Emission Factor Documentation for AP-42
Section 9.2.2

Pesticide Application

Final Report

For U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Inventory Branch

EPA Contract No. 68-D2-0159
Work Assignment No. I-08

MRI Project No. 4601-08

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For U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Inventory Branch
Research Triangle Park, NC 27711

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NOTICE

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PREFACE

This report was prepared by Midwest Research Institute (MRI) for the Office of Air Quality Planning and Standards (OAQPS), U.S. Environmental Protection Agency (EPA), under Contract No. 68-D2-0159, Assignment No. 005 and I-08. Mr. Dallas Safriet was the EPA work assignment manager for this project.

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SECTION 1

INTRODUCTION

The document *Compilation of Air Pollutant Emission Factors* (AP-42) has been published by the U.S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely issued to add new emission source categories and to update existing emission factors. The EPA also routinely updates AP-42 in response to the needs of federal, state, and local air pollution control programs, and industry.

An emission factor relates the quantity (weight) of pollutants emitted to a unit of source activity. Emission factors reported in AP-42 are used to:

1. Estimate areawide emissions;
2. Estimate emissions for a specific facility; and
3. Evaluate emissions relative to ambient air quality.

This background report supports preparation of a new AP-42 Section 9.2.2, Pesticide Application.

This report contains five sections. Following this introduction, Section 2 gives a description of the pesticide industry, including a brief characterization of the industry, formulations and application methods, and factors impacting pesticide emissions. Section 3 describes the literature search and criteria used to select and rate emission data and emission factors for use in AP-42 documents. Section 4 details emission factor development for pesticide application. Section 5 presents the proposed AP-42 Section 9.2.2, Pesticide Application.

SECTION 2

INDUSTRY DESCRIPTION

Pesticides are substances or mixtures—either derived from natural products or chemically synthesized—that are used to control populations of certain kinds of plant and animal life. Four major categories of pesticide users are: (1) agricultural; (2) industrial, commercial, and institutional; (3) home and garden; and (4) governmental. This report focuses solely on agricultural use of pesticides; in addition, it does not address the much smaller commercial use of selected pesticides in food product distribution.

Pesticide application is the process of applying or delivering various types of pesticides to target pests to increase and improve food production, protect public health, decrease pest-related property damage and injury, and reduce nuisance pest populations. In agriculture, pesticides are used primarily to control nuisance weeds (herbicides), insects (insecticides), fungi (fungicides), nematodes (nematicides), and rodents (rodenticides). Agricultural pesticides are used in the greatest quantities to protect field and orchard crops, but they are also used extensively to protect livestock. Pesticide application is used both preventively, as preemergence application (application before the appearance of the pest), and reactively, as postemergence application to reduce damage to infested crops and animals.

Pesticides are manufactured by firms under the Standard Industrial Classification (SIC) codes for pesticides and other organic agricultural chemicals (2869) and agricultural chemicals, NEC (2879). Pesticides are distributed by manufacturers, retail agricultural distributors, and farm service businesses (SIC 0711, 0721), such as farmer cooperatives. The application of pesticides for disease and insect control is incorporated in SIC 0721.

2.1 INDUSTRY CHARACTERIZATION[1]

Agricultural pesticides are used throughout all regions of the United States with the highest usage occurring in farm states. The five states with the highest pesticide usage by weight are:

1. Iowa
2. Illinois
3. Minnesota
4. Texas
5. California

Table 2-1 lists the top 10 herbicides in terms of usage in 1991 for the 10 major crops in the United States, and Table 2-2 lists the top 10 insecticides in terms of usage in 1991 for the same crops.

2.2 PESTICIDE FORMULATIONS AND APPLICATION METHODS[2-6]

Pesticide application methods vary according to the target pest and the crop or other value to be protected. In some cases the pesticide is preferably applied directly to the pest; in others to the host plant; and in others to the soil or an enclosed air space. Akesson and Yates concluded that "as a general rule, the more thorough the coverage and uniform the distribution of materials on the target or the plant host the more effective is the control." In some cases, however, much of the pesticide applied can be lost inefficiently to the soil or to the air. Since pesticide users desire cost-effective pest control, pesticide manufacturers have attempted to develop formulations that deliver optimal coverage to the target. Different formulations, including dry, liquid, and aerosol, are available to provide different coverages and distributions. Formulations generally contain several components in addition to the "active ingredient" (AI) (i.e., the principal chemical having pesticidal activity). These components may include solvents, emulsifiers, diluents, stabilizers, wetting agents, thickeners, anticaking compounds, and others, depending upon the specific product. These components are collectively termed inert ingredients. The AI content may vary from a percent or less of the total formulation to 50 percent or more, depending on the intended application, and a

TABLE 2-1. TOP 10 HERBICIDES USED ON MAJOR CROPS IN THE UNITED STATES[a]

		AI applied annually[b]	
	Herbicide	Pounds	Kilograms
1.	Atrazine	57,309,000	25,995,000
2.	Alachlor	51,155,000	23,204,000
3.	Metolachlor	50,280,000	22,807,000
4.	Cyanazine	24,958,000	11,321,000
5.	Trifluralin	22,753,000	10,321,000
6.	EPTC	15,547,000	7,052,000
7.	Pendimethalin	12,817,000	5,814,000
8.	Butylate	8,478,000	3,846,000
9.	2,4-D	7,918,000	3,592,000
10.	Propanil	6,696,000	3,037,000

[a] Source: Reference 1.
[b] AI = active ingredient.

TABLE 2-2. TOP 10 INSECTICIDES USED ON MAJOR CROPS IN THE UNITED STATES[a]

		AI applied annually[b]	
	Insecticide	Pounds	Kilograms
1.	Chlorpyrifos	8,024,000	3,640,000
2.	Terbufos	6,130,000	2,781,000
3.	Fonophos	3,011,000	1,366,000
4.	Carbofuran	2,797,000	1,269,000
5.	Phorate	2,735,000	1,241,000
6.	Methyl parathion	2,643,000	1,199,000
7.	Aldicarb	1,071,000	486,000
8.	Acephate	609,000	276,000
9.	Dicrotophos	440,000	200,000
10.	Dicofol	423,000	192,000

[a] Source: Reference 1.
[b] AI = active ingredient.

formulation can have more than one AI. In addition, applicators may field mix two or more products immediately before use for specific needs and economy of application. The following sections discuss the three most common types of formulations.

2.2.1 Dry Formulations

Dry formulations can be obtained as dusts, granules, wettable and soluble powders, water dispersible granules, and baits. Dusts contain relatively small particles and are subject to wind drift; they may also present a coverage problem if they do not remain on target plant surfaces. Granulars are of larger size (50 micrometers [μm] to 2,500 μm in diameter) and are usually intended for soil application. They present less of a drift problem than dusts. Wettable powders and water dispersible granulars both form suspensions when mixed with water. Baits may be approximately the same size as granules or larger, but in the application of baits, the AI is mixed with something such as bran or sawdust, which the target pest will eat.

2.2.2 Liquid Formulations

Solutions and emulsions are examples of liquid formulations. True solutions are formed when soluble liquid or solid AIs are dissolved in water or organic solvent for application. Emulsifiable concentrates are made up of the AI dissolved in an organic solvent with an emulsifier that will allow the AI to be field-mixed with water to form a suspension. The emulsifiers prevent phase separation and settling until application. A flowable formulation is a liquid mixture or powder suspension of an AI, that is nearly insoluble in either organic solvents or water, together with a petroleum base and emulsifiers. The emulsifiers keep the formulation from separating before use and also enable it to mix readily with water for application.

2.2.3 Aerosols

Aerosols are liquids with the active ingredient in solution with a solvent and a propellant. They are used for fog or mist applications. Optimum droplet size ranges are as follows: 10 to 50 μm for flying insects; 30 to 50 μm for foliage insects; 40 to 100 μm for foliage; and 250 to 500 μm for soil to avoid drift.

2.2.4 Pesticide Application Equipment

Pesticides may be applied in a number of different formulations as liquids, dry solids, or gases. Liquid formulations are usually applied as a spray of an aqueous solution or as oil droplets containing a solution or suspension of active ingredient. Pesticides formulated as dusts or granules are normally applied dry. Those active ingredients that exist in a gaseous state at ambient temperature may be applied by soil incorporation as gases or pressurized liquids. Some pesticides have a very high vapor pressure at ambient temperature; formulations of these pesticides are usually incorporated into the soil during application. Those pesticides that are gases or have very high vapor pressure are used as fumigants. A fumigant is a substance or mixture of substances which produce gas, vapor, fume, or smoke intended to destroy insects, bacteria, or rodents. The following sections provide a brief overview of the application methods for liquids, dry solids, and gases or volatile liquids.

2.2.4.1 Liquid Application Equipment—

Different application equipment is required depending on the characteristics of the crop or area treated. A listing of common liquid application equipment and common areas of usage is shown below.

- Low-pressure sprayers—Landscape, right-of-way, and agricultural;
- Powered backpack sprayer—Aquatic, landscape, forest, right-of-way, and agricultural;
- Controlled droplet sprayer—Contact herbicides and insecticides;
- High-pressure hydraulic sprayer—Landscape, dense foliage, large trees, agricultural, and right-of-way;
- Air blast sprayer—Trees, shrubs, and vines;
- Ultralow-volume sprayer—Agricultural and aquatic; and
- Electrostatic sprayers—Row crops, trees, and vines.

Liquid application equipment ranges from small aerosol cans to air blast sprayers with tank capacities up to 1,000 gallons which are capable of spraying up to 1,000 gallons per acre. Of the application methods listed, the most common are the low-pressure sprayers, powered backpack sprayers, and the high-pressure hydraulic sprayers.

Low-pressure sprayers are the common boom-nozzle field and row crop sprayers used for low-growing agricultural row crops and tall crops like corn and cotton. Booms for both low and high crops can be mounted on the back of the tractor or trailer unit or between the front and rear wheels. Powered backpack sprayers are the portable sprayers commonly used for spot applications of pesticides. These units are seldom used for large scale applications. High-pressure hydraulic sprayers used to treat dense foliage, tall trees, or large surface areas are usually vehicle-mounted units. These units discharge the pesticide using either compressed air or an electric motor to directly propel the liquid.

2.2.4.2 Dry Application Equipment—

There are basically two different types of dry pesticide formulations: dusts and granules (including pellets). The large scale application of agricultural pesticides as dust formulations has declined considerably due to concerns for operator safety, low application efficiency, and the high susceptibility of dusts to drift. Particles that do reach the target often do not adhere to the target surface. The application of granules is much more common than dusts because it does not suffer the disadvantages of the dusts.

The most common application methods for dusts are bulb applicators, compressed air dusters, mechanical dusters, and power dusters. Bulb applicators and compressed air dusters are used to treat very small areas such as small cracks and crevices, wall voids, and other confined areas. Mechanical dusters are used for treating landscapes and small agricultural areas. Power dusters are used to treat vine crops and buildings.

Common application methods for granules or pellets are hand-operated applicators, mechanically driven applicators, and powered granule applicators. Hand operated units are used primarily to treat landscapes or aquatic areas; their use is limited for agricultural purposes. Mechanically driven applicators are used principally for the treatment of turf, landscape, and some agricultural areas. Powered applicators are used primarily for agricultural areas, usually row crops.

2.2.4.3 Soil Incorporation Equipment—

Soil fumigants are generally applied to the soil by one of three methods:

(a) the liquid or condensed gas can by injected directly into the soil using soil incorporation equipment;

(b) a gas can be released above the soil surface but beneath a sealed plastic cover; and

(c) a solid fumigant can be applied to the soil and incorporated into the soil by cultivation.

Solid fumigants are compounds that react with water (i.e., soil moisture) to form a gaseous product; the gaseous product is the actual fumigating compound, not the original solid compound.

