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Jeff Jenkins

Empirical data regarding the evaporative flux of pesticides from sprayed droplets is essential for preparing accurate pesticide exposure estimates for risk assessment. Data on pesticide evaporative flux from droplets is scarce and other investigators in the field have not examined free-falling droplets. The Pesticide Volatilization Column (PVC) was utilized to assess the evaporative flux of the butoxyethyl ester of triclopyr from simulated spray droplets of Garlon® 4. Pesticide droplets were allowed to free fall through a glass column of temperature and humidity-controlled air. Volatilized triclopyr ester was quantified by collecting acetone rinses of the column walls and extracting a PUF air trap. Samples were analyzed using gas chromatography with a nitrogen/phosphorus detector (GC-NPD). Analytical results were compared with a predicted evaporative flux estimate prepared using a stagnant two-film (STF) model. Results of studies by Bentson (1988) on triclopyr ester volatilization from glass slides were also compared with the STF model predictions and the empirical data from this experiment. The average measured flux of 107.8 $pg/cm^2 \cdot sec$ at 35°C was approximately two times the STF model-predicted flux of 55.3 $pg/cm^2 \cdot sec$ at 25°C and about the same as the average flux of 106.9 $pg/cm^2 \cdot sec$ at 25°C from glass slides measured by Bentson (1988). Total evaporative losses of triclopyr ester from a spray application can be estimated using a spreadsheet model based on data from this experiment and wind tunnel droplet size distribution results from Yates et al. (1986). Using the spreadsheet model, the predicted total evaporative loss of triclopyr ester from 50 gallons of a 3 percent aqueous emulsion of Garlon-4 sprayed from a D8-Jet nozzle at 0 degrees azimuth, 50 mph flight speed, and 12 meters above ground was 8.23 mg. Evaporative loss estimation methods developed in this project may be applied to many pesticides in use today, thus enhancing efforts at modeling their environmental transport and fate.

A Novel Apparatus for Estimating Pesticide Volatility from Spray Droplets

by

Jeff D. Poel

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Jeff D. Poel, Author

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DEDICATION

This thesis is dedicated to my father, Jerry D. Poel, who as an aerospace engineer, computer scientist, and technical writer provided me with a standard of excellence I have tried to emulate in my scholastic and professional efforts. His attention to detail and never-ending quest for perfection set an example that helped bring the completion of this thesis project within my grasp. This document is also dedicated to my mother, Corinne, who managed to pass along enough of her gift of patience to allow me to complete my graduate work while somehow maintaining my sanity.

A NOVEL APPARATUS FOR ESTIMATING PESTICIDE VOLATILITY FROM SPRAY DROPLETS

1. INTRODUCTION

1.1 Problem Definition

Offsite movement of aerially-applied pesticides is recognized as a significant source of air, water, and soil pollution. It is of importance both locally and globally. There are many examples in the literature of the deleterious effects of pesticide spray drift on local non-target biota. Glotfelty et al. (1990) found that atrazine and simazine, two herbicides applied primarily to cornfields during spring near the Wye River in Maryland, could be measured in air at all times of the year, even during the winter. Although the possible negative effects of persistent organochlorine pesticides in the environment is currently in dispute, it has been shown by researchers that many of these compounds are distributed globally. For example, long-lived organochlorine insecticides such as dichlorodiphenyltrichloroethane (DDT) have been found at measurable concentrations in the polar regions, areas quite remote from their application sites (Muir et al., 1990; Bidleman et al., 1990).

Once released from application equipment such as aerial or ground sprayers, pesticides are free to begin dispersing in the environment. Although some pesticides are degraded rapidly (e.g. triclopyr), others, such as the aforementioned organochlorine pesticides, are long-lived and subject to long-range transport. A good deal of research has been dedicated to examining spray drift, or the offsite movement of fine spray droplets (Akesson et al., 1982; Miller, 1993; Ware et al., 1970; Ware, et al. 1972). Other research has measured the change in droplet size of different pesticides in temperature and humidity controlled airstreams (Freiberg and Crosby, 1986; Sundaram, 1985). However, comparatively little work has focused on the volatilization of active ingredient directly from spray droplets. Many pesticides have relatively low volatility; therefore, direct evaporation of active ingredient from spray droplets would be expected to play a minor role compared to droplet

drift in the greater picture of offsite transport. Given the tremendous volume of pesticides used annually in the U.S., however, it is likely that significant amounts of pesticides are lost to evaporation from spray droplets in flight. Therefore, it is necessary to understand the dissipation of a chemical from spray droplets before one can adequately model the environmental behavior and fate of that chemical.

A given pesticide may escape the application site as either fine droplets subject to offsite drift or as active ingredient that volatilizes directly into the atmosphere during droplet descent. The environmental fate of the two forms can be distinct. When a chemical remains within a droplet, the droplet may eventually leave the atmosphere by impacting a surface. Alternatively, chemical residues volatilized directly from the droplet may remain in the atmosphere until the chemical is transformed, precipitated from the atmosphere in solution with moisture, or adsorbed to particulates. Little information is available on the factors influencing these mechanisms or how they might be altered to improve on-target deposition of sprayed chemicals.

Damage to nontarget organisms by pesticide spray drift is a widely recognized problem. Research has confirmed that significant quantities of sprayed chemicals are subject to offsite transport. For example, the quantity of phenoxy herbicides in surface deposits that can be accounted for immediately after an aerial application is generally about 70 to 80 percent of the material released (Norris, 1981). In other applications using different pesticides, target deposits may range from 30 to 95 percent of the sprayed pesticide (Ware et al., 1972). In an earlier study, Ware et al. (1970) found that average on-target deposits of toxaphene and methoxychlor applied to cotton and alfalfa fields were 53 percent. It is unknown whether simple droplet drift or volatilization of active ingredient directly from the droplet accounts for the majority of "lost" pesticide. Because forestry applications release herbicides from greater heights than is typical of agriculture, longer exposure to evaporation could result in

greater losses of active ingredient than that which occurs in agricultural spraying. Greater evaporative losses of herbicides would increase the likelihood of off-site impacts from herbicide vapor drift.

An accurate estimation of the quantity of active ingredient that is lost to the atmosphere during pesticide application is important for determining exposure to non-target organisms downwind from the application site. This information is essential for preparing exposure estimates in human health and ecological risk assessments. Empirical data on the rate of loss of pesticide from spray drops is essential to our understanding of pesticide fate and transport processes. This information may also prove useful to spray drift modeling and drift mitigation.

1.2 Literature Review

The following literature review includes a discussion of emulsion properties, evaporation of pesticides from spray droplets, pesticide formulations, properties of triclopyr, the properties of falling droplets, and a proposed method for estimating the evaporative flux of pesticides from spray droplets.

1.2.1 Emulsion Properties

A pesticide emulsion consists of an emulsifiable concentrate (EC) formulation and a carrier solvent (water or diesel oil). An EC pesticide formulation is composed of a surfactant(s), hydrophobic solvent(s), and the active ingredient. When an EC is mixed with a polar carrier solvent (such as water) and agitated, the immiscible phases are broken down into very small compartments called micelles. Micelles make up the dispersed phase (droplets) in the continuous phase (carrier solvent).

When two immiscible liquids are combined, they separate into phases. With stirring or agitation, the interfacial surface area expands and micelles are formed. Large micelles result when low mechanical energies are added to the system, while with greater agitation the

micelles become smaller. Micelles are comprised of a liquid that is immiscible in the continuous liquid (Sharma and Shah, 1985). Depending on the design of the formulation and the energy input to the system by stirring, an emulsion may assume one of two forms, a microemulsion or a macroemulsion. Microemulsions are defined as clear, thermodynamically stable dispersions of two immiscible liquids where the dispersed phase consists of small droplets with diameters in the range of 0.01 to 0.1 micrometers (μm). Macroemulsions are turbid or milky in color, thermodynamically unstable, and typically form dispersed-phase droplets of > 0.1 μm diameter. Macroemulsions are widely used in industry and include diverse forms such as mayonnaise, cosmetics, and pesticides (Sharma and Shah, 1985). Macroemulsions are inherently unstable, and with the cessation of stirring, will gradually precipitate or dissociate into two separate phases (Rosen, 1978).

Virtually all current EC pesticide formulations form macroemulsions. Macroemulsions may be classified as single, double, or multiple emulsions (Sharma and Shah, 1985). Single emulsions are formed by two immiscible phases (e.g. water and an oil such as kerosene or diesel) that are separated by a surfactant film (Figure 1.1). An oil-in-water (O/W) emulsion contains oil as the dispersed phase (droplets) and water as the continuous phase or solvent. A water-in-oil (W/O) or invert emulsion is formed when water is the dispersed phase and oil acts as the continuous phase (Sharma and Shaw, 1985). A W/O emulsion can be formed in a pesticide spray mix by adding inverting chemicals such as Bivert-TM® and changing the ratio of water to oil in the mix (Newton, verbal communication). Both O/W and W/O emulsions are used in pesticide spray mixes, depending on the application technique and target organisms (Dow Chemical, 1993). Double and multiple emulsions can be formed by two or more than two immiscible phases that are separated by at least two emulsifier films (Sharma and Shaw, 1985). These more complex emulsions are used in pharmaceutical and industrial applications and will not be considered further in this discussion.

The presence of surfactants, or surface-active chemicals, allows the formation of micelles (Rosen, 1978). Surfactant molecules are composed of a hydrophobic end (nonpolar

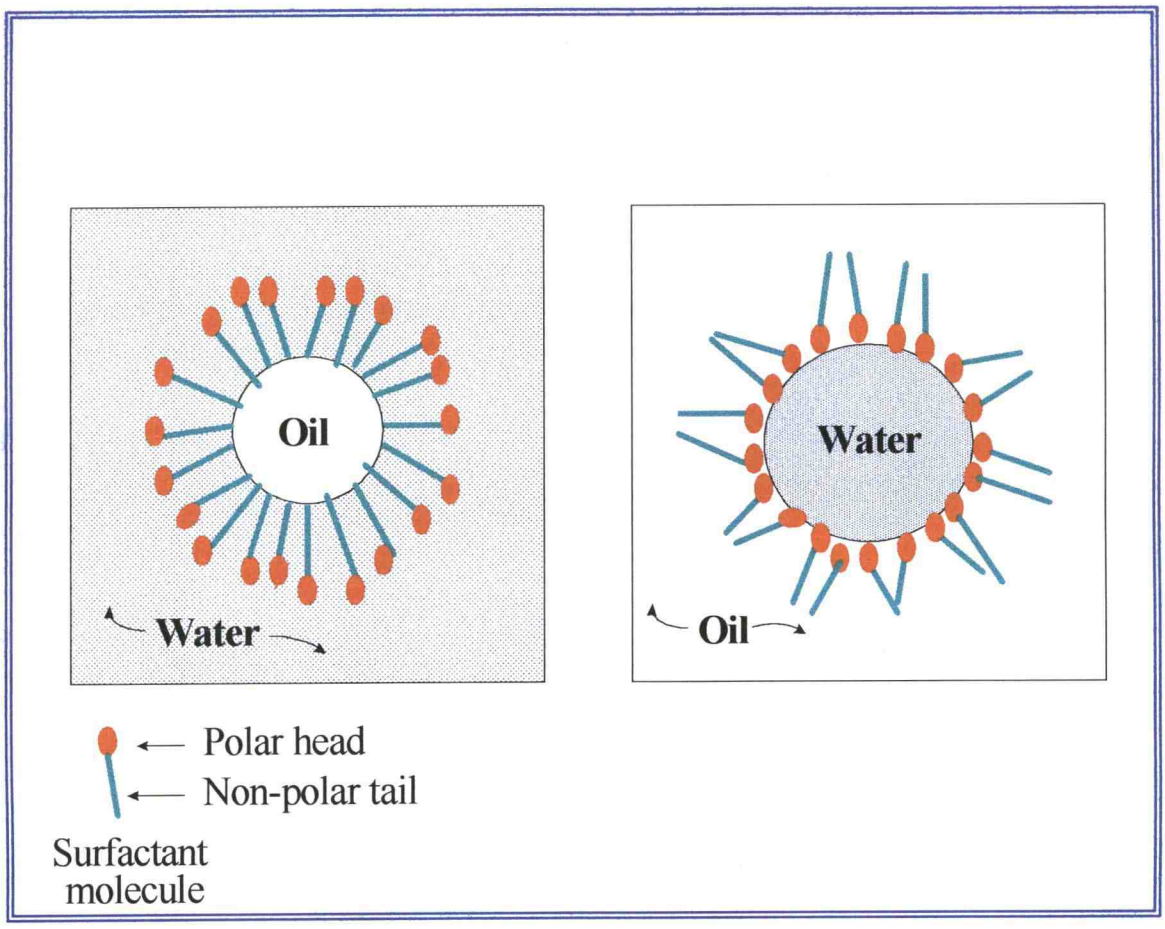

Figure 1.1 Schematic of oil-in-water and water-in-oil macroemulsions

tail) and a hydrophilic end (polar head). At micellization, the hydrophilic ends of the surfactant molecules align themselves to face the aqueous solution and the hydrophobic ends associate with the oil phase away from the aqueous solution (Figure 1.1) (Sharma and Shah, 1985). Surfactant molecules will also arrange themselves at gas-liquid or liquid-solid interfaces. Thus, on the outer surface of an emulsion spray droplet there will be a monomolecular layer of surfactant. This reduces the surface tension of the droplet below that of pure water (Rosen, 1978). Reduction of surface tension means that droplets will spread further on impacted surfaces and it takes less energy for evaporation of substances in the droplets to occur, particularly the bulk phase solvent.

The critical micelle concentration (CMC) is the lowest surfactant concentration at which micelles form; the lower the CMC, the greater the tendency of a system to form micelles (Scamehorn, 1986). At the CMC, the surfactant molecules have aggregated sufficiently at phase interfaces to permit micelle formation. The aggregation of surfactant molecules reduces the interfacial surface tension between the immiscible liquids (Sharma and Shah, 1985). The aggregation number is the minimum number of surfactant molecules that aggregate at a micellar interface. Changes in temperature, concentration of surfactant, additives in the liquid phase, and structural groups in the surfactant all may cause change in the size, shape, and aggregation number of the micelles (Rosen, 1978).

Surfactants used in pesticide formulations are rarely a single chemical. Usually they are a mixture of different surfactant molecules, because:

- Production of isomerically pure surfactant product is prohibitively expensive, and
- A blend of surfactants with different properties can improve micellization and reduce costs (Scamehorn, 1986).

The remaining ingredient in the EC formulation is the hydrophobic solvent. Solvents chosen are those that (Scamehorn, 1986):

- The pesticide is soluble and stable within
- Are suitable for micelle formation
- Meet regulatory requirements for safety, health, and environmental considerations.

Often a blend of solvents is used in formulations to improve the formulation's properties, reduce costs, or reduce unwanted effects such as phytotoxicity (with insecticides) or human toxicity (Hudson and Tarwater, 1988). Design of formulations is an art as much as a science and depends upon trial and error to develop an effective product. Thus, the formulation composition is a proprietary secret of the formulator.

1.2.2 EVAPORATION FROM DROPLETS

A falling pesticide spray droplet is a complex, dynamic system. During flight, mass consisting of solvents, surfactants, and active ingredients is being transferred to the environment as a result of basic physical processes. The evaporation rate depends on the following factors (Ranz and Marshall, 1952a):

- The rate of heat transfer to the droplet surface
- The rate of evaporation and mass transfer from the droplet surface
- The temperature and concentration at the droplet surface during evaporation
- The effect on evaporation rate of original drop temperature, heats of solution and crystallization, and the way in which solid surfaces form on the droplet surface.

It is apparent from the discussion in Section 1.2.1 that an oil-soluble pesticide such as the butoxyethyl ester of triclopyr (triclopyr ester) would be concentrated in the inner oil droplet of an O/W emulsion such as the one used in this experiment. Evaporative flux (the mass lost per unit area per unit time) of triclopyr ester from the droplet would be a function of:

- The diffusivity of triclopyr ester in oil
- The diffusion rate of triclopyr ester across the oil-water-surfactant interface
- The diffusivity of triclopyr ester in water
- The diffusion rate of triclopyr ester across the water-air-surfactant interface.

The diffusion of the pesticide across the water/air interface (at constant temperature, pressure, and droplet size) would initially depend on:

- The pesticide's Henry's Law constant
- The stagnant air boundary layer thickness surrounding the droplet (Ranz and Marshall, 1952a).

For neutral compounds at dilute solute concentrations in pure water, the air-water distribution ratio is referred to as the Henry's Law constant (K_H). It may be thought of as the ratio of a compound's abundance in the gas phase to that in the aqueous phase at

equilibrium. For real aqueous solutions containing many other chemical species, the air-water distribution ratio can be approximated by K_H. It can be expressed:

$$K_H = \frac{P_i}{C_w} \quad (1)$$

where P_i is the chemical's partial pressure in atm, C_w is its aqueous molar concentration, and K_H is in atm · L/mol (Schwarzenbach, et al., 1993). K_H is also commonly given in unitless form or in atm · m^3/mol (Section 1.2.5.2).

Due to changes in droplet composition during evaporation, the rate of volatilization of a pesticide or other solute from a falling droplet is dynamic. A solute's concentration in the aqueous, continuous phase would tend to increase as the droplet evaporates. With increasing concentration in the continuous phase, the concentration gradient between the droplet and the atmosphere would increase, thereby increasing the rate of solute loss. At the same time, the equilibrium between the solute concentration in the aqueous phase and the oil micelles would shift. An oil soluble compound like triclopyr ester would begin diffusing into the micelles where it is more soluble. With continued evaporation of the aqueous phase, the oil droplets would begin coalescing. Once the aqueous phase was completely lost, the coalesced oil droplets would be exposed directly to the atmosphere. Volatilization of the pesticide from the oil (at constant temperature, pressure, and droplet size) would then depend on:

- The diffusivity of triclopyr ester in oil
- The stagnant air boundary layer thickness surrounding the oil
- The diffusivity of triclopyr ester in air.

This process is complex and has not been examined in the literature. Thus, the evaporative flux of triclopyr ester from Garlon® 4 emulsions is difficult to predict. However, an order-of-magnitude estimate of the flux based on several simplifying assumptions may be useful (Section 1.2.5.2).

Ranz and Marshall (1952a, 1952b) examined the following four fundamental aspects of droplet evaporation:

1. The rate of heat transfer to the droplet surface
2. The rate of evaporation and mass transfer from the droplet surface
3. The temperature and concentration of solutes at the droplet surface during evaporation
4. The effect of evaporation rate on original droplet temperature, heats of solution and crystallization, and the way that solid surfaces form on the droplet surface.

