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AIR POLLUTION EMISSIONS ASSOCIATED WITH PESTICIDE APPLICATIONS IN FRESNO COUNTY

FINAL REPORT

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ABSTRACT

This report presents the findings in estimating the air pollution emissions associated with pesticide applications in Fresno County, California. The investigation covers the calendar year 1976.

To achieve the program objectives, this project was conducted in three parts. The primary concern of the first part was data collection which involved both reported and unreported pesticide use data. The reported data were obtained from the Pesticide Use Report; the unreported data were obtained by questionnaire surveys of farmers, pesticide dealers, and pesticide suppliers. The second part involved an inventory of emissions resulting from pesticide applications in Fresno County. The emission inventory was conducted in two steps. The initial step was to compile a list of the total pesticides applied in Fresno County classified as synthetic, inorganic and nonsynthetic products. Synthetic and inorganic products were further broken down into three groups: inorganics, organics, and inert materials. The synthetic organics, inert organics, and nonsynthetic organics were separated according to their acreage and nonacreage applications. The second step of emission inventory was to calculate the emissions of each organic compound based upon vapor pressure, molecular weight, relative humidity, and temperature, etc. Possible alternatives to pesticide use and methods of pesticide applications are discussed in the last part of the report.

Based on the findings of this study, the estimated pesticide application in Fresno County for the calendar year 1976 was 22 million pounds. This quantity represents 25.2 percent synthetic organics, 29.8 percent inorganics, and 45.0 percent of nonsynthetic petroleum oils. The major pesticide end user is the agricultural industry which is responsible for an estimated

89.1 percent of the total consumption. Estimatied home and garden application is a distant second with 3.8 percent consumption. This rate of pesticide application leads to an estimated total organic gas (TOG) annual average emission of 19.3 tons per day (TPD), and 18.6 TPD for reactive organic gas (ROG) emissions. The highest monthly emission for 1976 occurred in December with estimated TOG and ROG averages of 50.5 and 50.4 TPD respectively. The total pesticide emissions in December, 1976 would account for 3.9 percent of the ROG emissions and 3.0 percent of the TOG emissions from all Fresno County emission sources (stationary and mobile) during 1973.

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ABBREVIATIONS AND SYMBOLS

Abbreviations and Symbols	Definitions
α	Alpha
CARB	California Air Resources Board
CFR	Code of Federal Regulations
cm^2	Square centimeter
4-CPA	(4-chlorophenoxyacetic acid)
DDT	Dichlorodiphenyltrichloroethane
DFA	Department of Food and Agriculture
EPA	Environmental Protection Agency
ET	Evapotranspiration
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
$h\nu$	Light energy (photon)
IGR	Insect Growth Regulator
IPM	Integrated Pest Management
JH	Juvenile hormone
km/hr	Kilometer/Hour
m^3	Cubic meter
MH	Molting hormone
ml	milliliter
mm Hg	Millimeters of Mercury (Torr)
ng	nanogram (10^{-9} g)
PE	Potential Evapotranspiration
PUR	Pesticide Use Report

Abbreviations and Symbols	Definitions
RH	Relative Humidity
ROG	Reactive Organic Gas
SIRM	Sterile Insect Release Method
sp. gr.	Specific Gravity
SVC	Saturation Vapor Concentration
TOG	Total Organic Gas
TPD	Tons Per Day
µm	micron (10^{-6} meter)
USDA	United States Department of Agriculture

ACKNOWLEDGEMENTS

This report is the product of nine months of intensive investigation and analysis. A large number of people, organizations, and agencies in Fresno County and the California state government were contacted, and most were very helpful in providing information. Gratitude is extended to the many farmers, pesticide dealers, and pesticide suppliers who took time to respond to our survey questionnaires. The assistance and cooperation of all the pesticide manufacturers who provided confidential information for their products are gratefully acknowledged. Their assistance and cooperation was essential to the successful completion of this project.

There are several individuals that the authors wish to acknowledge and thank for their contributions: Robert Reynolds, our project officer, for his outstanding performance in coordinating this project between the contractor and the staff of the California Air Resources Board as well as for his assistance in project planning and technical input; and Jerry Weins, Nancy Matthews, Francis Torrance, and Dean Sato, also of the California Air Resources Board, who provided important technical suggestions for the project.

In completing our data collection, three individuals were indispensable: Dr. Ming-Yu Li of the Food Protection and Toxicology Center at UC Davis, Robert Emparan of the Fresno County Agricultural Commission, and Robert Rollins of the California Department of Food and Agriculture.

Dr. Ming-Yu Li, our project consultant, has been a constant source of information and advice. He and David Squire, the programmer, were instrumental in deciphering the pesticide use report data and in generating new

data to provide a basis for extrapolating pesticide use patterns for this project. We wish to extend our sincere thanks to them.

During the course of this study, Robert Eparam and his staff gave us complete access to the pesticide use report file of Fresno County. In addition, Mr. Emparan constantly provided us with valuable advice on statistics and pesticide use patterns in Fresno County. We wish to convey our most sincere thanks to Mr. Eparam and his staff.

Robert Rollins served as our "answer man" throughout the duration of this project. Mr. Rollins was most helpful in assisting us in assembling information on the inert ingredients contained in selected pesticide files to which permission of access had been obtained from manufacturers. His cooperation and patience are gratefully acknowledged.

1.0 CONCLUSIONS

The following conclusions are based on the interpretation of data presented in this study:

1. In 1976 the estimated pesticide application in Fresno County was 22 million pounds. The quantity is comprised of 25.2 percent synthetic organics, 29.8 percent inorganics, and 45.0 percent nonsynthetic petroleum oils.
2. The major pesticide end user in Fresno County is the agricultural industry which is responsible for 89.1 percent of the pesticides used, while the home and garden sector is a distant second, accounting for 3.8 percent of the total pesticide applications.
3. The estimated total organic gas (TOG) emission from the 1976 pesticide applications in Fresno County was 19.3 tons per day (TPD), and 18.6 TPD for reactive organic gas (ROG) emissions.
4. The emissions of TOG and ROG resulting from pesticide applications in Fresno County in 1976 are significant from an air quality perspective. When compared to ARB's 1973 Emission Inventory for Fresno County, the 1976 pesticide emissions would account for 33 percent of the ROG emissions and 22 percent of the TOG emissions from all stationary sources, and 17 percent of the ROG emissions and 13 percent of the TOG emissions from both stationary and mobile sources.

   There were four definite emission peaks during the year: February, May, August, and December. The peak in August corresponds best to both the high ambient levels of TOG in Fresno and a high frequency

of oxidant standard violations. It appears that pesticide applications, particularly those of nonsynthetic pesticides, during the latter part of the summer could contribute to oxidant problems in the Fresno area.

5. Pesticide use contributed significantly to hydrocarbon emissions in Fresno County in 1976. Emission control efforts should be directed toward reducing the use of organic pesticides responsible for producing ROG emissions during the summer and fall months with special emphasis on nonsynthetics.

6. A reduction in the use of chemical pesticides can be achieved without appreciable reduction of agricultural output by employing appropriate alternative pest control methods. Integrated Pest Management (IPM) is one alternative method which may be able to reduce pesticide applications by 50 percent or more in some crops where methods are developed. IPM is largely unexploited both with regard to development of methods for many crops and implementation of methods already developed.

2.0 RECOMMENDATIONS

1. A more comprehensive survey of farmers should be conducted to obtain a clearer picture of unreported pesticide applications, particularly nonsynthetic. Such a survey may also help to determine the reasons for farmers reluctance and concern in responding to surveys such as those employed in this study.
2. Pesticide use in home and garden applications should be investigated more thoroughly. Although the relative amount of pesticide use in this sector is rather small in an agricultural region such as Fresno County, it would probably be significant in urban and suburban areas of California.
3. A new and improved reporting system for governmental agencies should be considered. At present, federal agencies are not required to accurately account for their pesticide use; as a consequence, these agencies are very likely to under-report.
4. Emission control efforts should be directed toward reducing, during the summer and fall months, the use of those organic pesticides that produce ROG emissions; special emphasis should be given to nonsynthetics.
5. A more intensive effort should be directed toward the development and validation of more accurate methodologies for estimating pesticide emissions. This effort should consider relevant parameters such as pesticide persistence and degradation in soil and water and on vegetation. In addition, calculated emission factors should be validated with experimental data where possible.
6. Integrated Pest Management (IPM) should, as an alternative pest

control measure, be encouraged by governmental agencies by providing resources in method development as well as guidance and education to farmers for implementation of methods already developed.

7. The agricultural community should be better informed on how reactive hydrocarbons contribute to photochemical oxidant formation which adversely impacts crops, livestock, and humans.

3.0 INTRODUCTION

3.1 Air Pollution from Pesticide Uses

Pesticides have been effective in pest control and are responsible for up to a 25 percent increase in the agricultural production of crops and livestock.[1] Because of these great benefits, the annual production of pesticides has been gradually increased. In 1973 some 1.32×10^9 pounds of pesticides were manufactured in the U. S.;[2] this represents a 20 percent increase since 1970. California is one of the biggest agricultural states and pesticide user in the nation.

The Pesticide Use Report (PUR)[3] published by the California Department of Food and Agriculture states that over 90 million pounds of pesticides were used in California in 1976, and about 10 percent of this quantity was used in Fresno County which is the largest agricultural county in the state. From the standpoint of air pollution, the major question of interest is the quantity of pesticides which may enter the atmosphere.

Pesticides can enter the atmosphere in a number of ways. These include:[4]

- spray drift during application,
- volatilization from crops and soils,
- entrainment with dust,
- evaporation from water,
- emissions from manufacturing and formulating plants, or
- emissions through waste disposal.

Of all the modes of entry, spray drift and volatilization from crops and soils are the two major routes through which pesticides gain entry into

the atmosphere.

These topics will be treated in more detail as background information in Section 4.0.

The proportion of pesticides applied that may enter the atmosphere from different sources have been estimated.[5, 6, 7] These estimates vary and are as high as 63 percent. The quantity of pesticide that reaches the atmosphere depends on many factors such as volatility, environmental temperature, and nature of the target surface (soil, water, foliage, etc.).

The primary question of interest is how extensively the hydrocarbons derived from atmospheric pesticides contribute to the formation of photochemical smog. Although the mechanisms of photochemical smog formation have been studied by many, some aspects of the process remain in the theoretical realm. According to Calvert,[8] all hydrocarbons are involved in the production of photochemical smog to different degrees. This implies that all the organics in pesticides have a role in smog production. The extent to which a pesticide product is involved in photochemical smog formation depends largely on its reactivity. Research
relating pesticides to smog production has been neglected.

3.2 Program Objectives

In defining the role of a pesticide in photochemical smog formation, the initial step is to determine the quantity of the compound that will enter the atmosphere and the extent to which it will react with other chemical species in the air to form photochemical oxidants. With this mission in mind, the California Air Resources Board initiated a program to provide technical inputs to that effort. The objectives of the program are:

1. To provide an inventory, both temporal and spatial, of synthetic and nonsynthetic organic emissions resulting from agricultural and other identifiable applications of pesticides in Fresno County for the calendar year 1976. The inventory includes categorizing pesticide use and classifying the reactivity of organic emissions,
2. To provide an application inventory of inorganics, including some important heavy metals such as arsenics and lead, associated with pesticide usage in Fresno County, and
3. To present discussions on alternatives to pesticide use and methods of pesticide application that may minimize the effects of pesticide organic emissions on ambient air quality.

3.3 Scope

This report presents the results of the inventory program which consisted of three parts. The primary concern of the first part was data collection. The second part was to conduct an inventory of emissions resulting from pesticide applications in Fresno County. The last part was to discuss possible alternatives to pesticide use and methods of applications.

The data collection effort in the first part involved both reported and unreported pesticide use data. The reported data were obtained from the PUR through the data bank of the Food Protection and Toxicology Center at UC Davis. The unreported data were obtained by questionnaire surveys of farmers, pesticide dealers and suppliers. Appropriate statistics from the literature were also used.

The emission inventory was conducted in two steps. The initial step was to compile a list of the total pesticides applied in Fresno County

and classify them as synthetic and nonsynthetic products. The synthetic products were divided into three groups: inorganics, organics, and inert materials. The synthetic, inert organics, and nonsynthetic organics were separated according to their acreage and nonacreage applications. The second step of the emission inventory was to calculate the emissions of each organic compound based upon vapor pressure, molecular weight, relative humidity, and temperature, etc. Each organic compound was also grouped under the California Air Resources Board's (CARB) three-tiered reactivity classification.

Possible alternatives to pesticide use and methods of pesticide applications are discussed in the last part of this report; only an overview of the subject matter is presented since this part was not the central focus of this project.

Very few studies have been made to correlate pesticide use with air pollution problems, specifically that of photochemical smog production. The most relevant, recent report was published by Wiens[8] of the California Air Resources Board. Wiens observed that the 1975 California PUR included only 14 percent of the nonsynthetic organic materials actually applied and 52 percent of the synthetic organics. The volatility for petroleum products used as/or with pesticides was estimated to be 90 percent instead of 10 percent as found using existing assessment methodology. Wiens concluded that the reactive organic gas emissions resulting from pesticide use in 1975 in California was estimated to be 339 tons/day. This quantity is 7.9 times the amount published in the 1973 inventory.

With the many variables and uncertainties contained in the pesticide use data, Wiens' study is no doubt a pioneering and courageous effort.

However, there is much room for improvement. The emission factors used by Wiens were based primarily on professional opinion which sould serve to delineate priority areas for generation of sound experimental data.

The present study sought to improve and contribute to existing information by:

1. Determining the amount of total and reactive organic gases (TOG, ROG) emitted from pesticides applied in Fresno County using the PUR data and questionnaire survey results,
2. Determining the amount of inorganic pesticides applied in Fresno County,
3. Estimating the unreported amounts of pesticides used in Fresno County, including petroleum oils and other unrestricted chemicals,
4. Recommending methods for conducting inventories of pesticide applications and emissions,
5. Identifying the general use pattern of some of the most widely used pesticides, and
6. Providing a summary to identify alternatives to the use of pesticides which would result in reduced reactive hydrocarbon emissions.

3.4 References

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4.0 BACKGROUND INFORMATION

4.1 Air Quality In Fresno County

California has a number of air quality problems, but the most serious state-wide problem is the excessive concentration of photochemical oxidants. Based on their effect on health, the U. S. Environmental Protection Agency (EPA) established a national ambient air quality standard for oxidants of 0.08 parts per million averaged over one hour.[a] Photochemical oxidants comprised primarily of ozone are formed in the atmosphere in a series of complex chemical reactions involving the oxides of nitrogen, reactive hydrocarbons, and ultraviolet light.

Like much of the state, Fresno County experiences numerous oxidant standard violations during the course of the year. During the summer and fall these violations are frequent and, at times, relatively serious. Figure 4-1 shows the frequency of oxidant standard violations at Fresno's Olive St. monitoring station during 1976. The highest hourly average concentration recorded in each month is indicated in parentheses.[1] The figures demonstrate that numerous violations occurred at this station from July through November and that oxidant levels ranged to over twice the ambient air quality standard. Figure 4-2 shows the hydrocarbon concentrations detected at Fresno's Olive St. monitoring station throughout 1976; both the highest hourly averages occurring each month and the averages of the daily high hourly averages occurring each month are indicated. When compared with Figure 4-1, this figure shows the relationship between oxidant formation, sunlight, and hydrocarbons. Oxidant concentrations are the highest and oxidant standard violations are most frequent

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[a] In June, 1978, the EPA changed the oxidant standard from 0.08 ppm to to 0.10 ppm. Nevertheless, 0.08 ppm was the applicable standard in 1976.

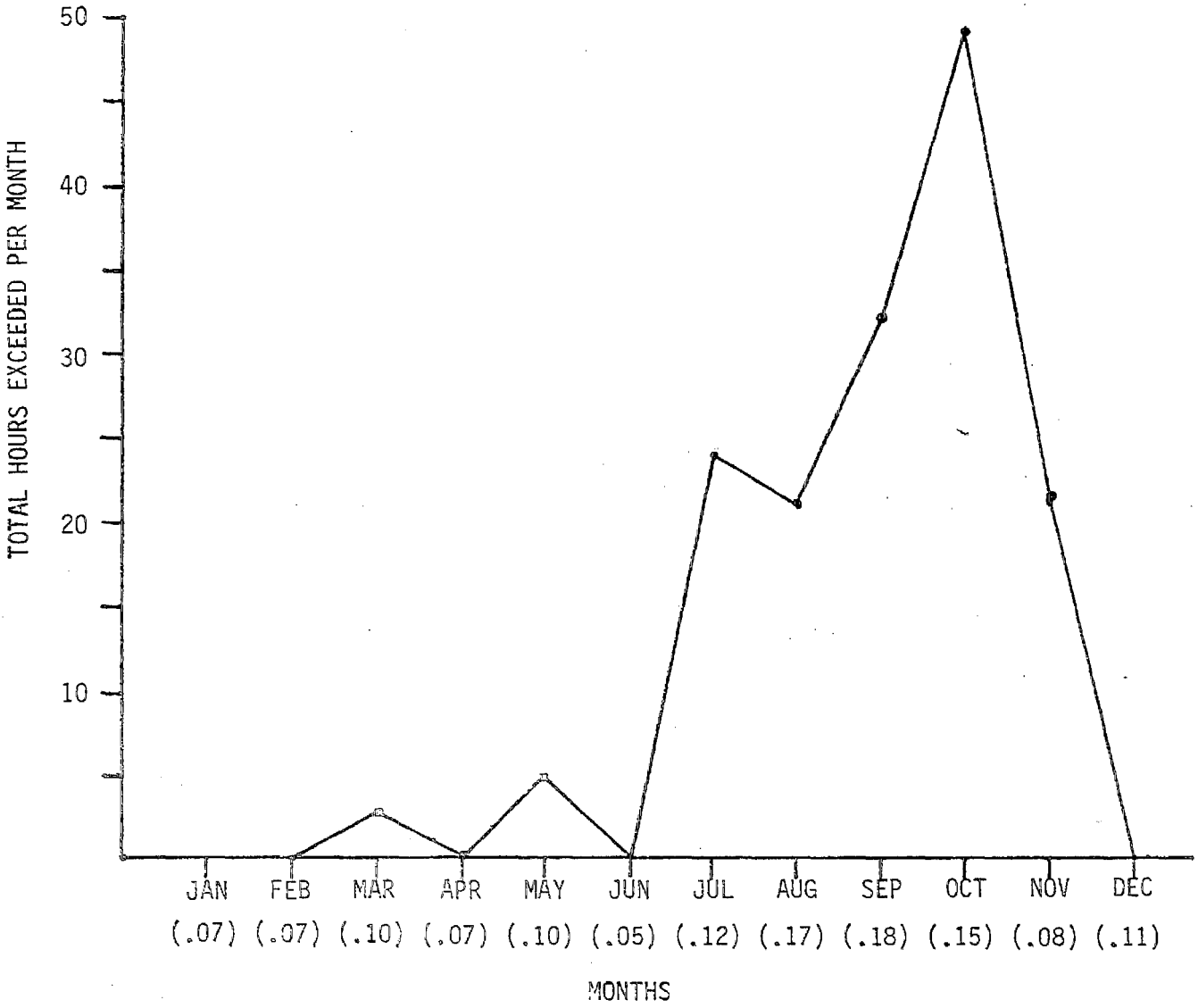


Figure 4-1. Frequency of Oxidant Standard Violations (.08 ppm or Greater) at the Fresno Olive Street Station in 1976.[7] Highest hourly average reading for the month is indicated in parentheses.

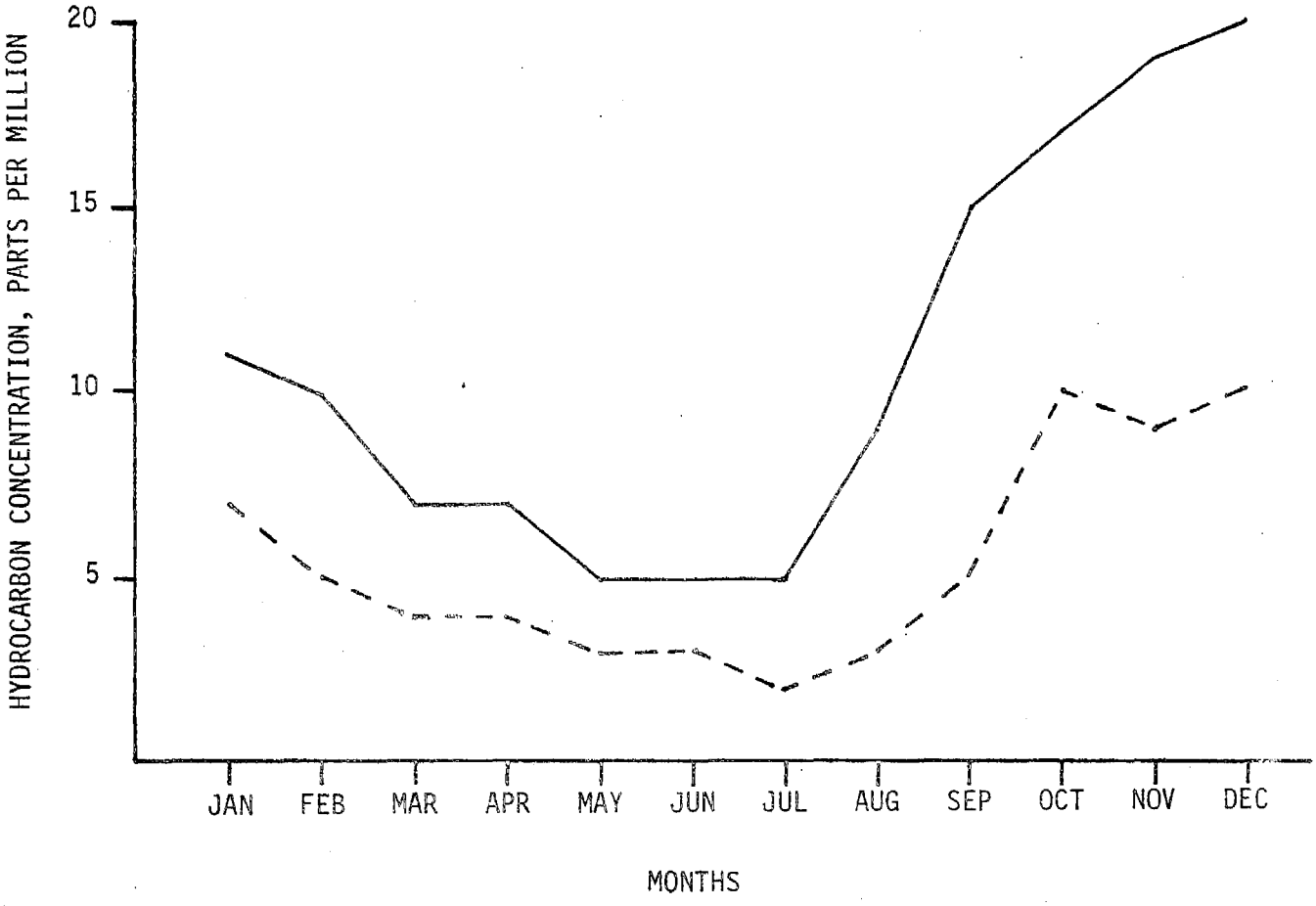


Figure 4-2. Hourly Average Hydrocarbon Concentrations at the Fresno Olive Street Station in 1976.[7]

_____ Highest Hourly Average in Month

--------- Average of Highest Hourly Averages Occurring Each Day of the Month

during the summer and fall when hydrocarbon levels are also very high. However, high hydrocarbon concentrations in December (and to a lesser extent in January and February) do not result in oxidant standard violations because of the much more limited amount and intensity of available sunlight.