As with granule applications, soil conditions are most influential in determining fumigant effectiveness. The soil must be neither too wet nor too dry when applying a fumigant. Wet soils tend to trap the fumigant in the soil water, slowing down or preventing fumigant movement through the soil. In soils that are too dry, the gas may diffuse so rapidly that it is not retained long enough to be lethal to the target organism. Fumigation effectiveness is also improved by higher soil temperatures. Higher temperatures enhance vaporization and diffusion of the fumigant in the soil, decreasing the concentration and time required for a lethal dose.

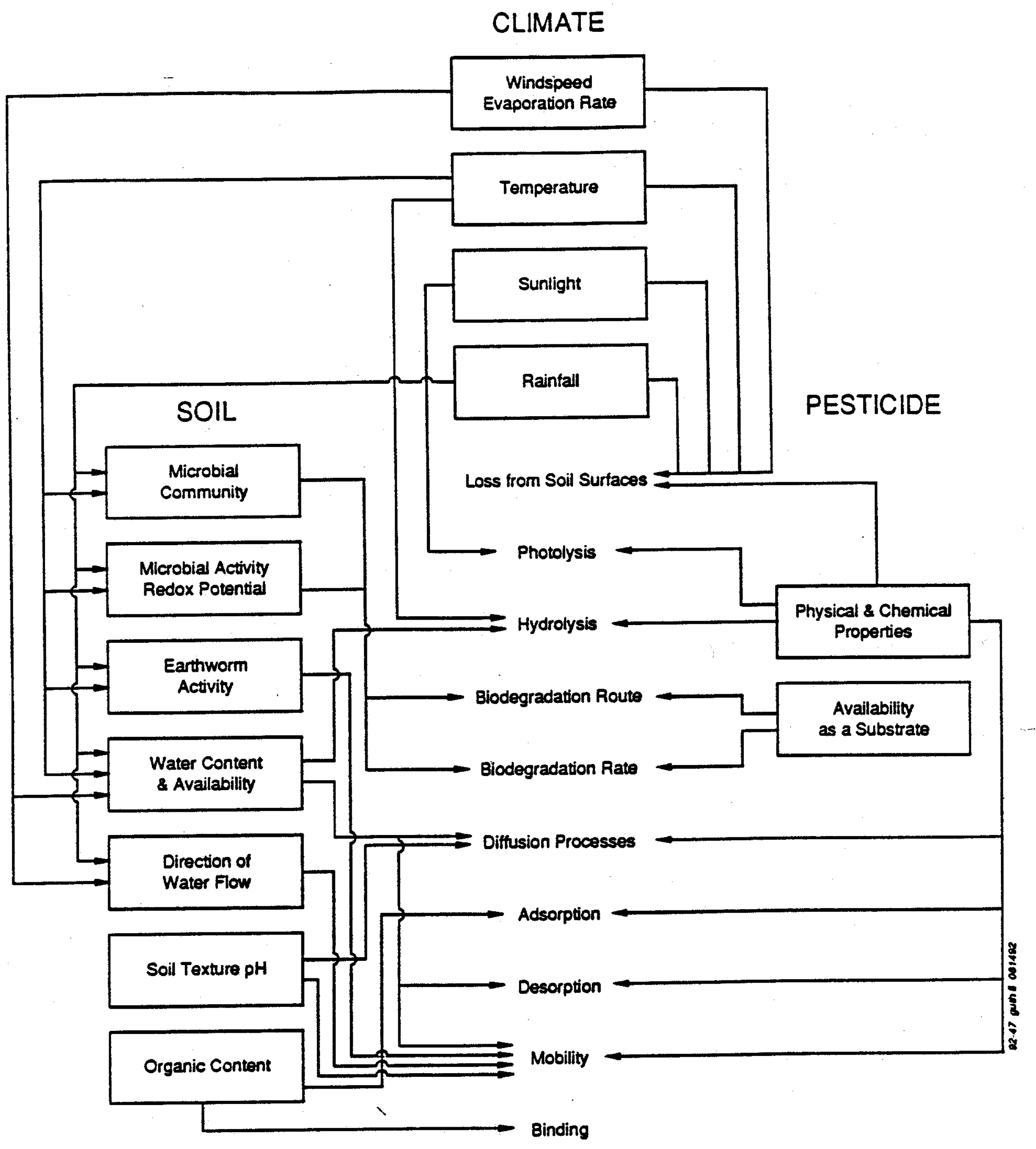
2.3 PESTICIDE EMISSIONS[6]

Constituents of pesticide products may be emitted to the atmosphere both during application and for some months following application. Emissions can occur as particulate matter, mists or droplets, and as vaporous substances. Particulates can consist primarily of inorganic matter used to carry and dilute the active ingredient (AI), or they can contain significant amounts of AI adsorbed on the carrier dust. Mists or droplets occur in spray applications of liquids. Vaporous substances can consist of chemicals having high vapor pressures at ambient conditions that evaporate soon after application or chemicals with lower vapor pressures that require some months to evaporate in significant amounts.

The term "volatile organic compounds" is used differently in different publications, and is abbreviated as both VOC and VOCs. 40 *CFR* Part 51 defines VOC as organics that participate in atmospheric reactions, excluding certain compounds having negligible reaction. (Excluded compounds are C_2H_6, CH_2Cl_2, CH_3CCl_3, and some chlorofluorocarbons and fluorocarbons.) Analytical chemists distinguish volatile organic compounds (VOCs) from semivolatile organic compounds (SVOCs) on the basis of their amenability to EPA-approved analytical methods; a VOC in that context usually has a vapor pressure of about 0.1 mmHg (0.1 torr) at 25°C. Still others may consider all organics that are liquids at ambient temperature to be VOCs. For present purposes, substances in formulations other than AIs will be called inert ingredients. Depending on the formulation, some or all of the inert ingredients may be VOC; these compounds are used as solvents, diluents, emulsifiers, etc. Most pesticide AIs are organic compounds, but few are very volatile (some fumigants are); most are either semivolatile organics or essentially nonvolatile under field conditions.

The following discussion focuses on the volatilization of ingredients in pesticide formulations applied to plants or soils because little information was found on volatilization from other applications or on particulate emissions. Note that the term volatilization is used in some literature sources to include spray drift losses during application as well as true evaporation. In this document, spray drift is not included in volatilization losses because very little information is known concerning loss mechanisms during drift. For this reason, aerial applications are not considered in this AP-42 section.

Many references describe the processes that affect the volatilization (evaporation) of agricultural pesticides applied to soils or plants. Numerous laboratory and field studies have been conducted in an effort to understand these processes. Figure 2-1 summarizes factors that influence volatilization, such as the nature of the pesticide itself, climatic factors, and soil characteristics. An alternative pathway for pesticide emissions is semivolatile pesticides being adsorbed to soil particles that become airborne in the wind.



D.J. Arnold, "Fate of Pesticides in Soil: Predictive and Practical Aspects", *__Environmental Fate of Pesticides__* *(D.H. Hutson, T.R. Roberts, Eds), Wiley & Sons, New York (1990)*

Figure 2-1. Factors that influence pesticide volatilization.

Brief summaries of the major factors impacting pesticide volatilization are given below. In addition, two important volatilization mechanisms, diffusion and volatilization from plant surfaces, are briefly discussed.

2.3.1 Nature of the Pesticide and Formulation

The molecular structure of a pesticide determines its physical properties, such as vapor pressure and solubility, and its chemical reactivity. The vapor pressure of most pesticides is sufficiently low that they are considered to be semivolatile rather than volatile in chemical analysis. The rate of evaporation of a pesticide is determined primarily by its vapor pressure, which in turn is usually increased by temperature and decreased by adsorption to the soil surface to which the pesticide is applied. The rate of evaporation can also be decreased if the pesticide dissolves in the oils or waxes of vegetation.

The nature of the formulation also affects emissions during application. Dusts of small particle size would likely give higher emissions of particulates (probably containing AI) than granulars, for example. Also, the several types of liquid formulations might yield still different emissions based on droplet sizes and applicator characteristics. For some formulations, volatile organic inert ingredients may be the major constituents volatilizing rather than the AI.

2.3.2 Meteorological Conditions[7-9]

Studies have shown that meteorological conditions can have a significant effect on the rate of pesticide volatilization from soil. This effect is observed especially in field tests when the amount of pesticide volatilizing from the soil surface changes according to the cycle of daytime and nighttime temperatures.

The extent of pesticide volatilization also depends in part on temperature. A pesticide is applied as a formulation of AIs and inert ingredients. Temperature will have a different effect on each component of the formulation, depending on its vapor pressure. An increase in temperature can increase or decrease volatilization, depending on its influence on other factors, such as diffusion of the pesticide towards or away from the soil surface and mass flow in the water present in the soil. Usually an increase in temperature enhances volatilization because the vapor pressure of the pesticide increases. If temperature increases enough, however, the soil surface will dry out, which decreases soil water movement and mass transport of the pesticide to the surface, and therefore volatilization.

Wind conditions also affect volatilization. A layer of stagnant air exists above an evaporating soil surface. An increased flow of air decreases the depth of the stagnant layer, increases turbulent mixing of the air near the surface, and reduces the concentration of volatilizing substance in the atmosphere, thereby increasing the volatilization rate. Glotfelty described the dispersion process that gradually takes place as the airstream above the stagnant layer comes in contact with, dilutes, and transports the pesticide from the soil surface.[9] Researchers routinely use wind profiles in combination with measured pesticide concentrations to calculate vertical flux intensities.

2.3.3 Soil Characteristics[9-13]

Adsorption-desorption of a pesticide depends on its chemical makeup and, to a great extent, on the characteristics of the soil. Increased amounts of organic matter or clay in soils decrease the volatilization rate of pesticides, probably because adsorption is increased, and the water content of the soil influences the rate of vaporization of the pesticide present in the soil. When soil is very dry, the volatilization of the pesticide is lowered significantly, while volatilization increases as the soil moisture content increases. (Note that in some cases the hydrolysis rate of a pesticide is greater in wet soils so that overall all volatilization can be decreased.) As water evaporates from the soil surface, pesticide present in the soil is transported to the surface in solution. Hartley refers to this as the "wick effect" because the soil acts as a wick for movement of the pesticide. The extent of this mass flow to the surface depends on the amount of solar radiation. Normally, at solar noon the movement is greatest, resulting in increased pesticide volatilization. The extent of the wick effect would be expected to vary with the solubility of the pesticide in water.

When pesticides are well-incorporated into soil during application, this mass flow mechanism limits volatilization and results in a lower rate of volatilization than when the pesticide is surface-applied.

2.3.4 Diffusion[9-11]

As vaporization occurs from the surface, a pesticide concentration gradient forms between the depleted surface and the more concentrated subsurface. Pesticide in the subsurface of the soil then diffuses upwards to the surface as pesticide at the surface volatilizes. Temperature, pesticide concentration, and soil composition influence the rate of diffusion. An extensive discussion on diffusion is provided by Hamaker. Mathematical equations for diffusion have been developed by Mayer for predicting volatilization of surface applied and soil-incorporated pesticides.

2.3.5 Volatilization from Plant Surfaces[14]

The rate of pesticide volatilization from plant surfaces depends on the manner in which the pesticide residue covers the plant structure. For example, higher volatilization losses occur from plant surfaces if the pesticide is present as droplets on the plant. After these droplets evaporate, volatilization slows down because remaining residues are left in the regions of the plant structure less exposed to air circulation or are adsorbed onto the plant material.

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SECTION 3

GENERAL DATA REVIEW AND ANALYSIS PROCEDURES

This section describes the literature search to collect emissions data and the EPA quality rating systems applied to data and to any emissions factors developed from those data.

3.1 LITERATURE SEARCH AND SCREENING[1]

A literature search was performed to collect pertinent emissions data for operations associated with agricultural pesticide application. The majority of emission data reports were found in journals such as the *Journal of Agricultural Food Chemistry*, *Journal of Environmental Quality*, *Pesticide Monitor*, and *Residue Reviews*. Information on pesticide application techniques was found in standard pesticide application handbooks and manuals. A comprehensive list of these references is found in the references for Sections 2 and 4 of this report.

During the review of each document, the following criteria were used to determine the acceptability of reference documents for emission factor development:

1. The report must be a primary reference:

    a. Source testing must be from a referenced study that does not reiterate information from previous studies.

    b. The document must constitute the original source of test data.

