaces and water surfaces respectively,

where:  $E$  = inches of water evaporated x 226,600 pounds  
per inch of water on one acre

Since the evaporation rate of applied pesticide does not remain constant, it is assumed that the initial rate is established from Equation 6-2, but the change in rate follows first order kinetics as calculated from Equation 6-8. In calculation of emission from vegetated land surfaces, the emission rate and change of rate were adjusted by use of 2 first order rate constants to more closely approximate observed loss kinetics.

#### 5. Calculation of the monthly emission from deposited pesticide.

The quantity of pesticide evaporated per acre in each month is calculated by using Equation 6-8 after the rate constant,  $k$ , is evaluated from the initial emission rate obtained from Equation 6-2.

In the calculation of emissions from pesticide applications to vegetated surfaces, the amount deposited per acre,  $\bar{A}_4$ , was divided into 2 equal parts which may be designated part 1 and part 2. Emission for each part was then calculated in exactly the same way as emissions from soil or water applications except that in the calculation for part 2 the rate constant,  $k$ , was multiplied by 8 after it was obtained. This was done so that the calculated loss curve would more closely match the empirical loss curves shown in Figure 6-1.

The first order equation used to calculate emission is:

$$2.303 \log \frac{\bar{A}_4}{\bar{A}_4 - A_x} = kt \quad (\text{Eq. 6-8})$$

where:  $\bar{A}_4$  = the quantity per acre of pesticide i available for evaporation in any month

$A_x$  = the quantity per acre of pesticide i evaporated at time t

k = the rate constant

t = time

The constant, k, is first evaluated in each month that pesticide i was available for evaporation by substitution of  $E_p$  (pounds/acre/day) x R into Equation 6-8 such that  $E_p \times R = A_x$  when t = 1 day and

$$\text{where: } R = \frac{\bar{A}_4 - A_x}{\bar{A}_4}$$

That is, R is the fraction of the initially available pesticide deposit,  $\bar{A}_4$ , remaining at the time of evaluation. The emission from the pesticide for the month,  $A_x$ , and the quantity per acre remaining,  $\bar{A}_4 - A_x$ , are then determined by substitution of the calculated rate constant into Equation 6-8, with t = the number of days in the month. Then  $(A_x \times \text{acres in the application}) + (A_1 - A_2) = \text{emission in that month}$ . If  $\bar{A}_4 - A_x < 0.1$  pounds per acre it was assumed that there was no pesticide remaining to evaporate the next month. If  $\bar{A}_4 - A_x \geq 0.1$  pounds per acre it was assumed that there was carry-over of pesticide to the next month. A calculation was then made for emission the next month (see heading 6 on next page).

Calculation of emissions were made separately for pesticide

applications in different months, and if there was carry-over the total pounds of emissions for one pesticide were summed for each month.

6. Calculation of monthly emission and carry-over for pesticides partially evaporated during any month. If from emission calculation with Equation 6-8,  $\bar{A}_4 - \bar{A}_x > 0.1$  pounds per acre at the end of the month, the quantity  $\bar{A} - A_x$  was carried to the next month. In emission calculations for the second or succeeding months  $(\bar{A} - A_x) \times$  acres was treated in the same way as  $A_3$  in the first months calculation, that is, degradation of 4 percent was subtracted,  $E_p$  was calculated for the second month, the rate constant for Equation 6-8 was estimated and the pounds of emission and pesticide remaining were determined from Equation 6-8.

The calculations of carry-over and emissions were continued until the applied pesticide ran out ( $A_y - A_x < 0.1$  lb./acre) or up to 12 months, whichever came first. Pesticide remaining in December was carried over to January on the assumption that applications in the previous year would be similar to the current year.

Non-acreage applications. Calculation of emissions from reported non-acreage applications of NSHC pesticides were made in the same way as for acreage applications for the following quantities:

- 1) Emission during application.
- 2) Pesticide loss by sequestration.
- 3) Pesticide remaining after loss by degradation,  $A_4$ .

Since no application rate (pounds/acre) was presented with

the non-acreage data, an emission rate could not be calculated from Equation 6-2 and 6-8. The pesticide remaining after loss by degradation,  $A_4$ , was assumed to evaporate in the month of application. Therefore, the total emission in that month was estimated as  $A_4 + A_1 - A_2$  (emission during application).

Oil applications for vector control are reported as non-acreage applications but are treated here as acreage applications to water. The application poundage is divided by the average recommended application rate of 2.0 pounds per acre<sup>48</sup> to get an estimated value for acreage. Calculations thereafter are the same as for other acreage applications.

Data for emission estimation. For emission estimation data was required on physical characteristics of the pesticides, the climatic conditions during and after application and the type of surface to which application was made. The source and methods of obtaining these data are indicated.