Ranz and Marshall were concerned primarily with spray droplets used in industry (e.g. painting) where temperatures could be extreme; however, they produced useful data on drying of aqueous and solute-containing droplets at room temperature that can provide some insight into the more complex behavior of pesticide emulsions. Unfortunately, their experimental treatments and equations dealt with the change in size of droplets and evaporation of the bulk phase, not the loss of solutes.

According to Ranz and Marshall (1952a), droplet drying is divided into two periods, called the constant-rate period, which is linear, and a non-linear falling-rate period wherein the droplet concentrates to the point where it no longer presents a free liquid surface to the gas stream. Thus, the rate of evaporation decreases with decreasing moisture content. This was shown to be true for emulsions of the phenoxy herbicide MCPA by Freiberg and Crosby (1986), as the droplets were quickly dehydrated to a persistent, oily film. Evaporation of a droplet occurs because heat for evaporation is transferred by conduction and convection from the surrounding gases to the drop surface from which vapor is transferred by diffusion and convection back into the gas stream. The rate of transfer per unit area of interface is a function of the temperature, humidity, and transport properties of the gas, and the diameter, temperature, and relative velocity of the drop. The effects of the evaporative process on a falling drop is not an even one, that is the rate of heat transfer is greatest on the side facing the airstream, and is effected by the presence of a stagnant air boundary layer (Ranz and Marshall, 1952a).

A literature search found only a single study of herbicide loss (dimethyl amine salt of MCPA: [4-chloro-2-methyl-phenoxy]acetic acid) from droplets in airstreams (Freiberg and Crosby, 1986). MCPA salt is soluble in water, and therefore not formulated as an emulsifiable concentrate. Thus, the pesticide is relatively non-volatile from water. Losses from 1 μL droplets suspended from a glass bead were measured over five days in sunlight in a cylindrical glass wind tunnel and compared to losses from deposits in glass beakers. Airflow through the chamber began at 1 meter per second (m/sec) and was reduced to an unspecified velocity during the exposure to simulate decreasing settling velocity with decreasing droplet size. One μL droplets rapidly evaporated to an oily film on the glass bead in 15 minutes. The initial decrease in droplet surface area with time was linear, but decreased slightly with time in accordance with the predictions made by Ranz and Marshall (1952a, b). The non-linear rate of droplet size change was attributed to decreasing vapor pressure as the MCPA solute concentration increased. The oily residue remaining on the glass bead contained all of the MCPA, and the study concluded that photolysis was the primary contributor to the calculated half-life of 4.6 days. This compared to a calculated half-life of 3.9 days in sunlight for MCPA as a thin film in a beaker. Losses of the amine salt of MCPA were about 15 to 20 percent in the dark and 80 to 90 percent in sunlight after eight days. The behavior of triclopyr ester should be different than that of MCPA because of its greater volatility and lower aqueous solubility (giving a higher K_H).

Sundaram (1985) compared a gravimetric method of measuring insecticide volatility to a visual, volumetric method. For the gravimetric method, he estimated the evaporation rates of several insecticides by applying single drops to filter paper in a temperature and humidity-controlled environment and recording their change in weight with time. The volumetric method involved spraying droplets onto glass fibers and monitoring their size reduction with time using a dissecting microscope. Airflow in the chamber was maintained at 0.15 to 0.25 m/sec for the volumetric method. Airflow rates for the gravimetric method were not mentioned. He found that the gravimetric method was more precise and eliminated the effect that changing droplet surface area has on evaporation rate. However, possible

interaction between the volatile components of the mixture and fibers in the filter paper were neither mentioned nor accounted for. Water-based emulsions did not spread uniformly on the filter paper; therefore, the gravimetric method is likely not suitable for examining the behavior of largely aqueous formulations such as the Garlon® 4 tank mixes used in this project. In addition, this study examined the loss to evaporation of the bulk solution, not the active ingredient alone.

1.2.3 Pesticide Formulations

Both O/W (direct) and W/O (invert) emulsions are used in forestry, depending on the target organisms and the season of application (Dow Chemical, 1993). Diesel oil is included in the formulation as a surfactant extender and as a means of increasing penetration of bark and waxy leaves. The formulation typically used with Garlon® 4 in forestry to make an O/W (direct) emulsion consists of 2 to 4 percent Garlon® 4, 5 to 10 percent diesel oil, and the balance water (Newton, verbal communication). However, oil is not included in formulations applied by air during the growing season of non-target organisms due to its phytotoxicity. For applications during the growing season, a Garlon® 4/water emulsion is typically prepared (Dow Chemical Company, 1993). Because a large proportion of the Garlon® 4 formulation is kerosene, the Garlon® 4/water emulsion is essentially a direct, O/W emulsion. This is the type of emulsion that was used in this experiment. Surfactants such as Tronic, Sponto 712, or Ortho X-77 may also be added to aid in emulsification and leaf penetration (Dow Chemical, 1993). Drift control agents such as Nalco-Trol, and other herbicides including 2,4-D (ester or amine) and Tordon® 10, may be included in the tank mix for some applications. The effects of these agents on the evaporative flux of triclopyr ester were not examined in this study.

1.2.4 Physical and Chemical Properties of Triclopyr

Triclopyr ([3,5,6-trichloro-2-pyridinyloxy]acetic acid) is formulated in Garlon® 4 as an emulsifiable concentrate of the butoxyethyl ester (Figure 1.2). The formulated product of Garlon® 4 contains 61.6 percent of the butoxyethyl ester of triclopyr and 38.4 percent inert

ingredient (Dow Chemical, 1993). The bulk of the inert ingredients is kerosene (Dow Chemical, 1990). Depending on the time of year and target pests, Garlon® 4 may be applied either as an aqueous O/W emulsion or as a W/O emulsion (Section 1.2.1).

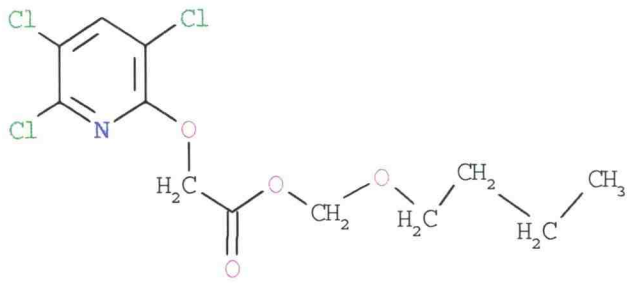

Figure 1.2 Butoxyethyl ester of triclopyr

Triclopyr is a selective systemic herbicide that is rapidly absorbed by the foliage and roots, with translocation throughout the plant, accumulating in the meristematic tissue. There it induces auxin-type responses in susceptible species, mainly broad-leaved weeds. It is used for control of woody plants and broad-leaved weeds, including nettles, docks, brambles, gorse, and broom in grassland, uncultivated land, industrial areas, coniferous forests, oil palm and rubber plantations, and rice fields (Farm Chemicals Handbook, 1996). Some important chemical and physical characteristics of triclopyr are presented in Table 1.1.

The vapor pressure of triclopyr acid is 1.26×10^{-6} millimeters mercury (mm Hg) at 25 degrees Centigrade (°C), and 3.6×10^{-6} mm Hg for the butoxyethyl ester. The higher vapor pressure of the ester formulation may be due to its lack of charge and polarity relative to the acid. Triclopyr acid is not susceptible to hydrolysis; however, the ester is rapidly converted to the acid by hydrolysis (Dow Chemical, 1993).

1.2.5 Droplet Properties

Spray droplets used in aerial forestry herbicide applications can range in size from a volume median diameter (VMD) between 150 and 1,130 μm (Parker, verbal communication; Yates et al., 1985). The VMD is the droplet diameter that divides the volume of material sprayed in half. Thus, for an 1,130 μm VMD spray application, one half the spray volume was smaller in diameter than the VMD and the other half larger. The 150

to 1,130 μm VMD droplets can be produced by the D6 or D8 spray nozzles used for forestry herbicide applications. The droplet size formed depends on the nozzle angle of incidence to the air stream, pesticide formulation, line pressure, and wind speed. Droplets of 2 mm or less in diameter falling at terminal velocity tend to be spheroid in shape (Goering et al., 1972). The droplets examined in this experiment are less than 2 mm in diameter; therefore, they will be treated as being spherical for all calculations.

TABLE 1.1
PHYSICAL AND CHEMICAL
PROPERTIES OF TRICLOPYR

Chemical Species	Soil ½-Life (Days)	Vapor Pressure (mm Hg @ 25°C)	K_H (atm-m^3/mol)	K_{OC} (ml/g)	Solubility (H_2O @25°C)	Solubility (Acetone @ 25°C)
Acid	<50 @ 25°C	1.26×10^{-6}	9.66×10^{-10}	15-78	440 mg/l	9.89×10^{7} mg/l
Ester	46	3.60×10^{-6}	2.28×10^{-7}	780	7.4 mg/l	NA

NA = Not available Source: USEPA Environmental Fate One-Liner Database

1.2.5.1 Rate of Fall

Very small drops settle at velocities according to Stokes law that depend on the difference between the droplet density and the density of the medium through which it is falling ($\Delta\rho$), droplet diameter (d), gas viscosity (η), and gravity (g) (Clift, 1978).
The relationship is:

$$V_t = \frac{g d^2 \Delta\rho}{18\eta} \qquad (2)$$

where V_t is the droplet's terminal settling velocity. However, Stokes law is only applicable for small particles with small Reynolds numbers (Re). Above about 300 μm diameter, Stokes law would greatly exaggerate the fall speed of a particle because Re becomes large

relative to its fall rate. The Reynolds number, shown for various droplet diameters in Table 1.2 below, is the non-dimensional ratio of inertial to viscous forces (Linsley et al., 1982). The Reynolds numbers presented in Table 1.2 were determined using the following relationship (Scorer, 1978):

$$Re = \frac{2rW_t}{\nu} \qquad (3)$$

where r is the droplet radius in cm, W_t is the fall speed in cm/sec, and $\nu = \mu/\rho$ for air = 0.15 cm^2/sec at 20°C where μ is the viscosity of air and ρ is the density. Very small particles, with correspondingly small Re, quickly reach their terminal velocities. However, as can be seen from Fig. 1.3, for larger droplets the terminal velocity increases more slowly relative to Re, and hence they do not reach their terminal velocity as rapidly. Water drop fall rates in air are summarized in Table 1.2. (adapted from Scorer, 1978).

Because small droplets do not descend as rapidly as larger droplets of the same density, smaller droplets have a longer period during which their constituents may equilibrate with the atmosphere. For example, a 100 μm droplet would have a fall rate of 0.27 m/sec (Table 1.2). This droplet released from an aerial sprayer at 12 m would take about 45 seconds to impact the ground, giving it ample opportunity to evaporate before reaching the target surface. Droplets less than 100 μm diameter can have very short lives: the model proposed by Goering et al. (1972) predicted that a 45 μm droplet sprayed at 21°C and 50 percent relative humidity would evaporate completely within 6 inches of the spray nozzle.

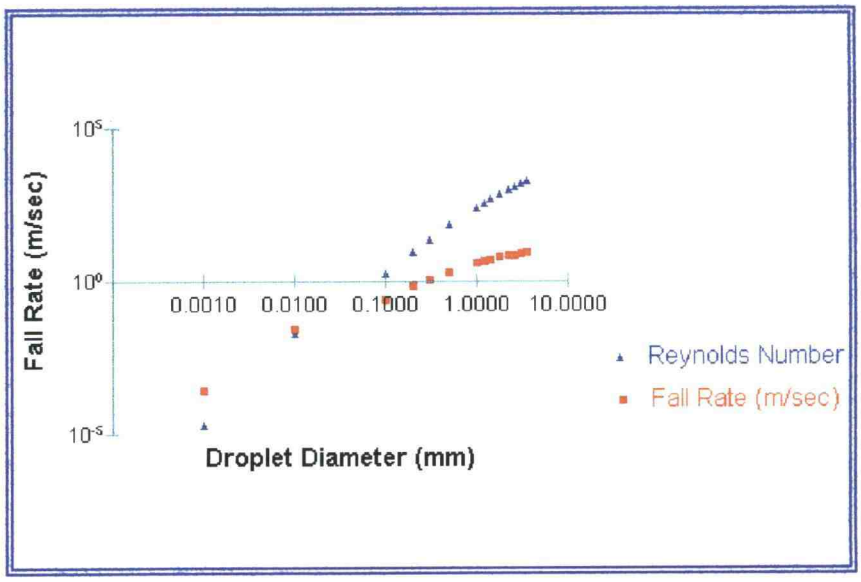

Figure 1.3 Droplet Diameter vs. Fall Rate and Reynolds Number

The droplets studied in this experiment fell approximately 1 meter from the top of the column to the point where they exited the airstream. They were ~ 2 μL (~ 1.6 mm diameter), and thus will not be subject to Stokes law. An approximation of their total fall time and the maximum velocity reached in the column can be calculated (neglecting air friction) (Bueche, 1977):

$$s = V_0 t + 0.5 a t^2 \qquad \textbf{(4)}$$

where s is distance = 1 m, V_o is initial velocity = 0 m/sec, t is time, and a is acceleration due to gravity = 9.8 m/sec^2.

Solving for t:

$$t = \sqrt{\frac{1m}{0.5 \cdot 9.8\, m/\text{sec}^2}} = 0.45 \text{ sec.} \qquad \textbf{(5)}$$

Because air friction is neglected, this approximation underestimates the true droplet exposure time by an unknown (however probably quite small) amount. This approximation will be important in estimating droplet exposure time to the airstream in the experiment. The

following equation was used to estimate final velocity (V_f) for a droplet falling 1 meter (again neglecting air friction) (Bueche, 1977):

$$2as = V_f^2 - V_o^2 \quad (6)$$

where V_f^2 is the square of final velocity and V_o^2 is the square of the initial velocity = 0. Solving for V_f:

$$V_f = \sqrt{2 \cdot 9.8\, m/sec^2 \cdot 1\, m} = 4.3\, m/sec. \quad (7)$$

Without considering air friction, this value is less than the terminal velocity shown in Table 1.2 of 5.7 m/sec for a 1.6 mm diameter droplet; therefore, the droplets will not reach their terminal (or settling) velocity within the one meter fall distance used in this experiment.

1.2.5.2 Estimation of Triclopyr Ester Evaporative Flux from Droplets

Ranz and Marshall (1952a,b) examined the factors influencing the rate of evaporation of pure liquid drops and that of water drops containing dissolved and suspended solids. Goering et al. (1972) expanded on their work and modeled the movement and evaporation of sprayed droplets in still air and induced airstreams. However, both groups of investigators described the change in volume of droplets due to the loss of water (or of the continuous phase for solutions) and did not deal with evaporative loss of solutes from solution.

In this section, an estimate of the evaporative loss of triclopyr ester from falling drops is given. This method of estimation, employing Henry's Law, is based on a number of simplifying assumptions. It should, however, provide a rough (perhaps order of magnitude) estimate of the evaporative flux.

TABLE 1.2
WATER DROP FALL SPEED IN AIR

Diameter (mm)	Volume (μL)	Fall Rate (m/sec)	Reynolds # (dimensionless)	Surface Area (cm^2)	Fall Time (sec/m)
0.001	5.24×10^{-10}	0.0003	0.00	3.14×10^{-8}	3333.3
0.010	5.24×10^{-7}	0.03	0.02	3.14×10^{-6}	33.3
0.1	5.24×10^{-4}	0.27	1.80	3.14×10^{-4}	3.7
0.2	4.19×10^{-3}	0.72	9.60	1.26×10^{-3}	1.39
0.3	0.01	1.2	24.00	2.83×10^{-3}	0.83
0.4	0.03	1.6	42.67	5.03×10^{-3}	0.63
0.5	0.07	2.1	70.00	7.85×10^{-3}	0.48
0.6	0.11	2.5	100.00	1.13×10^{-2}	0.40
0.7	0.18	2.9	135.33	1.54×10^{-2}	0.34
0.8	0.27	3.3	176.00	2.01×10^{-2}	0.30
0.9	0.38	3.7	222.00	2.54×10^{-2}	0.27
1.0	0.52	4	266.67	3.14×10^{-2}	0.25
1.2	0.90	4.6	368.00	4.52×10^{-2}	0.22
1.4	1.44	5.2	485.33	6.16×10^{-2}	0.19
1.6	2.14	5.7	608.00	8.04×10^{-2}	0.18
1.8	3.05	6.1	732.00	1.02e-01	0.16
2.0	4.19	6.5	866.67	1.26e-01	0.15
2.2	5.58	6.9	1012.00	1.52e-01	0.14
2.4	7.24	7.3	1168.00	1.81e-01	0.14
2.6	9.20	7.6	1317.33	2.12e-01	0.13
2.8	11.49	7.8	1456.00	2.46e-01	0.13
3.0	14.14	8.1	1620.00	2.83e-01	0.12
3.2	17.16	8.3	1770.67	3.22e-01	0.12
3.6	24.43	8.6	2064.00	4.07e-01	0.12
4.0	33.51	8.8	2346.67	5.03e-01	0.11
4.6	50.97	9	2760.00	6.65e-01	0.11
5.2	73.62	9.1	3154.67	8.49e-01	0.11

The United States Department of Agriculture (USDA) Forest Service examined the size distribution of droplets sprayed from various nozzles typically used in forestry herbicide

applications. Depending on the nozzle type used (D8-46 or D8 jet) and the nozzle angle incident to the airstream (0, 45, or 90 degrees), they determined that the VMD for 50 mph airspeed ranged between 382 and 1,130 μm. The larger droplets were produced by reducing the nozzle angle incident to the airstream. The percent of spray volume under 122 μm (the normal cut-off size for "driftable" droplets) ranged between 1 and 4 percent. The 382 μm VMD spray produced the largest number of driftable droplets and the 1,130 μm VMD spray produced the least (Yates et al., 1985). Based on these numbers, the droplets under consideration here (1,600μm diameter) are approximately 1.4 times the upper VMD of what is seen in a typical forestry application. Therefore, it will be necessary to compare the theoretical predictions regarding mass transfer and the empirical results seen in the larger experimental droplets and use this information to model the behavior of smaller droplets seen in typical forestry spray applications.

Schwarzenbach et al. (1993) proposed a model for predicting chemical flux at the air-water interface of surface waters. They called this model the stagnant two-film (STF) model (Schwarzenbach, R. P., Gschwend, P. M. & Imboden, D. M. in *Environmental organic chemistry* Vol.1st, 215-240. Copyright ©1993 John Wiley & Sons, New York, NY. Reprinted by permission of John Wiley & Sons, Inc.). For this experiment, the STF model was adapted for modeling the evaporative flux of triclopyr ester in spray droplets. The STF model envisions an unstirred or stagnant condition in both a water layer and an air layer adjacent to the interface. The stagnant layers represent the two "films" (modified for falling droplets in Figure 1.4). These films act as "bottlenecks" arranged in series, where molecular transport, unaided by the eddy mixing occurring in the bulk solution and the surrounding air, depends solely on diffusion. Therefore, the rate-limiting step in this model is molecular movement across the stagnant boundary layers.