2. The referenced study must generally contain test results based on more than one test run or that are collected over a relatively long time frame.

3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions.

3.2 DATA QUALITY RATING SYSTEM[1]

Based on Office of Air Quality Planning and Standards (OAQPS) guidelines, the following data are always excluded from consideration in developing AP-42 emission factors:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods; and
3. Test series in which the production and control processes are not clearly identified and described.

If there is no reason to exclude a particular data set, data are assigned a quality rating based on an A to D scale specified by OAQPS as follows:

A—This rating requires that multiple tests be performed on the same source using sound methodology and reported in enough detail for adequate validation. Tests do not necessarily have to conform to the methodology specified by EPA reference test methods, although such methods are used as guides.

B—This rating is given to tests performed by a generally sound methodology but lacking enough detail for adequate validation.

C—This rating is given to tests that are based on an untested or new methodology or that lack a significant amount of background data.

D—This rating is given to tests that are based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following are the OAQPS criteria used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated should be well documented in the report, and the source should be operating within typical parameters during the test.

2. Sampling procedures. The sampling procedures should conform to a generally accepted methodology. If actual procedures deviate from accepted methods, the deviations must be well documented. When this occurs, an evaluation should be made of how such alternative procedures could influence the test results.

3. Sampling and process data. Adequate sampling and process data should be documented in the report. Many variations can occur without warning during testing and sometimes without being noticed. Such variations can induce wide deviations in sampling results. If a large spread between test results cannot be explained by information contained in the test report, the data are suspect and are given a lower rating.

4. Analysis and calculations. The test reports should contain original raw data sheets. The nomenclature and equations used are compared to those specified by EPA (if any) to establish equivalency. The depth of review of the calculations is dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn is based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM[1]

EPA guidelines specify that the quality of the emission factors developed from analysis of the test data be rated utilizing the following general criteria:

A—Excellent: The emission factor was developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category* was specific enough to minimize variability within the source category population.

B—Above average: The emission factor was developed only from A-rated test data from a reasonable number of facilities. Although no specific bias was evident, it was not clear if the facilities tested represented a random sample of the industries. As in the A-rating, the source category was specific enough to minimize variability within the source category population.

C—Average: The emission factor was developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias was evident, it was not clear if the facilities tested represented a random sample of the industry. As in the A-rating, the source category was specific enough to minimize variability within the source category population.

D—Below average: The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there was reason to suspect that these facilities did not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are footnoted in the emission factor table.

E—Poor: The emission factor was developed from C- and D-rated test data, and there was reason to suspect that the facilities tested did not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are footnoted.

As part of the analysis of the emission data, the quantity and quality of the information contained in the final set of documents used for emission factor estimation in Section 4 were evaluated. Three types of references were reviewed: field study reports, theoretical discussions on volatilization, and emission-estimating algorithm presentations.

The theoretical discussions on volatilization were not rated because they did not discuss a particular source test, but instead provided important background information.

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* Source category: A category in the emission factor table for which an emission factor has been calculated.

The use of the above criteria is somewhat subjective depending to a large extent on the individual reviewer. Details of how each candidate emission factor was rated are provided in Section 4.

3.4 EMISSION TESTING METHODS[2-5]

Pesticide volatilization has been measured successfully in both the laboratory and the field. In a laboratory setting, the experimental conditions used during measurement can be more closely controlled and monitored than in the field. Much of the current understanding of the process of volatilization is credited to early laboratory studies by Hartley.

The field testing that began in the late sixties and early seventies attempted to provide a more realistic picture of the complex process of pesticide volatilization. Changing meteorological conditions and pesticide application losses are examples of the factors that complicate the measurement process in the field.

The objective in typical field tests is to apply one or more pesticide formulations to a test plot of tilled or vegetated soil and collect air, soil, and sometimes crop samples near the surface over a measured period of time. These samples are analyzed for active ingredient (AI) residues and, in some instances, for biodegradation products of the AI.

The characteristics of the test plots used vary according to the objective of the research. Sometimes the plots are sprayed with water or even flooded to determine the effects of water on movement of the pesticide in the soil. Several experiments performed in the past were designed to determine if different soil types affected the rate of volatilization.

Two of the major factors in any of the field testing studies conducted to determine pesticide volatilization are the existing meteorological conditions and the air sampling and analysis methods. Each of these factors is discussed in the following paragraphs.

3.4.1 Meteorological Conditions

The meteorological conditions monitored during field testing are important in the interpretation of data obtained for residue measurement. Factors such as temperature, rainfall, humidity, wind speeds, and water evaporation play a major role in the extent of pesticide volatilization.

Pesticide volatilization is influenced greatly by the turbulent flow of the atmosphere above the soil or vegetation surface. Pesticide vertical flux densities reported in grams per hectare per day or grams per hectare per hour are calculated using pesticide air concentrations and meteorological conditions such as wind speeds.

3.4.2 Air Sample Collection[6]

Air sampling studies are typically performed at a number of heights above the ground or crop canopy. A sampling station is constructed with sample collection devices at each of the desired heights as in Figure 3-1. Typically, several sampling stations are positioned in the test plot, usually in the center and on the downwind edge. Pesticide samples are taken by drawing air through impingers containing a solvent such as ethylene glycol or hexylene glycol at sampling rates ranging from 1 to 25 liters per minute (L/min). The impingers are changed frequently (once every 2 to 4 hr) during the first several days of a field test. The frequency of sampling is normally decreased over time as the amount of pesticide remaining on the treated plot decreases.

Many of the field tests used porous polyurethane foam plugs for air sample collection. The sampling equipment used for this method is similar to those described above, but the organic compounds are collected onto the plugs rather than absorbed into liquid. The advantage of this method over the impinger method is that higher volumes of air can be sampled without the risk of pesticide breakthrough.

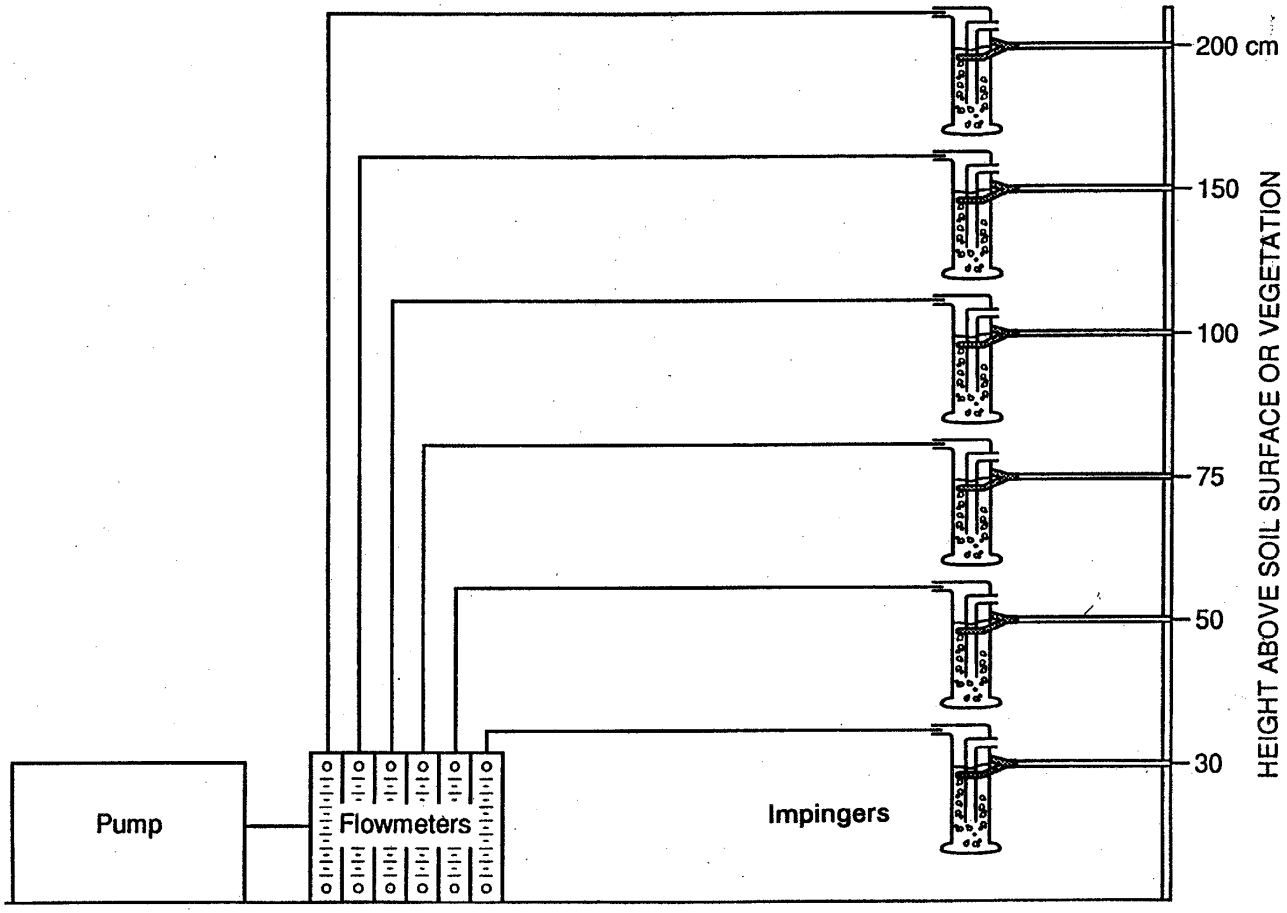

Figure 3.1 Air Sampling Aparatus

3.4.3 Air Sample Extraction and Analysis Methods

Impingers—Air samples collected in a solvent using impingers are normally extracted with hexane. The hexane extract is reduced in volume, and sometimes a Florisil chromatography column cleanup is performed. Recoveries of pesticides are reported to be greater than 90 percent using this extraction method. The final extract is typically analyzed using gas chromatography (GC) with an electron capture detector or other appropriate detector.

Polyurethane foam plugs—Air samples collected using polyurethane foam plugs are Soxhlet-extracted using hexane. After the volume of the extract is reduced, the sample is analyzed using GC with an electron capture detector. Recoveries using this technique are also reported to be greater than 90 percent.

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SECTION 4

AP-42 SECTION DEVELOPMENT

This section describes the literature surveyed, test data evaluated, and method considered for estimating emissions associated with applying agricultural pesticides to crops. An algorithm and its use are then described. The results serve as the basis for a new addition to Chapter 9 of AP-42: Section 9.2.2, Pesticide Application.

The discussion focuses on emissions of volatile organic substances, including the organic active ingredients (AI) and inert volatile organic compounds.* (Inert VOCs include a range of solvents, diluents, emulsifiers, etc., used in pesticide formulations.) This discussion does not address particulate emissions during or following application of pesticide formulations. Insufficient data were found on these topics to develop emission factors.

The emission factor algorithm development reflects current insights on pesticide application practices and volatilization processes as obtained from industry, literature, application handbooks, and research articles. Information on emissions was developed primarily from mathematical pesticide volatilization models in the literature.

4.1 REVIEW OF SPECIFIC DATA SETS

A search was conducted for published data pertaining to emissions due to application of agricultural pesticides. From this search, 16 references were found to contain sufficient documentation to be of value for developing the section on pesticide application. Fifteen of these references described field tests performed between 1964 and 1990 that contained data on losses within 30 days after application. The volatilization estimates reported in these references were based on either flux measurements or residue measurements taken in the field. Table 4-1

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* See Section 2.3.