The high oxidant levels occurring in summer and fall can also be attributed to stable meteorological conditions which permit the oxidant precursors (hydrocarbons and oxides of nitrogen) to accumulate and reach higher concentrations. Air stagnation is especially common in the fall and winter months. Consequently, pollutant levels are not always indicative of high rates of emissions from pollutant sources.

This in no way implies that emission rates are unimportant, but rather that good air quality management practice dictates the need for careful planning to reduce ambient pollutant concentrations. To reduce oxidant standard violations in Fresno County, the following factors must be considered: (1) emissions of oxidant precursors; (2) temporal (and perhaps spacial) distribution of these emissions; and (3) meteorological parameters including atmospheric stability, intensity of sunlight, and temperature. Only when all of these factors are known can pollution control efforts be most effective. The responsible air pollution control agency is then in a position to decide which specific emissions are most important to regulate during specific times of the day or months of the year.

An inventory of reactive hydrocarbon emissions resulting from pesticide applications, including a temporal distribution of such emissions, is of particular importance to air pollution control efforts in Fresno County. This county is an agricultural area of major importance, and there is a large amount of pesticide usage there. The last ARB-published state-wide emissions

inventory[2] (1973) indicated that the total emission of reactive organic gases from stationary sources in Fresno County was 43.3 tons per day. Of this total, 4.9 tons per day or 11 percent were derived from pesticide applications. Although 4.9 tons per day was only an approximation, it is apparent that pesticides contribute significantly to Fresno County's reactive hydrocarbon pollutant burden and therefore to the County's oxidant problem. With a more accurate and complete inventory of pesticide use and associated emissions in the County, responsible air pollution control officials can develop pesticide use strategies which will minimize reactive hydrocarbon emissions during periods when photochemical oxidants are likely to be formed.

4.2 Environmental Fate of Pesticides--With Emphasis on Atmospheric Occurrence

4.2.1 Introduction

By definition, pesticides are compounds that are toxic to certain members of the biota; their usefulness lies in their abilities to terminate or alter the natural life cycles of certain living organisms which we call pests. It would be ideal if pesticides could be applied just to such pests without contaminating other biota, the soil, the water, and the air or if the applied pesticides could be confined within the pests and degraded or mineralized rapidly into simple materials like carbon dioxide, chloride ion, sulfur, or molecular oxygen after fulfilling their functions. Unfortunately, perfect pesticides and such accurate application techniques are not yet available, and for the time being, the following problems will persist:

- Pesticides are distributed into the biosphere, lithosphere, hydrosphere, and atmosphere during and following applications;
- Pesticides move between the above four components; and

·Although pesticides can be degraded within each of the four components, degradation is not always rapid and complete.

While a vigorous address to the above problems is beyond the scope of this project, an attempt will be made here to discuss the occurrence of pesticides in the atmosphere and some of the environmental factors that can affect such an occurrence.

4.2.2 Introduction of Pesticides into the Atmosphere

The surface of the earth can be divided into two components--the hydrosphere, which consists of 140 million square miles of oceans, lakes, rivers, and ponds, and the lithosphere of 57 million square miles of land. Surrounding the surface--the hydrosphere and the lithosphere--is the atmosphere, a 20-mile-thick layer of various gases. Lastly, all living things together form the biosphere. Except for those originating from a few pesticidal bombs and strips, almost no pesticides are added to the atmosphere intentionally, and while considerable amounts of aquatic herbicides, algaecides, and mosquito control pesticides are added directly to the water, the bulk of the pesticides are aimed at the biota in the lithosphere. The presence of pesticides in the atmosphere results from the failure of sprayed pesticide particulates to settle from the atmosphere and from the transport of pesticides between the four spheres. According to estimates made by Cope[3] and Cowishee,[4] as little as 20 percent of an applied pesticide hits the target with the remaining 80 percent being distributed between the air, the soil, the water, and non-target biota. Freed[5] suggested that only about 50 percent to 70 percent of a sprayed pesticide ultimately finds its way to the soil surface within the target area, and the majority of the rest ends up in the atmosphere due to air currents and volatil-

ization. Spencer et al.[6] indicated that volatilization from plant, water and soil surfaces is a major pathway for loss of applied pesticides. For chlorinated insecticides, loss due to volatilization can range from a few percent to as much as 50 percent.[7, 8] In a more recent study with MCPA, an herbicide used in rice fields, Soderquist[9] reported that almost all of the applied chemical ended up in the atmosphere due to volatilization.

4.2.3 Volatilization Processes

Water. Volatilization of pesticides from water is governed by Henry's Law which describes the partitioning between the two phases. Mackay and Wolkoff[10] indicated that the volatilization rates of pesticides that are completely mixed with water are directly proportional to the pesticides vapor pressures and, at the same time, indirectly proportional to their solubilities. Other variables such as temperature, the pH of water, suspensions of organic matter and soils in water, depth of the water, and the presence of an organic film on the water surface[11] also contribute to the volatilization rate of pesticides from water. With the use of Henry's Law, taking into consideration the variables, equations can be derived to predict the volatilization rates.[10]

Soil. Volatilization of pesticides from soil can be very significant and is greatly dependent on the pesticides vapor pressures which, in turn, can be affected by the interaction between them and the soils. Many reports[12, 13, 14] have indicated that increases in soil water content and water loss were accompanied by greater loss of pesticides through volatilization. This is not due to "codistillation" of pesticides with water but, as pointed out by Spencer,[15]

is a result of displacement of the pesticides from the soil surfaces by water. Spencer demonstrated that vapor density of dieldrin and lindane increased rapidly with soil water content until the amount of water was equivalent to a monomolecular layer on the soil surface; water content beyond that amount had no effect on the vapor densities of the pesticides. Therefore, variables such as molecular structure of the pesticides, the pH of water, pesticide concentration, soil types, and temperature which affect the adsorption of pesticides by soils also govern the rate of their volatilization from soil surfaces. Igue et al.[16] also found that water loss, per se, without being accompanied by an increase in the vapor density of dieldrin did not increase the compound's volatilization.

Crop surface. There is very little information about the vaporization of pesticides from crop surfaces. According to Spencer and Cliath,[17] the initial deposit vaporizes at about the same rate as does the pure material, but subsequent vaporization is severely retarded by factors such as adsorption, penetration into the surface, and partition into the plant waxes and oils.

Most dissipation curves of pesticides from plants show a very sharp decrease of residues right after application followed by a much slower "leveled-off" rate. Frear[18] measured the amount of methoxychlor on alfalfa and found that about 70 percent of the residue dissipated within the first day; it took an additional six days for the remaining 30 percent to disappear. The fast decline in the pesticide concentration on plants right after application is a result of removal by wind, by water deposited on plant surfaces, by vaporization, and by photodecomposition. Thus, it appears that the transfer of pesticides from the biota to the other components in the environment is primarily an immediate and significant process. Since most pesticide sprayings a

carried out on sunny days, the amount of pesticides and their degradation products being transferred into the atmosphere is probably much greater than those remaining in the soil and plants.

4.2.4 Volatilization and Environmental Transformation of Pesticides

As mentioned in the previous sections, the transfer of a pesticide from water and soil to the atmosphere depends heavily on its vapor pressure, solubility, and adsorbability to particulates; therefore, a change in its molecular structure will certainly change its characteristics and subsequently affect its volatilization rate. Although a comprehensive account of all environmental degredation processes will not be discussed here, the following types of reactions and examples can be used for purposes of illustration.

Chemical reactions. Because of the abundance and chemical nature of water in the environment, hydrolysis is perhaps the most frequent and typical chemical reaction a pesticide undergoes in the environment. For example, chlorophenoxyacetic herbicides such as 2,4-D and 2,4,5-T are often applied as esters which can be easily hydrolyzed, especially in alkaline water. Zepp et al.[19] was able to hydrolyze the butoxyethyl ester of 2,4-D in water, which was slightly basic (pH 8.1), obtained from the Withacoochee River in southern Georgia. The transformation from ester to carboxylic acid resulted in an increased solubility of the compound in water and its adsorption to soil surfaces; the volatilization rate was thus reduced. On the other hand, soil water can hydrolyze DMIT (Mylone) and vapam to the very volatile isothiocyanate;[20, 21] the conversion of vapam in a sandy loam was 87 percent within a few hours.

The triazines also undergo hydrolysis in soil water. While the reactions can be catalyzed by organic matter in the soil,[22] they can also be inhibited by montmorillonite.[23]

Photodegradation. Solar ultraviolet light in the range of 290 nm to 450 nm provides enough energy for many types of photochemical reactions. A typical example is the photolysis of 4-CPA (4-chlorophenoxyacetic acid, see Figure 4-3).[24]

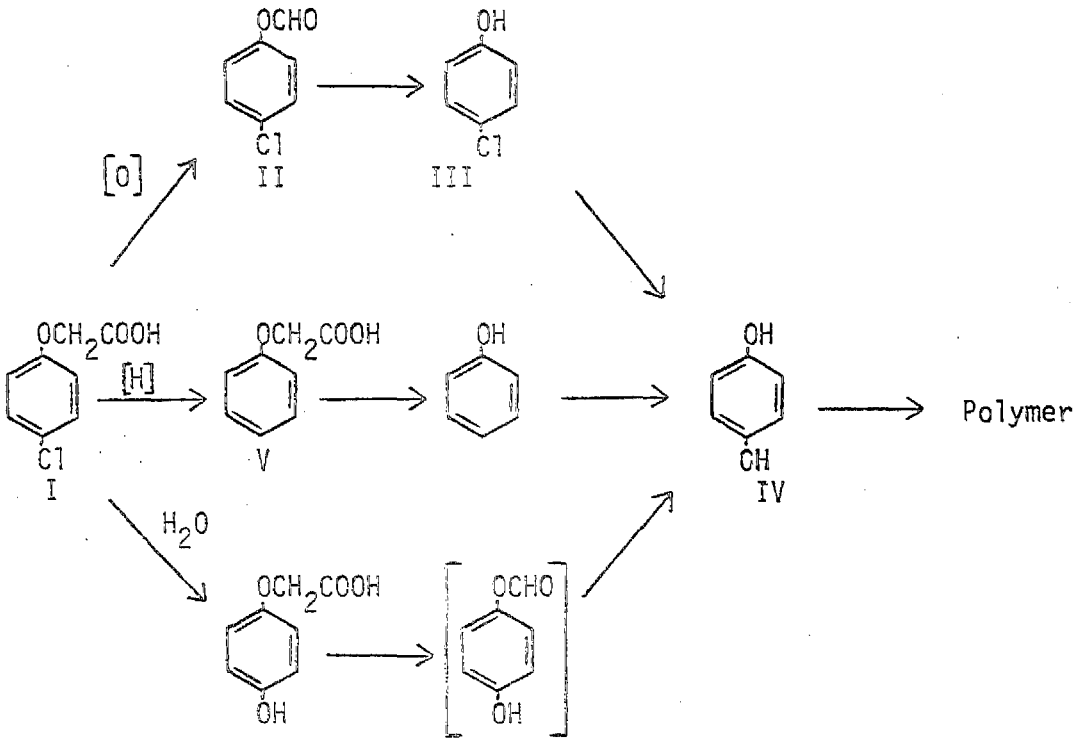


Figure 4-3. Photolysis of (4-Chlorophenoxyacetic Acid) in water.[24]

The formation of the 4-chlorophenyl formate (II) is the result of photooxidation. The replacement of the chlorine by a hydroxyl group is a photonucleophilic reaction which is the most common photodegradation pathway for chlorinated aromatic compounds in water. The reductive dechlorination, which is a replacement process of chlorine by hydrogen, is a major reaction when irradiation is carried out with organic solvents such as methyl alcohol. This dechlorination process may produce end products with different chemical characteristics, and

it may transform a single compound, such as 4-CPA, to products (such as the formate and the phenols) that are more volatile than the parent compound. However, if a complete photodegradation of 4-CPA takes place, a humic acid-type polymer may be formed which can be adsorbed very firmly to the organic matter in the water and on the soil surface. Similar results were also obtained from 2,4-D,[25] 2,4,5-T,[26] MCPA,[9] and pentachlorophenol.[27, 28]

Biological reactions. The resident time of pesticides in the soil together with the large number and varieties of soil microorganisms make microbiodegradation a very important mechanism of pesticide degradation. Similar to the dechlorination process, microbiodegradation induces the formation of products having volatilities which may be quite different from the parent compounds. For example: (a) the degradation of 2,4-D[29] and parathion[30] to phenols and the methylation of pentachlorophenol to anisole[36] result in the formation of very volatile products; (b) the hydroxylation of the aromatic ring in 2,4-D by Asperigillus niger[32, 33] and the reduction of parathion to aminoparathion[34] result in more polar and less volatile compounds.

In summary, many pesticides find their way into the atmosphere as unsettled particulates formed during applications by volatilization from water and soil surfaces and, to a lesser extent, by wind erosion. Many factors such as vapor pressure of the pesticides, their solubility and concentration in water and soil, the pH of water, temperature, the depth of the water, and the types of soil govern the volatilization rates of pesticides. Molecular transformations caused by chemical, photochemical, and biological reactions also affect the transport and persistence of pesticides and their degradation products between and within the atmosphere, the hydrosphere, and the lithosphere.

4.2.5 Removal of Pesticides from the Atmosphere

While spraying and the subsequent volatilization add pesticides to the atmosphere, precipitation and degradation are probably the major processes for removing them from the atmosphere; drifting only transfers pesticides from one locality to another. Cohen and Pinkerton[39] reported the presence of high concentrations of organochlorine hydrocarbons in rainwater. The degradation of pesticides in the atmosphere as a result of thermal and photochemical reactions is conceivable. However, only a few studies on these types of degradation have been conducted such as those reported by Crosby and Moilanen[40] on the photolysis of dieldrin and trifluralin in the vapor phase. Degradation of pesticides in the atmosphere only represents the disappearance of the parent compounds; the total amount of hydrocarbons in the atmosphere is not affected.

Drifting during and after spraying may lead to a movement of chemicals and the rapid dilution of concentrated pesticides in the local atmosphere; it is generally agreed that pesticides move mainly as particulates in the atmosphere. Cohen and Pinkerton[39] reported that dust containing DDT and DDE moved from western Texas to Cincinnati, Ohio. Tarrant and Tatton[41] suggested that a reduction of particulates over London would result in the lowering of DDT levels in the air. Risebrough et al.[42] speculated that windborne contaminants from the major river systems are responsible for the residues in the tropical Atlantic. Movement of pesticides in the atmosphere, together with water transport, has succeeded in complete global contamination by pesticides while even involving such remote areas as the Antarctic snow.[43]

4.3 Photochemical Reactions of Pesticides

Organic compounds used as pesticides for both agricultural and non-agricultural purposes are potential sources of hydrocarbon emissions that may contribute significantly to the formation of photochemical air pollution. Synthetic and nonsynthetic pesticides, acting as any other hydrocarbons (R) in the ambient air, may react with $[O]$ and O_3 in the presence of a third body "M".

$$NO_2 + h\nu \text{ (sunlight)} \rightarrow NO + [O]$$
$$R + [O] \rightarrow R'O\cdot + \text{Other Products}$$
$$[O] + O_2 + M \rightarrow O_3 + M$$
$$R + O_3 \rightarrow R'O\cdot + \text{Other Products}$$
$$O_3 + NO \rightarrow NO_2 + O_2$$

The free radicals ($R'O\cdot$) resulting from reactions between hydrocarbons, O_3 and $[O]$ are very reactive because of their unpaired electrons. By reacting with primary pollutants, other free radicals, and the normal constituents in the air, these free radicals produce a complex mixture commonly referred to as photochemical smog. High concentrations of oxidants such as O_3 and NO_2 will result from these photochemical processes.

Although all hydrocarbons are, to some extent, involved in photochemical smog formation, some hydrocarbons are more likely than others to produce oxidants. The photochemical reactivities of all organic pesticides can be categorized according to the ARB three-tier reactivity classification (see Appendix A). This scheme was designed to classify organic compounds based on their chemical potential to react with other constituents in the ambient air and cuase the formation of oxidants. Table 4-1 lists the photochemical reactivities of the top ten organic pesticide ingredients used in Fresno

TABLE 4-1

Structures, Formulas, and Photochemical Reactivities of the Top Ten Organic Pesticide Ingredients Applied in Fresno County in 1976.

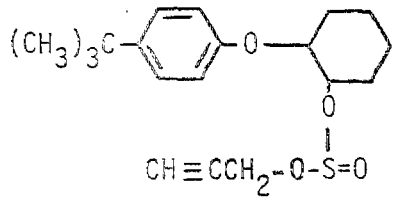
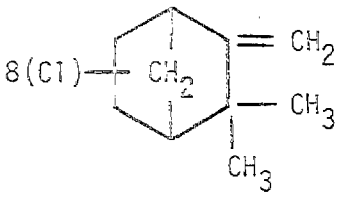
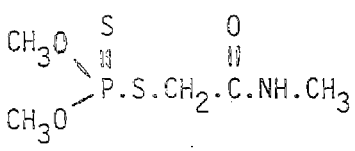
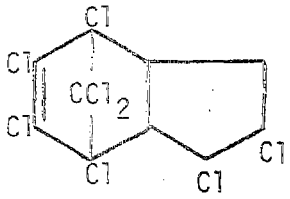
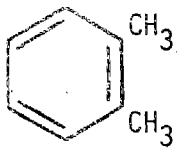
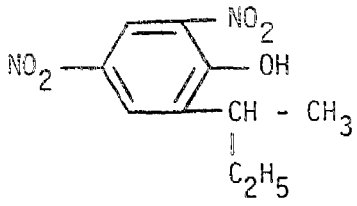
Pesticide Ingredient	Structural Formula	Compound Type	Reactivity
Omite-R		All olefinic hydrocarbons	III
Methyl Bromide	CH_3Br	Partially halogenated paraffins	I
DEF	$(C_4H_9S)_3PO$	C_3+ paraffins	II
Toxaphene		All olefinic hydrocarbons	III
Folex-R	$(C_4H_9S)_3P$	C_3+ paraffins	II
Dimethoate		N-alkyl Ketones	II
Chlordane		Partially halogenated Olefins	III

TABLE 4-1 (continued)

Pesticide Ingredient	Structural Formula	Compound Type	Reactivity
DBCP	$CH_2Br - CHBr - CH_2Cl$	Partially halogenated paraffins	I
Xylene		All other aromatic hydrocarbons	III
DNBP		All other aromatic hydrocarbons	III

County in 1976. Class II and III organics are referred to as Reactive Organic Gas (ROG), and the sum of all three classes is referred to as Total Organic Gas (TOG).

Ozone, atomic oxygen, and even molecular oxygen may react with photochemically-derived free radicals or photoexcited states of pesticides to form peroxides, epoxides, aldehydes, and ketones. Pesticides containing aromatic moieties, double bonds, and heteroatoms with non-bonding electrons (e.g., oxygen, nitrogen, sulfur) are particularly well suited for photochemical reactions. The by-products formed in the photochemical reaction processes may themselves cause more severe problems than are suggested by the photochemical reactivities of the specific pesticides. Some of these by-products may be less desirable than the parent compounds; they may be more toxic and/or more persistent. The formation of paraoxon from parathion,[35] photodieldrin from dieldrin,[36] methyl isocyanate from carbaryl[37] are some examples.