The STF model was chosen for estimating the evaporative flux of triclopyr ester from falling droplets for the following reasons:

- Droplets in moving airstreams have been shown using temperature sensors to possess a stagnant air boundary layer that is approximated by their diameter (Ranz and Marshall, 1952a)
- Droplets are very small, thus it is unlikely that turbulent mixing of the fluid would have a large effect on molecular transport within the droplet.

The following simplifying assumptions were made for using the STF model to estimate triclopyr ester evaporative flux:

- The surface of a spherical droplet would behave the same as an equivalent area of surface water
- Air moving past a falling droplet would have the same effect on molecular transport as air moving across flat surface water
- The rate limiting step for evaporative loss of active ingredient from a complex emulsion droplet is molecular diffusion across the two stagnant films.

The model was employed using empirical mass transfer coefficients that account for the effect that air moving past the droplet has on the triclopyr ester flux at the air-water interface. These empirical constants were derived from experiments by various investigators and combined into "average" values by Schwarzenbach et al. (1993). The effect of a surface surfactant layer on solute movement across the air-water interface was not considered. The pesticide droplets under consideration here are more complicated in some respects than dilute aqueous systems; however, the STF model will likely suffice for a rough, order-of-magnitude estimate of triclopyr ester evaporative flux.

The rate of movement of molecules out of the droplet is controlled by the chemical's ability to diffuse across the two stagnant boundary layers. From Ficke's first law, the flux F_a, across the stagnant air boundary layer of thickness Z_a, is the diffusivity times the gradient, given by:

$$F_a = -D_a \frac{dC}{dZ} = -D_a \frac{C_a - C_{a/w}}{Z_a} \quad [mols/cm^2 \cdot \text{sec}] \qquad \textbf{(8)}$$

where D_a is the chemical's diffusivity in air in cm^2/sec, C is the concentration in the surrounding air in mol/cm^3 , and $C_{a/w}$ is the concentration at the air/water interface in mol/cm^3. The gradient is the difference in concentration across the layer divided by the layer thickness. The same relationship holds for the flux F_w across the stagnant boundary layer of water:

$$F_w = -D_w \frac{dC}{dZ} = -D_w \frac{C_w - C_{w/a}}{Z_w} \qquad \textbf{(9)}$$

where D_w is the chemical's molecular diffusion coefficient in water, C_w is the concentration in the droplet, and $C_{w/a}$ is the concentration at the water/air interface. At steady state, the number of molecules passing from one boundary layer to its adjacent boundary layer must be the same; therefore $F_a = F_w = F$, and:

$$F = -D_a \frac{C_a - C_{a/w}}{Z_a} = -D_w \frac{C_{w/a} - C_w}{Z_w}. \qquad \textbf{(10)}$$

Assuming the layer of air molecules immediately above the interface is always equilibrated with the layer of water molecules immediately below, the compound's Henry's Law constant can be used to relate $C_{a/w}$ and $C_{w/a}$:

$$K'_H = \frac{C_{a/w}}{C_{w/a}} \qquad \textbf{(11)}$$

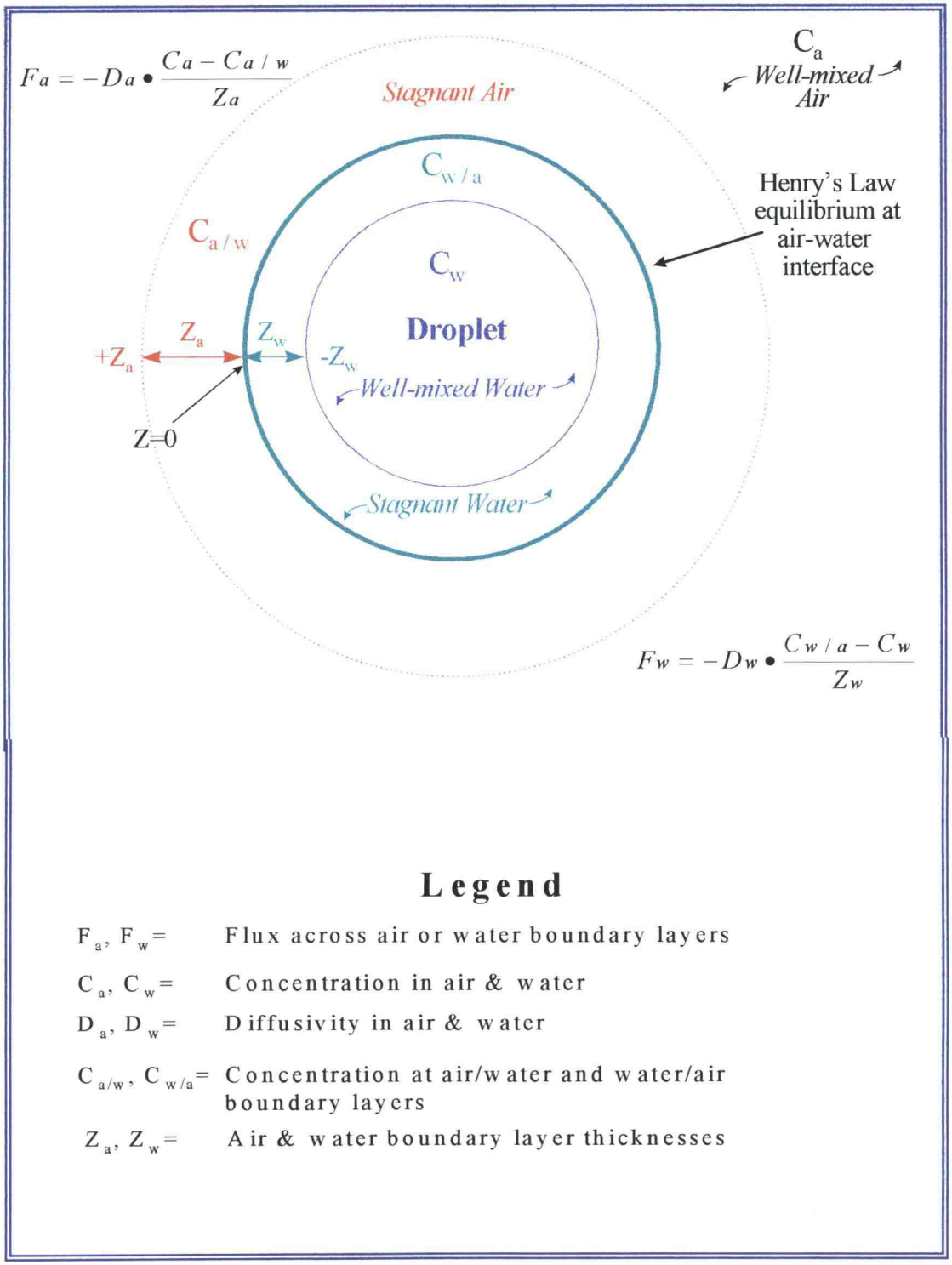

Figure 1.4 Stagnant Two-Film Model Adapted for Droplets

where $C_{a/w}$ is in units of mol/L_a and $C_{w/a}$ is in mol/L_w. Substituting in for Eq. 10 in terms of bulk media concentrations C_a and C_w which can be measured:

$$D_w \frac{C_w - C_{w/a}}{Z_w} = \frac{D_a(K'_H C_{w/a} - C_a)}{Z_a} \tag{12}$$

$$C_{w/a} = \frac{(D_w/Z_w)C_w + (D_a/Z_a)C_a}{(D_w/Z_w) + (D_a K'_H/Z_a)} \tag{13}$$

Substituting this result into Eq. 10 gives a quantitative description of the chemical flux through the transport bottlenecks in series:

$$F = \left(\frac{1}{(Z_w/D_w) + (Z_a/(D_a K'_H))} \right) \left(C_w - \frac{C_a}{K'_H} \right). \tag{14}$$

A positive flux denotes movement from the water to the air when the bulk water concentration C_w is larger than C_a/K'_H, the water concentration in equilibrium with the bulk air concentration C_a. The first term in the expression represents the total mass transfer velocity for the model. Dimensional analysis shows that it gives units in length per unit time, or velocity. Using the units of moles, centimeters, and seconds gives:

$$F = V_{tot} \cdot \left(C_w - \frac{C_a}{K'_H} \right) \quad [mol/cm^2 \cdot \text{sec}]. \tag{15}$$

The mass transfer coefficient V_{tot} can be expressed in terms of the partial transfer velocities for the two stagnant layers:

$$V_w \equiv \frac{D_w}{Z_w},\ V_a \equiv \frac{D_a}{Z_a}. \tag{16}$$

Combining Eq. 16 with Eqs. 14 and 15 yields:

$$\frac{1}{V_{tot}} = \frac{1}{V_w} + \frac{1}{V_a K'_H} \tag{17}$$

where $1/V_{tot}$ is the resistance to diffusion.

Evaporative flux depends on two controlling parameters, the partial mass transfer velocities in water (V_w), and in air (V_a), in the two stagnant boundary layers. The sum of these two parameters, V_{tot} is the total mass transfer velocity for the system. Stagnant air and water boundary layers at the air-water interface act to control the flux because they are unmixed and molecular movement depends on the rate of diffusion, which is slow compared to the movement by eddy mixing that occurs in the bulk fluid or surrounding well-mixed air. The rate of diffusion, or molecular movement from an area of higher to lower concentration, depends on the molecule's diffusion coefficient and the ambient medium. The diffusion coefficients (diffusivities) in air and in water and the Henry's Law constant of a chemical are determined by its structure.

Diffusion coefficients in water and air are not available for many organic compounds. However, they can be estimated based on what is known about the behavior of air in water and water in air. Considerable research on the evaporative flux of pure water and on gases soluble in water has given the following empirical relationships for estimating the diffusivity of other chemicals in water and air:

$$D_a(est) = (0.26\,cm^2/\text{sec}) \cdot \left(\frac{MW(H_2O)}{MW(chemical)} \right)^{0.5} \quad (cm^2/\text{sec}) \tag{18}$$

where D_a(est) is the chemical's estimated diffusivity in air relative to water's, and

$$D_w(est) = (2.1 \times 10^{-5} cm^2/\text{sec}) \cdot \left(\frac{MW(O_2)}{MW(chemical)} \right)^{0.5} \quad (cm^2/\text{sec}) \qquad \textbf{(19)}$$

where $D_w(est)$ is the chemical's estimated diffusivity in water relative to oxygen's.

The mass transfer coefficient of the chemical in air and water v_{tot} is estimated from the experimentally-determined mass transfer velocities of water in air $V_a(H_2O)$, and oxygen in water $V_w(O_2)$, using the following relationships:

$$V_a(compound) = V_a(H_2O) \cdot \left(\frac{D_a(compound)}{D_a(H_2O)} \right)^{\alpha} \qquad \textbf{(20)}$$

and

$$V_w(compound) = V_w(O_2) \cdot \left(\frac{D_w(compound)}{D_w(O_2)} \right)^{\beta} \qquad \textbf{(21)}$$

where D_a is diffusivity in air (cm^2/sec), α is an empirically-derived constant ($0.5 \geq \alpha \leq 1$), D_w is diffusivity in water, and $\beta = 0.5$ for water.

Empirical data suggest that $V_a(H_2O)$ is typically 0.3 to 3.0 cm/s for stagnant air boundary layer thicknesses between 1.0 and 0.1 cm (Schwarzenbach et al., 1993). For this estimate, the value of $V_a(H_2O) = 3.0$ cm/s was used because it corresponds to a stagnant air boundary layer thickness that approximates that of a 1,600 μm diameter droplet (stagnant air boundary layer ≈ droplet diameter)(Ranz and Marshall, 1952a). The STF model assumes that in slowly flowing bodies of water where turbulence is not a factor, the motion of air

across the water surface controls the nature of the air-water interface. Wind transfers energy to the water, thinning the stagnant water boundary layer, and increases the rate of molecular transfer out of aqueous solution. For winds of 2-10 m/sec, laboratory and field studies yield $V_w\ (O_2)$ estimates of 5×10^{-5} to 5×10^{-4} cm/sec (Schwarzenbach et al., 1993). For this estimate, the value of $V_w\ (O_2) = 5 \times 10^{-5}$ cm/sec was selected because it corresponds to a wind speed of 2 m/sec, a value near the fall rate of a 1,600 μm diameter droplet (Table 1.2).

The final term necessary to complete the flux estimate is K'_H. The unitless Henry's Law constant can be calculated from the universal gas law using the following relationship:

$$K'_H = \frac{K_H}{RT} \qquad \textbf{(22)}$$

where K_H (Eq. 1) is the chemical's Henry's Law constant in (atm · L)/mol, R is the gas law constant in L·atm/°K·mol, and T is the temperature in degrees Kelvin (°K).

1.2.5.3 Example Triclopyr Ester Flux Calculation

The following flux estimate is for a falling droplet in the PVC. Column conditions are 25°C, airflow set at 2.4 L/min. Humidity is not considered in the calculation. Note: constants provided are for 25°C.

Droplet diameter (d) = 1,600 μm

Volume (V) = 2.14 μL

Surface area = 0.0804 cm^2 (Table 1.2)

$K_H = 2.28 \times 10^{-7}$ atm-m^3/mol

$D_a\ (H_2O)$ = 0.26 cm^2/sec

$D_w\ (O_2) = 2.1 \times 10^{-5}$ cm^2/sec

$V_a\ (H_2O)$ = 3.0 cm/sec (for ≈ 0.1 cm stagnant air boundary layer)

$V_w\ (O_2) = 5 \times 10^{-5}$ cm/sec (for ≈ 2 m/sec wind speed)

$C_a \approx 0$ (constant flushing of air in column)

C_w = 7.4 mg/L (solubility of triclopyr ester in water).

The average rate of fall for the droplet plus the upward air velocity in the column gives the total air velocity (V_{air}) across the droplet:

$$V_{avg} = \frac{D}{t} \qquad (23)$$

where V_{avg} is the average fall rate, D is the fall distance in meters, and t is time in seconds. For a 1.0 m fall distance:

$$V_{avg} = \frac{(1\,m\ fall\ distance)}{(0.45\,\text{sec}\ fall\ time)} = 2.2\,m/\text{sec} + column\ upward\ air\ velocity = V_{air}.$$

To estimate the upward air velocity in the column (converting L/min to m^3/sec):

$$2.4\,\frac{L}{\text{min}} \times \frac{1\,m^3}{10^3\,L} = 2.4 \times 10^{-3}\,\frac{m^3}{\text{min}} \times \frac{1\,\text{min}}{60\,\text{sec}} = 4 \times 10^{-5}\,\frac{m^3}{\text{sec}}$$

Dividing by the cross-sectional area of the column will give the linear velocity of upward-moving air in the column:

$$4 \times 10^{-5}\,\frac{m^3}{\text{sec}} \cdot \frac{1}{(0.05\,m)^2 \cdot \pi} = 5.1 \times 10^{-3}\,\frac{m}{\text{sec}}.$$

This velocity is very small and adding it to V_{avg} would have a negligible effect on V_{air}, therefore, it will not be considered further.

Using Eq. 15, an estimate of the flux (F) in mol/cm^2 · sec can be calculated:

$$F = v_{tot} \cdot \left(C_w - \frac{C_a}{K'_H} \right).$$

To find V_{tot}, V_a and V_w must first be calculated for triclopyr ester from what is known about the behavior of water in air, and of oxygen in water. First, the diffusivity in air of triclopyr ester relative to water's is calculated using Eq. 18:

$$D_a(triclopyr\ ester) = (0.26\ cm^2/\text{sec}) \cdot \left(\frac{18\ g/mol}{356.62\ g/mol} \right)^{0.5} = 0.0584\ cm^2/\text{sec}.$$

And using Eq. 19 to estimate triclopyr ester's diffusivity in water relative to that of oxygen's:

$$D_w(triclopyr\ ester) = (2.1\times10^{-5} cm^2/\text{sec}) \cdot \left(\frac{32\ g/mol}{356.62\ g/mol} \right)^{0.5} = 6.29\times10^{-6} cm^2/\text{sec}.$$

Substituting $D_a(triclopyr\ ester)$ and $D_w(triclopyr\ ester)$ into Eqs. 20 and 21:

$$V_a(triclopyr\ ester) = (3.0\ cm/\text{sec}) \cdot \left(\frac{0.0584\ cm^2/\text{sec}}{0.26\ cm^2/\text{sec}} \right)^{0.67} = 1.103\ cm/sec$$

$$V_w(triclopyr\ ester) = (5\times10^{-5} cm/\text{sec}) \cdot \left(\frac{6.29\times10^{-6} cm^2/\text{sec}}{2.1\times10^{-5} cm^2/\text{sec}} \right)^{0.5} = 2.73\times10^{-5} cm/\text{sec}.$$

Now using Eq. 22 to convert the Henry's Law constant to unitless form:

$$K'_H = \frac{2.28\times10^{-7}\ \frac{atm\cdot m^3}{mol}}{8.21\times10^{-5}\frac{atm\cdot m^3}{mol^\circ K}\cdot 298^\circ K} = 9.32\times10^{-6}\ (unitless).$$

Then determining the resistance to mass transfer, $1/V_{tot}$ using Eq. 17:

$$\frac{1}{V_{tot}} = \frac{1}{2.73\times10^{-5} cm/\text{sec}} + \frac{1}{1.103\ cm/\text{sec}\cdot 9.32\times10^{-6}} = 1.33\times10^5\ \text{sec}/cm.$$

Then taking the inverse:

$$V_{tot} = 7.47\times10^{-6} cm/\text{sec}.$$

Now an estimate of the evaporative flux *(F)* can be calculated by substituting the above numbers into Eq. 15:

$$F = 7.47 \times 10^{-6}\ cm/\text{sec} \cdot [2.075 \times 10^{-8}\ mol/cm^3 - 0] = 1.55 \times 10^{-13}\ \frac{mol}{cm^2 \cdot \text{sec}}.$$

Note: $C_a \simeq 0$ because the air in the column is constantly being replaced (Section 2.2.1) and thus $C_a/K'_H = 0$. For a falling droplet, it is useful to have F in units of mass/unit area · unit time. Thus,

$$1.55 \times 10^{-13}\ mol/cm^2 \cdot \text{sec} \times 356.62\ g/mol = 5.53 \times 10^{-11}\ g/cm^2 \cdot \text{sec} = 55.3\ pg/cm^2 \cdot \text{sec}.$$

1.3 Experimental Objectives

The objectives of this experiment were the following:

1. Develop a protocol for measurement of herbicide volatilization rates from aqueous Garlon® 4 emulsion droplets in airstreams of different temperatures and humidities.
2. Quantify the loss by evaporation of triclopyr ester from falling droplets of Garlon® 4 aqueous emulsions.
3. Determine the effects of varying temperature and humidity on the volatilization rate of triclopyr ester from the falling droplets.
4. Evaluate the relationship between triclopyr ester volatilization and droplet time-of-flight.
5. Determine the effect of varying droplet size on the volatilization rate of triclopyr ester.
6. Develop a predictive model of triclopyr ester loss from droplets under different environmental conditions based on experimental data.