TABLE 4-1. SUMMARY OF FIELD TESTS OF PESTICIDE VOLATILIZATION

Active ingredient	Vapor pressure (mmHg)[a]	Formulation type	Application method	Soil type	Loss/time[b]	Report Date	Reference
2,4-D	8×10^{-6}	Aq. soln.	Surface spray	Not stated	1%-8%; application	1978	2
2,4-D (butyl ester)	—	Aq. soln.	Surface spray	Not stated	30%-40%; 2 hr	1978	2
2,4-D (octyl ester)	—	Aq. soln.	Surface spray	Not stated	10%-15%; 2 hr	1978	2
2,4-D (isooctyl ester)	—	Aq. soln.	Surface spray	Clay/silt	21%; 5 days	1985	11
Chlordane	1×10^{-5}	Aq. emul.	Surface spray	Dry sandy loam	2%; 2 days	1984	7
Chlordane	1×10^{-5}	Aq. emul.	Surface spray	Moist silt loam	50%; 2.5 days	1984	7
DCPA (Dacthal)	2.5×10^{-6}	Wet powder	Surface spray	Moist silt loam	2%; 1.5 days	1984	7
DCPA (Dacthal)	2.5×10^{-6}	Wet powder	Surface spray	Yolo	10%; 21 days	1990	14
DDT	1.5×10^{-7}	Aq. emul.	Surface spray	Not stated	72%; applica-tion	1983	3
Dieldrin	9.9×10^{-6}	Aq. emul.	Surface spray	Sandy loam	89%; 30 days	1977	1
Dieldrin	9.9×10^{-6}	Aq. emul.	Surface spray	Silt loam	43%; 2 days	1976	6
Dieldrin	9.9×10^{-6}	Aq. emul.	Surface spray	Sandy loam	12%; 12 hr[c]	1977	1
Dimethoate	2.5×10^{-5}	Aq. emul.	Surface spray	Sandy loam	94%; 14 days	1964	5
Dyfonate	2.1×10^{-4}	Aq. emul.	Surface spray	Silt loam	13%; applica-tion	1971	4
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Wet sandy loam	69%; 24 hr	1965	9

TABLE 4-1. (continued)

Active ingredient	Vapor pressure (mmHg)[a]	Formulation type	Application method	Soil type	Loss/time[b]	Report Date	Reference
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Wet sandy loam	44%; 15 min	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Moist sandy loam	49%; 24 hr	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface irrig.	Clay loam	74%; 2.25 days	1980	8
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Moist sandy loam	27%; 15 min	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Wet loam/ sand	90%; 6 days	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Moist loam/ sand	68%; 6 days	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Dry loam/ sand	44%; 6 days	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Clay loam	55%; 24 hr	1980	8
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Dry sandy loam	23%; 24 hr	1965	9
EPTC	3.4×10^{-2}	Aq. soln.	Surface spray	Dry sandy loam	20%; 15 min	1965	9
Heptachlor	3×10^{-4}	Aq. emul.	Surface spray	Sandy loam	45%; 12 hr[c]	1977	1

TABLE 4-1. (continued)

Active ingredient	Vapor pressure (mmHg)[a]	Formulation type	Application method	Soil type	Loss/time[b]	Report Date	Reference
Heptachlor	3×10^{-4}	Aq. emul.	Surface spray	Silt loam	43%; 2 days	1976	6
Heptachlor	3×10^{-4}	Aq. emul.	Surface spray	Moist silt loam	90%; 6 days	1984	7
Heptachlor	3×10^{-4}	Aq. emul.	Surface spray	Sandy loam	96%; 30 days	1977	1
Heptachlor	3×10^{-4}	Aq. emul.	Surface spray	Dry sandy loam	14%-40%; 2 days	1984	7
Heptachlor	3×10^{-4}	Aq. emul.	Surface spray	Moist silt loam	50%; 6 hr	1984	7
Lindane	3.3×10^{-5}	Aq. emul.	Surface spray	Moist silt loam	90%; 6 days	1984	7
Lindane	3.3×10^{-5}	Aq. emul.	Surface spray	Dry sandy loam	12%; 2 days	1984	7
Lindane	3.3×10^{-5}	Aq. emul.	Surface spray	Moist silt loam	50%; 6 hr	1984	7
Methoxychlor	—	Aq. emul.	Aerial	Not stated	47%; application[d,e]	1970	10
Toxaphene	4×10^{-6}	Aq. emul.	Aerial	Not stated	26%; 5 days	1980	12
Toxaphene	4×10^{-6}	Dust	Aerial	Not stated	86%; application[d]	1970	10
Toxaphene	4×10^{-6}	Aq. emul.	Aerial	Not stated	52%; application[d]	1970	10
Toxaphene	4×10^{-6}	Aq. emul.	Surface spray	Not stated	54%; applica-tion	1983	3
Toxaphene	4×10^{-6}	Aq. soln.	Surface spray	Not stated	17%; applica-tion	1983	3

TABLE 4-1. (continued)

Active ingredient	Vapor pressure (mmHg)[a]	Formulation type	Application method	Soil type	Loss/time[b]	Report Date	Reference
Triallate	1.1 x 10^{-4}	Aq. emul.	Surface spray	Clay	70%-100%; 5 days	1993	13
Trifluralin	1.1 x 10^{-4}	Aq. emul.	2.5 cm soil incorp.	Cecil soil	3.5%; application	1979	15
Trifluralin	1.1 x 10^{-4}	Aq. emul.	2.5 cm soil incorp.	Cecil soil	20%; 35 days	1977	15
Trifluralin	1.1 x 10^{-4}	Aq. emul.	Surface spray	Clay	61%-79%; 5 days	1993	13
Trifluralin	1.1 x 10^{-4}	Aq. emul.	Surface spray	Moist silt loam	50%; 5 hr	1984	7
Trifluralin	1.1 x 10^{-4}	Aq. emul.	Surface spray	Moist silt loam	90%; 7 days	1984	7
Trifluralin	1.1 x 10^{-4}	Aq. emul.	Surface spray	Dry sandy loam	2%-25%; 2 days	1984	7
Zinophos	3 x 10^{-3}	Aq. emul.	Surface spray	Silt loam	40%; applica-tion	1971	4

[a] Reference 17.

[b] Losses were believed to be primarily by volatilization of AI, but experimental conditions and parameters measured varied substantially between investigators. Some of the tests do not appear to have distinguished between true evaporation and drift, particulate wind reentrainment, or rain losses. Studies without data collected within 30 days after application were excluded.

[c] Includes losses upon application.

[d] Includes losses due to drift during application.

[e] Average of 15 separate studies over a 5-year period using methoxychlor applied at temperatures ranging from 2 ° to 41°C.

summarizes important parameters for the 15 field tests. Excerpts from the various technical publications cited in Table 4-1 are contained in Appendices A through O. The 16th reference reviewed summarized information on the use of control technologies to reduce emissions. In addition, five other publications, cited in support of emission factor development, are identified in the references, and other documents reviewed are listed. The references cited in this section represent the most recent field application studies available for the volatilization of pesticides. It is reported that the U. S. Department of Agriculture (USDA) and the U. S. Environmental Protection Agency (EPA) are initiating studies directed specifically towards the development of data on volatilization from formulated pesticides under field application conditions. However, these studies are only in the initial stages.

Of the 15 references cited in Table 4-1, only 4 of the studies occurred after 1983. Because the majority of the studies were prior to 1983, many of the AIs cited in these studies are no longer registered for use in the U. S. The use of volatilization data based on AIs that are no longer registered would pose a potential problem only if the ultimate goal was to calculate emission factors only for these nonregistered AIs, but this is not the case. The use of these referenced studies is only to create a data base of vapor pressure and percent loss by volatilization. The fact that many of the compounds used to create this data base are no longer in use has no impact on the validity of either the vapor pressure values or the volatilization loss measured in these studies.

The use of volatilization data only within 30 days of pesticide application was selected primarily for two reasons: (1) there are very few data available in the published literature on pesticide volatilization based on field application studies with sampling times greater than 30 days, and (2) after 30 days, the impacts of other mechanisms, such as plant uptake, soil adsorption, and biological or physical degradation can become very significant. There are very few published studies based on actual field application that address these other impacts, either cumulatively or on an individual basis. In addition, it is recognized that some AIs may be significantly impacted by these loss mechanisms in times less than 30 days and also that the level of the impact will vary between AIs.

Reference 1

This 1977 report describes emission of dieldrin and heptachlor surface-applied to a grass pasture. Vapor density profiles were measured over a 23-day period. During the first 12 hours after application, 12 percent of the dieldrin and 45 percent of the heptachlor were volatilized. It is estimated that during application about 60 percent of the dieldrin and 42 percent of the heptachlor were lost directly to the atmosphere as vapor or spray drops that never reached the target area. Volatilization declined rapidly over the first 7 days and after 30 days, 89 percent of the applied dieldrin and 96 percent of the heptachlor had volatilized. Marked diurnal variation in vertical flux intensities of both insecticides were observed during the initial period of rapid volatilization.

A rating of B was assigned to the data contained in this report. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated. Note that a similar study conducted by Taylor is described in reference 6. In this study, the pesticides were surface-applied, while in the Taylor study, the pesticides were incorporated into the soil after application.

Reference 2

This 1978 emission report describes a series of field trials undertaken on the Canadian prairies using ground rigs and aerial spraying to ascertain the relative magnitudes of droplet and vapor migration of various 2,4-D formulations from target areas. The results indicated that 30 to 40 percent of the initial quantity of the butyl ester of 2,4-D evaporated and drifted downwind, as vapor, in the 2 hours following spraying; the corresponding evaporation rate for the octyl ester was 10 to 15 percent. Off-target droplet drift during spraying varied between 1 and 8 percent for ground rig application and 20 to 35 percent with aircraft spraying.

A rating of B was assigned to these data. Vertical flux densities were calculated. Documentation of the study was thorough, and sampling and analysis methods were sound. Losses during application were calculated based on the quantity of AI collected in ground samples in the spray swath.

Reference 3

This 1983 report describes emissions of toxaphene and/or DDT during two application periods to a cotton field. Air samples for the two tests were collected over a period of 11 days and 33 days following application. In the first application, only toxaphene was applied to the cotton plants; in the second application, a mixture of toxaphene and DDT was applied. For the first application, 17 percent of the toxaphene was lost during application and within the first three hours after application. For the application of the toxaphene-DDT mixture, 54 percent of the toxaphene and 72 percent of the DDT were lost during the same time interval. Pesticide disappearance rates were observed to be a linear function of the pesticide loads on the plants. No measurable pesticide volatilization occurred from the soil, but very dry weather may have been a major factor. The study provided additional evidence that postapplication volatilization from plants is a major pathway of pesticide transport.

A rating of B was assigned to the data contained in this report. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated.

Reference 4

This 1971 emission report accounts for losses of dyfonate and zinophos during application and within the first 24 hours after spray application. The results showed that major losses of pesticide occurred during the application process. Nearly 40 percent of the zinophos and 13 percent of the dyfonate failed to reach the soil surface. In some tests, the pesticide was soil-incorporated after application for comparison to plots that were not soil-incorporated. Soil samples were taken at 0.5, 4, and 22 hr to determine evaporation. Neither pesticide showed significant losses during the 22 hours following application, regardless whether or not the pesticide was soil incorporated. Samples were analyzed by gas chromatography.

A rating of C was assigned to these data. The report does not present thorough documentation of analytical methods and sample collection. No air samples were taken. Losses during application were estimated rather than measured.

Reference 5

In this 1964 emission study, dimethoate was spray-applied to a plot and incorporated to a depth of 6 inches (in). Soil samples were taken immediately after application and then seven times throughout the next 2 weeks to determine dimethoate content. The results showed that within 3 inches of the soil surface, 94 percent of the dimethoate had disappeared within 14 days after application.

A rating of C was assigned to these data. No flux densities were calculated. The report did not document the analytical procedures used other than a statement of the method and it generally lacked sufficient background data. No air samples were taken. Agricultural application methods were simulated on a small area of land.

Reference 6

This 1976 report describes emissions of dieldrin and heptachlor incorporated 7.5 centimeters (cm) into soil immediately before maize was planted. Air samples were taken over a 6-month period to evaluate daily flux densities. No measurements were conducted for pesticide concentrations in the air either over or downwind of the site during application. However, the loss during application was estimated from soil analyses taken on the day after application. These analyses indicated that 43 percent of the limited application was not present in the soil. Marked diurnal variations with noon day maxima were observed during this study.