Simple halogenated hydrocarbons have long been reported to have the potential to deplete the ozone in the stratosphere.[38] Ozone is the component of the stratosphere that absorbs most of the ultraviolet light in solar radiation before it reaches the earth's surface. Depletion of the stratospheric ozone is believed to have serious consequences on human health by increasing the incidence of skin cancer resulting from the increased exposure to ultraviolet radiation. Halogenated compounds can photodecompose to yield free radical halogens and oxyhalogens which reduce the ozone concentration in the stratosphere if they reach there. Since heavier, less volatile halogenated hydrocarbons cannot escape from the troposphere, they should not be a threat to the ozone layer. Lighter, more volatile halogenated hydrocarbons, su

as methyl bromide and ethylene dichloride, are photochemically less reactive; therefore, they have a much longer lifetime, and more of them will be transported to the stratosphere. Once reaching the stratosphere, methyl bromide rapidly photolyzes to form methyl and bromine free radicals. Since large amounts of methyl bromide and ethylene dichloride are applied as fumigants, more attention should be given to research in this area.

4.4 Pesticide Regulations

California has developed a detailed pesticide regulatory system which is administered by the state and, at the local level, by the counties. The state agency responsible for overseeing the California Agricultural Pesticide Regulatory System is the Department of Food and Agriculture (DFA). Local implementation of the pesticide regulatory system is the responsibility of each County Agricultural Commissioner (hereafter referred to as "Commissioner"). Under the California Food and Agricultural Code, joint responsibility for the enforcement of many pesticide laws and regulations is shared by the Commissioners and the DFA Director. The Director himself is responsible for furnishing the counties with assistance in planning and in developing county enforcement programs.

Both the state and the U.S. EPA require the registration of any pesticide or "economic poison" prior to its sale by the manufacturer. Federal registration is required either concurrent with or prior to registration in California. In this state, a manufacturer, importer, or dealer must obtain a license and register each individual pesticide annually with the DFA. Registration involves two primary steps: evaluation and labeling. Each pesticide is eval-

uated to determine its performance, its effects on the environment, and its effects on public health and safety. Registration is refused or cancelled if it is determined: (a) that the pesticide has serious adverse environmental impacts; (b) that its advantages do not outweigh its disadvantages to the public and the environment; (c) that reasonable alternatives exist which are less environmentally deleterious; (d) that there are detrimental effects to vegetation (except weeds) , to domestic animals or to the public health and safety even when properly used; (e) that it is generally ineffective for its intended purpose, or (f) that the registrant or his agent provided false or misleading information.[b]

Labeling of a pesticide controls its use. The EPA, under the Federal Insecticide, Fungicide and Rodenticide Act as amended in 1972 (FIFRA), specifies the information which must be included on labels: a statement of ingredients; a caution or warning statement which if complied with will prevent harm to humans, domestic animals, useful plants and the environment; directions for use; and the name and address of the producer, registrant, or person for whom the manufacturer has produced the pesticide.[c] The law also prohibits the use of a pesticide in conflict with labeling unless authorized by the Director or Commission.

Although there is some overlap between state and EPA registration programs, the state program still fills a need. First, the EPA registration program has been halted since 1975 while that agency develops a proper

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[b]California Food and Agriculture Code, Sec. 12825.

[c]40 CFR 162.10.

approach to validating data. Second, California has some need to apply different restrictions than EPA (allowed under FIFRA as amended if the state does not allow any sale or use prohibited by EPA) in accordance with special local needs or problems. Finally, the California program utilizes the Pesticide Reporting System under which pesticide use information is compiled. Data on all restricted pesticide use and on all pesticides applied by commercial applicators is collected for use by the government, universities, and private businesses. A summary of this data, the Pesticide Use Report, is published quarterly and annually by the DFA, and includes the amount of pesticides used by crop and county.

However, some degree of control beyond registration is also required to assure proper use of pesticides. Therefore, the Director has established a list of closely-controlled or restricted substances. All of these restricted pesticides have the potential of endangering public health, worker health, crops, domestic animals, or the environment. The Director may "adopt regulations which will prescribe the time when, and the conditions under which, a restricted material may be used or processed in different areas of the state."[d] A list has also been established for "exempt," or non-restricted pesticides.

Many pesticide uses are also conditioned upon obtaining a permit. The County Agricultural Commission has the primary responsibility for administering and enforcing the permit system. The use of any restricted pesticide requires a permit, as does the application of any pesticide by a commercial

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[d]Ref (1), Secs. 14005-14006.

applicator.[e] Permits may be issued subject to a wide variety of conditions, including area, time, concentration or quantity, specified safety-related conditions, or any other limitation or condition which the Director or Commissioner feels is necessary. The Commissioner may refuse to grant a permit if he finds that the pesticide has excessive detrimental effects.

Applicants for permits are interviewed orally by the County Agricultural Commissioner before permits are granted, and the permittees are subject to inspection and surveillance when restricted pesticides are applied. The Commission may also inspect the property to which the pesticide is to be applied and the applicator's equipment and facilities to determine whether a permit should be granted or additional conditions should be applied. In the case of commercial applicators, the Commissioner has the option to issue a seasonal permit which enables the applicator to apply specific pesticides throughout the county for a given time period.

There are numerous other regulations and restrictions which apply to all pesticides and pesticide users. These regulations, found in the California Administrative Code, relate to the condition of application equipment; application techniques; and storage, transportation, and handling of pesticides and pesticide containers. Special care must be taken by the applicator not to damage or endanger property or persons not involved in the application process. If the pesticides are known to be harmful to bees, beekeepers must be advised 48 hours in advance of applications to blossoming plants in which bees are working. The California Food and Agriculture Code

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[e]Under the regulations applicable in 1976.

(Secs. 12980-12982) also includes regulations which require employers to provide safe conditions for agricultural workers; specific safety precautions are stipulated.

Enforcement of pesticide regulations is the responsibility of the Agricultural Commissioners. Commissioners and their staffs perform thousands of inspections of equipment, facilities, and application processes each year. Enforcement actions vary from informal warning to more stringent measures such as revocation of permits or registrations and the filing of criminal complaints.

The Director is responsible for the licensing program in California. Licenses are required for three levels of pesticide-related activity: recommendation, sale, and application. Any person seeking a license must provide the Director with personal information bearing on his financial and personal responsibility, and must pass a written test.

The first level of pesticide-related activity, recommendation, includes pest control advisors. These advisors provide guidance to the farmer seeking help with specific pest control problems. By law they must provide their advice in writing and include specific items of information, including necessary warning and precautions.

The second level of activity, sale, includes pesticide manufacturers, distributors, and retailers. These dealers must keep, for one year, a record of all pesticides sold or delivered. When a restricted pesticide is sold, the dealer must verify the buyer's restricted materials permit. The Commission may audit a dealer's records to determine compliance with pesticide sale requirements.

The last level of activity, application, is subject to the closest control. In addition to obtaining a state license, pesticide operators must register with the Commissioner in any county where they operate. A license is granted only if the operator meets certain criteria, including possession of qualified staff, proper equipment, and an adequate record system. The operator must also comply with safety requirements. The operator must maintain, for a period of three years, a record of specified information pertaining to each pesticide application. A license is not required if an individual wishes to apply pesticides to his own property or that of his neighbors (if not done "under hire").

The penalties connected with improper or illegal activities by a licensed pest control advisor, dealer, or applicator include prosecution, revocation or suspension of his license.

In summary, California's pesticide regulatory system is well-structured. It receives central direction under state law but is administered principally at the county level. California's system also provides for recordkeeping at state and local levels enabling special studies such as this emission inventory to be conducted more accurately and efficiently.

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5.0 PESTICIDE APPLICATION INVENTORY

5.1 Introduction

This section presents the methodology for and findings of the pesticide application inventory. Since a major part of the inventory methodology involves the identification of pesticide ingredients, a brief description of pesticide formulations is in order.

Most pesticide products are made up of two components: the active ingredients and the inert materials. The active ingredient component of a product may include one or more chemical compounds with the major chemical ingredient often referred to as the parent compound. The active ingredients are usually identified on the label of each product. The composition of inert materials, however, is confidential, and they are usually collectively labeled as "inert materials" with the percentage of composition identified.

Pesticide products are sold in different forms. They may be sold as technical active ingredients or in formulated packages. Most technical active ingredients cannot be used for control of pests without undergoing formulation processing. "Formulation" is the process by which technical active ingredients are made ready to be used by mixing liquid or dry diluents, grinding, and/or by the addition of emulsifiers, stabilizers, and other formulation adjuvants.

In California all pesticide products sold on the market fall under one of sixteen formulation types. Table 5-1 presents these formulation types. For the purpose of this project, the primary interest is organics. Of all the types applied in Fresno County in 1976, only three types (formulation codes 4, 9, and 10) are identified as having significant organic inert

TABLE 5-1

List of Pesticide Formulation Types Used in California.

Formulation Code	Formulation	Remarks
1	Bait	Product that a pest consumes as food, usually labeled "bait."
2	Coatings	Products used on the outside of an object, such as paints, preservatives, or animal smears.
3	Dust	Finely divided solid applied "dry," usually labeled "dust."
4	Emulsifiable Concentrate	Liquid product mixed with water to form an emulsion before application.
5	Fertilizer	Dry product used as a fertilizer as well as an insecticide.
6	Gels, Creams, Pastes, Waxes	---
7	Granular	Solid products in granular, tablet, crystaline, or other similar form.
8	Impregnated Materials	Products impregnated with an insecticide, such as dog collars and pest strips.
9	Liquid	Liquid phase materials not coded as anything else.
10	Oil	Products containing 98% or more petroleum derivatives as active ingredients.
11	Pressurized Dust	Spray powder, "aerosol" type.
12	Pressurized Fumigant	Pressurized gas, such as methyl bromide, chloropicrin, etc.
13	Self-generating Smokes	Smoke bombs, mosquito coils, etc.
14	Pressurized Sprays	"Aerosol" type sprays.
15	Wettable Powder	Finely divided solid for application as a dust or a suspension in water. Does not dissolve.
16	Soluble Powder	Finely divided solid which dissolves in water for application.

Source: California Department of Food and Agriculture.

ingredients. Since products in formulation code 10 contain 98 percent or more petroleum derivatives as active ingredients, only the inert materials in formulation 4 and 9 require elucidation.

5.2 Application Inventory Methodology

5.2.1 Overview

An overview of the application inventory is presented in Figure 5-1. Reported synthetic and inorganic pesticide application data were obtained from the Pesticide Use Report (PUR) for Fresno County. The synthetic pesticides were grouped according to the classification of the parent compounds (restricted or nonrestricted). The quantities of parent compounds, active ingredients, and inert ingredients in formulations 4 and 9 were then calculated separately and modified according to the grouping classification. The quantities in the restricted group were modified to account for reporting errors and improper applications and to account for unrecorded applications based upon DFA information. Attempts were made to assess the illegal application of pesticides, but such data were not available. The quantities in the unrestricted group were subjected to the same modifications as the restricted group plus an additional modification for unreported applications based upon survey data and assumed use ratio calculations. Likewise, the restricted and nonrestricted inorganic pesticides were grouped according to whether they were restricted or nonrestricted and modified as were the synthetics. The combined result of the modified restricted and nonrestricted pesticide application data was a synthetic and inorganic pesticide application inventory. To this synthetic and inorganic pesticide application inventory was added a nonsynthetic pesticide (oils) inventory based upon

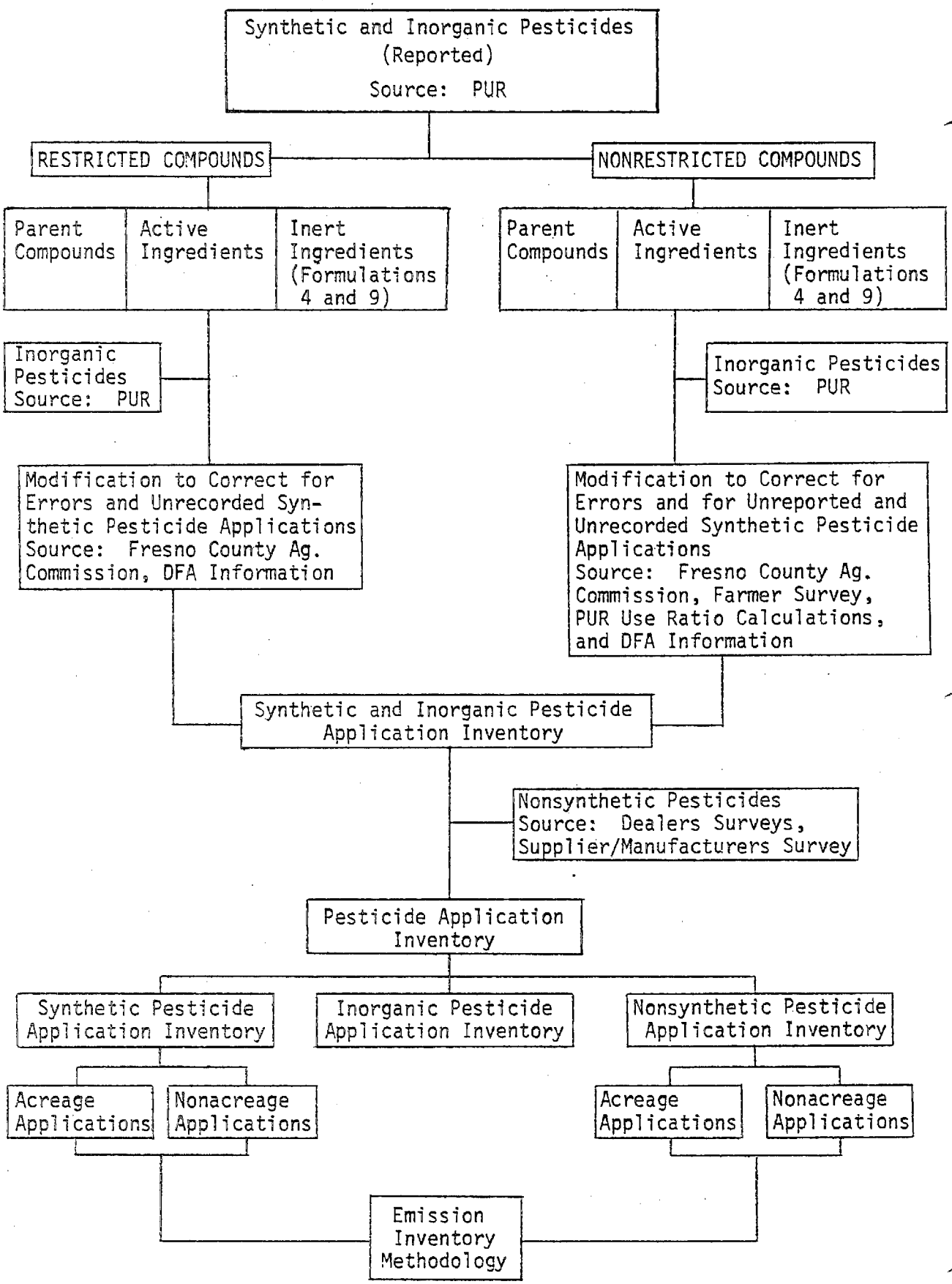

Figure 5-1. Application Inventory Overview.

surveys of dealers and suppliers/manufacturers.

To determine the actual emissions resulting from the pesticide applications, the synthetic and nonsynthetic pesticide applications (inorganics were excluded) were grouped according to "acreage" and "nonacreage" (e.g., animals, buildings) applications. It was assumed that all pesticides used in agriculture were "acreage" applications, and all nonagricultural applications were "nonacreage" applications. At this point, the emission inventory methodology was applied as described in Chapter 6. An application inventory was calculated for each month of 1976.

5.2.2 Synthetic and Inorganic Pesticide Application Inventory

For the purposes of the application inventory, the synthetic and inorganic pesticide applications were classified as either reported or unreported. Reported applications were those which were accounted for in the PUR. By law, all restricted pesticides applications by growers and all applications by commercial applicators (whether restricted or nonrestricted) had to be reported in 1976.

Reported pesticide application data were obtained from a data tape of the Environmental Toxicology Library at UC Davis. The UC Davis' data outputs included the amount of pesticides used recorded by registration number and by month. Two sets of data were obtained: one indicating acreage for the pesticides applied on acreage and the other showing amounts of those pesticides not applied on acreage. The Master Label File obtained from the California Department of Food and Agriculture (DFA) lists the parent compounds and active ingredients in each pesticide according to its registration number. With the combined use of the UC Davis' data outputs

and the Master Label File, a monthly application inventory of all individual pesticide ingredients, except inert ingredients, was compiled. Of the 965 pesticide products reported to be used in Fresno County in 1976, only those pesticides with annual usages of 100 pounds or more--about 150 chemicals--were included in this inventory. These 150 chemicals account for approximately 99.98 percent of all reported applications by weight. For classification purposes, all pesticides in this inventory were grouped according to the pesticide group list shown in Appendix C.

As stated earlier, only the inert ingredients in formulation codes 4 and 9 are important to this inventory study, since these are the only formulations which may contain significant quantities of organic inert ingredients.[a] Since the compositions of the inert ingredients in pesticides are generally considered to be confidential by the pesticide manufacturers, special permission to obtain such information was necessary. A letter, signed by Dr. John Holmes of the Air Resources Board, was sent to manufacturers of formulation 4 and formulation 9 pesticides requesting that the manufacturers grant Eureka Laboratories, Inc. access to the information on the inert ingredient composition. This information is contained in the files of the Department of Food and Agriculture (DFA). Permission for access to DFA files was granted by 24 of the 72 companies that were contacted. These 24 companies manufacture 39 formulation code 4 pesticides and 44 code 9 pesticides. As shown in Table 5-2, the organic and inorganic inert ingredients in the 39 code 4 and 44 code 9 pesticides were assumed to be

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[a]Hydrocarbons are used as propellants for some formulation code 11, 12, and 14 pesticides. However, pesticides using such propellants are generally for home and garden use only. Since home and garden pesticides comprised such a small proportion of overall pesticide applications (see Section 5.4), the quantity of hydrocarbon propellants released was assumed to be insignificant.

representative of all code 4 and code 9 pesticides, respectively, applied in Fresno County in 1976. Consequently, the inventory of the total organic inert ingredients of all reported code 4 and 9 pesticides applications in Fresno County in 1976 was calculated by extrapolating the quantities of these ingredients found in the 39 code 4 pesticides and the 44 code 9 pesticides.

Synthetic and inorganic pesticides were grouped as either restricted or nonrestricted. The grouping of each pesticide was based upon the classification (restricted or nonrestricted) of the parent compound. The restricted and nonrestricted chemicals are identified in Appendix C. This also means that minor active ingredients and inert ingredients in any particular pesticide were grouped in the same category as the parent compound.[b] The purpose of this grouping was to assure that the proper modification or correction factor was applied to the appropriate pesticide application data. Table 5-2 indicates correction factors of 1.377 and 1.387 applied to the extrapolated inert ingredient inventory (for formulation codes 4 and 9, respectively). The derivation of these factors will be described later in this chapter.

All reported pesticide usage in Fresno County in 1976 was subject to a small percentage of error. The staff of the Fresno County Agricultural Commission indicated that approximately 0.5 percent of all pesticide use application forms were incomplete, illegible, or otherwise improperly filled out, and could not be corrected by follow-up action by the Commission. The staff also estimated that "improper applications" (defined as overspray during applications and product use in conflict with labeling) amounted to

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[b] In some instances, nonrestricted minor active ingredients or inert ingredients were classified for calculation purposes as restricted because the parent compounds were restricted. Eleven chemicals fell into this "crossover" situation, and they are identified in Appendix C.

TABLE 5-2

Summary Calculations of Inert Ingredients
for Pesticide Products Used in Fresno County in 1976

Items	Pesticide Products with Formulation Code 4	Pesticide Products with Formulation Code 9
A. No. of Products Checked	39	44
B. Total Weight of Products Checked (lbs.)	572,947	278,916
C. Inert Ingredients of Product Checked (lbs.)	154,961	84,815
D. Organic Inert Ingredients (lbs.)	149,379 (96.4%)	19,956 (23.5%)
E. Inorganic Inert Ingredients (lbs.)	5,582 (3.6%)	64,859 (76.5%)
F. Active Ingredients of Product Checked (B - C)	417,986	194,101
G. Active Ingredients Applied (PUR) (lbs.)	1,533,296	1,971,244
H. Percentage of Products Checked by Weight (F/G x 100)	27.26%	9.85%
I. Quantity of Reported Inert Organic (D/H) (lbs.)	547,979	202,600
J. Quantity of Reported Inert Inorganic (E/H)	20,477	658,467
K. Adjusted Total Reported and Unreported Inert Organics (lbs.) (Code 4 = I x 1.381; Code 9 = I x 1.377)[a]	756,759	278,980

[a]See page 52 for the derivation of these factors.

less than 1 percent of the total reported use. Thus, it was determined that approximately 99 percent of "reported" pesticide usage was reflected in the PUR for Fresno County in 1976. For calculation purposes in this inventory, the correction factor was 0.99. This correction factor does not account for any pesticide application which by regulation required reporting to the agricultural commissioner but was not reported.

The next step in the application inventory was to correct for all unreported and unrecorded synthetic and inorganic pesticide applications. The determination of unreported applications was originally intended to be accomplished exclusively through a survey of farmers and pesticide dealers in Fresno County. Explanatory letters and questionnaires developed with assistance from the ARB and the Fresno County Agricultural Commission were mailed to 221 farmers and 124 distributors. Copies of these questionnaires are shown in Appendix B. The 221 farmers were selected at random by the Fresno County Agricultural Commission. Few of the farmers and only about 20 percent of the dealers responded to this survey. Consequently, a follow-up survey of 251 additional farmers (randomly selected by the Commission) was conducted. Of the total 472 farmers surveyed, only 80 responded. These 80 farmers indicated that 53 percent of all pesticides they used were reported.