These objectives lead to the following hypotheses:

1. Sufficient amounts of triclopyr ester volatilizes from falling droplets during aerial applications of Garlon® 4 to be of environmental consequence.

2. The volatilization rate of triclopyr ester from droplets is a function of air temperature during aerial spray applications.
3. The volatilization rate of triclopyr ester is a function of droplet diameter.

2. EXPERIMENTAL DESIGN

2.1 General Description

The equipment utilized in this experiment will be referred to as the Pesticide Volatilization Column (PVC) (Figures 2.1 and 2.2). The experimental protocol consisted of releasing a series of herbicide drops from a needle and allowing them to free fall through a water-jacketed glass column of temperature and humidity-controlled air. Droplet size was controlled by:

- Using needles of differing outside diameter (OD)
- Adjusting the concentration of formulated product in the emulsion
- Adjusting the fluid flow rate from the pumps.

Air in the column flowed in a countercurrent against the falling droplets, entering at the bottom of the column and exiting through a polyurethane foam (PUF) cartridge attached to the top of the column. The system was designed so that volatilized triclopyr ester would adsorb to the inside walls of the glass column or be scavenged by the PUF. Unvolatilized triclopyr ester remained in the drops as they exited the column where they were instantaneously frozen in a freezer vessel kept in a thermos filled with liquid nitrogen. Liquid nitrogen has a boiling point of -195.8°C at one atmosphere ambient pressure; thus when a droplet entered the freezer vessel, its vapor pressure was immediately reduced to zero and no further volatilization occurred. The volatilized triclopyr ester was quantified by collecting two acetone rinses of the column walls and extracting the PUF with 1:1 acetone/hexane, then analyzing the samples with a gas chromatograph (GC) equipped with an nitrogen/phosphorus detector (NPD).

2.2 Experimental Apparatus

The experimental apparatus used to evaluate the volatilization rate of triclopyr ester from Garlon® 4 spray droplets and its setup and calibration procedures are described in this section.

2.2.1 PESTICIDE VOLATILIZATION COLUMN

The equipment consisted of the following (Figures 2.1 and 2.2):

1. Two pumps:
   a. An XL-3000 syringe pump (Cavro Scientific Instruments, Inc., Sunnyvale, California). This pump was powered by a 24-volt regulated power supply and supplied with pesticide from a reservoir with a magnetic plate and stir bar, polyetheretherketone (PEEK) plastic tubing (Upchurch Scientific, Oak Harbor, Washington), and connectors. This pump was used alone in the majority of the experimental runs to pump Garlon® 4 (DowElanco, Midland, Michigan) solution to the needle and for system purging and cleaning. In later experiments it was used only to purge the system with cleaning solution or water.
   b. A pressure pump (Figure 2.3), magnetic plate and stir bar, and valves. This pump was developed to allow constant flow of pesticide to the needle and minimize droplet "shake" on the end of the needle which occurred when the Cavro pump cycled. Droplet "shake" increased the frequency that droplets impacted the column walls (Section 3.1). The Cavro pump was used in conjunction with the pressure pump for line purging and cleaning.
2. A 0.2032 mm diameter stainless steel needle (Hamilton Company, Reno, Nevada).
3. An IBM compatible 486 DX4-100 personal computer (PC) running Windows 3.1™ (Microsoft Corporation, Redmond, Washington). Windows™ Terminal was used to send serial commands to the Cavro pump. Pump control commands were specified in the Pumper program software supplied by Cavro. Labtech® NotebookPro (Laboratory Technologies Corp., Wilmington, Massachusetts) for Windows™ was used for monitoring and recording column temperature and humidity.
4. A model HX-11 temperature/humidity probe and PSU-24B unregulated 24-volt power supply (Omega Instruments, Stamford, Connecticut) connected via a DT-707 screw terminal panel to a model DT-2801 analog-to-digital (A/D) converter

card (Data Translation, Marlborough, Massachusetts). The DT-2801 was installed in an ISA slot on the PC's motherboard.

5. A 1 meter tall, 50 mm diameter jacketed glass column and 500 cm long, 50 mm diameter jacketed glass air inlet column (Ace Glass, Inc., Vineland, New Jersey) (Figure 2.2). Connected to the bottom of the column was a 400 mL freezer vessel that was kept in a thermos filled with liquid nitrogen.
6. A glass column top with a top port for the needle and three side ports: one for the PUF cartridge, and two at 90 degrees to one another with glass rods for needle alignment (Figure 2.4).
7. A PUF cartridge (Supelco, Inc., Bellefonte, Pennsylvania) attached to the column top's side port.
8. 50 mm diameter Teflon® (E. I. du Pont de Nemours and Company, Wilmington, Delaware) connectors by Ace Glass, Inc. to join column parts.
9. A model RTE-110 temperature-controlled water bath (Neslab Instruments, Union City, California) connected to the column jacket with Tygon® tubing (Norton Performance Plastics Corporation, Akron, Ohio).
10. Medical grade air supply (Industrial Welding Supply, Corvallis, Oregon) connected with Tygon® tubing to separate molecular sieve and activated carbon cartridges. Tubing on the downstream side of the cartridges was all made of Teflon®. The clean, dehumidified air was split using a glass "y" into two parts:
    a. Air routed to a glass bubbler for humidification and then to a second "y" at the head of the inlet column, and
    b. Air that flowed through a needle valve directly to the remaining fork of the second "y" at the head of the inlet column. Humidity control was achieved by varying the flow of the dehumidified air into the inlet column using the needle valve. When the flow rate of the dehumidified air was reduced, the flow rate through the bubbler increased and the inlet air became more humid. The column inlet air humidity was reduced by increasing flow of dehumidified air through the needle valve.

11. A gas flow control valve (Cole/Parmer Instrument Company, Niles, Illinois) for controlling the airflow rate into the column. Airflow into the column was set at a constant rate of 2.4 L/min. This represents a flushing rate of approximately 1.3 column volumes/minute, fast enough to ensure that triclopyr ester did not build up in the column air and affect the volatilization rate of the compound and slow enough to avoid excessive turbulence.

2.2.2 Probe and A/D Board Calibration Procedure

Temperature and humidity readings were collected using the HX-11 temperature/humidity probe in conjunction with the DT-2801 A/D board in one of the PC's ISA slots. The DT-2801 interfaced with the HX-11 temperature/humidity probe via the DT-707. The HX-11 provided an analog voltage output that could vary between 1 and 5 volts DC, depending on the temperature and humidity measured. Humidity and temperature signals were output on separate leads that were attached to the DT-707 on channels 0 and 1, respectively. The DT-2801 converted the received voltage to a digital signal of 0s and 1s that were in turn interpreted by the Labtech® Notebook software and output on the computer screen.

Prior to data collection, both the probe and the DT-2801 required calibration. The A/D board was calibrated so that readouts on the Labtech® Notebook screen reflected the measured temperature and humidity. The HX-11 was calibrated separately so that its voltage output was correct for a given temperature and humidity. Before beginning the A/D board calibration, a Labtech® Notebook calibration block called "Humidcal" was created. "Humidcal" was a digital readout of the signal received from the HX-11 on Channel 0 of the DT-2801. The software options were set so the hardware selected was a unipolar, 0-10 volt (v) DT-2801 with the DT-707. The DT-2801 was calibrated using a precision voltage source consisting of a 1.5 v and a 9 v battery connected in series to a variable-resistance potentiometer. Outputs between 0.1 millivolts (mv) and 10.5 v could be selected using this device. To minimize drift and signal interference, all of the channels

except Channel 0 on the DT-707 were returned to analog ground prior to calibration. Calibration was performed on Channel 0. First, the zero, or bottom of the signal was calibrated by applying a 2.4 mv current to Channel 0. The Labtech® Notebook readout designated "Humidcal" was adjusted to 0.00244 v using the trimpot R3 on the DT-2801. Next, the span or maximum signal was calibrated by applying a 9.95 v signal to Channel 0 and adjusting the trimpot R4 on the DT-2801 until Humidcal gave a readout of 9.95 v. The A/D board was now ready to convert analog voltage signals from the HX-11 to a digital data stream interpretable by the computer software.

The HX-11 was calibrated for both humidity and temperature. Humidity calibration was a two-point calibration using low (33 percent relative humidity) and high (75 percent relative humidity) calibration standards (Panametrics, Inc., Waltham, Maryland). The HX-11 probe was first inserted into the low humidity standard and allowed to equilibrate a minimum of 6 hours. The humidity output lead and the common lead were connected to a digital multimeter at the DT-707 interface. The "zero" trimpot inside the probe was adjusted until a reading of 2.32 v was maintained on the multimeter readout. This corresponds to a relative humidity of 33 percent using the manufacturer-provided equation $\%RH = \frac{(v-1)}{0.04}$. The probe was then placed in the high humidity standard and the "span" trimpot inside the probe was adjusted until a reading of 4.0 v, corresponding to 75 percent relative humidity, was maintained on the multimeter. A single point calibration procedure was used for the temperature output of the probe by comparison to a digital thermometer at room temperature and adjusting the "offset" trimpot using the manufacturer-provided equation $T°C = \frac{(v-1)}{0.04}$.

2.3 Garlon® 4 Solution Preparation

An emulsion of Garlon® 4 was prepared as necessary, on a weekly basis at a minimum, using the procedures outlined below. The Garlon® 4 emulsion used in this experiment was approximately a 3 percent by volume solution of Garlon® 4 herbicide and water. In the early stages of the experiment, a 50 mL solution was prepared and used for several runs. Left over solution was stored in the refrigerator between experiments. When variability in

the data indicated the possibility that triclopyr ester volatility decreased as the solution aged, a fresh emulsion was prepared before each experiment. This is noted in the data tables in Section 3. Two methods (described below) were used for mixing the Garlon® 4 solution, one for the Cavro pump and one for the pressure pump.

2.3.1 CAVRO PUMP SOLUTION PREPARATION

A 3 percent herbicide solution was prepared by pipetting 1.5 mL of Garlon® 4 herbicide into a vial containing 48.5 mL water while stirring. For some runs, 0.5 mL green food coloring was used with 48 mL water and 1.5 mL Garlon® 4. The dye aided in visually determining whether droplets impacted the column walls. Approximately 20 mL of the herbicide mixture was then transferred using a graduated pipette into the pump reservoir. Following each run, the pump reservoir containing the remaining herbicide was placed in the refrigerator for storage.

2.3.2 PRESSURE PUMP SOLUTION PREPARATION

The herbicide mixture was prepared by pipetting 0.5 mL Garlon® 4 into the pump vessel containing 14.5 mL distilled water and 3 parts per million (ppm) Rhodamine-6G fluorescent dye (Fischer Scientific, Pittsburgh, Pennsylvania). The Garlon® 4 was added to the solution of water while stirring the pump with a magnetic stir bar. The pipette was then flushed with the stirred emulsion repeatedly to remove any pesticide that had adhered to the walls of the pipette. The pump was then capped and continuously stirred prior to starting each run.

2.4 EXPERIMENTAL RUN PREPARATION

Prior to beginning each run, the following steps were performed:

1. The column temperature was raised to 65 °C by turning up the bath temperature. It was then rinsed twice with 400 mL acetone while still hot using the column pressure washer (Figure 2.5). Acetone vapors were vented out the top of the column into an aluminum