A rating of B was assigned to the data in this report. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated.

Reference 7

This 1984 emission report describes the application of various combinations of heptachlor, chlordane, lindane, trifluralin, and dacthal (DCPA) to fallow soil in three separate tests using two different soil types. Air samples were taken over a period of 23 hr in one test and 18 hr in each of two tests. The results showed that for trifluralin, the losses ranged from 2 to 25 percent over 2 days in dry sandy loam whereas in moist silt loam, the losses were 50 percent in 5 hours and 90 percent in 7 days. Heptachlor showed losses between 14 and 40 percent over 2 days in dry sandy loam but for moist silt loam, the losses were 50 percent and 90 percent for 6 hours and 6 days, respectively. Lindane losses were 12 percent in dry sandy loam over 2 days; in moist silt loam, the losses were 50 percent in 6 hours and 90 percent in 6 days. For chlordane, the loss from dry sandy loam was 2 percent in 2 days but 50 percent in 2.5 days for moist silt loam. Dacthal loss was measured only in moist silt loam and found to be 2 percent in 1.5 days. Soil moisture content in an obvious major factor in evaluating vaporization loss from bare soils.

A rating of B was assigned to these data. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated.

Reference 8

This 1980 emission report describes the application of the herbicide *S*-ethyl, *N,N*-dipropylthiocarbamate (EPTC) to an alfalfa field by "herbigation" (i.e., in irrigation water). After 52 hours, it was found that 74 percent of the EPTC had volatilized from the irrigation water. Studies of the soil prior to irrigation showed a 55 percent loss of EPTC within 24 hours of application.

A rating of B was assigned to the data in this report. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated.

Reference 9

This 1965 emission report describes volatilization of EPTC from soil. Soil samples were analyzed by steam distillation of the EPTC from substrate. The results of the study showed that during the first 15 minutes after spraying on the soil surface, 20 percent of the EPTC disappeared from dry soil, 27 percent from moist soil, and 44 percent from wet soil. The losses were 23, 49, and 69 percent after 24 hours and 44, 68, and 90 percent after 6 days on dry, moist, and wet soils, respectively. The amount of soil moisture was identified as the most important factor affecting volatilization. A rating of C was assigned to the data contained in this report. No air samples were taken. Agricultural application methods were simulated.

Reference 10

In this 1970 report, deposition data for aerial application from 16 pesticide studies were presented and used to estimate the percent of methoxychlor and toxaphene deposited on target from the aerial application to irrigated alfalfa and cotton fields. Of the 16 studies, 14 were results for aerial application of solutions of methoxychlor for varying application rates and meteorological conditions. The other 2 studies used toxaphene; one application was for a dust and the other was an aqueous emulsion. The application of toxaphene dust resulted in 86 percent of the quantity applied missing the target area whereas using toxaphene in the aqueous emulsion resulted in only 52 percent missing the target area. In the methoxychlor studies, the percentage of the quantity applied that missed the target area ranged from 27 to 72 percent; the average loss rate was 47 percent.

A rating of C was assigned to the emission data presented in this report. Analytical methods were not documented thoroughly in this report.

Reference 11

In this 1985 study, the isooctyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D) and its acid metabolite were applied to a field of wheat. The total or cumulative vapor loss of the isooctyl ester over a 5 day sampling period was estimated to be 21 percent of the amount applied. The crop canopy was determined to have intercepted 52 percent of the applied ester.

A rating of B was assigned to these emission data. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated. Data were also presented for the acid metabolite, which was observed to form rapidly after application, followed by a slow decline.

Reference 12

This 1980 study describes the results of aerial application of toxaphene to a cotton field. Air samples were taken from above the crop canopy over a period of 5 days. For the 5-day period following application, the cumulative volatile loss of toxaphene was 26 percent. Increased volatilization rates were observed when leaves were drying after heavy dew or light rain.

A rating of B was assigned to these data. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated.

Reference 13

For this 1993 emission study, a study plot was sprayed with trifluralin and triallate as an emulsified aqueous suspension and not incorporated into the soil. Air samples from above the fallow soil were taken immediately after spraying and continued for 120 h. Soil samples were taken at 12-h intervals for 3 days and then once per day for 2 days.

Two techniques were used to measure volatilization from the fallow soil: the relaxed eddy accumulation (REA) technique and the aerodynamic-gradient (AG) technique. A mass balance based on the quantity of pesticide volatilized over the 5-day period should losses of 100 and 70 percent for triallate and 79 and 61 percent for trifluralin by the AG and REA techniques, respectively.

A data rating of B was assigned to these data. Documentation of all aspects of the study was thorough. Pesticide fluxes were calculated. Two measurement methods were used. The relaxed eddy accumulation method was compared to the aerodynamic gradient technique.

Reference 14

This 1990 report describes a study to determine which transport mechanisms (drift, volatilization and deposition, windblown particles, or plant uptake) contribute to dimethyl tetrachloroterephthalate (DCPA) contamination of nontarget crops. Air, soil, and vegetation were sampled for DCPA. An estimated 10 percent of the DCPA (Dacthal) applied was lost to the atmosphere within 21 days after application. The overall test results indicated that drift during application, and volatilization with subsequent air transport after application are potentially important sources of DCPA contamination on nontarget crops.

A data rating of B was assigned to these data. Volatilization fluxes and soil dissipation of DCPA were measured. The study was well documented.

Reference 15

This 1977 study describes the measurement of trifluralin volatilization losses from a field during application at soybean planting and for a period of 120 days after planting. Volatilization losses during application were estimated to be 3.5 percent of the applied quantity. Total seasonal volatilization losses, excluding application losses, were estimated to be 22 percent, of which about 20 percent occurred within 35 days.

A rating of B was assigned to these data. Documentation of all aspects of the study was thorough, and sampling and analysis methods were sound. Vapor density profiles and vertical flux intensities were calculated. Both losses during application and seasonal losses were calculated.

Reference 16

This document does not contain original test results, but it discusses estimated emissions of agricultural pesticides in the United States based on data compiled by the Resources for the Future, EPA, and the California Department of Pesticide Regulation (DPR). Various alternative control technologies for reducing pesticide usage and emissions are discussed. Control technologies include microencapsulation of pesticides, reformulating pesticides to reduce solvent usage, improved efficiency application equipment, and integrated pest management techniques. Estimates were given for the potential of different control technologies to reduce pesticide emissions. The document discusses methods for estimating pesticide emissions.

This report was given a C rating because the emission calculations were based on equations and pesticide physical properties data, and represented an untested methodology for estimating volatilization losses.

4.2 DEVELOPMENT OF CANDIDATE EMISSION FACTORS

Pesticides are applied to agricultural crops in many forms and in many ways. Specific application techniques are numerous and vary considerably, depending upon the form of the pesticide. The form in which a specific pesticide is made available for application to agricultural crops is termed the formulation. Formulations are generally composed of the pesticide's active ingredient (AI) and a number of other materials that have little or no pesticide activity. These materials, collectively termed the inert ingredients, may include solvents, emulsifiers, diluents, fillers, carriers, and many others. The pesticide AI may be present in formulations in very small proportions (<1 percent) or up to relatively large proportions (>50 percent of the total formulation). Conversely, the inert ingredients may range from less than 50 percent to over 99 percent of the formulation.

Field conditions such as weather, soil characteristics, and application technique have been shown to influence the degree of pesticide volatilization. The chemical composition and physical properties of the formulation also affect volatilization. An emission factor model is based on knowledge of specific formulations, methods of application of the formulation, and the available data base of pesticide properties.

The emission model developed in this document considers only vaporous organic substances, and does not include particulate emissions. However, it does consider the contributions of both the inert ingredients and the AIs to the total emissions of organics resulting from the application of agricultural pesticide formulations. The model is separated into two parts: emissions of the AI and emissions of inert volatile ingredients in the formulation.

All organic constituents in the formulation that are not AIs are considered, for present purposes, to be potential volatile organic compounds (inert VOCs). No recognized published model is currently available that specifically estimates VOC emissions resulting from the inert ingredient portion of the pesticide formulation. Consequently, an emission model for the inert ingredients was developed based on information developed from existing data bases to estimate the quantity of VOCs in various types of pesticide formulations. Information on the nature of the specific VOCs typically present in these formulations was used to estimate an overall emission for these constituents.

Emissions resulting from the volatilization of the AI portion of the pesticide formulation have been investigated in a very limited number of studies as shown in Table 4-1. The models developed in some of the studies are focussed on vapor density profiles or vertical flux intensities, usually data intensive, and specific to the set of conditions existing during the specific field application test. No comprehensive models employing readily available physical or chemical properties have been developed for the estimation of the degree of volatilization of the AIs due to the surface application of pesticide formulations. The data obtained from the reports described in Section 4.1, and summarized in Table 4-1, were used to estimate emission factors for the surface application of pesticides based on a readily available physical property, the vapor pressure of the AI.

Comprehensive studies were published by Jury, Spencer, and Farmer for the application of pesticide formulations by soil incorporation.[18-21] The mathematical models developed in those studies were used herein, in conjunction with existing data for selected AIs, to estimate emission factors for that application method. Although other emission models are available, these models were selected because they were the most amenable to reducing the number of variables and could be converted into functions of a readily available physical property (i.e., vapor pressure) of the specific AI.

The emission factors based on the data presented in Table 4-1 or the soil incorporation model are E-rated because the estimates are derived solely from mathematic representations using averages of test results or physical properties of the AIs. In addition, the physical properties required for the soil incorporation model were available for only selected AIs within the different vapor pressure ranges. For this reason, the emission estimates for each vapor pressure range are based on data from a very small number of specific active ingredients. Because the total number of data points is small and the data within a vapor pressure range show considerable variation, the emission estimates obtained by use of these emission factors should be considered only as an approximation. However, no alternative emission estimation procedures have been suggested. As the USDA, EPA, and other studies are completed and additional data become available, the emission factors and the methodology used to derive the emission factors will be reviewed and revised, as appropriate, to incorporate the new data.

This emission model is not valid for the aerial application of pesticide formulations. A major factor in losses by this application technique is drift, and neither equations nor experimental data are currently available to permit predictions of these losses. Work is currently in progress by the Spray Drift Task Force, a joint venture of 28 basic manufacturers and end-use formulators, to compile a spray drift data base to satisfy registration requirements of the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Testing to complete the data base is expected to continue through 1994.

The following section discusses the development of the emission model into an AP-42 emission factor (algorithm).

4.3 ALGORITHM DEVELOPMENT

Emissions due to the applications of agricultural pesticides have been shown to be primarily functions of the physical properties of the specific AI and various field conditions including temperature, relative humidity, and soil moisture content. The modeling approach develops emission estimates for the inert ingredient portion of the pesticide formulation based on information derived from pesticide registration data. Emission estimates for surface application of the active ingredient (AI) portion of the formulation are based on the numerical averages of the data in Table 4-1 for two ranges of AI vapor pressure. The selection of the vapor pressure of the AI as the physical property for the emission estimates was based on the overall general availability of values for this property for a large number of AIs. Other properties, such as Henry's Law constant, may also be descriptive of the actual physical processes that occur after field application. However, values for these properties may not be generally found in readily available sources. One of the determinants in the selection of the physical property was that the values should be present in readily available sources.

For application by soil incorporation, the emission estimates use equations developed by Jury, Spencer, and Farmer. These methods have been developed into an algorithm for estimating AI emissions over a time interval of 30 days after application. One of the major objectives of the algorithm development was to estimate emission factors based on a straightforward relationship using readily available date. The following sections discuss the informational needs of the algorithm, the form of the estimating equations, and the use of the algorithm.

4.3.1 Information Requirements

Pesticide formulations contain both an AI and inert ingredients, and the pesticide volatilization algorithm uses separate steps to estimate emissions for both the AI and inert ingredients.

Ideally, the information used in the algorithm calculation matches as closely as possible the actual conditions under which the pesticide was used. The following information is necessary to use the algorithm.