Because of the low respons of farmers and dealers, it was suspected that the data obtained in these surveys might not be completely representative of unreported pesticide use. Consequently, a different approach was selected. Based on its field experience, the staff of the Fresno County Agriculture Commission suggested that in past years (including 1976) individual growers tended either to apply all pesticides themselves (whether the pesticides were restricted or unrestricted), or to hire all pesticide application

work out to commercial applicators. As a consequence, the relationship between quantities of pesticides applied by growers and commercial applicators may be expressed as:

$$\frac{\text{(a) Grower, nonrestricted}}{\text{(b) Grower, restricted}} = \frac{\text{(c) Commercial, nonrestricted}}{\text{(d) Commercial, restricted}}$$

$$\text{Reported} = (b) + (c) + (d)$$

$$\text{Unreported} = (a) = (b) \times \frac{(c)}{(d)}$$

This relationship may be used to determine the total nonrestricted synthetic and inorganic pesticide use by the development of a correction factor to be applied to reported nonrestricted pesticide use. For this inventory, the correction factor was calculated based on data obtained from over 3400 original pesticide use permits from Fresno County. These permits represented all reported pesticide applications in the following township-ranges during the months of January-February, April, July, and October of 1976:

West Side		East Side	
Firebaugh	12-13	Clovis	12-21
Mendota	14-14	Sanger	14-22
San Joaquin	15-16	Selma	16-22
Five Points	16-17	Orange Cove	15-24
Coalinga	20-13	Caruthers	16-19

The Fresno County Agricultural Commission staff recommended these township-ranges as a representative cross-section of Fresno County's agricultural areas. The staff also recommended these months as "busy months," representative of pesticide applications throughout the year.

The data obtained from each of the 3400+ permits included the pesticide's name and/or registration number, total pounds applied, the crop, and whether

the applicator was commercial or the grower. Once the pesticides applied were classified as restricted or nonrestricted, the following summary was developed:

From the information in Table 5-3, the ratio of reported synthetic and inorganic pesticide use to total synthetic and inorganic pesticide use was calculated. Using the equation presented earlier,

$$\frac{\text{(a) Grower, nonrestricted}}{\text{(b) Grower, restricted}} = \frac{\text{(c) Commercial, nonrestricted}}{\text{(d) Commercial, restricted}}$$

the quantity of nonrestricted, grower-applied (unreported synthetic and inorganic) pesticides was calculated as:

$$(a) = (b) \times \frac{(c)}{(d)} = 55{,}384 \times \frac{687{,}331}{185{,}420}$$

$$= 205{,}278 \text{ lbs.}$$

Also, it is evident that,

$$\frac{(a)}{(c)} = \frac{(b)}{(d)}$$

$$\frac{(a)}{(c)} = \frac{205{,}278}{687{,}331} = 0.2986, \text{ or approximately } 0.3$$

Since (a) = 0.3 x (c), the total nonrestricted pesticide use, (a) + (c), would equal 1.3 x (c).

Therefore, the correction factor of 1.3 should be applied to all nonrestricted products in order to include the grower nonrestricted applications in the inventory.

From the data obtained from 3400+ application permits, a list of the restricted and nonrestricted pesticide applications for several crops is

TABLE 5-3

Pesticide Use Report Totals of Synthetic Pesticides Used in Selected Months and Selected Areas of Fresno County[a] (Petroleum Oil Excluded)

	Pesticide Applicator and Inventory		
Month	GA-R (lbs.)	CA-NR (lbs.)	CA-R (lbs.)
Jan-Feb	9,042	31,038	11,648
April	23,524	24,287	12,625
July	22,734	196,674	130,116
October	84	435,332	31,031
TOTAL	55,384	687,331	185,420

GA-R = Restricted pesticide applied by grower applicator
CA-NR = Nonrestricted pesticide applied by commercial application
CA-R = Restricted pesticide applied by commercial applicator

[a]Based upon 3400+ pesticide use application forms

shown in Table 5-4. Also shown in Table 5-4 is the factor by which the reported commercial nonrestricted pounds should be multiplied to obtain an estimate of the total nonrestricted pesticide applied for the crops shown. The adjustment factor for all crops (1.30) is the average derived from the poundage applied to all crops included in the 3400 application permits. Table 5-4 presents only those crops that had the most poundage.

The correction for unrecorded pesticide applications was obtained from information supplied by the DFA.[1] Unrecorded applications were applications for which permits were issued, but these permits were incorrectly filled out. As a consequence, the DFA rejected the permit forms without entering the relevant data on data tapes or reporting the data in the PUR. Permit form data are rejected by the DFA for any of 24 possible errors. Examples of such errors include invalid county numbers, invalid or missing township or range numbers, and unit of measure errors.

A summary of PUR rejects due to errors for Fresno County in 1977 is shown in Table 5-5. This table consists of rejects for a period of twenty-five weeks in January and June through December, 1977. The average rate of rejection for all pesticide use permits in that period was 10.4 percent. It was assumed for purposes of this study that the rejection rate for 1977 in Fresno County was essentially the same as for the entire year of 1976. In addition, it was assumed that the proportion of rejected pesticide use permits was equivalent to the proportion of the actual pounds of synthetic pesticides applied in Fresno County which was unrecorded in the PUR. Based on these assumptions, the data which appear in the PUR for 1976 Fresno County pesticide applications represent 1 - 0.104, or 0.896 of the data which would have been reported had there been no permit errors.

TABLE 5-4

Pesticide Use for Selected Crops and Factors for Estimate of Nonrestricted Organic Pesticides.[a]

Crop	GA-R (lbs.)	CA-NR (lbs.)	CA-R (lbs.)	Estimated Pounds Unreported	Factor for Non-restricted Total[b]
All Crops	55,384	687,331	185,420	205,278	1.30
Almond	236	4,182	406	2,431	1.58
Cotton	14,812	124,154	35,356	51,990	1.419
Grapes	22,555	37,944	13,230	64,733	2.71[c]
Orange	4,767	9,655	6,421	7,150	1.74
Nectarine	1,023	6,962	1,098	6,486	1.93
Plum	332	2,561	1,795	474	1.185
Peach	1,220	4,338	373	3,989	1.920
Tomato	135	15,347	5,965	347	1.023

GA-R = Restricted pesticide applied by grower applicator
CA-NR = Nonrestricted pesticide applied by commercial applicator
CA-R = Restricted pesticide applied by commercial applicator

[a]Based on 3400+ pesticide use application forms from selected months and areas of Fresno County.

[b]The pounds under (CA-NR) multiplied by this factor gives the estimated total nonrestricted pesticide applied.

[c]This correction factor may lead to lower than actual unreported poundage due to grower application of an unusually high percentage of the total sulfur dust applied. Mr. L. Peter Christensen, the viticulture farm advisor for Fresno County, estimated that 95 percent of the sulfur dust used on grapes is applied by the growers and is unreported.

TABLE 5-5

Summary of Pesticide Use Report Rejects Due to Errors for Fresno County in 1977.[1]

Use Report	Use			
	Agricultural	Structural	Governmental	Total
Total Recorded	32,347	529	698	33,574
Number of Errors	3,247	163	92	3,502
$\frac{\text{Errors}}{\text{Recorded}} \times 100\%$	10.04	30.81	13.18	10.43

After combining the correction for unrecorded and improper pesticide applications, a resulting figure of 0.896 x 0.99 or 0.887 was calculated. The inverse of this figure, 1.13, is the factor which must be applied to all reported pesticide application data, restricted and unrestricted.

In summary, the correction factor for restricted synthetic and inorganic pesticides is 1.13, which includes the factors for improper and unrecorded applications. The correction factor for unrestricted synthetic and inorganic pesticides is 1.13 x 1.3 or 1.47, which includes the factors for improper and uncorrected applications, plus the factor for unreported applications. These correction factors, 1.13 and 1.47, were applied to all reported restricted and reported nonrestricted synthetic and inorganic pesticide applications, respectively, to calculate the total synthetic and inorganic pesticide applications reported in this inventory.

The restricted and unrestricted pesticide correction factors were also applied to inert organic ingredients although in a composite form as shown in line K of Table 5-2. These composite factors were developed in the following manner. First, the formulation code 4 and 9 data obtained from the PUR were broken down into four classes: 4-acreage applications; 4-nonacreage applications; 9-acreage applications; and 9-nonacreage applications. Next, factors were developed for each of these classes weighted according to the proportion of restricted and nonrestricted chemicals in each class. Hence,

ΣR = Summation of restricted chemicals (lbs.)

ΣNR = Summation of nonrestricted chemicals (lbs.)

$$\frac{1.13\Sigma R_1 + 1.47\Sigma NR_1}{\Sigma R_1 + \Sigma NR_1} = \underline{1.3806} \qquad \text{(Formulation 4-acreage)}$$

$$\frac{1.13\Sigma R_2 + 1.47\Sigma NR_2}{\Sigma R_2 + \Sigma R_2} = \underline{1.3967} \quad \text{(Formulation 4-nonacreage)}$$

$$\frac{1.13\Sigma R_3 + 1.47\Sigma R_3}{\Sigma R_3 + \Sigma R_3} = \underline{1.3730} \quad \text{(Formulation 9-acreage)}$$

$$\frac{1.13\Sigma R_4 + 1.47\Sigma R_4}{\Sigma R_4 + \Sigma R_4} = \underline{1.4463} \quad \text{(Formulation 9-nonacreage)}$$

Finally, one composite correction factor was developed for the formulation 4 pesticide products and another was developed for the formulation 9 pesticide products. For the formulation 4 products, this was accomplished by calculating the average of the two formulation 4 factors determined earlier (1.3806 and 1.3967) weighted according to the proportion of acreage and nonacreage applications for that formulation code. The composite factor for the formulation 9 products was calculated in a similar manner. These composite factors equal 1.381 and 1.377 for formulation codes 4 and 9, respectively.

The monthly distribution of the inert organic ingredient applications was determined from the PUR data. For each of the four classes of formulation code 4 and 9 data mentioned previously, the monthly application data reported in the PUR were corrected by the four weighted factors (1.3806, 1.3967, 1.3730, and 1.4463) described above. These corrected PUR data are shown in Tables D-4 through D-7 in Appendix D.

There are eleven other chemicals which are nonrestricted, but some portion of each was applied as an active ingredient in a restricted product and should be weighted the same as restricted chemicals. Another portion of these chemicals was applied in nonrestricted products. Since only one application poundage appears in the PUR for each chemical, this poundage was adjusted using a composite correction factor weighted according to the amounts applied as restricted and nonrestricted products. These factors were derived in the same manner as those for inert organic ingredients.

The correction factors for these chemicals are as follow:

Chemicals	Correction Factor
Sulfur	1.44
Naled	1.30
Botran-R	1.43
PCNB	1.13
Tetrazole-R	1.13
Borax	1.13
Aromatic Petroleum Solvent	1.18
Petroleum Distillates	1.13
Petroleum Hydrocarbon	1.37
Xylene	1.13
Xylene-Range Aromatic Solvent	1.13

5.2.3 Nonsynthetic Pesticides

Nonsynthetic pesticide products include the following seven classes of materials: aromatic petroleum solvents, petroleum oil (unclassified), petroleum hydrocarbons, petroleum distillate, mineral oil, petroleum distillate aromatic, and xylene including xylene-range aromatic solvents. The nonsynthetic pesticide applications in Fresno County reported for 1976 in the PUR totaled 1,043,249 lbs. This figure includes 521,539 lbs. of pesticides with formulation code 10 ("pure oils") and 521,710 lbs. of nonsynthetics used as active ingredients in other pesticides that were reported applied in the PUR.

There are 124 pesticide distributor/dealers registered with the Fresno County Agricultural Commission. A survey letter was mailed to each of them soliciting information on all pesticide sales to Fresno County users. Of the 124 distributor/dealers, approximately one-fourth responded. The information pertaining to nonsynthetic pesticides obtained from this survey ("1st survey") is summarized in Table 5-6. In an effort to obtain more information specific to nonsynthetic pesticides, a second series of survey

TABLE 5-6

Responses to Surveys on Nonsynthetic Pesticides

Respondents	Oil Type	Reported Sales (gal.) 1st Survey Total Sales	1st Survey % to Fresno Co.	2nd Survey Total Sales	2nd Survey % to Fresno Co.	Amt. Applied in Fresno Co.
1. Agri. Business Enterprises	Omni Supreme	675	100%	---	---	675
	Superior Oil	340	100%	340	100%	340
	Maxipreme	---	---	30	100%	30
2. Brea Agri. Service, Inc.	Weed Oil	3292	60%	---	---	1975
3. California Fresno Oil Co.	Weed Oil	19489	81%	---	---	15786
4. Currie Bros., Inc.	Weed Oil	35000	95%	47617	60%	33250
5. Mortin Oil Co.	Arco Weed Killer A	56243	90%	56243	100%	50619
6. Otten Oil	Weed Oil	8000	100%	16000	100%	16000
7. Oxchem Reedley	Oxy Super 94 Oil	600	4.9%	---	---	29
8. Panoche Chemical & Supply	Weed Oil	36146	100%	---	---	36146
9. Red Triangle Supply	Weed Oil	14299	20%	14000	60%	8400
10. Robert L. Vernon	Weed Oil	24049	100%	---	---	24049
11. Western Farm Service	Weed Oil	86200	100%	---	---	86200

TABLE 5-6 (continued)

Respondents	Oil Type	Reported Sales (gal.) 1st Survey Total Sales	1st Survey % to Fresno Co.	2nd Survey Total Sales	2nd Survey % to Fresno Co.	Amt. Applied in Fresno Co.
12. Leman Agri. Chem.	Super 94	---	---	210	100%	210
13. Vingro Agri. Enterprises	Volck Supreme	---	---	500	100%	500
14. Selma	Volck Supreme	---	---	2216	99%	2194
15. Chevron, U.S.A. [a]	Weed Oil					
Sales to following dealers/end users:						
Telles Ranch		---	---	120617	100%	120617
Giffen, Price and Assoc.		---	---	40814	100%	40814
Peck, Sumur Ranch		---	---	6740	100%	6740
Rusconi Farms		---	---	20286	100%	20286
Ketscher Div.		---	---	7000	100%	7000
R. V. Jensen [b]		---	---	13227	100%	13227
Great Western		---	---	417	100%	417
Consolidated Milling		---	---	55	100%	55
Beach, S. C.		---	---	474	100%	474
City of Clovis		---	---	54	100%	54
16. Keen Petr. Co. [a]						
Sales to following dealers/end users:						
Nicoletti Oil [b]	Weed Oil	---	---	60983	Assume 100%	60983
Tom Ward	Weed Oil #40	---	---	6746	Assume 100%	6746
	Weed Oil #60	---	---	7516	Assume 100%	7516
					GRAND TOTAL	= 561,332 gal = 4,024,649 lbs

[a] Manufacturer/Supplier

letters was sent to all the distributor/dealers requesting information on only nonsynthetic pesticide sales to Fresno County users. The results of this survey ("2nd survey") are also tabulated in Table 5-6. Some of the respondents to this survey did not respond to the first survey, and some of the first survey respondents corrected their earlier responses.

In addition to these distributor/dealers, several large manufacturer/supplier firms were also contacted to obtain further information on the use of nonsynthetic pesticides in Fresno County. These manufacturer/suppliers included Chevron, Martinez Petroleum, FMC, Keen Petroleum, Golden State, and Mobile Petroleum. Of these, FMC did not respond and all others except Chevron and Keen reported no sales in Fresno County. The quantities of nonsynthetic pesticides sold by Chevron and Keen to dealers and end users in Fresno County are also shown in Table 5-6. Finally, Table 5-6 summarizes all the nonsynthetic pesticides used in Fresno County which were reported in the surveys. It should be noted here that all survey data were reported in gallons. The conversion to pounds from gallons at the bottom of Table 5-6 was based upon an assumed oil density of 7.16 lbs/gal, representing a specific gravity of 0.86. This specific gravity was based upon the overall makeup of the nonsynthetics; approximately one-third of the total poundage was insecticides and two-thirds was herbicides. Most of the petroleum insecticides have density values of 0.80 to 0.86, while nonselective weed oils have specific gravities near 0.9. Consequently, the 0.86 figure used would be very near average for all nonsynthetics.

The data obtained in these surveys were extrapolated to estimate the total nonsynthetic pesticide use in Fresno County. The method of extrapolation is shown in Table 5-7. In this extrapolation, the assumption was made that the survey respondents were proportionally representative of all

TABLE 5-7

Response Patterns in Surveys on Nonsynthetic Pesticides

	Questionnaires Mailed[a]	Total Responses	Positive Responses	No Oil Sales	Uncooperative	Other[b]	Duplication between 2 Surveys
1st Survey	124	33	11	20	2	3	-
2nd Survey	124	35	8	23	2	2	5 positive responses, 9 no oil sale
Additional responses through manufacturer/ supplier survey			4[c]				

- Total dealers = 124 - 5 (assumed out of business) + 2 (extra dealers not included in Agriculture Commission list of 124) = 121.

- Total responses: 33 + 35 - 14 (duplications between 2 surveys) = 56.

- Total nonsynthetic pesticide use reported in surveys = 4,024,649 lb.

- Assuming 56 responses are representative of all 121 dealers Fresno County users, total nonsynthetic pure oil pesticide use in Fresno County = $4{,}024{,}649 \times \frac{121}{56} = 8{,}696{,}117$ lbs.

[a] All dealers registered with Fresno County Agriculture Commission.

[b] Questionnaires returned without forwarding addresses-- assumed to be out of business.

[c] Two of these were not included in the list of 124 dealers obtained from the Agriculture Commission.

the dealers, suppliers, and distributors who sell nonsynthetic pesticides to Fresno County users. As indicated in Table 5-7, the total estimated nonsynthetic pesticide use in Fresno County in 1976 was approximately 8.7 million pounds, more than 8.5 times the amount reported in the PUR. It should be noted here that because of the nature of the surveys upon which the nonsynthetic inventory is based, it was not possible to estimate the quantities of diesel oil and other non-pesticide oils which may have actually been used as pesticides.

As mentioned in the overview (Section 5.2.1), the combined results of the synthetic and nonsynthetic application inventory are inputs to the emission inventory. The inorganics were assumed to contribute no significant oxidant precursor emissions, and only the application inventory of these substances is reported.

As a summary, Table 5-8 presents all application inventory correction factors used in this study.

5.3 1976 Pesticide Application Inventory

5.3.1 Synthetic and Inorganic Pesticides

The tables in Appendix D indicate the monthly application of each type of synthetic, inorganic, and nonsynthetic pesticides in Fresno County during 1976. These pesticides are separated into five major classifications: organic, acreage; organic, nonacreage; inorganic; inert organic ingredient, acreage; and inert organic ingredient, nonacreage. The organic synthetic pesticides are further classified as insecticides, fungicides, herbicides, and nematocides. The tables in Appendix D include all parent compounds and minor active ingredients excluding nonsynthetics. All poundage figures have been corrected to

TABLE 5-8

Correction Factors for Application Inventory

Chemical	Correction Factor
Restricted Synthetic Organics	1.13
Nonrestricted Synthetic Organics	1.47
Restricted-Nonrestricted Synthetic Organics:	
Naled	1.30
Botran-R	1.43
PCNB	1.13
Terrazole-R	1.13
Restricted Inorganics	1.13
Nonrestricted Inorganics	1.47
Restricted-Nonrestricted Inorganics:	
Sulfur	1.44
Borax	1.13
Formulation 4 Inert Ingredients:	
Acreage Application	1.38
Nonacreage Application	1.40
Formulation 9 Inert Ingredients:	
Acreage Application	1.37
Nonacreage Application	1.45
Nonsynthetic Organics:	
Formulation 10 - Pure Oil	Based on survey
Nonrestricted Nonsynthetic Organics (Nonformulation 10 Chemicals)	1.47
Restricted-Nonrestricted Nonformulation 10 Chemicals:	
Aromatic Petroleum Solvent	1.18
Petroleum Distillate	1.13
Petroleum Hydrocarbon	1.37
Xylene	1.13
Xylene Range Aromatic Solvent	1.13

account for unreported pesticides. A summary of all synthetic and inorganic pesticide applications is shown in Table 5-9.

It should be noted from Table 5-9 that the major pesticide type, in terms of pounds applied, was inorganics. More inorganics were used in Fresno County in 1976 than all the synthetics combined, and of these inorganics, approximately 75 percent was sulfur (see Table D-3). Other inorganic pesticides applied in relatively large quantities included sodium chlorate (11 percent) and cryolite (9 percent). Approximately 9,000 lbs. of arsenate compounds (sodium and lead arsenate) were applied in Fresno County in 1976, but this only amounted to about 0.13 percent of the total inorganics applied. Of the remaining types of synthetic pesticides, only insecticides used on acreage accounted for a very large proportion (15.6 percent) of applications.

5.3.2 Nonsynthetic Pesticides

The data on pure oil use in the PUR were used to determine the split between acreage and nonacreage applications and to determine the application, by month, of each type of nonsynthetic pesticide. The nonsynthetic pesticide application figures shown in the tables in Appendix D were calculated by proportional extrapolation of the dealer survey data to arrive at the total nonsynthetic pesticide application figure of 9.9 million lbs. This figure was determined as specified in Section 5.2.3.