The average molecular weights, boiling points and vapor pressures of NSHC pesticides are shown in Table 6-2. Pesticide oils are placed in different chemical classes according to the DFA registration system. The molecular weights (petroleum hydrocarbons excepted) and boiling points for these chemical categories are based on values for 33 NSHC products of various types reported in returns from the survey of manufacturers. The molecular weight estimates for the 2 petroleum hydrocarbons were obtained from a plot of molecular weights versus boiling points for 11 aromatic hydrocarbons found in creosote.<sup>49</sup> The mean temperatures for 50 percent distillation which are reported

TABLE 6-2

Physical Characteristics of Nonsynthetic  
Hydrocarbon Pesticide Chemicals

Chemical, Pesticide Type and Major Application	Percent Chemical Use in Oil Type <sup>a</sup>	Boiling Point (Mean)	Molecular Weight (Mean)	Vapor Pressure (mm Hg at 20°C)
<u>Aromatic Petroleum Solvent</u>				
Herbicide, Aquatic Weed Oil	100	279°F	110	6.50
<u>Mineral Oil</u>				
Insecticide, Fruit and Nut Oil Spray	100	690°F	327	7.4 X 10 <sup>-6</sup>
<u>Petroleum Oil Unclassified</u>				
Insecticide, Fruit and Nut Oil Spray	99.3	680°F	307	2.89 X 10 <sup>-5</sup>
<u>Petroleum Distillate</u>				
Insecticide, Mosquito Larvicide	100	571°F	253	9.11 X 10 <sup>-4</sup>
<u>Petroleum Hydrocarbon</u>				
Herbicide, Non Selective General Contact Herbicide and Defoliant	56.7	569°F	160	9.54 X 10 <sup>-4</sup>
Herbicide, Selective Oil for Carrot, Other Vegetables	43.3	350°F	124	0.546
<u>Diesel Oil</u>				
Herbicide, Solvent or Adjuvant			200	2.0 x 10 <sup>-3</sup>

<sup>a</sup> Based on usage reported in the 1977 Pesticide Use Report.

in the manufacturers survey responses were used to estimate vapor pressure (Table 6-2) for each chemical based on the vapor pressure-boiling point correlation of Maxwell and Bonnell.<sup>50</sup>

The mean monthly temperature, relative humidity and water evaporation for each county were obtained from Environmental Data Service Publications<sup>18</sup> and in some cases from reports of the University of California Agricultural Experiment Stations. A complete set of climatological data was not available for each county. When a datum for a county was missing the value from the nearest county with similar conditions was substituted. The climatic data used for each county and the location of the recording station are listed in Appendix A.2.1.

In emission calculations, NSHC applications of insecticide, fungicide and defoliant to acreage were considered applications to vegetated surfaces and an  $E_A$  coefficient of 0.73 was used. Applications of herbicide were considered soil applications and an  $E_A$  coefficient of 0.40 was used. For a combination of insecticide and herbicide, the 0.73 coefficient was used. Vector control is the only major category under which oil is applied primarily to water. Emissions from vector control applications are calculated using an  $E_A$  coefficient of 0.70.

### 6.2.3 Emission Calculation for Wood Preservatives

#### 6.2.3.1 Introduction

Creosote evaporation studies<sup>51,52,53</sup> have shown that after creosote is impregnated into wood, it is not held tightly by the

wood but continually flows downward and outward as long as there is a volatile carrier present. The downward gravitational flow of creosote in poles and posts, for example, continually replenishes the creosote that is lost at the groundline where attack by wood destroying organisms is the greatest. Also, as creosote is lost at the surface of the treated products, it is continually replaced from the inner areas as long as there is a sufficient quantity of volatile carrier remaining.

An evaporation study with creosoted posts showed that a vapor loss of up to 37.5 percent for low-residue creosote occurred after just one year.<sup>51</sup> However, posts have a relatively large surface to volume ratio compared to ties and poles, and evaporation losses would be expected to be highest from posts.

A study with creosoted poles concluded that after three years, the evaporation loss was 27.5 percent for seasoned poles treated with low-residue creosote.<sup>53</sup> This averages out to an approximate loss of 9 percent per year. However, when the author of the study was asked if there was a greater loss during the first year than during the second and third years, he agreed that there would be a greater evaporation loss during the first year. As a result, a conservative value of 10 percent evaporative loss for the first year following treatment with creosote will be used for all wood products treated with creosote and used in California. The creosote emission estimation for 1977 only includes those emissions from wood treated in 1977 and does not include any residual volatilization from creosoted wood that was already in place or in storage prior to 1977.