- Method by which the formulation was applied (the algorithm cannot be used for aerially applied pesticides);
- Total quantity of formulation applied;
- Type of formulation (e.g., emulsifiable concentrate, granules, microcapsules, powder);

- Name of the specific AI (or AIs) and the percentage of AI (or each AI) in the formulation;
- Vapor pressure of the AI (or each AI);
- Percentage of inert ingredients; and
- Quantity or percentage of VOCs in the inerts.

Information on the formulation (name of AI, percent content of the AI, percent content of the inert ingredients) is required by FIFRA to be on the product label. If a label is unavailable, this information can be obtained from the manufacturer or end-use formulator. Tables are presented in Section 4.3.2 that provide information on default values for the percentage of VOCs in the inert ingredient portion of various formulations, active ingredients contained in common trade name formulations, and vapor pressure data for specific AIs.

4.3.2 Emission Estimation Methods

Two basic methods are used in the algorithm to estimate total emissions from the application of agricultural pesticides. One method estimates the quantity of active ingredient emissions for selected time intervals after application, and the other estimates emissions of VOCs present in the inert ingredients.

4.3.2.1 Emissions Due to the Active Ingredients—

Application of pesticide formulations occur by three general methods: (1) aerial application, (2) surface application, and (3) soil incorporation. The methods presented in this section are not valid for aerial applications. In addition, the method should not be used to estimate emissions due to fumigants because these liquid or gaseous products are highly volatile and would be rapidly discharged to the atmosphere. In many states, the gaseous fumigants and some of the liquid products are no longer used or are being replaced. The remainder of this section presents the methods used to estimate emissions of AIs due to surface application techniques and soil incorporation techniques.

Surface application - The behavior of the pesticide AI as it interacts with air, water, soil, and biota is strongly influenced by the physical and chemical properties of the specific AIs. Water solubility, vapor pressure or volatility, and the tendency to sorb to organic and mineral matter in the soil are major properties to be considered. Henry's Law constant has been used to describe air-water partitioning of pesticides and may provide a measure of the tendency to volatilize. Vapor pressure is an important property that can also provide a measure of AI volatility. Every AI has a characteristic vapor pressure, which varies with temperature. Vapor pressure is a key chemical characteristic controlling the vaporization potential of the AI. In this section, Henry's Law constant and vapor pressure will be evaluated to estimate volatilization rates from the soil surface.

Table 4-1 presented a summary of the results of studies conducted to measure the loss of AI from pesticide formulations applied to soil surfaces over a variety of conditions for time intervals ranging from immediately after application to 30 days after application. In the table, data are provided for a range of combinations of AI, formulation type, application method, soil type, and length of time after application. Of the 48 results listed in the table, 43 were the result of conventional surface application techniques (e.g., ground rig sprayers), 4 were due to aerial application, and one result was for soil incorporation. After results were excluded for aerial applications, soil incorporation, and those for which no vapor pressure data were available, 39 data points for AI loss remained. This set of data represents the available information on the percentage loss for the surface application of several AIs for time intervals up to 30 days after application. The rationale for limiting the volatilization losses to 30 days after application was provided in Section 4.1.

In Table 4-1, the 39 data points for AI loss represent 15 different AIs. The most recent compilation of Henry's Law constants for pesticides was published by Suntio, et al., in 1988.[22] In this review article, the constants were listed for 96 pesticide AIs and displayed a range of about 11 orders of magnitude between the highest and lowest constant. If the extreme high and low values are excluded, most of the constants fell within a 7 order of magnitude range. The compilation provided Henry's Law constant values for 12 of the 15 AIs in Table 4-1. Of the 12 values, 9 of the values were within a range of less than two orders of magnitude. This represents a very small portion of the total range of Henry's Law constants and would not result in estimated emission factors for a significant percentage of the AIs used in pesticide formulation. The AIs in Table 4-1 fall within a range that is too narrow for the use of Henry's Law constants to be an effective way to group AIs for emission factor purposes.

The use of vapor pressure provides a overall range that is more inclusive of a larger portion of the AIs in pesticide formulations. Most AIs typically have vapor pressures in the range of 10^{-3} to 10^{-6}mmHg at ambient temperatures. The data from Table 4-1 were segregated into groups based on the vapor pressure of the AI. Two vapor pressure ranges were selected: (1) greater than $1x10^{-4}$mmHg, and (2) between $1x10^{-4}$ and $1x10^{-6}$mmHg. Because only one data point was available for the group with vapor pressures less than $1x10^{-6}$mmHg, no emission factor was developed for this vapor pressure range. For an AI in this vapor pressure range, a possible default procedure would be to use the soil incorporation equation; however, these equations may provide a very low emission estimate.

For AIs with vapor pressures greater than $1x10^{-4}$mmHg, the data in Table 4-1 show that the average percentage loss of AI within 30 days after application was 58 percent. For AIs with vapor pressures in the range between $1x10^{-4}$ and $1x10^{-6}$mmHg, the data show the average percentage loss to be 35 percent. Within each of the vapor pressure groups, there is considerable variability of field conditions from one field test to the other and in the volatilization data in Table 4-1 so that the average percentage loss is subject to considerable uncertainty. However, based on the models and data available at this time, use of the average values may be the best simplistic and straightforward approach to provide emission estimates.

<u>Soil incorporation</u> - Vaporization of AIs from the soil can be estimated by considering the physical and chemical factors controlling concentrations at the soil surface. Most models developed for estimating volatilization rates of soil-incorporated AIs are based on equations describing the rate of movement of the AI to the surface by diffusion and/or convection.

Volatilization rates were calculated for AP-42 Section 9.2.2 for a number of pesticides using the screening model proposed by Jury, Spencer, and Farmer.[18-21] In the model, pesticides are divided into volatilization categories I, II, and III based on their rate of movement to the soil surface by diffusion and/or convection.

The volatilization of pesticides in category I is time-dependent, limited by soil resistance. Once the category I pesticides reach the soil surface, however, they behave as though there is no boundary layer resistance in the air above the soil. Therefore, in the absence of evaporation, the concentration of category I pesticides at the soil surface increases with time. The rate of volatilization of category I pesticides is given by equation (1):

$$J_{v1} = C_o \sqrt{\frac{D_G^a\ K_H\ (\phi - \theta)^{10/3} + D_L^w\ \theta^{10/3}}{\phi^2 \pi t\ [\rho_b f_{oc} K_{oc} + \theta + (\phi - \theta) K_H]}} \qquad \textbf{(1)}$$

where:

J_{v1} = rate of pesticide volatilization (g/m^2/d)
C_o = initial pesticide concentration = 1 g/m^3
D_G^a = gaseous diffusion coefficient in air = 0.43 m^2/d
K_H = Henry's constant (m^3/m^3)
ϕ = soil porosity = 0.5 m^3/m^3
θ = soil volumetric water content = 0.3 m^3/m^3
D_L^w = liquid diffusion coefficient for water through soil = 4.3 x 10^{-5} m^2/d
t = time after application = 30 d
ρ_b = bulk soil density = 1350 kg/m^3
f_{oc} = organic carbon fraction = 0.0125
K_{oc} = organic carbon partition coefficient (m^3/kg)

The values given for D_G^a, ϕ, θ, D_L^w, ρ_b, and f_{oc} can be used as default values if the actual values are unknown. Henry's Law constants can be found in Suntio, et al., (Reference 22) for 96 pesticides. Organic carbon partition coefficients for selected pesticides are available in Reference 18.

The volatilization of category III pesticides is dependent on the thickness of the boundary layer of air above the soil surface. However, as the category III pesticides proceed through the soil to the surface, they behave as though there is no soil resistance. Therefore, in the absence of evaporation, the concentration of Category III pesticides decreases at the surface with time. The rate of volatilization of category III pesticides (J_{v2}) is given by equation (2):

$$J_{v2} = \frac{Co\ D_G^a\ K_H}{d\,[\rho_b f_{oc} K_{oc} + \theta + (\phi - \theta)\ K_H]} \qquad \textbf{(2)}$$

All of the parameters for equation (2) were presented in equation (1), with the exception of the boundary layer thickness, d. A value of 0.005 m can be used as a default value for d if the actual value is unknown.

Category II pesticides have properties that create soil and boundary layer resistance of approximately similar size. As a result, they display behavior intermediate between these two extremes. For category II pesticides, both volatilization equations are equivalent, and, therefore, the volatilization of category II pesticides can be represented by either equation. For the purpose of the AP-42, the equation for category I pesticides was used for category II pesticides, because the time after pesticide application is more certain than the thickness of the boundary layer, which may be different for category II pesticides.

The rate of volatilization was obtained for Categories I and II pesticides by integrating equation (1) over the 30-day time interval. For Category III pesticides, equation (2) was used to estimate the rate of volatilization.

Emission factors were estimated for the AIs using the volatilization rates calculated from the model and the application rate of 1 kilogram per hectare (kg/ha) given in the model description. Because vapor pressure is a key chemical characteristic controlling AI vapor behavior, the emission factors for the AIs were averaged and presented over three AI vapor pressure ranges. Table 4-2 presents the vapor pressures for 90 selected AIs, including those for which emission factors were calculated. Table 4-3 presents the emission factors as a function of AI vapor pressure for the time interval from application up to 30 days after application of the pesticide formulation.

TABLE 4-2. SELECTED ACTIVE INGREDIENT VAPOR PRESSURES[a]

Active ingredient	Vapor pressure mmHg at 20° to 25°C
1,3-Dichloropropene	29
2,4-D acid	8.0×10^{-6}
Acephate	1.7×10^{-6}
Alachlor	1.4×10^{-5}
Aldicarb	3.0×10^{-5}
Aldoxycarb	9×10^{-5}
Amitraz	2.6×10^{-6}
Amitrole (aminotriazole)	4.4×10^{-7}
Atrazine	2.9×10^{-7}
Azinphos-methyl	2.0×10^{-7}
Benefin (benfluralin)	6.6×10^{-5}
Benomyl	$< 1.0 \times 10^{-10}$
Bifenox	2.4×10^{-6}
Bromacil acid	3.1×10^{-7}
Bromoxynil butyrate ester	1.0×10^{-4}
Butylate	1.3×10^{-2}
Captan	8.0×10^{-8}
Carbaryl	1.2×10^{-6}
Carbofuran	6.0×10^{-7}
Chlorobenzilate	6.8×10^{-6}
Chloroneb	3.0×10^{-3}
Chloropicrin	18
Chlorothalonil	1.0×10^{-3}[b]
Chlorpyrifos	1.7×10^{-5}
Clomazone (dimethazone)	1.4×10^{-4}
Cyanazine	1.6×10^{-9}
Cyromazine	3.4×10^{-9}
DCNA (dicloran)	1.3×10^{-6}
DCPA (dacthal; chlorthal-dimethyl)	2.5×10^{-6}
Diazinon	6.0×10^{-5}
Dichlobenil	1.0×10^{-3}
Dicofol	4.0×10^{-7}
Dicrotofos	1.6×10^{-4}
Dimethoate	2.5×10^{-5}
Dinocap	4.0×10^{-8}
Disulfoton	1.5×10^{-4}
Diuron	6.9×10^{-8}
Endosulfan	1.7×10^{-7}
EPTC	3.4×10^{-2}

TABLE 4-2. (continued)

Active ingredient	Vapor pressure mmHg at 20° to 25°C
Ethion	2.4×10^{-6}
Ethoprop (ethoprophos)	3.8×10^{-4}
Fenamiphos	1.0×10^{-6}
Fenthion	2.8×10^{-6}
Fluometuron	9.4×10^{-7}
Fonofos	3.4×10^{-4}
Isofenphos	3.0×10^{-6}
Lindane	3.3×10^{-5}
Linuron	1.7×10^{-5}
Malathion	8.0×10^{-6}
Methamidophos	8.0×10^{-4}
Methazole	1.0×10^{-6}
Methiocarb (mercaptodimethur)	1.2×10^{-4}
Methomyl	5.0×10^{-5}
Methyl parathion	1.5×10^{-5}
Metolachlor	3.1×10^{-5}
Metribuzin	$< 1.0 \times 10^{-5}$
Mevinphos	1.3×10^{-4}
Molinate	5.6×10^{-3}
Naled	2.0×10^{-4}
Norflurazon	2.0×10^{-8}
Oxamyl	2.3×10^{-4}
Oxyfluorfen	2.0×10^{-7}
Parathion (ethyl parathion)	5.0×10^{-6}
PCNB	1.1×10^{-4}
Pendimethalin	9.4×10^{-6}
Permethrin	1.3×10^{-8}
Phorate	6.4×10^{-4}
Phosmet	4.9×10^{-7}
Profenofos	9.0×10^{-7}
Prometon	7.7×10^{-6}
Prometryn	1.2×10^{-6}
Propachlor	2.3×10^{-4}
Propanil	4.0×10^{-5}
Propargite	3.0×10^{-3}
Propazine	1.3×10^{-7}
Propoxur	9.7×10^{-6}
Siduron	4.0×10^{-9}

TABLE 4-2. (continued)

Active ingredient	Vapor pressure mmHg at 20° to 25°C
Simazine	2.2×10^{-8}
Tebuthiuron	2.0×10^{-6}
Terbacil	3.1×10^{-7}
Terbufos	3.2×10^{-4}
Thiobencarb	2.2×10^{-5}
Thiodicarb	1.0×10^{-7}
Toxaphene	4.0×10^{-6}
Triallate	1.1×10^{-4}
Tribufos	1.6×10^{-6}
Trichlorfon	2.0×10^{-6}
Trifluralin	1.1×10^{-4}
Triforine	2.0×10^{-7}

Note: This table contains vapor pressure values for 90 active ingredients in pesticides. Additional data can be found in Reference 17.