A summary of nonsynthetic pesticide applications is shown in Table 5-10 which includes not only pure oil application data but also nonsynthetic minor active ingredients found in synthetic pesticides. As can be seen in this table, pure oils account for the vast majority (88 percent) of all

TABLE 5-9

Synthetic and Inorganic Pesticides Used in Fresno County in 1976
(Corrected Data)

Pesticide Type		Pounds	Acreage	Total (lbs.)	Percent
Insecticide:	acreage	1,889,685	1,687,492	1,979,113	16.31
	nonacreage	89,428			
Fungicide:	acreage	352,346	189,368	371,932	3.06
	nonacreage	19,586			
Herbicide:	acreage	673,030	814,379	714,676	5.89
	nonacreage	41,646			
Nematocide:	acreage	600,160	10,767	678,079	5.59
	nonacreage	77,919			
Plant Growth Regulators:	acreage	3,054	9,940	91,939	0.76
	nonacreage	88,885			
Adjuvants:	acreage	24,549	195,846	24,549	0.20
Defoliant:	acreage	658,413	637,718	661,497	5.45
	nonacreage	3,084			
Subtotal:	acreage	4,201,237	3,545,510	4,521.785	37.26
	nonacreage	320,548			
Inorganic:					
acreage and nonacreage		6,579,274		6,579,274	54.21
Inert Ingredient:					
acreage		976,699	5,127,086	1,036,014	8.53
nonacreage		59,315			
TOTAL				12,137,073	100%

TABLE 5-10

Nonsynthetic Pesticides Used in Fresno County in 1976 (Corrected Data)

Pesticide Type		Pounds	Acreage	Percentage
Pure Oil -	acreage	6,786,156	2,321,048	68.5
	nonacreage	1,909,951		19.3
Subtotal		8,696,117		87.8
Minor Active Ingredients -				
	acreage	955,020	403,330	9.6
	nonacreage	258,914		2.6
Subtotal		1,213,934		12.2
TOTAL NONSYNTHETIC		9,910,051		100%

nonsynthetic pesticide applications. Most of these pure oils were used in acreage applications.

A summary of all pesticide applications (synthetic and nonsynthetic) is shown in Table 5-11, along with the percentage proportions of major pesticide classes. This table indicates the large quantity of nonsynthetic pesticide applications (45 percent, by weight, of all pesticides applied) with respect to the organic synthetic applications (25 percent). The large quantity of inorganics (which are mostly sulfur) applied should be noted as well.

5.3.3 August 24, 31 Data

At the request of CARB, application data were obtained for the days of August 24th and August 31st. These data and the associated emissions will be used as input to an air quality modeling study of Fresno County, conducted by CARB's Research Division. Application data shown in Table 5-12 were obtained in the following manner. Data reported in the PUR for these two days were obtained from the data tapes of UC Davis' Environmental Toxicology Library. All synthetic and inorganic pesticide data from these tapes were multiplied by the 1.13 or 1.47 correction factors, depending on whether the specific pesticides were restricted or nonrestricted, respectively.

For nonsynthetic pesticide applications, the pesticide chemicals were grouped under pure oil and minor active ingredients. Each minor active ingredient figure thus determined was then multiplied by an appropriate correction factor (see Table 5-8). The pure oil figure, calculated earlier, was then corrected for unreported usage by multiplying by 16.67 (see footnote, Table 5-19).

TABLE 5-11

Pesticides Used in Fresno County in 1976 (Corrected Data)

Pesticide Type	Pounds	Percentage
Synthetic		
Organic[a]	5,557,799	25.2
Inorganic	6,579,274	29.8
Nonsynthetic	9,910,051	45.0
TOTAL	22,047,124	100%

[a]Include inert organic ingredients.

TABLE 5-12

Application of Pesticides in Fresno County on August 24 and August 31, 1976. (Corrected Data) (The upper number is lbs.; the lower number in () is acreage.)

Chemicals	August 24	August 31	Total
(A) Synthetic Organic Products			
Balan-R	42 (57)		42 (57)
Benomyl	125 (279)	88 (336)	213 (615)
Bidrin-R		299 (299)	299 (299)
Botran-R	300 (183)	123 (68)	423 (251)
Captan	624 (92)	49 (49)	673 (141)
Carbofuran	23 (91)		23 (91)
Carbaryl	1383 (760)	564 (400)	1947 (1160)
Chloropicrin	255 (11)		255 (11)
Chlorothalonil	1614 (719)		1614 (719)
DNBP	1872 (1731)	3451 (2437)	5323 (4168)
Diazinon	343 (196)	182 (582)	526 (778)
Difolatan-R	1085 (434)		1085 (434)
Dimethoate		51 (152)	51 (152)
Di-Syston-R	160 (164)		160 (164)
Endothall	242 (161)	489 (325)	730 (487)

TABLE 5-12 (continued)

Chemicals	August 24	August 31	Total
Ethion	170 (170)	170 (170)	340 (340)
Fundal-R	1951 (1951)	714 (714)	2665 (2665)
Kelthane-R		835 (557)	835 (557)
Kerb-R	42 (57)		42 (57)
Malathion	148 (43)		148 (43)
Maneb		58 (73)	58 (73)
Methyl Bromide	519 (11)		519 (11)
Methomyl	1017 (1708)	502 (1155)	1519 (2863)
Methyl Parathion	595 (1378)	164 (690)	759 (2068)
Monitor-R	1023 (1269)	295 (295)	1318 (1564)
Naled	1544 (1274)	441 (415)	1985 (1689)
Paraquat Dichloride	11 (23)		11 (23)
Parathion	490 (511)	398 (942)	888 (1453)
Phorate	89 (91)	231 (255)	320 (346)
Phosdrin-R	54 (299)	93 (240)	147 (540)
Supracide-R	35 (14)		35 (14)
Toxaphene	182 (45)	522 (130)	704 (175)
Subtotal:	15938 (13722)	9719 (10284)	25657 (24006)

TABLE 5-12 (continued)

Chemicals	August 24	August 31	Total
(B) Nonsynthetic Petroleum Products			
(1) Minor Active Ingredients			
Aromatic Petroleum Solvents	1663 (1776)	520 (580)	2183 (2356)
Petroleum Distillates		98 (198)	98 (198)
Petroleum Hydrocarbons	191 (457)	109 (315)	300 (772)
Xylene	1134 (1208)	194 (1280)	1328 (2488)
Xylene Range Aromatic Solvent	57 (45)	49 (39)	106 (84)
(2) Pure Oil			
Petroleum Oil, Unclassified	15494 (400)		15494 (400)
Subtotal:	18539 (3886)	970 (2412)	19509 (6298)
(C) Synthetic Inorganic Products			
Cryolite		1106 (200)	1106 (200)
Diammonium Phosphate	18 (373)	8 (339)	26 (712)
Lignin Sulfonic Acid	25 (167)	17 (110)	42 (277)
Sulfur	945 (184)	86 (22)	1031 (206)
Subtotal:	988 (724)	1217 (671)	2205 (1395)
Total:	35465 (18332)	11906 (13367)	47371 (31699)

5.4 Pesticide Use Patterns

The pesticide use patterns in Fresno County in 1976 include both the type of pesticide use and the geographical distribution of pesticide applications. Pesticide type and use classifications are defined in Tables 5-13 and 5-14, respectively.

Table 5-15 is a summary of all pesticide applications by use and type in Fresno County in 1976. The use patterns in this table are based on PUR data. As can be seen in this table, agricultural applications accounted for more than 89 percent of all applications in 1976. At 3.8 percent, home and garden applications were the second largest uses of pesticides in the county. The latter figure is relatively small in the light of some home and garden pesticide use. Dr. Jake MacKenzie, of the DFA, has stated that home and garden use may account for as much as 20 percent of total pesticide use.[c] However, the 3.8 percent figure (from the PUR) represents the only data available for Fresno County in 1976. Also, this figure does not appear unreasonable considering the heavy agricultural orientation of Fresno County. A 1972 study[2] of home and garden pesticide use in three U.S. cities: Philadelphia, Dallas, and Lansing, indicated an average pesticide use of 0.14 lb. per capita, as shown in Table 5-16. Fresno County's estimated home and garden pesticide use amounted to 1.80 lbs. per capita in 1976. The results of the three-cities study certainly give no indication that the Fresno County data are underestimates.

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[c]Statement made in testimony before the Assembly Committee on Environmental Quality's hearing on urban and suburban pesticides in California in October, 1973.

TABLE 5-13

List of Pesticide Types and Their Definitions (in California)

Type	Remarks
Adjuvant	Spreader-stickers, wetting agents, etc.
Algaecide	Control of algae or algae and fungus.
Disinfectant	Bacteriocide, germicide, etc.
Fungicide	Control of fungus.
Herbicide	Control of weeds, brush, any undesirable plant growth.
Insecticide	Control of insect pests.
Nematocide	Control of nematodes.
Rodenticide	Control of any animal pest.
Growth Regulator	For the promotion or hindrance of plant growth.
Defoliant	For defoliation of plants.
Repellent	For repelling animal and insect pests.

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 a 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 with type code "A".
Soil Fumigation	Use for preplanting or postplanting treatment of fallow land or noncrop land.
Agricultural Commissioner	Used by county agricultural commissioners. Usually rodenticides.

TABLE 5-15
Summary of Use Patterns of All Pesticide Types in Fresno County in 1976 (Corrected Data)

Use \ Type	Synthetic Organics											Inorganic	Nonsynthetic Products		Inert Organic Ingredients	Total (lbs.)
	Insecticides	Fungicides	Herbicides	Nematocides	Fun. & Ins.	Fun. & Herb.	Fun. & Herb. & Ins.	Plant Growth Regulators	Adjuvants	Defol.	Subtotal		As Pure Oil	As Minor Active Ingr.		
Agricultural	1883191	300636	1052118	92976	12834		7987	2767		433533	3786042	6557955	7516534	900435	871207	19632173 (89.05%)
Home Garden	2470										2470		773179	56432	593	832674 (3.78%)
Household													493	144	33	670 ---
Industrials	492	8031	92					81			8696		3287	7404	2089	21476 (0.1%)
Manufacturing	197										197				47	244 ---
Residential	4079										4079		110265	3628	980	118952 (0.54%)
Structural	40885		55		2						40942		5869	25033	9837	81681 (0.37%)
Noncrop	8758		27486				247	4			36495	5022	18652	198971	8702	267842 (1.21%)
Turf Areas	83							74728			74811		1183	144	17973	94111 (0.43%)
Nursery	1353										1353		1901	365	325	3944 ---
Spreader Sticker	1		100						35576		35677	14655	264754	21378	8571	345035 (1.56%)
Soil Fumigate	49660			209478	4797	5095	261993				531023				65327	596350 (2.70%)
Agricultural Commissioner												1642			50330	51972 (0.24%)
TOTAL	1991169	308667	1079851	302454	17633	5095	270227	77580	35576	433533	4521785	6579274	8696117	1213934	1036014	15467550 22047124 (100%)

TABLE 5-16

Summary of Population and Estimated Quantities of Home and Garden Pesticide Use.[2]

Study Area	Population	Total Pesticides Used (lbs.)	Pesticides Used Per Capita (lbs.)
Philadelphia	3,866,000	417,000	0.11
Dallas	1,327,000	301,000	0.23
Lansing	272,000	41,000	0.15
Total	5,465,000	759,000	0.14 (Average)
Fresno Co.	461,900	832,674	1.80

Tables 5-17 and 5-18 present additional details on synthetic and non-synthetic pesticide use patterns, respectively. These demonstrate the use of various types of pesticides on specific crops in Fresno County in 1976 based upon PUR data. From Table 5-17 it may be seen that considerably more synthetics are applied to cotton than to any other major crop. Table 5-18 indicates that more pure oils are applied to alfalfa (24 percent) than on any other crop and that applications to alfalfa, carrots, and peaches alone account for more than half (55.6 percent) of all pure oil applications. Unclassified petroleum oils comprise the single largest class of pure oil use. Appendix E includes other related information including a list of the top 50 pesticides, by weight, applied in Fresno County in 1976; leading crops in Fresno County; and the crops to which major pesticides are applied.

Table 5-19 indicates the use patterns of pesticides among governmental users in Fresno County. Pesticides are listed according to type and by pounds applied. "Other agencies" account for the majority (81 percent) of governmental use of pesticides. In addition, 80 percent of the pesticides used by governmental agencies were petroleum products.

The spacial distribution of pesticide use in Fresno County in 1976 is depicted in a series of maps in Appendix E. These maps indicate the use density, by pounds, of 35 major pesticides. Since certain pesticides are used most extensively on specific crops, pesticide use distribution tends to reflect crop patterns. In general, the eastern portion of Fresno County is more oriented toward orchard crops and truck gardens while field crops are more dominant in the western portion of the county. Lists of crop types and the major pesticide applied to each type are found in Appendix F and in Tables 5-17 and 5-18, as mentioned earlier.

TABLE 5-17

Distribution of Synthetic Pesticide Uses (More than 1000 lbs.)
Among Fresno County's Five Leading Crops in 1976 (Corrected Data).

Pesticide Applied	Crops (lbs.)					
	Cotton	Grapes	Tomatoes	Alfalfa	Barley	Plums
Toxaphene	86116		78754	18284		
Paraquat Dichloride	50412	9242			2279	
Azodrin-R	45444					
Monitor-R	31200					
Aldicarb	23159					
Phorate	17197				15154	
Supracide-R	9842			6267		
Methomyl	5989		21049	14976		
Bidrin-R	5007			4396		
Methyl Parathion	3506		3714	13047	7312	
Parathion	1610	2948	3168	9672	9991	5641
Carbaryl	1214	23101	1138	1730		
Chlordane	73543					
Dialifor	16500					
Dialifor, Other Related	1834					
Endosulfan		1461	19411	12521		
Guthion-R		1333	2317			
TEPP				11772		
TEPP, Other Related				17657		
Carbofuran				7970		
Phosphrin-R				5196		
Phosphrin-R, Other Related				3457		
4(2,4-DB) Isooctyl Ester				2619		
2,4-D, Dimethylamine Salt					41919	

TABLE 5-17 (continued)

Pesticide Applied	Crops					
	Cotton	Grapes	Tomatoes	Alfalfa	Barley	Plums
2,4-D, Alkanolamine Salts					30462	
Di-Syston-R					8130	
2,4-D					7734	
2,4-D,N-Oleyl-1,3-Propylene					7147	
2,4-D, Buthyl Ester					2858	
MCPA, Dimethylamine Salt					2266	
Sodium Arsenate		9224				
Ethion		7187				
Carbophenothion		1323				
Methyl Bromide			9297			
Chloropicrin			2669			
TOTAL	372573	55819	141517	129564	135252	5641

TABLE 5-18

Reported and Calculated Quantities of Nonsynthetic Products (Pure Oils) Used in Fresno County in 1976. Listed by Individual Type and by Uses.

Pure Oil and Use	Quantities (lbs.) Reported		Calculated Based on Survey Data
Aromatic Petroleum Solvent			
Alfalfa	127,120	(24.37%)	2,119,593
Mineral Oil			
Peach	12,221	(2.34%)	203,756
Nectarines	6,085	(1.17%)	101,461
Almonds	2,759	(.53%)	46,004
Plum	2,466	(.47%)	41,118
Walnut	1,426	(.27%)	23,776
Petroleum Distillates			
Structural Control	142	(.03%)	2,368
Petroleum Hydrocarbons			
Carrot	88,800	(17.03%)	1,480,647
Agencies, Other	51,960	(9.96%)	866,379
Irrigation Districts	9,440	(1.81%)	157,402
Petroleum Oil, Unclassified			
Peach	74,098	(14.21%)	1,235,506
Almonds	56,162	(10.77%)	936,442
Plum	38,288	(7.34%)	638,412
Nectarines	27,362	(5.25%)	456,233
Olives	8,722	(1.67%)	145,430
Orange	2,509	(.28%)	41,834
Prune	1,490	(.29%)	24,844
Grapes	1,277	(.25%)	21,292
Apricot	10	(.002%)	167
Residential Pesticides	6,613	(1.27%)	110,265
Federal Agency	1,288	(.25%)	21,476
Agencies, Other	636	(.12%)	10,604
University of California	270	(.04%)	4,502
Structural Control	210	(.02%)	3,501
Turf	71	(.01%)	1,183
Deciduous Ornamental Trees	114	(.02%)	1,901
TOTAL	521,539	(100%)	8,696,117

TABLE 5-19

Distribution of Pesticide Types Among Governmental Users in Fresno County in 1976.

Agency	Pesticide Type and Amount Used (lbs.)[a]								
	Adjuvants	Fungicide	Growth Regulator	Herbicide	Insecticide	Nematocide	Petroleum Product	Inorganic	Total
Agencies, Other	12,369	11,526	88,884	15,850	6,007	77,300	893,677	16,403	1,122,016
County Agricultural Commission	---	43	---	2,577	8,135	5,392	16,729	4,952	37,828
Federal Agency	---	---	---	2,276	---	---	21,482	---	23,758
Irrigation Districts	---	---	---	9,698	---	---	176,593	---	186,291
State Highway	1,045	---	---	8,086	27	---	34	1,226	10,418
University of California	---	7	---	70	285	---	4,503	522	5,387
Water Resources	---	---	---	2,685	1	---	---	238	2,924
TOTAL	13,414	11,576	88,884	41,242	14,455	82,692	1,113,017	23,342	1,388,622

[a]All values presented here have been adjusted (individual values of restricted chemicals multiply 1.13 and that of nonrestricted, 1.47) except values for the petroleum products. 94 percent of the petroleum products here is from Formulation Code 10; petroleum product values have been adjusted by, $\left(\frac{\text{Survey Estimates}}{\text{PUR Formulation 10}} = \frac{8,696,117}{521}\right) = 16.67$ (adjustment factor).

Finally, the time of day during which pesticides were applied in Fresno County during each month of 1976 is indicated in Table 5-20. This table was based on data obtained from approximately 500 pesticide use application forms selected at random from the Fresno County Agricultural Commissioner's 1976 files. This table indicates that during the spring and summer months the greatest number of pesticide applications occur in the morning hours while middle-of-the-day applications predominate during the fall and winter applications.

5.5 Discussion and Recommendations

The data reported in this application inventory was based on a number of estimates and assumptions, as noted earlier. Major estimates, the 1.13 and 1.47 factors used to correct for improper, unrecorded, and unreported synthetic and inorganic pesticide applications, are in line with an earlier DFA estimate. In their 1975 Report to the Legislature (pursuant to the California Food and Agriculture Code, Sec. 14104), the DFA estimated that 80 - 85 percent of pesticide use is reported in the PUR ($\frac{1}{1.13} \times 100\% = 88\%$; $\frac{1}{1.47} = 68\%$). However, this DFA estimate probably included nonsynthetics, while the 1.13 and 1.47 factors do not apply to pure oils. The use of pure oils has been underestimated because they are nonrestricted pesticides, and growers are not required to report their applications.

A second significant estimate involved the organic inert ingredient application inventory. The makeup of all formulation 4 and 9 pesticides, the only pesticides having a significant quantity of organic inert ingredients, was determined by extrapolating data obtained from a relatively small sample. As explained in Section 5.2.2, the inert constituents of the formulation

TABLE 5-20

Percentage of Time for Pesticide Applications in a Day

Month \ Hrs.	0-3	3-6	6-9	9-12	12-15	15-18	18-21	21-24
Jan			15	33	38	14		
Feb			13	37	44	6		
Mar		4	46	12	20	18		
Apr		5	42	23	20	6	4	
May		5	38	17	21	15	4	
June		14	49	13	8	12	4	
July	4	19	32	24	14	4	1	2
Aug		5	34	28	19	14		
Sept		19	30	25	12	13	1	
Oct			8	49	23	19	1	
Nov			7	39	42	12		
Dec			8	44	39	9		

code 4 pesticides (27.3 percent, by weight) and the formulation code 9 pesticides (9.8 percent, by weight) applied in Fresno County in 1976 were determined after gaining access to the proprietary files of numerous pesticide manufacturers. This information was assumed to be representative of all pesticides of those formulation codes applied in Fresno County. This assumption gains credence from the fact that a relatively large number of manufacturers (24) and pesticides (83) were represented in the sample upon which the extrapolation was based.

Another important estimate was the extrapolation of all "pure oil" nonsynthetic pesticide applications based on survey responses from 46 percent of the pesticide dealers and distributors who sell to Fresno County users. The primary assumption here was that these dealers were representative of all dealers selling to Fresno County users, i.e., they sold 46 percent of all the pure oils used as pesticides in Fresno County. Although this assumption could be questioned, it is the best position which could be taken under the circumstances. The survey effort (two direct-mail surveys of every dealer registered with the Fresno County Agriculture Commission plus a survey of major manufacturers and suppliers) was intensive, and it is not even certain that personal surveys could have yielded a higher response rate.

A final point is that the use patterns presented in this inventory are not representative of all pesticide applications. Within the scope of this study, the use pattern information could only be obtained from the PUR. Nevertheless, sufficient use pattern information is presented to illustrate general trends in spacial, temporal, and crop-specific pesticide application patterns.

Overall, the data reported are credible. This study relied upon several assumptions, but, at the same time, it represents a major pioneering effort in developing an inventory of reported and unreported pesticide applications. More importantly, it illustrates the large quantity of pesticides which are not included and recorded in the PUR.

Several recommendations for further study are in order. First, the use of pesticides in home and garden applications should be investigated more thoroughly. Although the relative amount of pesticide use in this sector may be rather small in an agricultural region such as Fresno County, it would most likely be significant in urban and suburban areas in California.

Secondly, a new and improved reporting system for governmental agencies should be considered. At present, there is no requirement for federal agencies to give an accurate accounting of their pesticide use, and, as a consequence, these agencies are likely to under report. In addition, the "other agency" user category in the PUR needs to be refined. This category was found to include private pest control users as well as public agency users.

Finally, a more comprehensive survey of farmers should be conducted to obtain a clearer picture of unreported pesticide applications, particularly nonsynthetics. Such a survey, particularly if conducted in conjunction with a limited face-to-face survey, may also help to determine the reasons for the farmers' concern and reluctance in responding to surveys of this nature.

5.6 References

1. Rollin, R. 1978. California Department of Food and Agriculture. Private communication.

2. Von Rumker, R., R. M. Matter, D. P. Clement, F. K. Erickson. 1972. "The Use of Pesticides in Suburban Homes and Gardens and Their Impact on the Aquatic Environment," Pesticide Study Series - 2, Environmental Protection Agency.