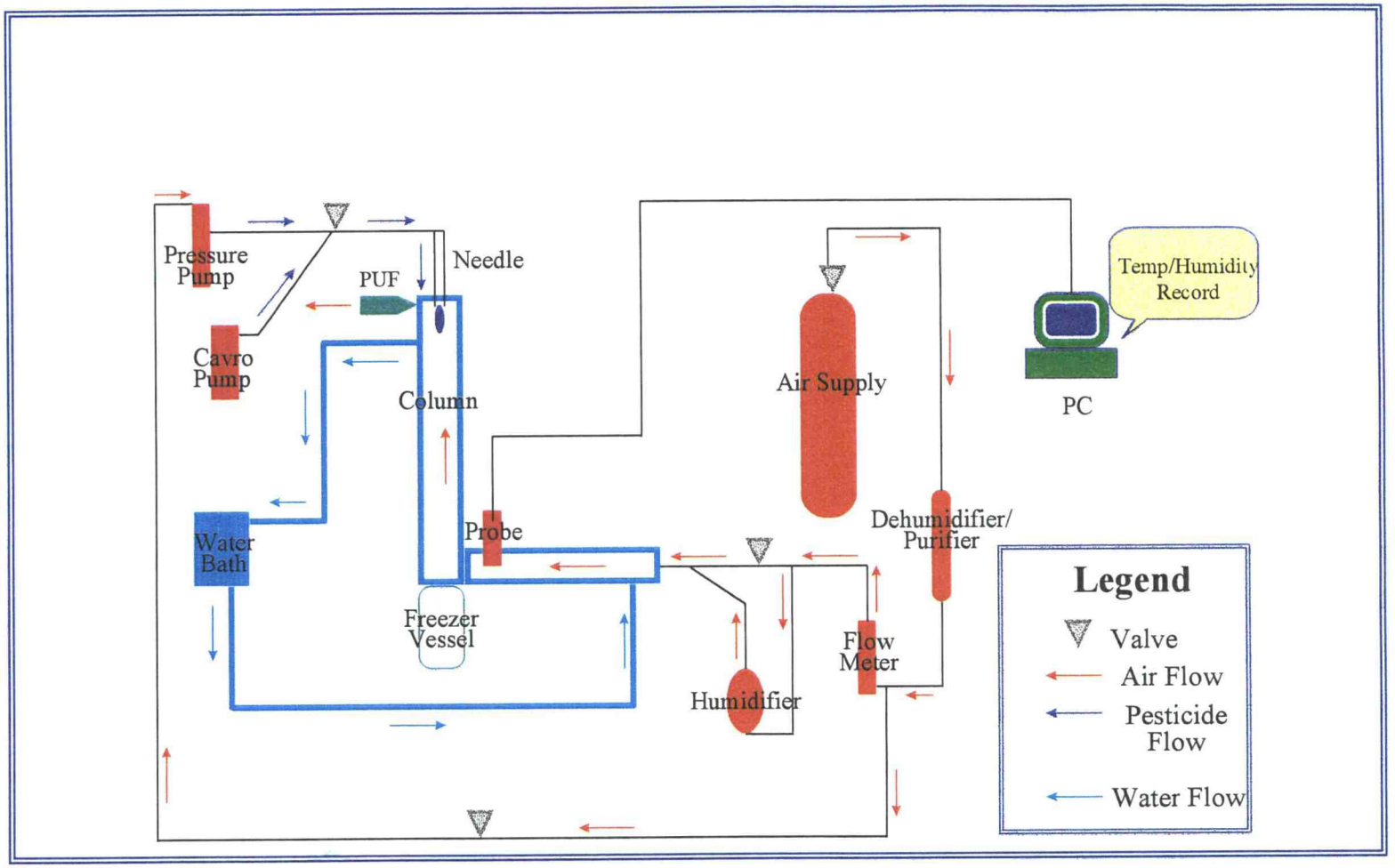

Figure 2.1 PVC Schematic

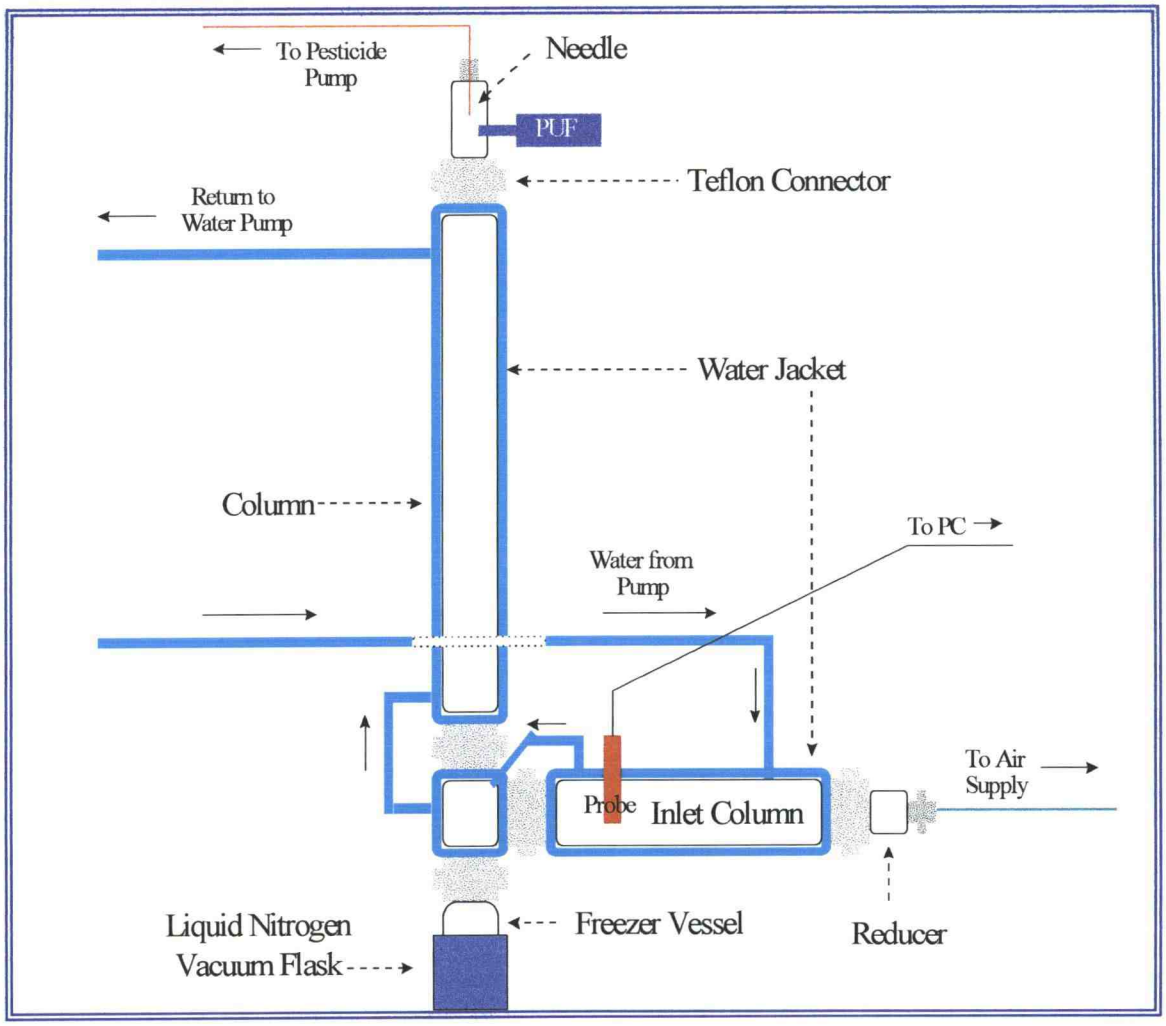

Figure 2.2 Expanded Column View Schematic

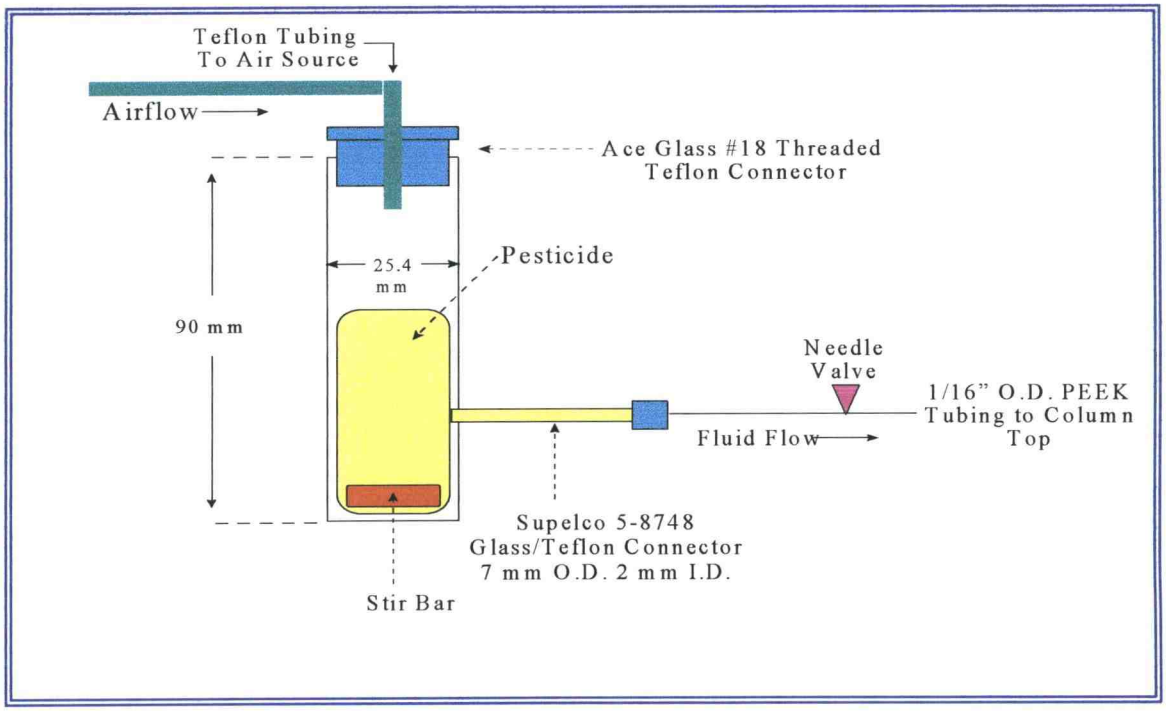

Figure 2.3 Pressure Pump Schematic

pipe attached to the lab fume ventilation system. Acetone rinsate was collected in a freezer vessel and placed in a container for recycling. Freezer vessels used for column cleanup were kept separate from those used for sample collection. After rinsing, the column was allowed to cool to room temperature.

2. The removable column top with the needle and associated plumbing was soaked in hot, soapy water, triple rinsed with distilled water, allowed to air dry, then rinsed with acetone.
3. The column temperature for the run was set on the water bath controls and the temperature was allowed to equilibrate between the bath and the column.
4. The column top and freezer vessel were connected to the column. A thermos was placed around the freezer vessel and filled with liquid nitrogen.
5. If the Cavro pump was used as the pesticide delivery system, previously prepared Garlon® 4 solution was removed from the refrigerator and allowed to equilibrate to room temperature while being stirred. Approximately 10 mL of the pesticide was

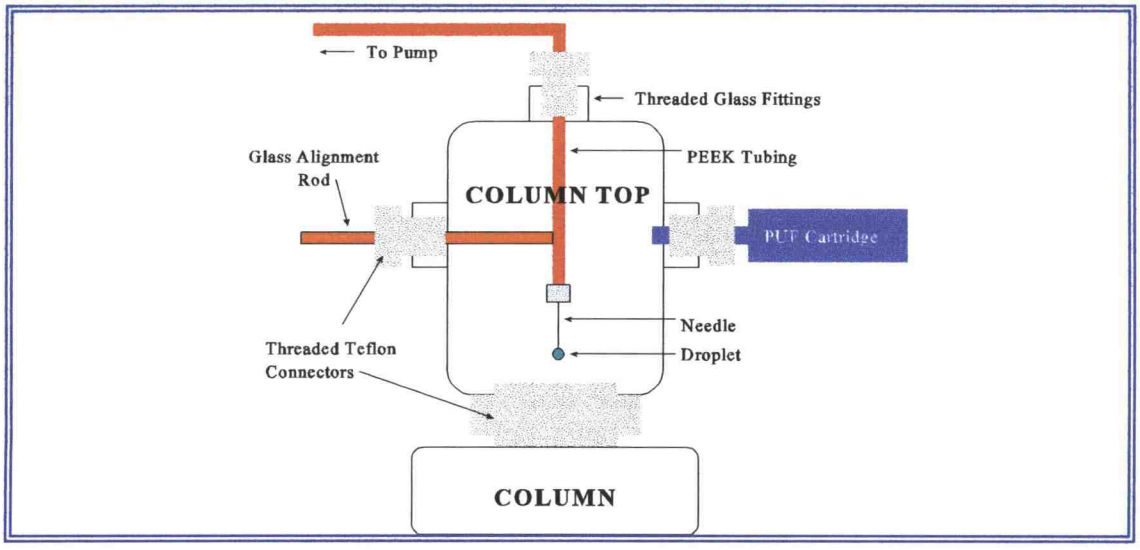

Figure 2.4 Column Top Schematic

pipetted into the pesticide reservoir. If the pressure pump was used, the herbicide solution was prepared in the pump. The pump was then connected to the fluid delivery lines.

6. The column air flow was set to 10 mm on the Cole Parmer flow gauge (≈2.4 L/min flow rate).
7. The temperature and humidity inside the column, monitored by computer, were allowed to equilibrate to the desired levels .
8. When the Cavro pump was employed to deliver the pesticide, the pump was cycled rapidly several times into a sealed waste reservoir. The pump output line was then connected to the column top and the command given via computer to start the pump for the two-hour run. Simultaneously, computer temperature/humidity logging was initiated with Labtech® Notebook. When the pressure pumper was used to deliver pesticide, the air pressure was set so that droplets fell evenly off the end of the needle.

2.5 Data Collection and Temperature/Humidity Control

During each two-hour run, the column was continuously monitored for correct temperature and humidity via the HX-11 probe and LabTech® Notebook. The temperature in the column was controlled using the external water bath. A temperature between 0 and 100°C could be selected on the bath using its digital rheostat. Before entering the main, vertical section of the column, humidity-controlled air was conditioned to the correct temperature inside the horizontal inlet column. Minor adjustments were occasionally made with the humidity control valve to keep the relative humidity close to the planned experimental conditions.

Droplet trajectory and size were also monitored at the beginning of the experiment and periodically thereafter. The column and/or needle were adjusted as required to minimize the likelihood of droplet impact to the sidewalls of the column. (This was frequently not possible, as the data indicate.) The number of droplets produced by a 20 μL syringe stroke were counted for ten consecutive strokes and recorded in the project notebook. The mean number of droplets per stroke was used to compute an average droplet size for each run as discussed in Section 2.10. The droplet sizes produced are shown in Tables 3.2 and 3.3.

2.6 Sample Collection

Triclopyr ester in the simulated spray droplets was predicted to distribute to one of three places in the system:

- Remaining as solute in frozen droplets in the freezer vessel
- As volatilized compound in the PUF cartridge
- As volatilized compound adsorbed to the column walls.

The experiment was designed to segregate and determine the mass of triclopyr ester in each of these three locations. Samples were collected and analyzed in a manner to avoid cross-contamination between the media. The total amount of triclopyr ester delivered to the system could then be determined using a mass balance approach (Section 3).

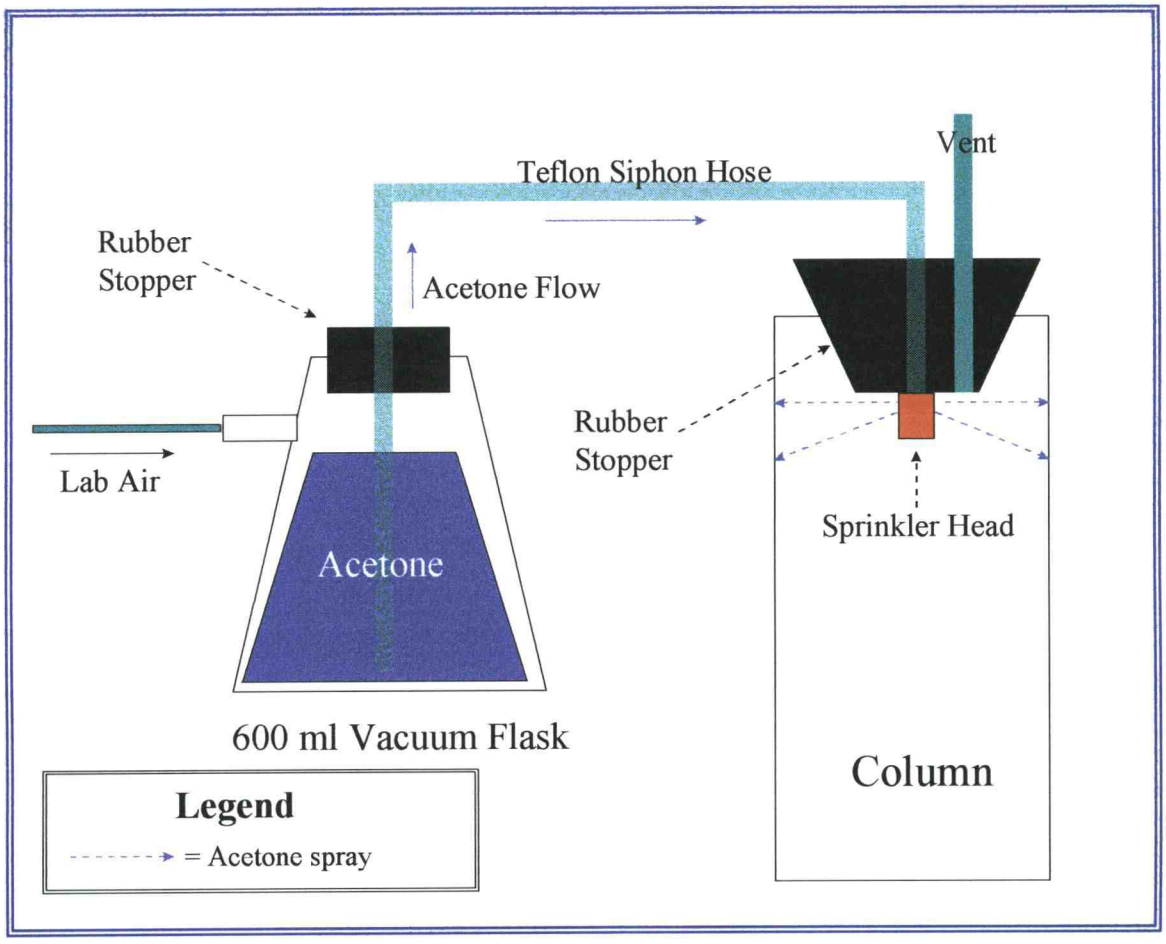

Figure 2.5 Column Pressure Washer

2.6.1 PUF CARTRIDGES AND COLUMN TOP

Following each run, the PUF cartridge was removed from the head of the column, labeled, and both ends of the cartridge were capped. It was then either stored in the refrigerator or set aside for extraction. The column top was removed from the column and carefully rinsed five times with 10 mL of Omnisolve® GC grade acetone (EM Science, Gibbstown, New Jersey) into a labeled Turbovap® tube (Zymark Corporation, Hopkinton, Maryland). The Turbovap® tube was placed in a Turbovap II® concentration work station for volume reduction. In early experiments, the column top rinse was combined with the

first column rinse (Section 2.6.2). In later experiments, it was analyzed separately to help determine the source of experimental variability.

2.6.2 Freezer Vessel and Column Rinses

The freezer vessel was removed from the bottom of the column and stored in the fume hood to allow evaporation of liquefied air that collected in the bottom of the vessel. A clean freezer vessel, labeled "CR-*i*A" (where "*i*" was an integer corresponding to the run number), was then placed on the bottom of the column. The column walls were rinsed into the freezer vessel with 400 mL of acetone using the column pressure washer (Figure 2.5). The freezer vessel containing the first, or "A" rinsate, was then removed and a second, clean freezer vessel (labeled "CR-*i*B") was put in its place and the procedure repeated. The freezer vessels containing the column rinsate were covered with aluminum foil and stored in the fume hood pending sample preparation.

2.7 Sample Extraction and Preparation

Triclopyr ester is slightly polar and quite soluble in acetone. However, acetone has a very high coefficient of expansion and thus is not suitable for injection into the GC, where it tends to expand resulting in sample loss from the injection port. Thus for GC analysis, it was necessary to exchange acetone for hexane (which has a lower coefficient of expansion than acetone) in the sample preparation process.

2.7.1 PUF Cartridges

PUF cartridges were extracted in large test tubes using 40 mL of 1:1 acetone/hexane. The test tubes were shaken for 15 minutes on a wrist-action shaker and the extract decanted into a labeled Turbovap® tube. The extraction procedure was repeated 3 times. The extract was then evaporated to 1 mL in the Turbovap®. Two mL Omnisolve® hexane (EM Science, Gibbstown, New Jersey) was then added to the tube and the mixture again evaporated to 1 ml. This was repeated with an additional 2 mL hexane. The remaining 1 mL concentrate was quantitatively transferred to a volumetric concentration tube and

brought to a final volume of 4 mL using hexane. A 1 mL aliquot of the sample was transferred to a GC sample vial for analysis on the HP-5880 gas chromatograph.

Initially, the PUF was extracted after each run and the extract analyzed. After it became apparent that the quantity of triclopyr ester adsorbed onto the PUF was very small in relation to that absorbed on the column and the analytical results for the PUF were very consistent between runs (Fig. 3.1), the PUF was used for several runs before analysis. If the PUF was used for more than one run, it was stored in the refrigerator between runs. The PUF was used for all replicates of the same temperature /humidity regime and the results were averaged for the replicates.

2.7.2 FREEZER VESSEL

The freezer vessel sample for the vessel containing the frozen pesticide droplets was prepared using the following procedure:

1. After allowing the liquefied air to evaporate, the frozen pesticide droplets were quantitatively transferred to a 100 mL volumetric flask (labeled FV-*i*A) using repeated rinses of 10-15 mL acetone. The flask was then allowed to equilibrate to room temperature and brought to volume using acetone. The flask was inverted at least 15 times until the sample was well mixed.
2. A 1 mL aliquot of FV-*i*A was placed in a second 100 mL volumetric flask (labeled FV-*i*B) using a 1 mL volumetric pipette. The flask was brought to volume using hexane. The flask was inverted at least 15 times until the sample was well mixed.
3. A 100 μL aliquot of FV-*i*B was transferred to a GC sample vial containing 900 μL of hexane (total dilution = $1{:}10^5$) for analysis on the HP-5880 GC. The serial dilution served two purposes:

- To dilute the sample to within the concentration of the calibration curve, and
- To dilute the acetone and water present in the sample to insignificant quantities.

2.7.3 COLUMN RINSE

The column rinse samples were prepared using the following procedure:

1. About half the 400 mL rinsate in the freezer vessel was decanted into a Turbovap® tube labeled CR-*i*A or CR-*i*B. The rinsate in the Turbovap® tube was evaporated to 1 ml. The rinsate remaining in the freezer vessel was then quantitatively transferred using acetone into the Turbovap® tube. The sample was then evaporated to 1 mL in the Turbovap®, solvent exchanged twice with 2 mL hexane, and quantitatively transferred using hexane to a 10 mL volumetric concentration tube.
2. The sample volume in the concentration tube was adjusted to 4 mL using hexane.
3. A 1 mL aliquot of the sample was transferred to a GC vial for analysis on the HP-5880 GC.

   Note: After run 23, about 0.5 g of Na_2 SO_4 was added to the bottom of the concentration tube to absorb water in the samples. Water in the sample was produced from condensate due to cooling of the column walls during the acetone rinse. Method validation experiments showed that adding 5 mL H_2O and 0.5 g Na_2 SO_4 had no effect on the recovery of spike samples (Table 3.9).

2.8 INSTRUMENTAL ANALYSIS

The instrumentation and equipment utilized to analyze the samples collected using the PVC are described in this section.

2.8.1 GAS CHROMATOGRAPH

Analysis of triclopyr ester residues was performed using a model 5880A GC (Hewlett-Packard, Palo Alto, California) equipped with a nitrogen phosphorus detector (NPD), an autosampler, and a 30 m DB-5 column with a 0.25 μ film thickness (J&W Scientific, Folsom, California). GC data collection and analysis was by Chemstation® software by Hewlett-Packard run on a remote PC. Samples were analyzed against a standard curve generated for each run. The standard curve included at least five points, ranging in

concentration from 0.1 μg/ml to 6.6 μg/ml. A complete description of equipment used and column conditions is provided below.

2.8.2 COLUMN CONDITIONS

The injector port was a split/splitless port with an HP 900μL inlet liner using a 0.6 min purge time. Injector port temperature was 240°C. The NPD was maintained at 300°C. The carrier gas was helium with a 1 ml/min flow rate. Initial oven temperature was 90°C, ramped to a final temperature of 250°C at 20 degrees per minute. Sample injection volume was 1.0 μL.