[a] Reference 17.

[b] This value is an estimate.

TABLE 4-3. EMISSION FACTORS FOR ACTIVE INGREDIENTS AS A FUNCTION OF APPLICATION METHOD AND VAPOR PRESSURE

Vapor Pressure (mmHg at 20° to 25°C)[a]	Emission factor[b,c]	
	kg/Mg	lb/ton
Surface application (SCC 24-61-800-001)		
10^{-4} to 10^{-6}	350	700
$>10^{-4}$	580	1,160
Soil incorporation[d] (SCC 24-61-800-002)		
$<10^{-6}$	2.7	5.4
10^{-4} to 10^{-6}	21	42
$>10^{-4}$	52	104

[a] See Table 4-2 or reference 17 for vapor pressures of specific AIs.

[b] Emission factors expressed as equivalent weight of AI volatilized per unit weight of AI applied. All emissions are uncontrolled.

[c] Emission factor applicable for the 30 day period following application.

[d] References 18-21 (particularly reference 19).

No emission factors were estimated after 30 days because after that time, degradation processes, such as hydrolysis and microbial degradation, can have a major impact on the loss of AI so that volatilization may not be the primary loss mechanism. (Note that in Table 4-1 the data do not extend beyond 30 days). The use of equations (1) and (2) may not be appropriate to estimate volatilization rates over extended periods of time.

4.3.2.2 Emissions Due to Inert VOC Ingredients—

Many of the materials used as inert ingredients in pesticide formulations are classified as VOCs. During the application of the pesticides and for a period of time subsequent to the application, the VOCs are volatilized into the atmosphere. The degree of volatilization with time is a function of many factors. Among the more predominant are the vapor pressure of the specific component, the moisture content of the soil, air temperature, and wind speed. While the precise degree of VOC loss during application is not known, a review of the data in Table 4-1 ndicates that a substantial portion, probably greater than 50 percent, of the pesticide formulation is lost upon application and during the subsequent 7 days. Many of the liquid inert ingredients in pesticide formulations have vapor pressures much higher than those of the active ingredients, which typically have vapor pressures in the range of 10^{-3} to 10^{-6}mmHg at ambient temperatures. These inert ingred-ients are the major contributors to the VOC emissions that occur within the first 30 days after the application of agricultural pesticides. In the AP-42, it is assumed that 100 percent of the VOCs present in the inert ingredients volatilize within those 30 days.

Information on the percentage of total inert ingredients in a specific formulation can be obtained from the product label, which denotes the percentage of AI in the product within the container and the percentage of inert ingredients. However, not all inert ingredients are VOCs. Most liquid formulations contain amounts of water as a portion of the inert ingredients. The percentage of water may range from several percent to greater than 95 percent. Solid formulations typically contain inert ingredients such as talc, finely ground clay, ground corn cobs, and other solid, nonvolatile components. Although solid formulations are composed almost entirely of nonliquid constituents, small quantities of liquid organic compounds are contained in the matrix. The compounds are often incorporated as carriers, stabilizers, surfactants, or emulsifiers. After field application, these compounds are susceptible to volatilization from the formulation. If information on the content of VOCs in the inert ingredient portion of the formulation cannot be obtained from the label or the manufacturer, an average percentage of the VOC content of the inert portion in typical formulation types can be found in Table 4-4. These data show the VOC content as a percentage of the inert portion. These estimated average percent values can be used as default values if the actual data cannot be obtained.

These estimated average VOC percentages were calculated by analyzing the inert formulations of approximately 9,000 products registered in the State of California. The nonvolatile portions of the inert formulations were subtracted out and the remaining (assumed) volatile portions averaged across each formulation type. The list of nonvolatile ingredients was compiled by review of nearly 3,200 individual ingredients in California's chemical data base. This cursory review, conducted by staff in the Pesticide Registration Branch of the California Department of Pesticide Regulation, determined if a component was volatile or nonvolatile. No attempt was made to establish the degree of volatility. Of the 3,200 ingredients, 981 were identified as being nonvolatile or exempt (e.g., selected CFCs are exempt). Many inert ingredients were not identifiable as to their chemical composition and, by default, were categorized as volatile. This may explain the rather high averages calculated for many of the solid formulation types. An inert ingredient contribution factor to VOC emissions was calculated for each individual product. Using a unique factor for each product allows a more accurate estimate of emissions because of variations in reported individual product usage. The formulation averages are only used when inert formulation information is unavailable. This estimation methodology is conservative, assuming that each ingredient, unless excluded as nonvolatile or exempt, is 100 percent volatilized.[23]

4.3.3 Use of the Algorithm

The algorithm is applied in a six-step procedure as follows:

1. Determine the application method and the quantity of pesticide product of concern that will be or has been applied (aerial application is not covered by the algorithm).

2. Determine the type of formulation used.

3. Determine the specific AI (or AIs) in the formulation.

TABLE 4-4. AVERAGE VOC CONTENT OF PESTICIDE INERT INGREDIENT PORTION, BY FORMULATION TYPE[a]

Formulation type	Average VOC content of inert portion, %[b]
Oils	66
Solution/liquid (ready-to-use)	20
Emulsifiable concentrate	56
Aqueous concentrate	21
Gel, paste, cream	40
Pressurized gas	29
Flowable (aqueous) concentrate	21
Microencapsulated	23
Pressurized liquid/sprays/foggers	39
Soluble powder	12
Impregnated material	38
Pellet/tablet/cake/briquette	27
Wettable powder	25
Dust/powder	21
Dry flowable	28
Granule/flake	25
Suspension	15
Paint/coatings	64

[a] Source: Reference 23.
[b] Weight percent of VOC in inert portion of the formulation.

4. Determine the percentage of the AI (or each AI) present.

5. Determine the VOC content of the formulation.

6. Perform calculations of emissions.

Information for these steps can be found as follows:

- Item 1—The quantity can be found either directly from the weight purchased or used for a given application, or alternately by multiplying the application rate (e.g., pounds/acre) times the number of units (acres) treated.

- Items 2, 3, and 4—This information is presented on the labels of all pesticide containers. Alternatively, it can be obtained from the manufacturer, end-use formulator, or a local distributor. If the trade name of the pesticide and the type of formulation are known, the specific AI in the formulation can be obtained from the *Farm Chemicals Handbook*. Table 4-5 presents the specific AIs found in several common trade name formulations. Information on the various formulations for specific AIs applied in individual States may be available from the National Agricultural Statistics Service, U. S. Department of Agriculture, Washington, D.C. This service compiles numerous statistics on pesticide usage in individual States and may provide assistance in determining annual quantities of specific AIs used by crop by State and the type of formulations used in specific States.

- Item 5—The percent VOC content of the inert ingredient portion of the formulation can be requested from the manufacturer or end-use formulator. Alternatively, an estimated average VOC content of the inert portion for several common types of formulations is given in Table 4-4.

- Item 6—Emissions are calculated separately for AIs and inert VOCs and then summed, as described and illustrated below.

4.3.3.1 Emissions Due to Active Ingredients—

The total quantity of AI applied to the crop can be calculated from the percent content of the AI in the formulation and the total quantity of applied formulation. Determine the vapor pressure of the specific AI at 20-25°C from Table 4-2, reference 17, or other sources.

Table 4-3 presents emission factors for AIs within specified vapor pressure ranges. Find the vapor pressure range in Table 4-3 corresponding to the vapor pressure of the specific AI and determine the emission factor for the AI. Based on the total quantity of applied AI (determined in the first paragraph), use the emission factor to determine the total quantity of AI emissions 30 days after application. This table is not applicable for emissions due to the use of fumigants because these gaseous or liquid products are highly volatile and would be rapidly discharged to the atmosphere. Fumigants, such as methyl bromide and 1,3-dichloropropene (1,3-D or Telone®), are no longer used in several states.

TABLE 4-5. TRADE NAMES FOR SELECTED ACTIVE INGREDIENTS[a,b]

Trade names[c]	Active ingredient[d]
INSECTICIDES	
AC 8911	Phorate
Acephate-met	Methamidophos
Alkron®	Ethyl Parathion
Alleron®	Ethyl Parathion
Aphamite®	Ethyl Parathion
Bay 17147	Azinphos-methyl
Bay 19639	Disulfoton
Bay 70143	Carbofuran
Bay 71628	Methamidophos
Benzoepin	Endosulfan
Beosit®	Endosulfan
Brodan®	Chlorpyrifos
BugMaster®	Carbaryl
BW-21-Z	Permethryn
Carbamine®	Carbaryl
Carfene®	Azinphos-methyl
Cekubaryl®	Carbaryl
Cekudifol®	Dicofol
Cekuthoate®	Dimethoate
CGA-15324	Profenofos
Chlorpyrifos 99%	Chlorpyrifos
Chlorthiepin®	Endosulfan
Comite®	Propargite
Corothion®	Ethyl Parathion
Crisulfan®	Endosulfan
Crunch®	Carbaryl
Curacron	Profenofos
Curaterr®	Carbofuran
Cyclodan®	Endosulfan
Cygon 400®	Dimethoate
D1221	Carbofuran
Daphene®	Dimethoate
Dazzel®	Diazinon
Denapon®	Carbaryl
Devicarb®	Carbaryl
Devigon®	Dimethoate
Devisulphan®	Endosulfan
Devithion®	Methyl Parathion
Diagran®	Diazinon

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
Methyl	Methyl Parathion
Metiltriazotion	Azinphos-methyl
Nipsan®	Diazinon
Niran®	Ethyl Parathion
Nivral®	Thiodicarb
NRDC 143	Permethryn
Ortho 124120	Acephate
Orthophos®	Ethyl Parathion
Panthion®	Ethyl Parathion
Paramar®	Ethyl Parathion
Paraphos®	Ethyl Parathion
Parathene®	Ethyl Parathion
Parathion	Methyl Parathion
Parathion	Ethyl Parathion
Parawet®	Ethyl Parathion
Partron M®	Methyl Parathion
Penncap-M®	Methyl Parathion
Phoskil®	Ethyl Parathion
Piridane®	Chlorpyrifos
Polycron®	Profenofos
PP 557	Permethryn
Pramex®	Permethryn
Prokil®	Cryolite
PT265®	Diazinon
Qamlin®	Permethryn
Rampart®	Phorate
Rhodiatox®	Ethyl Parathion
S276	Disulfoton
SD 8530	Trimethacarb
Septene®	Carbaryl
Sevin 5 Pellets®	Carbaryl
Soprathion®	Ethyl Parathion
Spectracide®	Diazinon
SRA 5172	Methamidophos
Stathion®	Ethyl Parathion
Tekwaisa®	Methyl Parathion
Temik®	Aldicarb
Tercyl®	Carbaryl
Thimul®	Endosulfan