6.0 PESTICIDE EMISSION ESTIMATION METHODS

6.1 Introduction

Methods for estimating the rates of emission of pesticides and their related compounds can be categorized into five simple mathematical models depending on the sources of emission:

A. Emissions from water surfaces;

B. Emissions from water bodies;

C. Emissions from soil surfaces;

D. Emissions from incorporated soil; and

E. Emissions from vegetated land.

Models A and B can be used to predict the emissions resulting from pesticides applied to lakes, reservoirs, rivers, rice paddies and areas filled with irrigational water. Pesticides with high vapor pressure and those likely to evaporate relatively fast are most likely to fit into model A. Long-term evaporation of some pesticides, generally those with a low vapor pressure, would occur when they are dissolved in the water body. Model B would most likely apply in these situations.

Models C and D are used to predict the emissions from pesticides on the soil surface and those incorporated into soil. Model C can be used for pesticides and their related compounds that have high vapor pressures and would be released into the atmosphere relatively quickly. Model D is most appropriate for pesticides which have either high evaporation rates and are likely to be incorporated into the soil immediately after the application to achieve its planned effectiveness or have low evaporation rates and are likely to be incorporated into the soil by dissolving in the

irrigation water and rainfall.

Model E is used to predict emissions from vegetated land. Soil surfaces and vegetated land differ in the amount of available surface area. Vegetated land provides a much larger surface because of the leaf surfaces of the crop. Therefore, evaporative loss of pesticides is much greater on vegetated land.

6.2 Methods

6.2.1 Emissions from Water Surfaces

Most organic solvents and hydrocarbons are not soluble in aqueous systems. They usually remain in suspended form or float on the water surface. Mackay and Wolkoff[1] developed an evaporation model to describe the rate of emission from a water surface. If we consider m_i lb/acre of compound i on the water surface, the "equilibrium mole ratio" of compound i in the vapor above the water is P_i/P_w where:

P_i = partial vapor pressure of compound i; and

P_w = partial vapor pressure of water.

The mass ratio is thus $M_iP_i/18\ P_w$, where:

M_i = molecular weight of compound i; and

18 = molecular weight of water.

If the monthly evaporation rate E in lb/acre-month of water evaporates from the water body, the evaporation rate of compound i would be:

$$\frac{dm_i}{dt} = - E\ M_iP_i/18P_w \qquad \text{(EQ. 6-1)}$$

However, Spencer et al.[2] suggested that the ratio of compound i to water in the vapor phase was dependent not only on the amount of compound i vaporized but also on the amount of water vaporized which, in turn, was controlled by the relative humidity (R.H.) of the air above the surface. Water vapor was diffusing into an atmosphere already partially saturated with water vapor while the compound i was diffusing into air devoid of compound i; this is a valid assumption. Since water vaporization depends on the R.H. of the air overlying the water surface, water flux will be proportional to $P_w(1 - R.H.)$ rather than to P_w only. Therefore, the correct equation for predicting the evaporation rate for compound i would be:

$$-\frac{dm_i}{dt} = E\, M_i P_i / 18\, P_w\, (1 - R.H.) \qquad \text{(Eq. 6-2)}$$

The monthly water evaporation rate E can be accurately estimated using Meyer's evaporation formula (in lb/acre)[3]:

$$E = C\,(P_w - P_a)\,\left(1 + \frac{u}{10}\right) \qquad \text{(Eq. 6-3)}$$

where: P_w = saturated water vapor pressure at the mean monthly surface temperature, in mm Hg;

P_a = actual water vapor pressure measured about 7.5 meters above the water surface, in mm Hg;

u = wind velocity measured about 7.5 meters above the water surface, in mph; and

C = empirical constant having the following values;

C = 133,500 for shallow ponds and small puddles of water;

C = 98,000 for small lakes and reservoirs.

By substituting Equation 6-3 in Equation 6-2, the monthly loss of compound i from one acre of water surface can be formulated as:

$$-\frac{dm_i}{dt} = C\,(P_w - P_a)\,(1 + \frac{u}{10})\,M_i P_i / \left[18\,P_w\,(1 - R.H.)\right] \qquad \text{(Eq. 6.4)}$$

Acree et al.[4] suggested that a codistillation process operates in the vaporization of pesticides from water or moist surfaces. Hardley[5] and Hamaker,[6] however, concluded that codistillation does not play a role in pesticide volatilization since pesticide molecules and water molecules volatilize from water or a moist surface independent of each other; this can be predicted from known physical chemical principles.

6.2.2 Emissions from Bodies of Water

The exact rates of evaporation of organic compounds dissolved in aqueous systems depend on the relative rates of evaporation and of liquid diffusion or mixing with the slower process controlling the overall rate. Evaporation is a molecular transfer process occurring between air and water, and the interface between the two phases can be considered to be a two-layer (film) system. Since molecular diffusion is responsible for transport through the layer system, Liss and Slater[7] suggested that Fick's first law (in the one-dimension form) is applicable,

$$F = -D\,\frac{\partial C}{\partial Z} \qquad \text{(Eq. 6-5)}$$

where: F = flux of compound i through layer;

D = molecular diffusion coefficient of compound i;

C = concentration of compound i; and

Z = thickness of the layer.

A more useful form of equation 6-5 is:

$$F = k\Delta C \qquad \text{(Eq. 6-6)}$$

where: ΔC = concentration difference across the layer; and

$K = D/Z$.

By applying Equation 6-6 to the two-layer system and assuming the evaporation of gas across the interface is a steady state process, it follows that:

$$F = k_g(C_g - C_{sg}) = k_l(C_{sl} - C_l) \qquad \text{(Eq. 6-7)}$$

where: K_g = exchange constant for gas phase;

K_l = exchange constant for liquid phase;

C_g = gas concentration in gas phase;

C_{sg} = gas concentration at the bottom of the gas film;

C_{sl} = gas concentration at the top of the liquid film; and

C_l = gas concentration in the liquid phase.

According to Henry's law,

$$C_{sg} = H\, C_{sl} \qquad \text{(Eq. 6-8)}$$

where: H = Henry's law constant.

If C_{sg} and C_{sl} in Equations 6-7 and 6-8 are eliminated, then,

$$F = K_g(C_g - H\, C_l) = K_l(C_g/H - C_l) \qquad \text{(Eq. 6-9)}$$

where: $$1/K_g = 1/k_g = H/k_l \quad \text{(Eq. 6-10)}$$

and: $$1/K_l = 1/k_l + 1/H\,k_g \quad \text{(Eq. 6-11)}$$

MacKay and Leinonen[8] have used the same approach to evaluate the process of evaporation of pesticides and other organic compounds from water surfaces. Under the valid assumption that the background level the compound in the atmosphere is low compared to the local level, they concluded that the rate of change in concentration would be:

$$\frac{dc}{dt} = - K_l\, C/L \quad \text{(Eq. 6-12)}$$

where: L = average depth of the water body.

Equation 6-12 can be integrated to express the concentration of the compound as a function of time:

$$C = Co \exp (- K_l t/L) \quad \text{(Eq. 6-13)}$$

According to Liss and Slater,[7] the gas and liquid exchange constants are:

$$K_l(H_2O) = 21{,}600 \text{ meter/month; } K_g(CO_2) = 144 \text{ meter/month.}$$

The following equations can be used to obtain K_l values for liquids other than water and K_g values for gases other than CO_2:

$$K_l(i) = K_l(H_2O) \times \left(\frac{18}{M_i}\right)^{1/2} \quad \text{(Eq. 6-14)}$$

$$K_g(i) = K_g(CO_2) \times \left(\frac{44}{M_i}\right)^{1/2} \quad \text{(Eq. 6-15)}$$

where: M_i = molecular weight of compound i.

The Henry's law constant can be obtained for compound i by using the following equation:

$$H_i = \frac{P_{is}}{C_{is}\ RT} \qquad \text{(Eq. 6-16)}$$

where: P_{is} = vapor pressure of compound i;

C_{is} = solubility of compound i;

R = gas constant; and

T = absolute temperature.

If the data on the vapor pressure and water solubility can be obtained, the values of K_g, K_l, and H_i can be calculated using Equations 6-14, 6-15, and 6-16. Thus K_l can be obtained by substituting these values in Equation 6-11. The monthly evaporation of compound i when completely dissolved in the water body can be obtained by the following equation:

$$-\frac{dm_i}{dt} = M_{io}\left[\exp\left(-K_l \frac{t-1}{L}\right) - \exp\left(-K_l \frac{t}{L}\right)\right] \qquad \text{(Eq. 6-17)}$$

where: t = number of months after the application of compound i to the water body; and

M_{io} = number of pounds applied.

Here, the total number of acres is not important provided that the initial concentration of compound i does not exceed its solubility.

6.2.3 Emissions from Soil Surfaces

The rate of loss of a pure substance into the atmosphere from a clean and inert surface is governed under stable conditions by two of its

properties: its saturation vapor concentration (SVC) and the rate at which its vapor diffuses through the still air layers next to the treated surface.[5] This principle can be applied to the volatilization of surface deposits or to initial volatilization of soil-incorporated pesticides before the concentration on the surface is depleted. Hartley[5] assumed that the rate of evaporation would be dependent on diffusion of the vapor away from the soil surface into the surrounding air. Thus, the rate of mass transfer by molecular diffusion would be proportional to the diffusion coefficient and the SVC.

Since SVC is proportional to the vapor pressure (P) times the molecular weight (M) and the molecular diffusion coefficient of organic vapors in air indicates an inverse proportionality to the square root of molecular weight, the rate of evaporation should be proportional to $P\ (M)^{\frac{1}{2}}$. Spencer[7] proposed the following equation to predict the rate of evaporation of compound 1 based on data for a model compound 2:

$$E_1 = E_2 \frac{P_1(M_1)^{\frac{1}{2}}}{P_2(M_2)^{\frac{1}{2}}} \qquad \text{(Eq. 6-18)}$$

where: E = evaporation rate;

P = vapor pressure;

M = molecular weight;

C_1 = vaporizing compound; and

C_2 = model compound.

Hartley,[5] however, pointed out that if the model compound is water, the water evaporation rate must be corrected for the relative humidity (R.H.) in the ambient air:

$$-\frac{dm_i}{dt} = \frac{E}{(1 - R.H.)} \times \frac{P_i (M_i)^{\frac{1}{2}}}{P_w (18)^{\frac{1}{2}}} \qquad \text{(Eq. 6-19)}$$

where: $\frac{dm_i}{dt}$ = monthly evaporation of compound i per acre; and

E = monthly water evaporation per acre.

6.2.4 Emissions from Soil-Incorporated Pesticides

According to Equation 6-19, the surface pesticide will evaporate at a constant rate under constant conditions, namely, constant rate of water evaporation, constant temperature, and constant relative humidity. But this is not the case for volatilization of pesticides incorporated into soil. Volatilization decreases rapidly as the pesticide on the surface is depleted, then volatilization levels off at a much reduced rate which depends on the movement of pesticide to the soil surface. Prediction of this movement to the surface is very complex. There is abundant evidence that movement will be affected by the pesticide's solubility and vapor pressure, the soil temperature, the air flow rate, the soil's moisture and organic content, the relative humidity, the pH, the type of soil, the water evaporation rate, precipitation, etc.[5, 9, 10, 11] Equations to predict volatilization rates that would include all these factors have not been developed.

Although Spencer[2] concluded that it will be necessary to use models which include both diffusion and mass-flow-movement of pesticides to the surface for subsequent volatilization, equations have not been developed to predict both processes simultaneously.

Meyer et al.[3] developed five mathematical models for predicting volatilization based on pesticide movement to the soil surface by diffusion only. The use of these models requires a knowledge of diffusion coefficients, of adsorption isotherm, and of other parameters that may or may not exist

for any individual pesticide. The boundary conditions involved in these models are either of no practical means (e.g., the background concentrations) or may be too detailed to be obtained (e.g., the depth of the soil).

Hartley[5] used the mass-flow-movement approach to explain that water can accelerate the evaporation of pesticides from the soil. When evaporation of pesticides occurs from the exposed surface, liquid solution moves up the capillaries of the wick to replenish that which was lost through evaporation at the top. Thus, pesticide dissolved in the soil water would be brought to the surface where it would evaporate or accumulate depending on its solubility and vapor pressure. Spencer and Cliath[12] demonstrated that the mass-flow-movement of pesticides toward the soil surface through water evaporation can accelerate the pesticides evaporation rates. The magnitude of the effect is related to the water evaporation rate and concentration of the pesticides in the soil water:

$$F_p = F_w \times C \qquad \text{(Eq. 6-20)}$$

Where: F_p = pesticide flux in ng/cm^2 per day;

F_w = water flux in ml/cm^2; and

C = concentration of pesticide in the soil water in ng/ml, which can be estimated from its solubility and its desorption isotherm.

However, using the mass-flow-movement approach, the amount of pesticide (F_p) that would be brought to the surface with soil water is not the same as the amount that would be evaporated. On the other hand, a simple diffusion model cannot be used to explain the acceleration of evaporation by the wick effect. In the absence of such a combined mathematical model, the

simplified model developed by Hamarker[6] can be used to accurately estimate the volatilization loss from soil:

$$Q_i = \frac{P_i M_i}{P_w M_w} \times \frac{D_i}{D_w} \times (QW)_V + C_i \times (QW)_L \qquad \text{(Eq. 6-21)}$$

where: Q = amount of loss per unit area;

C_i = concentration of compound i in the soil water;

i = compound i;

w = water;

V = loss as vapor; and

L = loss as liquid;

D = diffusion coefficient in soil.

The term $\left(\frac{P_i M_i}{P_w M_w}\right)$ in Equation 6-21 is an estimate of the vapor phase diffusion, and the term is an estimate of mass transfer. However, breaking down the water loss into loss due to water vapor diffusion and loss due to mass transfer of soil solution is, practically, very difficult to achieve. However, we can assume that the normal water loss due to water vapor diffusion can be calculated using Equation 6-3. If the total water loss (Qw) is smaller than the calculated normal water loss $\left[(Qw)_N\right]$, then all the water loss Qw will be used as $(Qw)_V$ in the equation because no matter how much of the pesticide was brought to the surface, it would accumulate on the surface. If Qw is larger than $(Qw)_N$, then $(Qw)_V = (Qw)_N$, and $(Qw)_L = Qw - (Qw)_N$, here the acceleration caused by the wick effect would be shown.

Green and Obien[13] developed the following equation to determine the

concentration of pesticide in the soil water:

$$C_i = \frac{Q_i}{m(W_e + K)} \qquad \text{(Eq. 6-22)}$$

where: Q_i = total amount of pesticide applied;

m = total solid weight;

W_e = effective water content; and

K = partition coefficient (the ratio of the concentration of compound accumulated at the soil surface to that in the soil water).

Since the information on the partition coefficients for all pesticides is very limited, the effective water content varies with time and place, and the calculation requires information that is not available. Thus, it is very difficult to obtain an accurate estimate of the concentration in the soil water. However, the solubility of the compound can be used as the upper limit of the concentration in the soil water. This is a valid substitution particularly for insoluble pesticides in the upper part of the soil.

Since the ratio of diffusion coefficients can be represented as the ratio of the square root of molecular weight,[5] the monthly loss of compound i incorporated in soil can be rewritten as:

$$\frac{dm_i}{dt} = (QW)_V \times \frac{P_i(W_i)^{\frac{1}{2}}}{P_w(18)^{\frac{1}{2}}} + (QW)_L \times C_i \qquad \text{(Eq. 6-23)}$$

6.2.5 Emissions from Vegetated Land

The rates of evaporation of pesticides and their related compounds from vegetated land may be quite different from the rates of evaporation from inert soil surfaces. The rate of water evaporation from the soil alone cannot be used to represent the rate of evapotranspiration from vegetated land. However, Hartley's Equation can still be applied here:

$$-\frac{dm_i}{dt} = \frac{ET_j}{(1 - R.H.)} \times \frac{P_i (M_i)^{\frac{1}{2}}}{P_w (18)^{\frac{1}{2}}} \qquad \text{(Eq. 6-24)}$$

where: $\frac{dm_i}{dt}$ = monthly evaporation of compound i per acre;

ET_j = monthly evapotranspiration from land with a crop j;

R.H. = monthly average relative humidity;

P_i = vapor pressure of compound i;

P_w = vapor pressure of water;

M_i = molecular weight of compound i;

18 = molecular weight of water.

The monthly ET rate can be obtained from its relation to the potential evapotranspiration (PE) rate of the vegetated land. However, most of the methods used to calculate the PE rate require detailed basic data which may not be available. The Blaney-Criddle method[14, 15] has been used for years to calculate the PE rate and only requires data on the monthly average temperature, the monthly percentage of daytime hours and the available moisture (precipitation, irrigation water, or natural ground water.) The monthly PE can be computed by the following equation:

$$u = ktp/100 \qquad \text{(Eq. 6-25)}$$

where: u = monthly PE in inches;

k = monthly PE coefficient for a specific crop and month;

t = mean monthly temperature (^{o}F); and

p = monthly percentage of the year's daytime hours.

The values of p for Fresno County are shown in Table 6-1.[16]

Equation 6-25 can be converted for use with metric units:

$$u = kp\ (45.7t + 813)/100 \qquad \text{(Eq. 6-26)}$$

where: u = monthly PE in mm; and

t = mean monthly temperature (^{o}C).

Examples of the Blaney-Criddle monthly PE coefficient are shown in Table 6-2.[17]

However, the monthly PE coefficients for most crops in Fresno County are not available. While it is recognized that a number of climatological factors affect the monthly PE coefficient, complete climatological data on the relative humidity, wind movement, hours of sunshine, evaporation, etc., are seldom available for a specific site. Phelan[18] found that the monthly PE coefficient can be approximated by the following equation:

$$k = kc \times (0.0173t - 0.314) \qquad \text{(Eq. 6-27)}$$

where: kc = monthly PE stage coefficient; and

t = temperature (^{o}F).

Thus, the local monthly PE coefficient k can be obtained only if the monthly PE stage coefficient kc and the local monthly average temperature are known.

TABLE 6-1

Monthly Percentage of Annual Daytime Hours in Fresno County[16]

Month	Latitude		
	36°N	37°N	38°N
January	6.98	6.92	6.87
February	6.85	6.82	6.79
March	8.35	8.34	8.33
April	8.85	8.87	8.89
May	9.80	9.85	9.90
June	9.82	9.89	9.96
July	9.99	10.05	10.11
August	9.41	9.44	9.47
September	9.36	8.37	8.37
October	7.85	7.83	7.80
November	6.93	6.88	6.83
December	6.81	6.74	6.68

TABLE 6-3

Monthly Potential Evapotranspiration (PE) Stage Coefficients[18]

Month	Alfalfa	Avocados	Citrus	Grapes
January	0.63	0.27	0.63	0.20
February	0.73	0.42	0.66	0.24
March	0.86	0.58	0.68	0.33
April	0.99	0.70	0.70	0.50
May	1.08	0.78	0.71	0.71
June	1.13	0.81	0.71	0.80
July	1.11	0.77	0.71	0.80
August	1.06	0.71	0.71	0.76
September	0.99	0.63	0.70	0.61
October	0.91	0.54	0.68	0.50
November	0.78	0.43	0.67	0.35
December	0.64	0.30	0.64	0.23

TABLE 6-4

Relationship of ET/PE to Available Soil Moisture[19]

Available Soil Moisture (%)					
10	20	30	40	50	100
ET/PE					
0.71	0.82	0.90	0.94	1	1

3. Exact and detailed data on crop distribution are needed to calculate the local PE rate.
4. The available data of kc for certain types of crops may or may not be applicable to Fresno County. Different farming seasons and different weather situations would change the value of kc considerably.

Estimating the water loss from evaporation or evapotranspiration from water, soil, or crop surfaces can also be accomplished through comparison with water loss from an evaporating pan (usually a U.S. Weather Bureau Class A pan). The pan should be placed near the crop surface where evaporation is to be estimated. The water loss from the pan (E_{pan}) must be related experimentally to the amount lost from the ground surface or water surface. The ratios of evapotranspiration of crops to pan evaporation must be determined for each growing stage of each kind of crop and for areas with fairly similar weather if the values are to be reasonably accurate.[20] Properly used, the pan evaporation method is more accurate than the Blaney-Criddle method and most of the other methods which are based on calculations using environmental factors.[21]

6.2.6 Emission During Pesticide Applications

When pesticides are applied in the field or even in the laboratory, the amount which can be measured on the target surface is in almost every case less than the amount applied. Part of the loss is a result of small particles or droplets drifting to off-target areas, and part is due to evaporative loss. It is difficult to separately assess the amounts lost to evaporation

and drift, and only estimates of the proportionate amounts have been found. Woodel et al.[23] found less than 50% reached the target from pesticides applied aerially to forests, a condition which might be conducive to high losses. Other losses reported during application vary depending on the pesticide and conditions of application.[22, 24, 25, 26] In addition, the evaporative loss of a pesticide may be different if it is mixed with other chemicals rather than being applied alone.[27, 28]

No procedure developed for estimation of evaporative loss during pesticide application has been found in the literature. The same is true for estimation of the changes in volatility which may occur on mixing of chemicals. An estimation of application losses must be based on observed experimental values and assumptions regarding the influences of environmental or other variables. The causes for observed changes in the evaporation rate of a pesticide on mixing with other chemicals are not clearly known at this time; therefore, no model or procedure can be used to quantitatively predict this effect.

6.2.7 Biological Degradation of Pesticides

Pesticides in the environment may be degraded to other chemicals through chemical reaction, photodegradation, and biological reaction as was pointed out in Chapter 4. It was also noted that these chemical conversions do not generally reduce the quantity of hydrocarbon which may be subject to vaporization and atmospheric reactions. Probably the only way that a pesticide may be essentially removed by degradation from the pool of chemicals which can be emitted into the atmosphere as reactive hydrocarbons is for the

pesticide to be modified through a series of chemical or biochemical reactions until it is converted into a natural chemical metabolite of a biological system. These biological metabolites may eventually be converted to carbon dioxide (CO_2), or in some instances, the carbon may be fixed into reasonably stable polymers such as cellulose or other components of living organisms.