2.9 METHOD VALIDATION

A rigorous set of experiments were conducted during various stages of the experimental design and data collection phases to verify internal column conditions and identify possible sources of experimental error. These experiments are described in the following sections.

2.9.1 FORMULATED PRODUCT TRICLOPYR CONCENTRATION

The listed concentration of triclopyr ester in Garlon® 4 is 61.6 percent. Prior to beginning the experiment, it was necessary to verify the actual concentration of triclopyr ester in the formulated product. A serial dilution of the formulated product was prepared by weighing approximately 0.16 g of the formulated product in a weighing boat on a model R-2000RS analytical balance (Sartorius Corporation, Edgewood, New York). The weighing boat was rinsed with hexane into a 100 mL volumetric flask and the flask brought to volume with hexane. This procedure was repeated for six separate primary standards. Each primary standard was further diluted to a predicted concentration of approximately 1.0 mg/L in 100 mL volumetric flasks and each flask was labeled A1-A through F1-A (Table 3.6). One mL of each diluted sample was placed in a sample bottle and the samples were analyzed against a concentration curve of triclopyr ester standards. Analytical results are presented in Table 3.6.

2.9.2 PUF Collection Efficiency

The collection efficiency of the PUF cartridges was tested using a simple U-tube experiment. A known mass (6.6 μg) of triclopyr ester in 1 mL hexane was placed in a glass U-tube (Ace Glass, Inc., Vineland, New Jersey) (Figure 2.6). Medical-grade air was passed through the U-tube. The air flow rate was set to 2.5 L/min and the U-tube was heated in a water bath to 50°C to enhance triclopyr ester volatilization. Air was run through the U-tube until the solution evaporated to dryness. The PUF was removed from the apparatus and extracted as previously described. The extract was analyzed by GC. To recover triclopyr ester remaining in the U-tube, it was rinsed several times with 5 mL 1:1 acetone/hexane into a Turbovap® tube. The extract was evaporated to 1 mL in the Turbovap II® concentration station. The concentrate was quantitatively transferred to a 10 mL concentration tube and the volume brought to 4 mL using hexane. One mL of the sample was placed in a sample vial and analyzed by GC. Results are presented in Section 3.2.2.

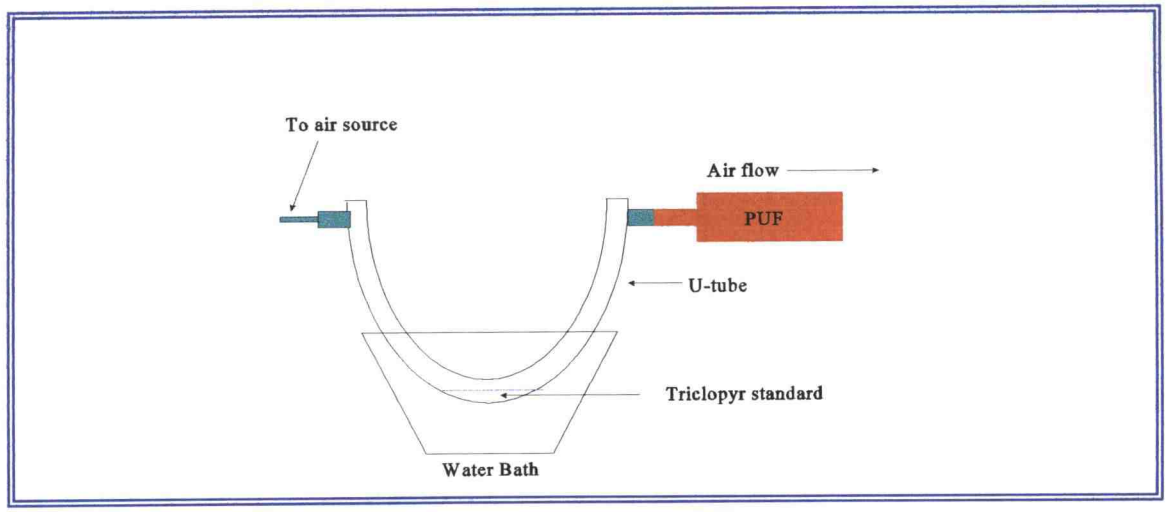

Figure 2.6 U-tube Schematic

2.9.3 Column Internal Temperature Gradient

The temperature inside the column was measured to determine whether it was consistent throughout its length. This was done by heating the external water bath to 25°C and lowering the HX-11 temperature/humidity probe from the top of the column to various distances down the column. The experiment was conducted while the freezer vessel was immersed in liquid nitrogen. Airflow was set to 2.4 L/min. Results are presented in Section 3.2.3.

2.9.4 Cavro Pump Precision and Accuracy

A high degree of variability was present in the freezer vessel analyses (Tables 3.2 and 3.3, column labeled "Total Mass Delivered"). One possible explanation for the variability was inaccuracy or imprecision in the amount of herbicide delivered to the system by the Cavro pump. Therefore, it was necessary to determine the precision and accuracy of the Cavro pump as it was being used in this experiment. The pump's manual listed its imprecision as 0.05 percent and its inaccuracy as <1 percent per stroke. According to a company representative, the listed specifications were for full length (100 μL) strokes of the pump. To keep the fluid moving as constantly as possible in the pump and lines, much shorter (20 μL) strokes were used for this experiment. Using many repetitions of short strokes greatly increased the error in the total amount of fluid pumped in an experiment. Therefore, to examine the accuracy and precision of the pump, the following experiment was performed:

1. A small plastic vessel with a sealable top was placed on the Sartorius analytical balance and the weight was tared to zero. The vessel was removed from the scale. The pump output line was connected to the vessel through a small hole in the lid.
2. The pump inlet line was connected to a separate vessel containing distilled water.
3. A command was issued to the pump to dispense 270 × 20 μL strokes = 5.4 ml.
4. Following the pump run, the plastic vessel was weighed on the balance. The results of five test replications are presented in Table 3.6.

2.9.5 Investigation of Active Ingredient Loss By Hydrolysis

Due to its polarity and charge, triclopyr acid tends to be trapped in the GC column and not "seen" by the detector. Thus, any triclopyr ester converted to its acid form would be lost and thereby reduce the recovery of the chemical in a given experiment. Therefore, some variability in the data might have been explained by:

- Hydrolysis of the ester to the acid on the column walls during the run, and
- Differing rates of hydrolysis between runs.

Following the completion of run 15X, an experiment was conducted to determine whether hydrolysis of triclopyr ester to the acid might be occurring and thereby contribute to the high degree of variability seen in the data. The experiment was performed using the following procedure:

1. The column walls were spiked with 550 μg of triclopyr ester in 4 mL hexane using a Pasteur pipette.
2. The pipette and concentration tube containing the standard were rinsed with an additional 5 mL hexane onto the column walls to complete a quantitative transfer and help distribute the triclopyr ester along the length of the column.
3. The column was run with normal air flow for 1 hour at 35°C and 15 percent relative humidity.
4. The column top and walls were rinsed with acetone as described in Section 2.7.3 and the fractions were combined into one sample for analysis by GC. Results are presented in Section 3.2.5.

2.9.6 Investigation of Freezer Vessel Analysis Methodology

The data showed a great degree of variability in the amount of active ingredient found in the freezer vessel fraction. Therefore, it was of interest to determine whether the freezer vessel sample collection, preparation, and dilution methodology might be the cause of the variability. The following procedure was followed to investigate the freezer vessel methodology for analytical error:

1. Three fresh 3 percent emulsions of Garlon® 4 were prepared in 50 mL sample containers, labeled Gar-1, Gar-2, and Gar-3.
2. Five mL of the pesticide emulsion was pipetted from each container using a volumetric pipette into 100 mL volumetric flasks containing acetone. Five replicate dilutions of each of the three emulsions were prepared. The flasks were labeled Gar-1A through F, Gar-2A through F, and Gar-3A through F. The flasks was brought to volume with acetone and inverted 15 times to mix.
3. One mL from each of the diluted samples was transferred into 100 mL volumetric flasks containing hexane using a 1 mL volumetric pipette. The flasks were brought to volume with hexane and mixed.
4. 100 μL of each of the diluted samples was transferred to sample vials containing 900 μL of hexane using a micropipetter, giving a total dilution for each sample of $1{:}10^5$.
5. The samples were analyzed by GC. Results are presented in Table 3.8.

2.9.7 Investigation of Column Rinse Recovery

To determine whether column rinse sample handling and preparation methodology was affecting analytical results, the following experiment was performed:

1. Four clean freezer vessels were spiked with 2 mL of 110 μg/ml triclopyr ester in hexane standard.
2. The freezer vessels were filled with 400 mL acetone.
3. Two of the freezer vessels were spiked with an additional 2 mL distilled H_2O to simulate water condensation during acetone rinsing of the column.
4. The normal concentration and solvent exchange procedures described previously were performed on all four samples.
5. Following the final solvent exchange, 0.5 g Na_2SO_4 was added to the bottom of the Turbovap® tubes containing the samples with added water.
6. The samples were transferred to concentration tubes and GC sample vials as described previously.
7. The samples were analyzed by GC. Analytical results are presented in Table 3.9.

2.9.8 Analytical Blanks

For quality control, the following analytical blanks were collected prior to each run:

1. A PUF blank. Because PUF cartridges were reused for subsequent experiments, it was necessary to determine whether the extraction procedure was consistently removing the triclopyr ester to below detectable limits. Therefore, a PUF blank (labeled "PB-*i*") was selected at random from the available PUF cartridges for analysis. The blank was extracted and the sample prepared using the methods described in Section 2.7.1. This procedure was performed for several experiments until it became apparent that the PUF cartridge extraction procedure was sufficient to reduce triclopyr ester concentrations in the foam to below detectable limits. Results are presented in Table 3.10.
2. A rinse blank of the column walls. The rinse blank was collected in the freezer vessel by rinsing the column walls with 400 mL acetone using the column pressure washer. The rinse blank was quantitatively transferred from the freezer vessel into a Turbovap® tube, labeled as "CRB-*i*" and evaporated to 1 ml. This concentrated solvent was exchanged with hexane and quantitatively transferred to a volumetric concentration tube and brought to a final volume of 4 mL using hexane. A 1 mL aliquot of the concentrate was transferred to a GC vial for analysis on the HP-5880 GC. Analytical results of column rinse blanks are reported in Table 3.10.

2.10 Droplet Size

Methods used for controlling and determining droplet size are discussed in this section.

2.10.1 Control of Droplet Size

This study planned to examine the rate of triclopyr ester volatilization from droplets of two sizes:

- 2.8 μL (1.75 mm diameter)
- 2.0 μL (1.56 mm diameter).

However, due to technical difficulties and the lack of sufficient time and resources to correct them, only one droplet size was tested. The following discussion is included to demonstrate

the feasibility of examining different droplet sizes and the potential impact of droplet size on evaporative flux.

The above-listed droplet sizes are averages that were determined by pumping 20 μL of well-mixed 3 percent Garlon® 4 aqueous emulsion through the Cavro syringe pump and lines. The number of droplets that fell from the end of the needle from one pump stroke were counted. The experiment was repeated 10 times for each of two needle ODs:

- 0.254 mm (31 gauge) steel
- 0.2032 mm (33 gauge) steel.

The droplet volume was calculated by dividing the volume delivered (20 μL) by the number of droplets produced by each of the 10 replicates and taking the mean. This gave the mean droplet volume (V_μ):

$$V_\mu = \frac{Volume\ dispensed\ (\mu L)}{Mean\ number\ droplets\ produced}. \tag{25}$$

The mean droplet diameter was calculated by using the following formula for the volume of a sphere:

$$V_d = \frac{4}{3}\pi r^3 \tag{26}$$

where V_d is the droplet volume and r is its radius. The mean droplet diameter was calculated by rearranging Eq. 26 and substituting V_μ for V_d:

$$r = \sqrt[3]{\frac{3V_\mu}{4\pi}} \tag{27}$$

and using the relationship:

$$d_{\mu} = 2r \qquad \textbf{(28)}$$

where the mean droplet diameter is (d_{μ}).

2.10.2 EXAMPLE DROPLET DIAMETER CALCULATION

Needle: 0.2032 mm (33 gauge) steel Volume delivered: 20 μL × 10 strokes

Mean number drops formed/stroke: 10.0 $\sigma = 0.316$

First, the mean droplet volume (V_{μ}) was calculated using Eq 25:

$$V_{\mu} = \frac{20\,\mu L}{10.0} = 2.0\,\mu L.$$

Then using Eqs. 27 and 28 the droplet's radius and diameter were calculated:

$$r = \sqrt[3]{\frac{(3\times 2.0\,\mu L)}{4\pi}} = 0.78\ mm$$

$$d_{\mu} = 2\times 0.781\,mm = 1.56\ mm.$$

Thus, for a 0.2032 mm diameter needle, the mean droplet volume $V_{\mu} = 2.0\ \mu$L and the corresponding mean droplet diameter (d_{μ}) is 1.56 mm. The number of droplets produced per stroke (and thus the droplet diameter) varied between experimental runs. Therefore, the number of droplets produced during 10 successive strokes was recorded and an approximate average droplet diameter for each run was determined (Tables 3.2 and 3.3).

3. RESULTS

In this experiment, triclopyr ester in the simulated spray droplet could either remain in the droplet, volatilize and adsorb to the glass sides of the column, or volatilize and be scavenged by the PUF. A mass balance was utilized to determine the distribution of triclopyr ester in the system. The total amount of pesticide put into the system was the mass volatilized plus the mass found in the freezer vessel fraction. The amount volatilized theoretically consisted of the mass of triclopyr ester found on the PUF plus that found in the column rinse samples.

A total of 47 experimental runs for one droplet size and two temperature/humidity regimes were conducted using the PVC. The methodology for sample preparation was slightly different for experiments 4 through 28 than for experiments 2X through 25X; however, it is believed that these changes had little effect on the data. The analytical results of the experimental runs are presented in Section 3.1. The results of the method validation experiments are presented in Section 3.2. The method used for calculating droplet exposure time is discussed in Section 3.3.

3.1 Experimental Runs

The data are presented in three tables. Table 3.1 and Figure 3.1 show the distribution of triclopyr ester in the system for runs representative of the data as a whole. Tables 3.2 and 3.3 give the percent of triclopyr ester in the volatilized fraction as a function of the total mass of active ingredient delivered for each of the temperature/humidity regimes. The data presented are representative of the findings in the body of data.

As can be seen from the data presented below, there was a great deal of variability in the amount of triclopyr ester found on the column walls. The majority of volatilized pesticide

TABLE 3.1
DISTRIBUTION OF TRICLOPYR ESTER IN SYSTEM

Experiment Number	Total Mass Delivered (μg)	Column Rinse A (μg)	Column Top (μg)	Column Rinse B (μg)	PUF (μg)	Total Column Rinses + PUF (μg)
18	96,200	13.7		1.0	0.0	14.7
19	96,900	33.9		1.5	0.0	35.4
20	158,000	19.9		1.4	0.0	21.3
21	86,500	16.1		2.0	0.0	18.1
22	78,400	9.4		0.8	0.3	10.5
23	90,600	64.8		0.9	0.3	66.0
24	92,000	10.5		2.6	0.4	13.5
25	86,000	9.3		0.6	0.4	10.3
26	103,600	10.6		1.1	0.4	12.0
27	72,800	68.8		4.1	0.4	73.2
28	80,900	202.4		2.1	0.4	204.9
6X	97,400	285.6		4.8	1.2	291.6
7X	105,700	405.4		4.1	1.2	410.7
8X	93,100	530.0		4.9	1.2	536.1
9X	81,100	128.5		1.2	1.2	130.9
10X	87,400	51.6		1.0	1.2	53.8
11X	84,300	0.0	31.3	0.9	0.6	32.8
12X	88,600	0.0	20.6	1.0	0.6	22.2
13X	70,700	0.0	8.9	9.3	0.6	18.8
14X	98,300	116.1	20.1	1.5	0.6	138.3
15X	110,100	91.0	29.0	1.4	0.6	122.0
17X	106,600	15.8	25.2	1.7	0.6	43.2
18X	86,500	2.2	15.0	1.6	0.6	19.5
19X	106,900	2.1	4.9	0.0	0.6	7.6
20X	123,200	2.22	2.82	1.38	0.6	7.0
21X	122,400	1.86	3.88	0		5.7
22X	106,500	222.56	3.51	6.38		232.5
23X	133,100	19.37	7.67	5.5		32.5
24X	120,800	1.4	3.25	50.67		55.3
25X	110,400	1.19	1.89	16.33		19.4
Mean	**99,167**	**77.9**	**12.7**	**4.4**	**0.6**	**88.7**
SD [1]	**18,953**	**129.8**	**10.6**	**9.3**	**0.4**	**128.2**
RSD [2]	**19**	**166.6**	**83.2**	**212.8**	**67.9**	**144.6**

[1]SD = Standard deviation

[2]RSD = Relative standard deviation

was found in the column rinses (Table 3.1, Figure 3.1). This indicated that the pesticide had strong affinity for glass. This phenomenon is consistent with that seen for pendamethalin by Jenkins et al. (1990). The fraction of triclopyr ester found in the PUF and the column rinses ranged from a high of 0.57 percent of the total amount delivered to a low of 0.005 percent (Tables 3.2 and 3.3). Incremental changes in the methodology were tried in experiments 3 through 27; however, little or no reduction in the data's variability could be achieved. Thus, a series of method validation experiments were conducted to determine the cause of the variability (Section 2.9). These experiments revealed that the methods used for collecting, handling, extracting, concentrating, and analyzing the samples were not responsible for the variability in the amount of triclopyr ester in the column rinsate. This left one remaining possible cause of the variability: droplets impacting the side of the column. If a droplet impacted the side of the column, it would leave virtually all of its active ingredient on the column walls. An estimate of the amount of triclopyr ester in a 1.9 μL droplet of 3 percent Garlon® 4 in water solution can be calculated:

$$1.9\ \mu L\ drop \times \frac{3\ ml\ Garlon®\ 4}{100\ ml\ soln} \times \frac{0.616\ g\ triclopyr}{g\ Garlon®\ 4} \times \frac{1.002\ g}{ml} \times \frac{10^{-3}\ ml}{\mu L} \times \frac{10^{6}\ \mu g}{g} = 35.18\ \mu g\ triclopyr \quad (29)$$

where the gravimetrically-determined density of a 3 percent solution of pesticide is 1.002 g/ml. Thus, one droplet impacting the column could add as much as 35 μg of triclopyr ester to the "volatilized" fraction. (Because of heterogeneity in the emulsion, especially due to breakdown of the emulsion in the delivery lines, the amount of active ingredient in a given droplet could be more or less than 35 μg.) In some experiments, green dye was added to the pesticide emulsion. Occasionally, it was possible to see the dye on the column walls following the experiment, indicating droplet impact on the walls. However, several runs left no visible evidence of the dye, but the high amount of triclopyr ester in the "volatilized" fraction indicated that one or more droplets had impacted the column walls. The suspicion that droplets impacting the column caused the variability was confirmed by adding

ultraviolet (UV) fluorescent Rhodamine-6G dye (3 ppm) to the pesticide emulsion. Under a hand-held UV light in the dark, even very small traces of the emulsion were readily visible on the column walls. This was the case for three consecutive runs after 25X (the last run for which data were collected).