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
Dicarbam®	Carbaryl
Dicomite®	Dicofol
Dimethogen®	Dimethoate
Dimet®	Dimethoate
Dizinon®	Diazinon
DPX 1410	Oxamyl
Dyzol®	Diazinon
E-605	Ethyl Parathion
Ectiban®	Permethryn
Endocide®	Endosulfan
Endosol®	Endosulfan
ENT 27226	Propargite
ENT27164	Carbofuran
Eradex®	Chlorpyrifos
Ethoprop	Ethoprop
Ethoprophos	Ethoprop
Ethylthiodemeton	Disulfoton
Etilon®	Ethyl Parathion
Fezudin	Diazinon
FMC-5462	Endosulfan
FMC-33297	Permethryn
Fonofos	Dyfonate
Force®	Tefluthrin
Fosfamid	Dimethoate
Furacarb®	Carbofuran
G-24480	Diazinon
Gardentox®	Diazinon
Gearphos®	Methyl Parathion
Golden Leaf Tobacco Spray®	Endosulfan
Hexavin®	Carbaryl
Hoe 2671	Endosulfan
Indothrin®	Permethryn
Insectophene®	Endosulfan
Insyst-D®	Disulfoton
Karbaspray®	Carbaryl
Kayazinon®	Diazinon
Kayazol®	Diazinon
Kryocide®	Cryolite
Lannate® LV	Methomyl

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
Trimetion®	Dimethoate
UC 51762	Thiodicarb
UC 27867	Trimethacarb
Uniroyal D014	Propargite
Yaltox®	Carbofuran
None listed	Dicrotophos
None listed	Terbufos
HERBICIDES	
A-4D	2,4-D
AC 92553	Pendimethalin
Acclaim	Fenoxaprop-ethyl
Acme MCPA Amine 4®	MCPA
Aljaden®	Sethoxydim
Amiben®	Chloramben
Amilon®-WP	Chloramben
Amine®	MCPA
Aqua-Kleen®	2,4-D
Arrhenal®	DSMA
Arsinyl®	DSMA
Assure®	Quizalofop-ethyl
Avadex® BW	Triallate
Banlene Plus®	MCPA
Banvel®	Dicamba
Barrage®	2,4-D
Basagran	Bentazon
Bay 30130	Propanil
Bay DIC 1468	Metribuzin
Bay 94337	Metribuzin
Benefex®	Benefin
Benfluralin	Benefin
Bentazon	Bentazon
Bethrodine	Benefin
BH® MCPA	MCPA
Bioxone®	Methazole
Blazer®	Aciflurofen
Bolero®	Thiobencarb
Border-Master®	MCPA
Brominex®	Bromoxynil
C-2059	Fluometuron

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
Checkmate®	Sethoxydim
Chloroxone®	2,4-D
Classic®	Chlorimuron-ethyl
Clomazone	Clomazone
Command®	Clomazone
CP50144	Alachlor
Crisuron®	Diuron
Croprider®	2,4-D
Dacthal®	DCPA
Dailon®	Diuron
Depon®	Fenoxaprop-ethyl
Dextrone®	Paraquat
Di-Tac®	DSMA
Diater®	Diuron
DMA	DSMA
DMA-100®	DSMA
DPA	Propanil
DPX-Y6202	Quizalofop-ethyl
EL-110	Benefin
EL-161	Ethalfluralin
Emulsamine®	2,4-D
Esgram®	Paraquat
Excel®	Fenoxaprop-ethyl
EXP-3864	Quizalofop-ethyl
Expand®	Sethoxydim
Far-Go®	Triallate
Farmco Diuron®	Diuron
Farmco Atrazine Gesaprim®	Atrazine
Fervinal®	Sethoxydim
Ferxone®	2,4-D
Furore®	Fenoxaprop-ethyl
Fusilade 2000	Fluazifop-p-butyl
G-30027	Atrazine
G-34161	Prometryn
G-34162	Ametryn
Gamit®	Clomazone
Genate Plus®	Butylate
Glyphosate Isopropylamine Salt	Glyphosate
Goldquat® 276	Paraquat

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
Higalcoton®	Fluometuron
Hoe 002810	Linuron
Hoe-023408	Diclofop-methyl
Hoe-Grass®	Diclofop-methyl
Hoelon®	Diclofop-methyl
Illoxan®	Diclofop-methyl
Kilsem®	MCPA
Lasso®	Alachlor
Lazo®	Alachlor
Legumex Extra®	MCPA
Lexone® 4L	Metribuzin
Lexone® DF®	Metribuzin
Linorox®	Linuron
LS 801213	Aciflurofen
M.T.F.®	Trifluralin
Magister®	Clomazone
Mephanac®	MCPA
Merge 823®	MSMA
Methar® 30	DSMA
Mezopur®	Methazole
Monosodium methane arsenate	MSMA
Nabu®	Sethoxydim
Option®	Fenoxaprop-ethyl
Oxydiazol	Methazole
Paxilon®	Methazole
Pillarquat®	Paraquat
Pillarxone®	Paraquat
Pillarzo®	Alachlor
Pilot®	Quizalofop-ethyl
Plantgard®	2,4-D
Pledge®	Bentazon
PP 005	Fluazifop-p-butyl
Primatol Q®	Prometryn
Probe	Methazole
Prop-Job®	Propanil
Propachlor	Propachlor
Prowl®	Pendimethalin
Rattler®	Glyphosate
RH-6201	Aciflurofen

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
Saturno®	Thiobencarb
Saturn®	Thiobencarb
Scepter®	Imazaquin
SD 15418	Cyanazine
Sencor® 4	Metribuzin
Sencor® DF	Metribuzin
Shamrox®	MCPA
Sodar®	DSMA
Sonalan®	Ethalfluralin
Squadron®	Imazaquin
Squadron®	Pendimethalin
Strel®	Propanil
Surpass®	Vernolate
Targa®	Quizalofop-ethyl
Target MSMA®	MSMA
Telok®	Norflurazon
Tigrex®	Diuron
Total®	Paraquat
Toxer®	Paraquat
Trans-Vert®	MSMA
Tri-4®	Trifluralin
Tri-Scept®	Imazaquin
Tributon®	2,4-D
Trifluralina 600®	Trifluralin
Trinatox D®	Ametryn
Tritex-Extra®	Sethoxydim
Tunic®	Methazole
Unidron®	Diuron
VCS 438	Methazole
Vegiben®	Chloramben
Vernam 10G	Vernolate
Vernam 7E	Vernolate
Vonduron®	Diuron
Weed-Rhap®	MCPA
Weed-B-Gon®	2,4-D
Weedatul®	2,4-D
Weedtrine-II®	2,4-D
Whip®	Fenoxaprop-ethyl
WL 19805	Cyanazine

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
None listed	Molinate
None listed	Tridiphane
OTHER AIs	
A7 Vapam®	Metam Sodium
Aquacide®	Diquat
Avicol®	PCNB
Carbam (MAF)	Metam Sodium
Clortocaf Ramato®	Chlorothalonil
Clortosip®	Chlorothalonil
Cotton Aide HC®	Cacodylic
De-Green®	Tribufos
DEF®	Tribufos
Deiquat	Diquat
Dextrone®	Diquat
E-Z-Off D®	Tribufos
Earthcide®	PCNB
Exotherm Termil®	Chlorothalonil
Folex®	Tribufos
Folosan®	PCNB
Fos-Fall A®	Tribufos
Karbation®	Metam Sodium
Kobutol®	PCNB
Kobu®	PCNB
Kypman® 80	Maneb
M-Diphar®	Maneb
Mancozin®	Mancozeb
Maneba®	Maneb
Manebe	Maneb
Manzate® 200	Mancozeb
Manzeb	Mancozeb
Manzin®	Mancozeb
Maposol®	Metam Sodium
Metam for the Acid	Metam Sodium
Moncide®	Cacodylic
Montar®	Cacodylic
Nemispor®	Mancozeb
Pentagen®	PCNB
Quintozene	PCNB
Rad-E-Cate® 25	Cacodylic

TABLE 4-5. (continued)

Trade names[c]	Active ingredient[d]
SMDC	Metam Sodium
Soil-Prep®	Metam Sodium
Sopranebe®	Maneb
Superman® Maneb F	Maneb
Terrazan®	PCNB
Tersan 1991®	Benomyl
TriPCNB®	PCNB
Tubothane®	Maneb
Weedtrine-D®	Diquat
Ziman-Dithane®	Mancozeb
None listed	Dimethipin
None listed	Ethephon
None listed	Thiadiazuron

[a] Selected pesticides used on major field crops found in Agriculture Chemical Usage 1991 Field Crops Summary, USDA, March 1992.
[b] Source: Reference 24.
[c] Trade names can be found in alphabetized order in reference 24.
[d] Common name. Chemical name can be found in reference 24.

4.3.3.2 Emissions Due to Inert Ingredients—

The total quantity of emissions due to the VOC in the inert ingredient portion of the formulation can be obtained by using the percent of the inert portion contained in the formulated product, the percent of the VOCs contained in the inert portion, and the total quantity of formulation applied to the crop. First, multiply the percentage of inerts in the formulation by the total quantity of applied formulation to obtain the total quantity of inert ingredients applied to the crop. Second, multiply the percent of VOC in the inert portion by the total quantity of inert ingredient applied to obtain the total quantity of VOC inert ingredients. If the VOC content for the formulation is not known, use a default value from Table 4-4. The emission factor for VOC inert ingredients is assumed to be 100 percent within 30 days after application of the formulation.

4.3.3.3 Total Emissions—

Add the total quantity of emissions due to the AI as calculated in 4.3.3.1 to the total quantity of VOC inert ingredients volatilized as calculated in 4.3.3.2. The sum of these quantities represents the total emissions resulting from the application of the pesticide formulation.

4.3.4 Example Estimation

A total of 3,629 kilograms (kg), or 8,000 pounds, of Spectracide® were surface-applied to cropland, and an estimate is desired of the total quantity of emissions within 30 days after application.

1. The active ingredient in Spectracide® is diazinon (reference 22, or Table 4-5). Information from the pesticide container states that the formulation is an emulsifiable concentrate containing 58 percent active ingredient and 42 percent inert ingredient.
2. The total quantity of AI applied is

0.58 * 3,629 kg lb = 2,105 kg (4,640 lb) of diazinon applied

2,105 kg = 2.105 megagrams (Mg); 1 Mg = 1.1 tons

2,105 Mg * 1.1 tons/Mg = 2.32 tons of diazinon applied

From Table 4-2, the vapor pressure of diazinon is 6 x 10^{-5}mmHg. Using Table 4-3, the emission factor for AIs with vapor pressures between 1 x 10^{-6} and 1 x 10^{-4} during a 30-day interval after application is 350 kg/Mg

(700 lb/ton) applied. The estimated total quantity of diazinon volatilized is 737 kg (1,624 lb) over the 30-day interval.

3. From the label, it can be determined that the inert content is 42 percent and Table 4-4 shows that the average VOC content of the inert portion of emulsifiable concentrates is 56 percent.

   Total quantity of emissions due to inert VOC ingredients:
   0.42 * 3,629 kg * 0.56 = 854 kg (1,882 lb) of VOC inert ingredients

   One hundred percent of the VOC inert ingredients emissions is assumed to volatilize within 30 days.

4. The total quantity of emissions during this 30-day interval is the sum of the emissions due to VOC inert ingredients and AI. In this example, the total quantity of emissions is 854 kg (1,882 lb) plus 737 kg (1,624 lb), or 1,591 kg (3,506 lb).

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SECTION 5

PROPOSED AP-42 SECTION 9.2.2

[See instead current AP-42 Section 9.2.2.]