There are some pesticides which are known to be readily degraded by microorganisms in the soil to products which are common biological metabolites,[29] and there is a much larger group of pesticides which are not easily degraded or for which final degradation products are largely unknown. Among the easily degraded compounds are aliphatic acids such as dalapon, and the phenylalkanoates such as 2,4-D.[30, 31] Endosulfan is an example of a pesticide which can be biologically degraded but for which the end products are mostly unknown. In one experiment endosulfan was degraded by each of 49 bacteria or 10 fungi, some of them metabolizing more than 30 percent of the applied pesticide in 6 weeks; nevertheless, the average conversion to CO_2 was less than 0.2 percent.[32]

No procedures have been put forward in the literature, and data is not available on which a firm empirical estimate can be based for degradation losses of the kind that have been considered here.

6.2.8 Retention of Pesticides by Sorption

Adsorption of pesticides by soil or other materials is generally treated as a reversible process[33, 34, 35] whereby a pesticide is not considered to be permanently attached to the adsorbant. There is occasional mention by some

authors of possible irreversible adsorption and a recognition that some pesticide in the soil is to some degree unavailable to processes leading to degradation or removal.[36] Simulation models to be used for incorporating the concept of pesticide pools with varying degrees of availability into pesticide loss calculations are in the beginning stages of development.[36] However, at present there is an absence of data from which pesticide adsorption or other pesticide movement restricting processes can be calculated.[34]

6.3 Application of Methodology

In 1976 the farmers in Fresno County harvested 2,543,215 acres of crops,[37] which included 50 to 100 crop varieties and were reported to have consumed about 9 million pounds of pesticides sold under 900 different brand names.[38] In choosing an applicable method for estimating the hydrocarbon emissions resulting from pesticide use, the complexity and magnitude of pesticide use in Fresno County makes it evident that the method will have to be relatively simple in operation and will require the input of data which are readily available.

6.3.1 Emission from Deposited Pesticide

Of the methods reviewed in Section 6.2, the model developed by Spencer to estimate volatilization loss from soil surfaces emerges as the most appropriate one to be adopted for use in this study. This model is simple and requires input data which can be readily obtained. In addition, the accuracy of this model has been demonstrated in one study by direct

emission measurements.[6] The model is depicted by Equation 6-19 and was discussed in detail in Section 6.2.3.

In order to take into consideration the different evaporative losses from water, soil, and vegetated land, an appropriate adjustment of the E value (representing the water evaporation rate) will have to be made. The values of E for emission calculations are calculated using the monthly evaporation from a Class A pan reported from measurements made in 1976 at the Friant Government Camp station.[39] The evaporation and other weather data for Fresno County are shown in Table 6-5.

The pesticide-related water surfaces in Fresno County would consist primarily of irrigation canals and ditches and, for part of the year, rice plantings. The acreage planted in rice in 1976 was about one-half of one percent of the total crop acreage in Fresno County, and the water surface exposed during irrigation was comparatively small and highly variable. Therefore, the difference between evaporation of pesticide from water surfaces and other crop lands is negligible when compared to the total pesticide evaporation, and an estimate of this evaporation from water surfaces is not included in emission calculations.

Empirical data relating evapotranspiration from each crop on vegetated land in Fresno County to evaporation from an open pan are not available. In different, mature crops, this ratio has been reported to vary between 0.75 and 1.15.[20, 21] The mid-value of 0.95 may be taken as representative of the average condition and is used for calculating evapotranspiration from vegetated land although it may overestimate ET for early crop stages An additional factor of 0.77 was applied to the pan evaporation to correct

TABLE 6-5

General Climatological Data for Fresno County in 1976

Month	Wind Speed (mph)	R.H. (%)	Evaporation (inches)	Temperature (^{o}F)	(^{o}C)
January	3.4	75	1.76	44.3	6.8
February	5.1	80	2.39	49.6	9.8
March	6.7	65	4.13	52.4	11.3
April	6.2	60	5.49	57.2	14.0
May	6.9	44	10.81	69.7	20.9
June	8.4	41	12.48	73.0	22.8
July	9.0	44	14.71	79.4	26.3
August	8.1	58	10.07	72.7	22.6
September	6.4	62	7.96	72.2	22.3
October	4.3	65	4.98	65.1	18.4
November	4.1	80	2.33	53.4	11.9
December	4.0	69	1.72	46.5	8.1

for the excess evaporation which occurs when pan measurements are made in a drier area not surrounded by vegetated land.[40] Therefore, the value of ET will be designated E_A and for vegetated surface $E_A = 0.95E_{pan} \times 0.77 = 0.73E_{pan}$.

A separate value of E_A for evaporation from soil was used in the emission calculations since a large amount of pesticide is applied on to bare or nearly bare soil surfaces as pre-emergence sprays. The pan ratio for soil evaporation varies greatly depending on the amount of drying that has occurred after watering. An E_{pan} value of 0.40 has been found for soil kept moist enough to promote seedling growth and this value was used in the calculations.[17, 41]

The acreage treated was considered to be vegetated land when insecticide, fungicide, plant growth regulator or defoliant was applied and was considered to be soil when herbicide or nematocide was applied.

Pesticide emission from soil or crop surface is proportional to the water evaporation potential (E) as indicated in Equation 6-19. This relationship is shown in Figure 6-1 for three pesticide chemicals used in Fresno County in 1976 with vapor pressures varying between 0.2 and 5×10^{-7}. The August, 1976 pesticide emission under 58 percent relative humidity and 10.0 inches of water evaporation was taken as the basis for the calculation and determines the slopes of the curve.

It was noted above that pesticide emission is proportional to the water evaporation potential expressed in Equation 6-19, by the empirical water evaporation factor E.

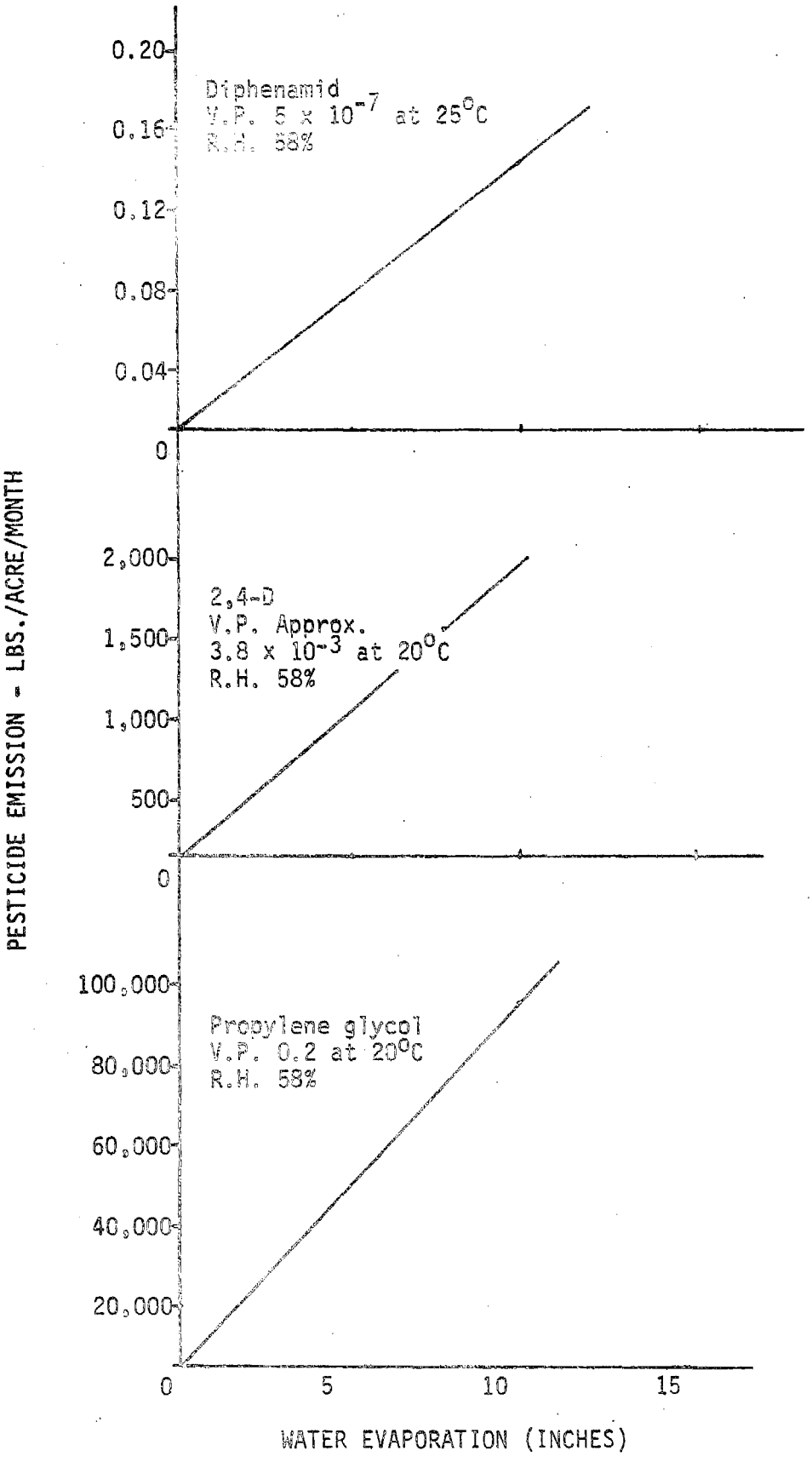

Figure 6-1. The Relationship Between Water Evaporation Potential and Pesticide Emission Rate.

$$-\frac{dm_i}{dt} = \frac{E}{(1 - R.H.)} \times \frac{P_i (M_i)^{\frac{1}{2}}}{P_W (18)^{\frac{1}{2}}} \qquad \text{(Eq. 6-19)}$$

Also, it was indicated previously in Section 6.2.1 that water evaporation is proportional to $P_W(1 - R.H.)^2$. In effect, in equation 6-19 we have the factor E in the numerator which is proportional to (1 - R.H.) and the factor (1 - R.H.) as part of the molecular diffusion coefficient in the denominator. Therefore, the pesticide evaporation rate - $\frac{dm_i}{dt}$ does not have a direct relationship to relative humidity.

6.3.2 Emission During Application

The estimation of evaporative loss of pesticides during application will be based on generalizations from the measured losses observed in the studies listed in Table 6-6.

From the data in Table 6-6, it is estimated that 18.5 percent of a pesticide with a vapor pressure of 10^{-3} mm Hg will be lost during application when the temperature is 68-8°F (20.4°C). Application loss of a pesticide appears to have an approximately linear relationship to the log of its vapor pressure, but loss may be assumed to be negligible from compounds with vapor pressures less than 10^{-7} mm Hg. Other data suggest that the pesticide evaporation rate is approximately proportional to the square of the temperature within the range of about 5 to 30° C.[28, 43, 44] By combining these considerations, the equations obtained for the calculation of emission during application are:

$$\text{Emission during application} = A - A'$$

where:

TABLE 6-6

Reported Pesticide Losses During Application

Pesticide	Vapor Pressure (mm Hg)	Application Temperature (°F)	Percent Loss During Application	Reference
Disulfoton	1.8×10^{-7} (20°C)	70	18	42
Phorate	8.4×10^{-4} (20°C)	70	0	42
Zinophos	3×10^{-3} (30°C)	71	46	25
Dyfonate	2.1×10^{-4} (25°C)	61	12.6	25
Dimethoate	8.6×10^{-6} (25°C)	72	16	26
Average	8.12×10^{-4}	68.8	18.5	

$$A' = A - A\left[(4.625)(\log Pi + 7))0.0024\ T^2)\left(\frac{1}{100}\right)\right] \qquad \text{(Eq. 6-28)}$$

and: A = the amount of pesticide applied,

A' = the amount of pesticide deposited on soil or other surface after application losses,

Pi = the vapor pressure in mm Hg of pesticide i at 20°C (adjusted in proportion to the water vapor pressure and temperature curve when needed).

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 values for application loss are treated as emissions in this calculation since the proportions of drift and evaporation in the reference data are not known. Nevertheless, they may be judged not to be overestimations for the majority of pesticide applications. Von Rumker[24] has estimated the average of drift and evaporation loss at 30 to 40 percent during application. In aerial applications to forests, DDT loss was estimated to be over 50 percent,[23] and in extreme cases more than 70 percent of aerially applied pesticide is reported to be lost.[22]

6.3.3 Biodegradation Losses

Established procedures and data are not available for calculation of the percentage of each pesticide removed by biological action, but since biological degredation is one of the main processes removing pesticide from the pool available for evaporation, the loss by this means will be estimated for this report to be 2 percent each month for most of the pesticides for which emissions are calculated.[29] Exceptions to this will be the aliphatic acids

and phenylalkanoates where it will be estimated that the loss is 30 percent of the amount available each month, and those pesticides classed as highly persistant (half-life >3 months) will not be considered to undergo biological degradation.

6.3.4 Pesticide Sorption Losses

Since it is recognized in this report that some portion of applied pesticide can be unavailable for evaporation due to adsorption and absorption[27] for a considerable or indefinite time, it will be estimated that 2 percent of deposited pesticides are bound except for compounds with high vapor pressures (1.0 mm Hg or greater at 20°C).

6.4 Conclusions and Recommendations

The method of estimating pesticide emissions, which was discussed and used in this study, is based on theoretical considerations and is modified by certain factors to account for various environmental differences. It is possibly the most appropriate method now available, and it may, in fact, be the only method which can be applied to the wide-range of pesticide chemicals and environmental conditions encountered in Fresno County. However, the method might be improved by making additional adjustments based on any of the specific experimental data which is available or which may become available in the future.

The calculation of emissions by the methods used here has been shown through a limited number of measurements to provide reasonably accurate values under some conditions.[6, 45] Different conditions and estimations

for other pesticides could lead to some error. In order to identify and reduce the error in future estimates of pesticide emissions, the following recommendations are made:

1. Calculated vaporization rates of individual pesticides should be compared (where possible) with literature reports of measured values. This is advised for the purpose of validating the method as well as for making adjustments in the emission calculations.
2. Calculated estimates of the persistance of specific pesticides should be compared with measured persistance of the same pesticides in soil, water, and on vegetation. The possible degradation products should be included in the measurements of persistance, and they should be considered in relation to differences in volatility from the parent compounds.
3. For applications made to soil, water, and vegetation, the pesticide emission calculations should be made separately. To do this, it would be necessary that accurate records be maintained of the kind of application of each pesticide including inert organic ingredients.

6.5 References

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7.0 PESTICIDE EMISSION INVENTORY

7.1 Introduction

The primary objective of this project was to conduct an inventory of hydrocarbon emissions associated with pesticide applications in Fresno County for the calendar year 1976. In meeting this objective, application data from the PUR and data obtained from farmer and pesticide dealer/supplier surveys were used. Based on these data, emissions were calculated.

Calculating the emissions resulting from pesticide use differs from similar efforts involving emissions from other sources. The more "conventional" air pollutant emission estimation is based on emission factors derived from engineering specifications and/or from actual measurements of specific sources. To calculate emissions resulting from pesticide applications, one has to consider the type of surfaces to which pesticides are applied. Emission rates will differ depending on whether the type of surface is soil, water, or crop. In addition, factors such as temperature, relative humidity, and the molecular weights and vapor pressures of the pesticide products will affect the overall emission rates. Details on some of the factors that are pertinent to emission rates of pesticides were discussed in Chapters 4 and 6.

Adding to these complexities, a considerable amount of data, such as the vapor pressures, molecular weights, and evaporation rates of pesticides from different surfaces, are either not available to this study or have not been developed. For the purpose of this study, some of these data were estimated.

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

7.2 Methodology and Assumptions

7.2.1 Calculation Methods

In calculating emissions, it was assumed that there were no emissions from inorganic pesticides or from nonvolatile organic pesticides. The assumption of no emissions from nonvolative organic compounds is not entirely accurate in the long-term, since, to an uncertain extent, emissions can possibly occur from these compounds after degradation in soil or elsewhere.[1, 2]

The estimate of emissions from organic pesticides was made through calculations based on principles and assumptions discussed in section 6.3.1. The estimate for pesticides with significant vapor pressure applied on acreage requires the following calculations:

1. Calculation of the maximum monthly emission rate using equation 6-19 with the following modifications:

$$E_p = -\frac{dmi}{dt} = \frac{E_A}{(1 - R.H.)} \times \frac{P_i(M_i)^{1/2}}{P_w(M_w)^{1/2}} \qquad \text{(Eq. 7-1)}$$

where: $E_p = -\frac{dmi}{dt}$, the monthly evaporation rate of compound i per acre;

E_A = the adjusted water evaporation rate ($E_A = 0.73E$ for applications to vegetated surface and $0.40E$ for applications to soil surfaces)

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

2. Calculation of evaporation during application using equation 6-28 to estimate the amount of pesticide deposited (A').

$$\text{Evaporation} = A - A' \qquad \text{(Eq. 7-2)}$$

where: $A' = A - A\left[(4.625)(\log P_i + 7)(.0024T^2)\left(\frac{1}{100}\right)\right]$;

(assume A' = 0 for $\log P_i < -7$)

A = the pounds of pesticide i applied;

P_i = the vapor pressure of pesticide i at 20°C;

T = average temperature (°C) reported during the month of application.

3. Calculation of the remainder (A'') after estimated loss to irreversible sorption and biodegradation for the first month using the equation:

$$A'' = A' - 0.02A' - 0.30A' \qquad \text{(Eq. 7-3)}$$

for aliphatic acids and phenylalkanoates, and

$$A'' = A' - 0.02A' - 0.02A' \qquad \text{(Eq. 7-4)}$$

for other pesticides with some volatility. However, it is assumed there is no loss to biodegradation or adsorption for compounds where the vapor pressure is ≥ 1.0 mm Hg at 20°C.

4. Calculation of monthly carry-over for pesticides partially evaporated during one month by comparing $\frac{A''}{acres}$ with the maximum emission rate for that month (E_p). If $E_p \geq \frac{A''}{acres}$, $A'' + (A - A')$ = the emission for the month. If $E_p < \frac{A''}{acres}$, $(E_p \times acres) + (A - A')$ = the emission for the month, and $\frac{A''}{acres} - E_p$ was carried to the next month. The same procedure was repeated for each succeeding month where the carry-over minus 2 percent for biodegradation was greater than the E_p for that month. The carry-over was continued until the pesticide ran out or up to 12 months, whichever came first.

Total emission for each month was found by multiplying lbs/acre emissions by the acres under the month of application. Applications made for each month were treated separately in the manner described above, and the total pounds of emissions were summed for each month. Some sample calculations are included in Appendix G.

Emission calculations for nonacreage applications were done for all chemicals having reported or estimated vapor pressures of less than 1.0 mm Hg. Two percent of the applied poundage was subtracted for adsorption, and two percent was subtracted for biological or other degradation to forms unavailable for production of hydrocarbon emissions, and the remainder of the application was considered to be evaporated in the month of application. Pesticides with vapor pressures of 1.0 mm Hg or greater were considered to be completely evaporated in the month of application.

Emissions for August 24 and 31, 1976, were calculated in the same manner as monthly emissions; although, no carry-over from previous days

was added. The reported water evaporation rates of 0.31 and 0.41 inches for August 24 and 31 respectively were substituted for the monthly water evaporation rate in making the calculations.[3]

7.2.2 Data for Emission Calculations

Emissions were calculated for pesticides of appropriate volatility from those in the inventory of pesticides applied in Fresno County in 1976.

Values for the vapor pressure and the molecular weight of a pesticide are required for calculation of the evaporation rate. Molecular weights are available for nearly all pesticides and related products; vapor pressures for many of them are reported in the literature. These values were used for emission calculations. For some compounds, values for vapor pressure were not found in the literature, and in these cases an estimated vapor pressure was used.

The vapor pressures and molecular weights used in emission calculations are listed in Appendix G. Reference compounds are given for estimated vapor pressures where applicable. In most instances, estimates of vapor pressures were based on the vapor pressures reported for reference compounds of similar structure. If the structural differences between the reference compound and the unknown were minor, it was estimated that they have the same vapor pressure. When there was greater structural dissimilarity, the vapor pressure was considered to be decreased by substitution of more polar groups such as -COOH, $-NH_2$, $-HPO_3$, and -OH, as well as by an increase in molecular weight with other things equal, by lower boiling point, and in some cases by lower melting

point. In a number of instances, no compound of generally similar structure and reported vapor pressure could be found. When this occurred, the vapor pressure estimate was made from a judgment based on the overall structure in relation to other compounds, the presumed influence of substituent groups and any reported physical characteristics such as boiling point and melting point. The accuracy of estimated vapor pressures may be expected to be highly variable.

Nonsynthetic organic pesticides consist of a mixture of compounds which vary depending on the region in which the oil was produced and on the fractionation and purification methods used. These oil products are generally not well characterized with regard to the specific chemicals contained in them nor by the range of their molecular weights.[4, 5]

The following procedure was used for obtaining estimates of molecular weights and vapor pressures of nonsynthetic hydrocarbons.

(1) Based on information from the Master Label File of the DFA, the kinds of products included under the various chemical headings (Petroleum distillates, Petroleum hydrocarbons, etc.) was determined, as well as the percentage under each heading used, such as insecticide, herbicide or others.

(2) The predominant types of insecticide or herbicide included in each category were determined from the names of products and from their uses listed in the Pesticide Use Report. Examples of the types considered are aquatic weed killer, pesticide solvent, selective herbicide, narrow-range tree spray and dormant tree spray.