TABLE 3.2
COLUMN CONDITIONS: 24°C
15% RELATIVE HUMIDITY

Experiment Number	Estimated Droplet Size (μL)	Mass in Column Rinses + PUF (μg)	Total Mass Delivered (μg)	% of Total Mass Delivered Found in Rinses + PUF
4	2.04	86.22	28,800	0.2994
5[1]	2.09	32.62	33,100	0.0986
6	2.09	18.40	26,800	0.0687
7[1]	2.00	59.64	20,400	0.2924
8	1.87	39.32	67,600	0.0582
9	1.90	27.78	72,400	0.0384
10	1.89	15.27	67,500	0.0226
11	1.80	15.50	100,000	0.0155
12	1.85	64.59	57,000	0.1133
13[1]	1.94	39.61	49,100	0.0807
14	1.89	70.85	49,100	0.1443
15	1.82	34.04	94,500	0.0360
16	1.87	19.34	96,600	0.0200
17	NR	46.84	104,700	0.0447
Mean	1.9	40.7	61,971	0.095
SD[2]	0.1	22.3	29,030	0.093
RSD[3]	5.1	54.8	46.8	97.6

Notes: [1] Fresh Garlon® 4 solution prepared [2] Standard deviation
[3] Relative standard deviation NR = Not recorded

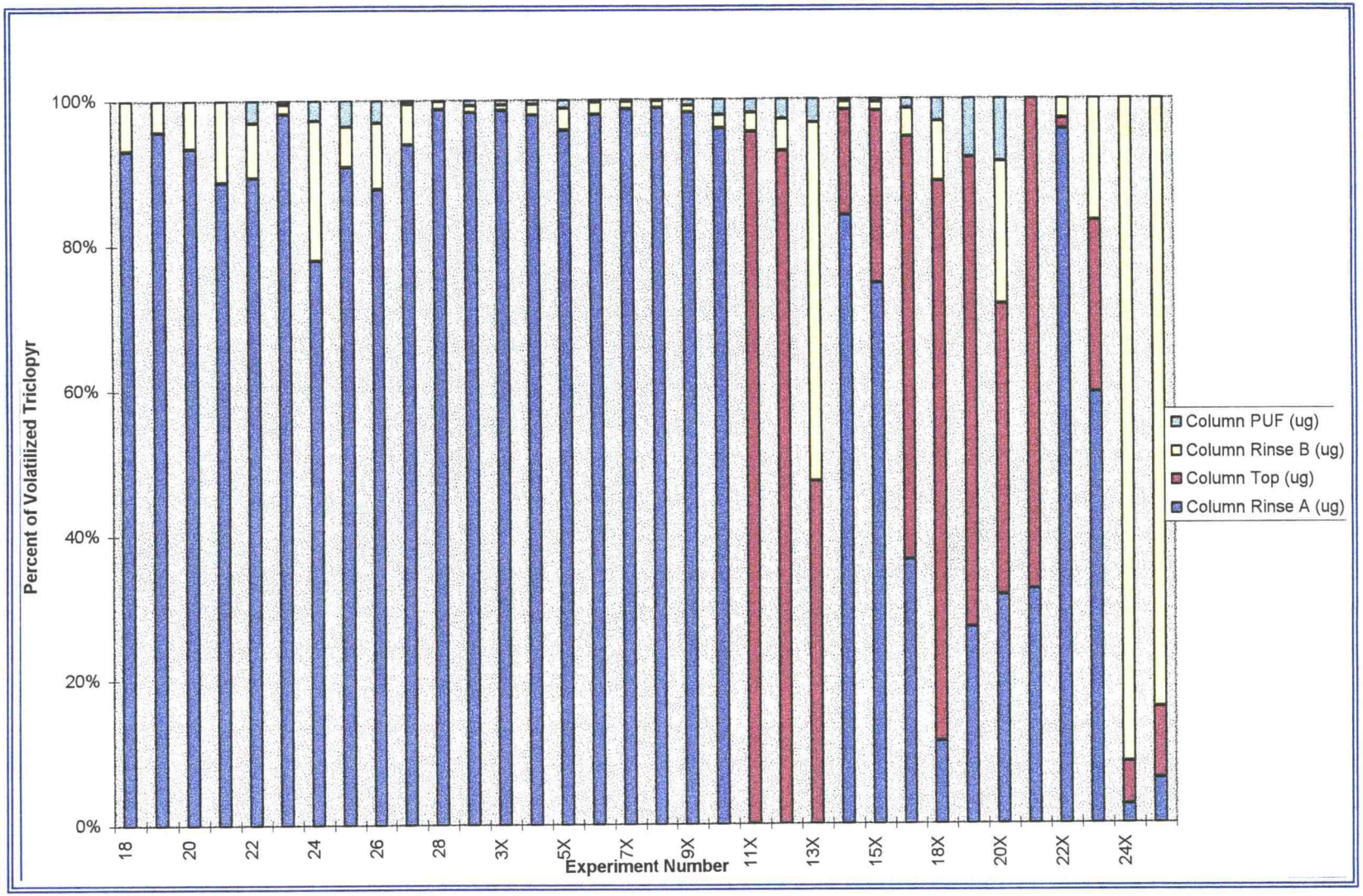

Figure 3.1 Distribution of Triclopyr Ester in System

TABLE 3.3
COLUMN CONDITIONS: 35°C
15% RELATIVE HUMIDITY

Experiment Number	Estimated Droplet Size (μL)	Mass in Column Rinses + PUF (μg)	Total Mass Delivered (μg)	% of Total Mass Delivered Found in Rinses + PUF
18	1.87	14.7	96,200	0.015
19	1.87	35.4	96,900	0.037
20	1.82	21.3	158,000	0.013
21	1.82	18.1	86,500	0.021
22	1.77	10.5	78,400	0.013
23[1]	1.9	66.0	90,600	0.073
24	1.9	13.5	92,000	0.015
25	1.89	10.3	86,000	0.012
28	1.83	204.9	80,900	0.253
2X[1]	NR	161.5	99,200	0.163
3X	NR	186.2	91,100	0.204
4X	1.85	200.1	95,700	0.209
5X	1.82	100.2	106,400	0.094
6X	NR	291.6	97,400	0.299
7X	1.79	410.7	105,700	0.389
8X	1.85	536.1	93,100	0.576
9X	NR	130.9	81,100	0.161
10X	NR	53.8	87,400	0.062
11X	NR	32.8	84,300	0.039
12X[1]	1.92	22.2	88,600	0.025
13X	2.2	18.8	70,700	0.027
14X	2.02	138.3	98,300	0.141
15X	1.92	122.0	110,100	0.111
17X	2.1	43.2	106,600	0.041
18X[1,2,4]	2.27	19.5	86,500	0.022
19X[1,2,4]	1.9	7.6	106,900	0.007
20X[1,2,4]	2.06	7.0	123,200	0.006
21X[1,2,4]	1.94	5.7	122,400	0.005
22X[1,2,3]	1.93	232.4	106,500	0.218
23X[1,2,3]	1.92	32.5	133,100	0.024
24X[1,2]	1.85	55.3	120,800	0.046
25X[1,2,4]	NR	19.4	110,400	0.018
Mean	1.92	100.7	99719	0.104
Standard Dev.	0.12	126.1	17800	0.131
RSD[5]	6.40	125.3	17.9	125.9

Notes: [1]Fresh Garlon® 4 solution prepared [2]Dye added [5]Rel. standard deviation
[3]Dye visible on column walls [4]No dye visible on column walls NR = Not recorded

It was noted during the experiment that 3 runs (19X, 20X, and 21X) had very low amounts of "volatilized" triclopyr ester relative to all the other experiments. Green dye was used for these runs, and no dye was visible on the column walls following the experiment. As stated earlier, the lack of visible evidence of droplet side impact was not the only criterion used to rule out the possibility that one or more droplets had impacted the column walls. However, it is possible that no droplets impacted the column side during runs 19X-21X and these three data points represent the actual amount of triclopyr ester volatilized under the experimental conditions. Runs 18X and 25X also showed no visible evidence of dye on the column walls. These runs had a higher mass of triclopyr ester in the "volatile" fraction than runs 19X-21X, but still had less than the estimated 35 μg triclopyr ester in one droplet. It is possible that a droplet glanced off the column walls in runs 18X and 25X and did not leave its full complement of triclopyr ester behind on the column. Support for this hypothesis was provided by experiments conducted after 25X using a highly visible, ultraviolet fluorescent dye in the pesticide emulsion. Two of these experiments showed small particles of spattered triclopyr ester visible on the freezer vessel collar. Therefore, the data were put into two groups, runs 19X-21X representing low flux, and runs 18X and 25X representing high flux. A Student's *t*-test comparison was conducted on the two groups of data (Tables 3.4 and 3.5) using the statistical data package SPSS version 7.0 (SPSS Ltd, Surrey, United Kingdom). The *t*-test indicated a difference ($p = 0.004$) between the "high" flux values of runs 18X and 25X (mean = 0.020 μg) and the "low" flux values of experiments 19X-21X (mean = 0.006 μg). Therefore, runs 18X and 25X were excluded from the data used to estimate evaporative flux. Droplet impact to the column walls in all experiments except runs 19X-21X was thought to be the primary source of bias observed in these data (see Section 3.2). Therefore, only data from runs 19X-21X were used for comparison with the predicted evaporative flux rate from Section 1.2.5.3.

TABLE 3.4
GROUP STATISTICS

Flux Values	N	Mean	Standard Deviation	Standard Error of Mean
High	2	0.020	0.0028	0.00200
Low	3	0.006	0.0010	0.00058

TABLE 3.5
INDEPENDENT SAMPLES TEST

Mass Volatilized	Levene's Test for Equality of Variances		Student's *t*-Test for Equality of Means						
	F	Sig.	t	df	Sig. (2-tailed)	Mean Diff.	Std. Error of Diff.	95% c.i. of Mean	
								Lower	Upper
Equal Variances Assumed	9.600	0.53	8.400	3	0.004	0.014	0.00167	0.0087	0.019
Equal Variances not Assumed			6.725	1.2	0.071	0.014	0.00208	-0.005	0.033

3.2 METHOD VALIDATION RESULTS

The results of the method validation experiments are presented in individual tables in this section. The results of each experiment are briefly summarized below each table.

3.2.1 GARLON® 4 TRICLOPYR ESTER CONCENTRATION TEST RESULTS

TABLE 3.6
TRICLOPYR ESTER CONCENTRATION
IN GARLON® 4

Garlon® 4 Dilution Number	Predicted Concentration (mg/L)	Measured Concentration (mg/L)	Normalized Concentration (mg/L)	Mean Concentration (mg/L)	Std. Dev.	95% c.i. of mean
A1-A	1.02	1.057	1.04			
B1-A	1.02	1.013	0.99			
C1-A	1.06	1.040	0.98			
D1-A	1.06	1.023	0.97			
E1-A	1.04	1.012	0.97			
F1-A	1.07	1.039	0.97	0.987	0.026	0.96 to 1.014

If the concentration of triclopyr ester in the Garlon® 4 samples tested was equal to the manufacturers stated concentration of 61.6 percent (Table 3.6), the normalized concentration in column 4 would be equal to 1.00 mg/L. Therefore, the mean of the normalized sample concentrations was compared to 1.00 mg/L using a Student's *t*-test. The null hypothesis that the actual concentration is 1.00 (H_o: μ = 1.00 mg/L) was tested against an alternative hypothesis that the sample concentrations are different from 1.00 (H_a: $\mu \neq$ 1.00 mg/L), resulting in a two-tailed statistical test. Using α = 0.05 (0.25 in each tail of the *t* distribution), the critical value for *t* was 2.571 for 5 degrees of freedom. The computed test statistic was t = 1.225, resulting in acceptance of H_o and the conclusion that the concentration of Garlon® 4 in the samples was not different from the manufacturer's stated concentration of 61.6 percent. The 95 percent confidence interval of the mean normalized concentration of triclopyr ester in the Garlon® 4 samples was 0.96 to 1.014 mg/L.

Therefore, it can be concluded that the listed concentration of 61.6 percent active ingredient in the formulated product is accurate and this quantity was used in all pertinent calculations.

3.2.2 PUF Collection Efficiency Test Results

The triclopyr ester mass recovered from the PUF was 3.66 μg, or 55.5 percent of the total mass spiked into the U-tube. The mass of triclopyr ester recovered from the U-tube rinsate was 2.34 μg, or 35.4 percent of the mass spiked. Thus, 90.9 percent of the total mass spiked was recovered in the experiment. Due to the design of the PUF cartridges, they could not conveniently be connected in a series to determine whether breakthrough might have occurred. However, given the tendency for triclopyr ester to adsorb to the column walls, it was unlikely that the PUF would become saturated under the experimental conditions. Therefore, 90.9 % recovery was deemed acceptable, demonstrating that the PUF could effectively be used to scavenge triclopyr ester from air under the experimental conditions.

3.2.3 Column Internal Temperature Gradient Test Results

The temperature was fairly uniform inside the column ($\pm 0.5\,^{\circ}C$) with the exception of about 1 inch into the connecting collar between the column and the freezer vessel where the temperature dropped rapidly. The temperature drop in the neck of the freezer vessel was acceptable because droplets entering this part of the column were to be frozen to prevent further volatilization of triclopyr ester.

3.2.4 CAVRO PUMP PRECISION AND ACCURACY TEST RESULTS

TABLE 3.7
CAVRO PUMP PRECISION AND ACCURACY TEST RESULTS

Replication Number	Predicted Dispense Volume (ml)	Predicted Weight @ 24°C (g)	Sample Net Weight (g)	Percent Difference	Mean Percent Difference
1	5.4	5.38	5.350	-0.56	
2	5.4	5.38	5.080	-5.57	
3	5.4	5.38	4.600	-14.49	
4	5.4	5.38	4.660	-13.40	
5	5.4	5.38	4.050	-24.72	11.8

The results of the Cavro pump accuracy and precision test presented in Table 3.7 characterized the pump's accuracy and precision under the experimental conditions. The pump's accuracy is represented by the value in the column labeled "Mean Percent Difference". The average difference between the amount the pump actually dispensed and the amount it was instructed to dispense was 11.8 percent. This value is excessively high for the needs of this experiment. The pump's precision can be estimated from the standard deviation of the values in column 4 = ±0.497 g. Based on this experiment and the other method validation experiments, it is likely that the variability between experiments in the freezer vessel sample analyses resulted primarily from variability in the amount of herbicide delivered by the pump. Therefore, for comparison purposes, the amount of triclopyr ester found in the freezer vessel analysis was used as the total amount of ester put through the system for a given experiment. In other words, to determine the percent total mass triclopyr ester "volatilized" for an experiment, the amount in the volatile fraction (PUF + CR-A + CR-B) was divided by the freezer vessel sample analysis result.

3.2.5 Active Ingredient Hydrolysis Test Results

A known mass of triclopyr ester was spiked on the column walls using a Pasteur pipette. The column was operated as normal for 1 hour, then rinsed as described above. The mass of triclopyr ester recovered in the rinsate from the spike of the column walls was 589.8 μg. The mass spiked was 550 μg, giving a 107 percent recovery for the experiment. This result indicates that hydrolysis of triclopyr ester to its acid is not occurring on the column walls under the experimental conditions of the test.

3.2.6 Freezer Vessel Analysis Methodology Validation Results

As shown in Table 3.8, results ranged from 84 to 114 percent recovery, with a mean percent recovery of 102.0 percent and a standard deviation of 7.5. Based on these data, it can be concluded that the methodology used for collecting and analyzing the Garlon® 4 droplets from the freezer vessel gave an accurate representation of the amount of pesticide input into the system. The amount volatilized is very small (~0.005 percent) of the total mass of pesticide input into the system. Leaving the volatilized pesticide out of the amount input into the system will not significantly impact the calculations. Therefore, it was reasonable to use the mass of triclopyr ester found in the freezer vessel as the total mass of pesticide delivered in the experiment.

TABLE 3.8
FREEZER VESSEL ANALYSIS
METHOD VALIDATION

Sample	Mass Triclopyr Ester Pipetted (mg)	Mass Recovered (mg)	Percent Recovery
Gar-1A	92.5	77.7	84.0
Gar-1B	92.5	103.4	111.8
Gar-1C	92.5	96.2	104.0
Gar-1D	92.5	93.7	101.3
Gar-1E	92.5	100.4	108.5
Gar-1F	92.5	95.9	103.7
Gar-2A	92.5	103.3	111.7
Gar-2B	92.5	105.9	114.5
Gar-2C	92.5	88.3	95.5
Gar-2D	92.5	90.1	97.4
Gar-2E	92.5	93.4	101.0
Gar-2F	92.5	92.2	99.7
Gar-3A	92.5	88.4	95.6
Gar-3B	92.5	102.4	110.7
Gar-3C	92.5	94.3	101.9
Gar-3D	92.5	92.7	100.2
Gar-3E	92.5	90.4	97.7
Gar-3F	92.5	89.9	97.2
Mean			102.0
SD[1]			7.5
RSD[2]			7.3

[1]SD = Standard deviation [2]RSD = Relative standard deviation

3.2.7 COLUMN RINSE ANALYSIS METHOD VALIDATION RESULTS

TABLE 3.9
COLUMN RINSE ANALYSIS
METHOD VALIDATION RESULTS

Sample	Mass Triclopyr Ester Spiked (μg)	Mass Recovered (μg)	Percent Recovery
CRS-A	220	214.40	97.5
CRS-B	220	199.51	90.7
CRS-C[1]	220	221.00	100.5
CRS-D[1]	220	230.11	104.6
Mean			98.3
SD[1]			5.9
RSD[2]			6.0

Notes: [1]Water and Na_2SO_4 added to sample.

Sample recovery ranged from 90.7 to 104.6 percent of the spiked amount (Table 3.9). The mean percent recovery was 98.3 percent of the spiked amount with a standard deviation of 5.9 and a relative standard deviation of 6.0. Based on these results, it can be concluded that the column rinse sample handling methodology was sound and did not contribute significantly to the data's variability. This experiment also demonstrates that triclopyr ester deposited on the column walls can be removed efficiently using the column rinsing apparatus. In addition, the presence of water in the samples and adding Na_2SO_4 to the sample appears to have had little effect on spike recovery.