(3) The usual boiling points for 50 percent distillation for different types of pesticide oils was found from a number of literature sources.[6, 7]

(4) Vapor pressure estimates were determined from the vapor pressure - boiling point correlation of Maxwell and Bonnell[8] using the boiling points at 50 percent distillation.

(5) Molecular weights were estimated to be the same as for straight chain paraffins with boiling points equal to the 50 percent boiling points of the pesticide oils. Interpolations were made to obtain molecular weights between n and n + 1 carbon atoms.

7.2.3 Classification Methodology for Photochemical Reactivity of Organic Pesticides

The photochemical reactivity of pesticides was estimated by reference to the California Air Resources Board (CARB) reactivity classification list (Appendix A).

While most of the organics used in crop protection are complex, multifunctional compounds, a look at each functional group within the compound revealed those molecular sites where reactions would most likely be initiated. It is generally accepted that for a molecular reaction to proceed, a specific stereochemical arrangement is required in addition to the basic electronic requirement between oxidized states.

To evaluate the stereochemical nature of each complex organic pesticide would have been a monumental task. It was assumed, therefore, that the kinetics of the postulated reactions would be dependent primarily on the existence of certain functional groups. In those instances where functional groups did not correspond directly to those of the CARB's reactivity classification, structural similarity was relied upon (e.g., double bonded oxygen was considered similar to ketonic oxygen or acidic oxygen).

Each molecular compound was then assigned a reactivity according to its functional group with the highest reactivity according to the CARB's classification. Since reactivities are generally limiting functions, the fastest route is usually taken in a reaction. For those compounds for which a molecular structure could not be identified, a Class II reactivity was arbitrarily assigned. Those compounds are identified in Appendix H by a (?).

Nonsynthetic hydrocarbon pesticides are mixtures of compounds of more than one reactivity class. It is presumed here that nonsynthetic hydrocarbons are composed of class 2 paraffins (including cycloparaffins) and class 3 aromatic hydrocarbons. The sulfonatable residue of oils is taken as the aromatic content where other measures of aromatic content are not available.

The estimated aromatic content of petroleum chemicals and distribution in reactivity Classes II and III is shown in Table 7-1.

The types of insecticides and herbicides in each petroleum chemical and their uses were determined from the PUR, and the usual or average aromatic content of these was obtained from a number of literature

TABLE 7-1

Estimated Aromatic Content and Reactivity Class
of Nonsynthetic Hydrocarbons
Used in Pesticides

Hydrocarbon Pesticide	Percent Insecticide and Herbicide Products, and Percent Aromatic, in ()		Chemical Content and Reactivity Class, Average Percent		Reference
	Insecticide	Herbicide	Aromatic (Class III)	Paraffin (Class II)	
Aromatic Petroleum Solvent	0	100 (85)	85	15	6
Mineral Oil	77 (8)	23 (70)	15	85	6
Petroleum Distillates	100 (15)	0	15	85	6
Petroleum Hydrocarbons	19 (8)	81 (85)	70	30	6
Petroleum Oil Unclassified	88 (8)	12 (70)	15	85	4, 6, 7
Petroleum Distillate, Aromatic	a		85	15	6
Xylene	a		100	0	6, 9
Xylene Range Aromatic Solvents	a		80	20	6
Diesel Oil	a		20	80	10
Kerosene	a		40	60	11

[a]The aromatic content of these compounds is the same for insecticides and herbicides.

sources. Both insecticides and herbicides are found under some of the petroleum chemical headings. When this was the case, an average value for percent aromatic was calculated from the proportionate number of products registered as insecticide or herbicide under each chemical and the percent aromatic found in the literature for each.

7.3 Emission Inventory

7.3.1 Inventory of Emissions from Organic Pesticide Applications

The methodology described earlier was applied to the pesticide application data in order to develop an inventory of emissions resulting from the application of organic pesticides in Fresno County during 1976. A summary of this inventory is shown in Table 7-2. The majority of emissions (68 percent) were due to nonsynthetic pesticides. In addition, the table illustrates the total amounts of reactivity Class I, Class II, and Class III emissions from synthetic organic and nonsynthetic pesticide applications. Only a small quantity (11 percent) of synthetic organic emissions are of low reactivity (Class I). In addition, all of the nonsynthetics were determined to be reactive (Class II or III). Consequently, it is apparent that nearly all the emissions associated with organic pesticide use are reactive organic gases.

Tables 7-3 through 7-5 expand on the emission inventory summary and describe the emissions resulting from the application of each type of organic synthetic and nonsynthetic pesticide (acreage and nonacreage applications) according to its reactivity classification and month. From these tables it is evident that nonacreage pesticide applications

TABLE 7-2

Summary of 1976 Emissions Calculated from Synthetic and Nonsynthetic Pesticide Applications in Fresno County Based on Reactivity Classifications

Pesticide Types	Emissions (lbs.)						
	Reactivity Class			ROG *		TOG **	
	I	II	III	Weight	%	Weight	%
Synthetic Organics	500562	623767	3364884	3988651	29	4489213	32
Nonsynthetic	-	4854340	4766078	9620418	71	9620418	68
TOTAL:	500562	5478107	8130962	13609069	100	14109631	100

* ROG = Reactive Organic Gas. (Reactivity Classes II + III)

** TOG = Total Organic Gas. (Reactivity Classes I + II + III)

TABLE 7-3

Summary of Monthly Emission Distribution for All Pesticide Types with Reactivity Class I Applied in Fresno County in 1976

Pesticide Type	Emissions (lbs.) Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Total
SYNTHETIC ORGANIC													
Insecticides:													
Acreage	3	6	6	330	5617	26363	44198	19442	2807	244	60	3	99079
Nonacreage	133	31		13						43	425	852	1497
Herbicides:													
Acreage	4822	2705	10083	5972	4033	1594	574	850	742	4344	5739	4414	45872
Nonacreage	637	697	76	193	24	156	12	547	167	475	1973	459	5416
Fungicides:													
Acreage	63	98	97	113	159	2635	2021	4435	2924	467	133		13145
Nonacreage	777		1017	1020	672	1662	621	621	1391	389	1041		9211
Nematocides:													
Acreage	14047		6840	26861	4275	97961	377	71843		1907	10103		251384
Nonacreage	7229	10714	4909	4457	4585	3518	4266	2709	5604	9970	12713	4127	74801
Inert Organic Ingredients:													
Acreage	1	1	11	6	10	18	29	25	20	21	4	3	149
Nonacreage			1		1	1	2	1	1	1			8
TOTAL:	27712	14252	23040	38965	19376	133908	52100	100473	13656	35031	32191	9858	500562

TABLE 7-4

Summary of Monthly Emission Distribution of All Pesticide Types with Reactivity Class II Applied in Fresno County in 1976

Pesticide Type	Emissions (lbs.) Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annua Tota
SYNTHETIC ORGANIC													
Insecticides:													
Acreage				189	11046	10386	762	116	528				230
Nonacreage			11	28	40	11	11	425	26	28	198	364	11
Herbicides:													
Acreage	23639	5962	5503	11813	10947	775	591	51331	66460	8910	3044	8901	1978
Nonacreage	618	1205	175	307	263	579	786	859	597	649	2279	128	84
Fungicides:													
Acreage		26	238	1291	2226	26842	39901	43784	1329	318			1159
Nonacreage	2110		1557		949				317	845	2428		82
Nematocides:													
Acreage		301	6189	5968	4277		100		632	12940	77162	33736	1413
Adjuvants:													
Acreage	58			1	84	187	618	365	214	4147	360		60
Inert Organic Ingredients:													
Acreage	1025	1243	8587	4286	7321	13255	22374	17669	15155	18649	3083	2126	1147
Nonacreage	145	88	532	290	506	796	1314	1102	884	992	206	133	69
NONSYNTHETIC													
Minor Active Ingredient:													
Acreage	76994	106058	25110	3753	18802	14918	23996	23610	17792	17040	1949	58826	3888
Nonacreage	3106	3766	6432	6619	30322	3376	3335	73076	9101	7375	4328	4584	1554
Pure Oil:													
Acreage	365704	1086745	44376	11471	327026	33456	27940	401731	61970	22250	16645	972408	33717
Nonacreage	102863	297682	12467	1558	93045	9352	7792	114812	17306	6233	73253	202071	9384
TOTAL:	576262	1503076	111177	47574	506874	113933	129520	728880	192311	100376	184931	1283277	54781

TABLE 7-5

Summary of Monthly Emission Distribution of All Pesticide Types with Reactivity Class III Applied in Fresno County in 1976

Pesticide Type	Emissions (lbs.) Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Total
SYNTHETIC ORGANIC													
Insecticides:													
Acreage	14667	25384	110641	94082	116086	245348	511976	394044	83782	47148	9750	8892	1661800
Nonacreage	5126	5287	5287	9175	5056	6559	6789	7607	3178	19739	4165	3807	83208
Herbicides:													
Acreage	3886	31426	53167	3682	25021	31661	9379	5534	6994	11704	6658	2721	191833
Nonacreage	842	1325	484	1310	54	---	95	124	407	3642	3967	340	12590
Fungicides:													
Acreage	---	16649	2051	825	364	7694	6177	23288	28936	4686	---	---	90670
Nonacreage	15	11	482	176	141	160	11	96	111	53	130	---	1386
Nematocides:													
Acreage	533	15951	485	---	---	3101	---	---	90062	6760	22129	68430	207451
Defoliants:													
Acreage	270	---	---	---	---	---	---	---	203194	251845	2982	---	459291
Inert Organic Ingredients:													
Acreage	5540	10721	42927	21164	38655	59365	102826	92424	77028	135919	17951	14350	618870
Nonacreage	817	443	2585	1922	4749	3525	5547	7187	3958	5226	1202	624	37785
NONSYNTHETIC													
Minor Active Ingredient:													
Acreage	14372	21817	22065	20451	36084	43524	95200	90487	34503	27094	2594	136998	545189
Nonacreage	1004	1308	1744	1841	53452	1594	1214	14025	11093	2429	1945	1490	93139
Pure Oil:													
Acreage	64537	191778	7831	2025	493091	5904	4930	814499	75992	3926	2937	1565118	3232568
Nonacreage	18153	52532	2200	275	137985	1650	1375	233555	21199	1100	389435	35660	895119
TOTAL:	129762	374632	253382	156928	910738	410085	745519	1682870	640437	522271	465845	1838430	8130899

account for only a small fraction (less than 20 percent) of total emissions, and the small quantity of Class I reactivity pesticide emissions which do exist are mostly derived from nematocide applications.

Figure 7-1, derived from these tables, illustrates the pattern of total emissions throughout the course of 1976. There were four definite emission peaks during the year: February, May, August, and December. This pattern and its significance will be discussed later.

It is important to emphasize the significance of nonsynthetic pesticide emissions because of their high reactivity and their great volume. Since the application of nonsynthetics as a class is rather loosely regulated, the quantities applied are difficult to monitor. Nevertheless, the use of this class of pesticides constitutes a much greater photochemical oxidant precursor source than does the use of synthetics. Table 7-6 indicates the relative proportion of TOG emissions from nonsynthetic pesticide applications as compared to TOG emissions from all pesticide applications. Nonsynthetic pesticide emissions comprise the bulk (more than 70 percent) of all pesticide emissions during the months of January, February, May, August, November, and December. The four peak months of the year for TOG emissions from all pesticide applications coincide with heavy nonsynthetic pesticide use months (Table 7-6 and Figure 7-1). In other words, nonsynthetic pesticide use is primarily responsible for the emission peaks.

Figure 4-1 depicted the frequency of violations of the oxidant standards in the City of Fresno during 1976. Oxidant violations were recorded in March and May; a dramatic increase in violations occurred

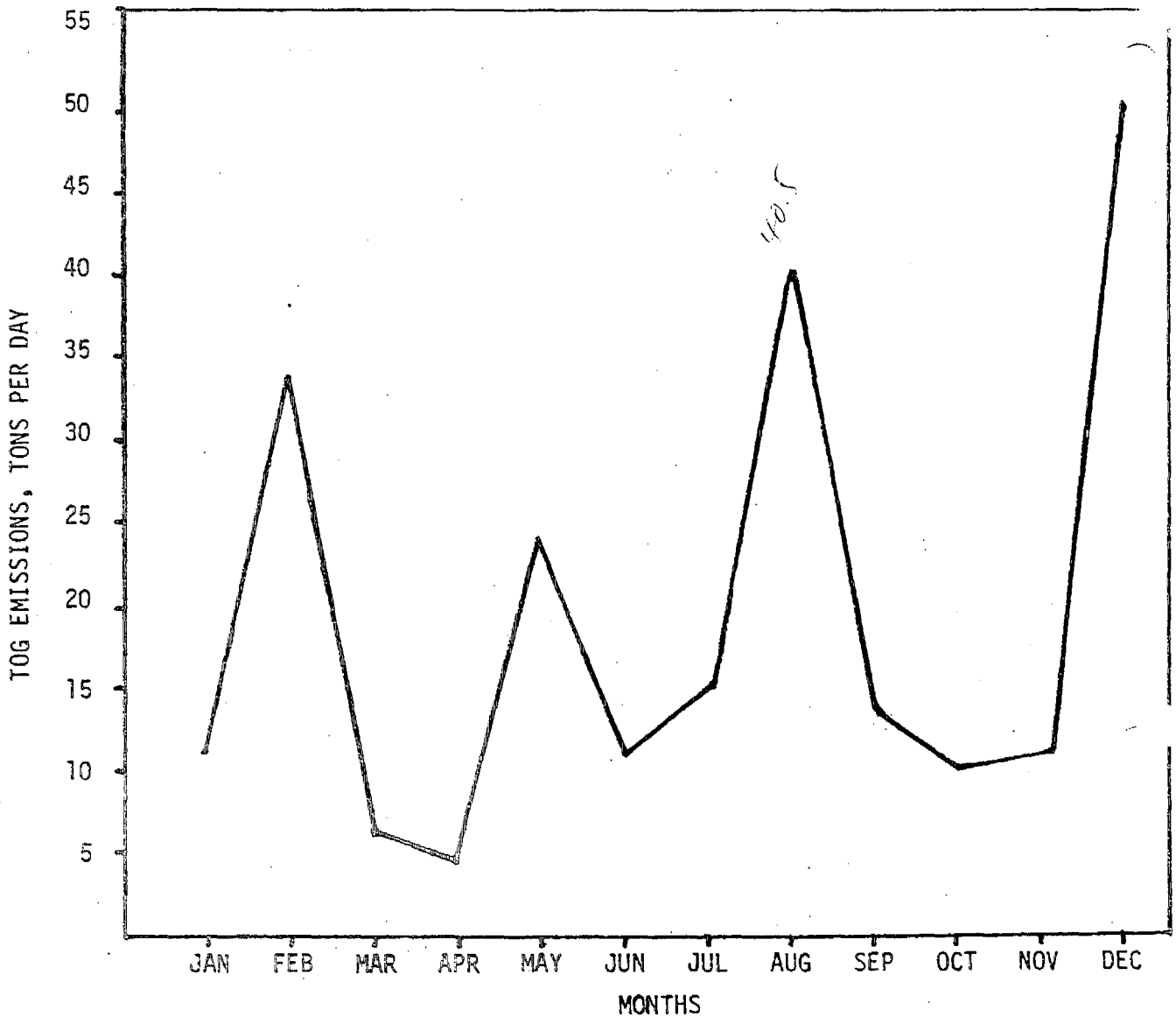

Figure 7-1. Emissions of Total Organic Gas (TOG) Resulting from Pesticide Use in Fresno County in 1976. TOG emissions are nearly equal to reactive organic gas (ROG) emissions; the difference is too small to depict on this graph.

TABLE 7-6

Total Organic Gas ("TOG") Emissions from Nonsynthetic Pesticide Applications Shown as a Percentage of TOG Emissions from All Pesticide Applications in Fresno County for Each Month of 1976.

Month	Percentage
January	88.1
February	93.1
March	33.5
April	23.5
May	83.9
June	21.7
July	18.9
August	73.2
September	29.9
October	14.0
November	75.8
December	95.4

in July, and a high frequency of violations continued through November. October was the worst month of the year for oxidant violations. Figure 4-2 showed the hourly average hydrocarbon (TOG) concentrations. The concentrations were relatively low during the spring and early summer but rose sharply in August and continued at a high level through December. Of the TOG emission peaks indicated in Figure 7-1, the peak in August corresponds best to both the high ambient levels of TOG in Fresno and a high frequency of oxidant standard violations. Consequently, it would appear that pesticide applications, particularly those of nonsynthetic pesticides, during the latter part of the summer contribute to oxidant problems in the Fresno area. This does not say that these pesticide emissions are a prime cause of the oxidant standard violations in Fresno, but they undoubtedly contribute to the problem on a county-wide basis.

A word of caution with regard to the interpretation of Figures 4-1 and 4-2 is necessary. These figures are based on air quality data collected at the Olive Street monitoring station in Fresno. These data are influenced by the Fresno urban area; emissions associated with urban development tend to decrease maximum oxidant levels due to oxidant-scavenging nitric oxide emissions and to increased hydrocarbon levels. The Olive Street station, however, was the only monitoring station in Fresno County for which complete oxidant and hydrocarbon data were available for 1976.

7.3.2 Pesticide Emissions for August 24 and August 31, 1976

The estimated emissions on August 24 and August 31, 1976, in Fresno County are shown on Table 7-7.

TABLE 7-7

Estimated Emissions of Synthetic and Nonsynthetic Pesticides Used on August 24 and August 31, 1976, in Fresno County.

Pesticides (Chemicals)	Emissions (lbs)									
	Reactivity Class						ROG		TOG	
	I		II		III					
	Aug 24	Aug 31	Aug 24	Aug 31	Aug 24	Aug 31	weight	(%)	weight	(%)
SYNTHETIC ORGANICS										
Insecticides										
Bidrin-R						175	175		175	
Carbofuran					19		19		19	
Carbaryl[C]					521	363	884		884	
Diazinon					269	136	405		405	
Dimethoate[C]						31	31		31	
Di-Syston-R					120		120		120	
Ethion[C]					6	8	14		14	
Fundal-R					1477	513	1990		1990	
Kelthane-R[C]		13							13	
Malathion[C]					28		28		28	
Methomyl					833	405	1238		1238	
Methyl Parathion[C]					125	43	168		168	
Monitor-R					732	198	930		930	
Naled					1097	293	1390		1390	
Parathion					401	315	716		716	
Phorate					65	160	225		225	
Phosdrin-R[C]					7	7	14		14	
Toxaphene					106	268	374		374	
Subtotal		13			5806	2915	8721	24.6	8734	24.0
Fungicides										
Botran-R[C]	9	5							14	
Captan					613	48	661		661	
Chlorothalonil			1592				1592		1592	
Subtotal	9	5	1592		613	48	2253	6.3	2267	6.3

[C]Compounds with carryover (Carryover not calculated).

TABLE 7-7 (continued)

Pesticides (Chemicals)	Emissions (lbs) Reactivity Class I Aug 24	I Aug 31	II Aug 24	II Aug 31	III Aug 24	III Aug 31	ROG weight	ROG (%)	TOG weight	TOG (%)
Herbicides										
Balan-R	41								41	
DNBP			1845	3404			5249		5249	
Kerb-R[c]					5		5		5	
Endothal[c]					3	8	11		11	
Subtotal	41		1845	3404	8	8	5265	14.8	5306	14.6
Nematocides										
Chloropicrin	255								255	
Methyl Bromide	519								519	
Subtotal	774								744	2.1
Total for Synthetic Organics	824	18	3437	3404	6427	2971	16239	45.8	17081	47.0
NONSYNTHETIC PETROLEUM PRODUCTS										
Aromatic Petroleum Solvent			249	78	1414	442	2183		2183	
Petroleum Distillate				84		14	98		98	
Petroleum Hydrocarbons			50	32	137	75	294		294	
Petroleum Oil, Unclassified			12955		2286		15241		15241	
Xylene					1134	194	1328		1328	
Xylene Range Aromatic Solvents			12	9	45	40	106		106	
Total for Non-synthetics			13266	205	5016	766	19253	54.2	19253	53.0
Grand Total	824	18	16703	3607	11443	3736	35489	100	36331	100

[c] = Compounds with carryover.

7.4 Conslusions and Recommendations

In summary, the emissions associated with pesticide applications in Fresno County are indeed significant from an air quality perspective. In the California Air Resources Board's 1973 Emissions Inventory,[12] the most recent official Emission Inventory published by the CARB, the ROG and TOG emissions associated with pesticide use in Fresno County were each estimated to be 4.9 tons per day. This 1976 inventory now indicates that ROG and TOG emissions averaged 18.6 and 19.3 tons per day respectively, which is an increase by a factor of nearly 4. Exclusive of emissions attributed to pesticides, the 1973 inventory listed ROG and TOG emissions from stationary sources in Fresno County as 38.4 and 67.9 tons per day respectively, while ROG and TOG emissions from both mobile and stationary sources were 91.3 and 126.1 tons per day respectively. If the 1976 pesticide inventory data were included in the CARB inventory of stationary sources for 1973, the pesticide emissions alone would account for 33 percent of the ROG emissions and 22 percent of the TOG emissions from all stationary sources in Fresno County. The 1976 pesticide inventory data would also account for 17 percent of the ROG emissions and 13 percent of the TOG emissions from all sources in Fresno County.

This report shows that pesticide use makes a significant contribution to hydrocarbon emissions in that county. As indicated in Section 7.3.1 and in earlier chapters, the timing of pesticide applications during the course of the day and, more importantly, the peak in late summer ROG emissions from pesticide applications when ambient oxidant problems are most acute make pesticide use a significant air quality issue. Emission control efforts should be directed toward reducing the use of organic pesticides responsible for producing ROG emissions during the summer and fall months with special emphasis on nonsynthetics.

7.5 References

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