3.2.8 BLANK SAMPLE ANALYTICAL RESULTS

TABLE 3.10
BLANK SAMPLE ANALYTICAL RESULTS
24°C and 35°C, 15% R.H.

Sample	Mass Detected (μg)	Total Mass Volatilized (Experiment, μg)	Percent Total Mass Volatilized	Mean CRB as % Total Mass Volatilized
PB- 4	BLQ[1]	32.62	3.07	
PB- 5	BLQ	18.40	0.00	
PB- 6	ND[2]	59.64	3.35	
PB- 7	ND	39.32	0.00	
PB- 8	ND	27.78	0.00	
PB- 9	ND	15.27	0.00	
CRB- 4	1.890	32.62	5.79	
CRB- 5	1.870	18.40	10.16	
CRB- 6	1.550	59.64	2.60	
CRB- 7	0.824	39.32	2.10	
CRB- 8	3.480	27.78	12.53	
CRB- 9	8.460	15.27	55.40	
CRB- 10	2.990	15.50	19.29	
CRB- 11	0.512	64.59	0.79	
CRB- 12	1.416	39.61	3.57	
CRB- 13	3.520	70.85	4.97	
CRB- 14	1.650	34.04	4.85	
CRB- 15	1.120	19.34	5.79	
CRB- 16	2.590	46.84	5.53	
CRB- 17	6.950	46.84	14.84	
CRB-18X	NR[3]	19.50	15.38	
CRB-19X	NR	7.60	0.00	
CRB-20X	1.540	7.00	22.00	
CRB-21X	NR	5.70	0.00	
CRB-25X	6.600	19.40	34.02	9.0

Notes: [1] BLQ = Below the limit of quantitation (0.1 μg/mL)
[2] ND = Not detected
[3] NR = Not recorded

Triclopyr ester concentrations in all PUF blanks were either below the limits of quantitation of 0.1 μg/ml or not detected (Table 3.10). Column rinse blank results ranged from a low of 0.79 to a high of 55 percent of the total mass of triclopyr ester found in the column rinses and PUF. The average column rinse blank value was 8.4 percent of the total triclopyr ester mass found in the column rinses and PUF. For experiments 19X-21X (the data used for the calculation of the average flux), column rinse blanks were taken only in experiment 20X. The column rinse blank value for this experiment was 22 percent of the total triclopyr ester mass found in the column rinses and PUF. From these results, it is apparent that triclopyr ester remaining on the column walls before the start of the experiment could have an effect on the experimental outcome. The magnitude of this effect is unknown, as the collection of the rinse blank further reduced the mass of triclopyr ester remaining on the column walls before the experiment was begun. (Possible contamination of the column was not considered in the evaporative flux estimates for this project presented in Section 4.2) It is likely that this problem can be eliminated by ensuring that droplets do not impact the column walls, thereby eliminating gross contamination of the column and carryover of triclopyr ester into subsequent experiments. For future experiments, it appears that additional measures, including mechanical scrubbing and additional column rinsing, should be implemented to insure that the column is clean before the experiment is started.

3.3 Droplet Exposure Time

The flow rate delivered by the pump was adjusted to allow each drop to individually form and fall off the needle when its mass exceeded the adhesive force holding it to the tip. The time required for a droplet to form and fall off the needle was approximately 1 second. The fall time for a droplet was estimated in Section 1.2.5.1 to be approximately 0.45 second. Since each droplet grew continuously while it formed on the needle, they did not instantaneously present their final surface area to the airstream. Therefore, a time-step approximation of the surface area and a mean droplet surface area exposed to the airstream was prepared using 0.2 second increments (Table 4.1). The sum of the mean droplet surface area exposed to the airstream during droplet formation (equal to 1.0 sec) and the fall time

of 0.45 seconds gives an approximate droplet exposure time/surface area relationship with a total exposure time of 1.45 seconds. This relationship was used for calculating evaporative flux per droplet in Section 4.2.

4. CONCLUSIONS

The PVC is a unique apparatus for estimating evaporative flux from falling pesticide spray droplets. The majority of work performed on this project involved the design, construction, testing, modification, and fine-tuning of the device. A good deal of effort was also put into the method development for triclopyr ester sample collection and analysis. Unfortunately, by the time the PVC's critical design flaw (column width) had been identified, both the available time and money for the project had run short and further development of the device was not possible. However, some useful data was collected. Analysis of the data demonstrates that the device, with a few modifications, could potentially be used to assess the volatility of many pesticides in use today.

Some of the unique elements of the PVC and associated problems are discussed in Section 4.1. Section 4.2 provides a comparison of the STF model predicted evaporative flux from spray droplets with the observed values. A method for estimating the total evaporative loss of triclopyr ester from spray droplets during flight from an aerial application is presented in Section 4.3. The project objectives, hypotheses, and findings are discussed in Section 4.4. Finally, the sources of experimental error are discussed in Section 4.5.

4.1 Some Critical Design Elements of the PVC

The PVC was designed with the specific idea of finding a way to assess pesticide volatility from free-falling droplets. It was designed and built using concepts originally proposed by Edward Palmes, Ph.D. Other investigators (Freiberg and Crosby, 1986; Sundaram, 1985) have examined pesticide droplets that were suspended on fibers or adsorbed to filter paper. In their experiments, interaction between droplets and the fiber or filter paper may have created experimental artifacts that affected pesticide volatility. By producing a free-falling droplet, this study sought to eliminate any potential effects that the fiber or filter paper might have on a pesticide's rate of volatilization. A pesticide droplet free-falling against a counter-current of temperature and humidity-controlled air in an

enclosed column should improve pesticide volatilization rate estimates compared to the methods used by others.

4.1.1 Freezer Vessel

An important design goal for the PVC was to find a way of stopping further evaporation of droplets once they left the main vertical column. This problem was solved by placing a freezer vessel in a liquid nitrogen bath at the bottom of the column. When droplets entered the freezer vessel, further volatilization was instantaneously arrested. This design feature had another important benefit: it allowed very accurate measurement of the total amount of pesticide delivered to the system during a given run. Because the droplets remained frozen solid throughout the run, they could be transferred in this state for serial dilution and analysis with virtually no loss of the pesticide.

4.1.2 Column Architecture

Another unique design aspect of the PVC was the "L" shape of the apparatus (Figs. 2.1 and 2.2). This design allowed fresh, preconditioned air to be brought into the system where it could be temperature-equilibrated in the inlet column without interfering with the droplets' fall paths. Because airflow was countercurrent to the falling droplets, volatilized pesticide was swept up the vertical column and away from the inlet column. One of the most important aspects of the "L" shape design was that it allowed temperature/humidity monitoring of the air as it entered the column without exposing the probe (which could not be washed with acetone!) to pesticide vapors.

The modular design of the column allowed easy removal of the column top, PUF cartridge, and the freezer vessel for acetone rinsing of the column walls. The PUF cartridge was placed at the head of the column to capture any volatilized pesticide that did not adsorb to the column walls. (Virtually all of the volatilized pesticide was taken up by the column walls.)

4.1.3 Droplet Delivery Systems

The most critical challenge of this project ended up being something relatively simple, and thus easily overlooked, in the design phase: droplets simply did not fall in a straight path down the middle of the column when released from the delivery needle. This phenomenon was caused by droplet adhesion to the delivery needle. When a droplet became heavy enough to break the attractive forces holding it to the needle, it broke away and fell through the column. Breaking the adhesive forces between the droplet surface and the needle imparted some angular kinetic energy to each droplet upon release. This deflected each droplet horizontally, causing a few droplets to impact the column walls during almost every run. Whether or not a given droplet impacted the column walls appeared to be a random event. The largest diameter commercially-available column proved to be too narrow for the experiment due to the magnitude of droplet deflection during release from the needle.

Several attempts were made at remedying the droplet deflection problem. Needles of various sizes, end cuts, and materials of construction were tested at various stages of the experiment. Applying a spray Teflon® coating to reduce droplet adhesion to the needle surface was tried. (Interestingly, the non-stick coating actually increased the angular deflection of most droplets.) Increasing the concentration of Garlon® 4 in the emulsion and/or adding surfactant to the mixture helped reduce the surface tension of the droplets and decreased the amount of energy imparted to the droplet at breakaway, thus reducing droplet deflection somewhat. As mentioned earlier, macroemulsions are inherently unstable and tend to separate into phases with time. Added surfactant/Garlon® 4 also helped minimize emulsion breakdown in the delivery lines.

The rate of droplet formation also had a significant effect on the angular deflection of droplets. Slower fluid delivery tended to decrease droplet deflection. However, if flow rates were too low, emulsion breakdown occurred in the delivery lines. The flow rate was optimized based on trial and error. Pesticide flow rates were optimal at about 2 μL/sec, which meant that a given volume of pesticide remained in the delivery lines ($\simeq$ 60 μL dead

volume) for approximately 30 seconds. This was sufficient time for partial emulsion breakdown to occur, causing some droplets to have a relatively greater fraction of water and thus greater surface tension than others. The shortest possible lengths of extremely small bore PEEK tubing was used to minimize the system's dead volume.

Cycling of the Cavro syringe pump also caused droplet "shake" on the end of the needle. The pressure pump was designed to eliminate this phenomenon by providing continuous fluid flow without cycling to refill. However, despite the efforts described above to reduce droplet deflection, during most experiments one or more droplets impacted the column walls. Therefore, it was concluded that the seminal design flaw with the PVC was inadequate width of the column. Rectifying this problem would have required custom ordering a wider column along with the associated fittings. The project budget could not accommodate additional expenditures of this magnitude; therefore, the project was terminated when all conceivable means of reducing droplet deflection failed to control the problem sufficiently for use of the 50 mm wide column.

4.2 Comparison of Predicted Evaporative Flux to Observed Values

A potentially useful estimate of triclopyr's volatilization rate was made by Bentson (1988). Based on a review of his data, the average evaporative flux of triclopyr ester from Garlon® 4 deposits on glass slides was calculated to be approximately 106.9 $pg/cm^2 \cdot sec$ over 35 hours at 25° C. The evaporative loss was higher initially and decayed with time. The estimated flux of 55.3 $pg/cm^2 \cdot sec$ @ 25°C from Section 1.2.5.3 is roughly half of the average flux value calculated from Bentson's data. The difference between the estimated flux and Bentson's findings is not surprising given the assumptions used in preparing the estimate. As was mentioned earlier, Freiberg and Crosby (1986) found the difference between evaporative loss of MCPA from droplets and that from liquid placed on glass slides to be insignificant.

The observed values of total volatilized triclopyr ester from three experiments (19X, 20X, and 21X) @ 35°C were compared below to the predicted flux from Section 1.2.5.3. First, the volume of Garlon® 4 dispensed in each experiment were approximated from the total mass of active ingredient collected in the freezer vessel. Calculations for experiment 19X (1.90 μL average estimated droplet size) are provided as an example. First, the volume dispensed can be determined (using a modification of Eq. 29) by multiplying the mass of triclopyr ester found in the freezer vessel sample by the known concentration of triclopyr ester in a 3 percent aqueous emulsion of Garlon® 4:

$$106{,}900\ \mu g\ t.e. \times \frac{100\ ml\ soln}{3\ ml\ Garlon®\ 4} \times \frac{1\ g\ Garlon®\ 4}{0.616\ g\ t.e.} \times \frac{1\ ml\ Garlon®\ 4}{1.002\ g} \times \frac{1\ g\ t.e.}{10^6\ \mu g\ t.e.} = 5.77\ ml\ soln. \quad \textbf{(30)}$$

where t.e. is triclopyr ester and the first term is the mass in the freezer vessel. Then the approximate number of droplets dispensed for the experiment can be determined:

$$5.77\ ml\ soln \times \frac{1\ droplet}{1.9\ \mu L\ soln} \times \frac{10^3\ \mu l\ soln}{1\ ml\ soln} = 3{,}036\ droplets. \quad \textbf{(31)}$$

Taking the mass volatilized for the experiment = 7.6 μg and dividing by the number of droplets, the mass volatilized per droplet @ 35°C can be calculated:

$$\frac{7.6\ \mu g\ t.e.}{3{,}036\ droplets} \times \frac{10^3\ pg}{\mu g} = \frac{2.5\ pg}{droplet}. \quad \textbf{(32)}$$

Alternatively, the evaporative loss can be expressed as flux (mass per unit area per unit time). However, the droplet did not instantaneously form on the end of the needle; its surface area started at zero and grew until it reached its maximum surface area when it broke

off the needle. Since flux is a function of surface area, it is necessary to divide the droplet exposure into two periods:

- The droplet formation period where its surface area continuously grew, and
- The droplet flight period, where its surface area was constant.

Calculations detailed below are for 2.0 μL droplets because that is the approximate average droplet size from the experimental data used in the flux calculations (runs 19X-21X).

The simplest part of the equation, the droplet flight period, will be discussed first. To determine the droplet's maximum surface area, the radius of a 2.0 μl droplet was calculated using Eq. 27:

$$r = \sqrt[3]{\frac{(3 \times 2.0\ \mu L)}{4\pi}} = 0.781\ mm \times \frac{1\ cm}{10\ mm} = 0.0781\ cm$$

and its maximum surface area was found (cm^2):

$$s.a.\ cm^2 = 4\pi r^2 = 4\pi(0.0781)^2 = 7.67 \times 10^{-2}\ cm^2 \qquad \textbf{(33)}$$

where *s.a.* is the surface area of the fully-formed droplet. This quantity was used to determine flux during the 0.45 sec droplet flight period. To determine the droplet surface area/time relationship during droplet formation, the integral of the droplet surface area with respect to time was determined. The droplet formed in about one second and its final volume was 2.0 μL. Therefore,

$$\frac{dV}{dt} = 2.0\ \mu L, \qquad \textbf{(34)}$$

$$V = 2t + c.$$

where dV/dt is the droplet's change in volume with time and c is a constant. Since the initial condition is $V(0) = 0$, then,

$$V = 2t. \qquad \textbf{(35)}$$

Substituting this result into Eq. 26 gives:

$$\frac{4}{3}\pi r^3 = 2t \tag{36}$$

and solving for r,

$$r = \left(\frac{3}{2\pi}\right)^{\frac{1}{3}} \ (mm) = \frac{\left(\frac{3}{2\pi}\right)^{\frac{1}{3}}}{10} \ (cm). \tag{37}$$

Then defining surface area in terms of time (t) using Eq. 33:

$$s.a. \ (cm^2) = \frac{4\pi\left(\frac{3}{2\pi}t\right)^{\frac{2}{3}}}{10^2}. \tag{38}$$

When $0 \le t \le 1$, the general formula of the integral is:

$$\int_0^1 s.a. \, dt \tag{39}$$

Substituting Eq. 38 for surface area into the integral gives:

$$\int_0^1 \frac{4\pi\left(\frac{3}{2\pi}t\right)^{\frac{2}{3}}}{10^2} \, dt \tag{40}$$

for a 1 sec droplet formation period and a final volume of 2.0 μL. Then taking the integral:

$$\frac{8\pi^2}{5 \cdot 10^2}\left(\frac{3}{2\pi}\right)^{\frac{5}{3}} = 4.60 \times 10^{-2} \ cm^2 \cdot \text{sec}. \tag{41}$$

This quantity represents the contribution of the growing droplet surface area to flux for the

time interval of 0 to 1 sec. Again, the droplet surface area/time relationship for a 2.0 μL droplet was used for all flux calculations because it represent the average droplet size for the three droplet sizes in experiments 19X, 20X, and 21X. The flux for the droplet formation and flight periods was determined by multiplying the mass flux per droplet for each experiment (Mass/Drop, Table 4.1) by the adjusted surface-area-and-time-of-exposure relationships as shown for experiment 19X in Eq. 42 below:

$$F = \frac{2.5\,pg}{droplet} \cdot \left(\left[\frac{1\ droplet}{7.41 \times 10^{-2}\ cm^2} \times \frac{1}{0.45\,\text{sec}} \right] + \left[\frac{1\ droplet}{\int_0^1 s.a.\ dt}\ cm^2 \cdot \text{sec} \right] \right) =$$

$$\frac{2.5\,pg}{droplet} \cdot \left(\left[\frac{1\ droplet}{7.41 \times 10^{-2}\ cm^2} \times \frac{1}{0.45\,\text{sec}} \right] + \left[\frac{1\ droplet}{4.60 \times 10^{-2}\ cm^2 \cdot \text{sec}} \right] \right) = \quad \textbf{(42)}$$

$$74.97\ \frac{pg}{cm^2 \cdot \text{sec}} + 54.35\ \frac{pg}{cm^2 \cdot \text{sec}} = 129.32\ \frac{pg}{cm^2 \cdot \text{sec}}.$$

Flux values calculated using the above equations for experiments 19X-21X are presented in Table 4.1.

TABLE 4.1
CALCULATED FLUX VALUES
FROM EXPERIMENTAL DATA @ 35°C

Experiment Number	Drop Volume (μL)	Max. Drop Surface Area (cm^2)	Mass Volatilized (μg)	Garlon Dispensed (ml)	Mass /Drop (pg)	Flux ($pg/cm^2 \cdot sec$)	Mean Flux
19X	1.90	7.41×10^{-2}	7.6	5.77	2.5	129.32	
20X	2.06	7.89×10^{-2}	7.0	6.65	2.17	108.28	
21X	1.94	7.52×10^{-2}	5.7	6.61	1.67	85.65	107.8

The mean flux of 107.8 $pg/cm^2 \cdot sec$ @ 35°C is about twice the estimated flux for a 2.1 μL droplet of 55.3 $pg/cm^2 \cdot sec$ @ 25°C. It is about the same as the estimated flux of 106

$pg/cm^2 \cdot sec$ @ 25°C from Bentson's data. As would be expected, the flux at the higher experimental temperature is greater than the STF model estimated flux @ 25°C. Future investigators using the PVC producing differing droplet sizes under a variety of temperature/humidity regimes should be able to gather sufficient data to evaluate the validity of these results.

4.3 Flux Extrapolation from Discrete Droplets to Spray Applications

The value of the data produced in this experiment hinges upon the utility of extrapolating evaporative flux from single droplets, or a known quantity of monodisperse droplets, to an actual spray application that contains a range of droplet sizes. Sophisticated models used by the US Forest Service (e.g. FSCBG model) are capable of predicting spray drift based on a number of input parameters, including the chemical properties of the spray material (Dumbauld, 1984). However, the models treat the volatile components as if they are water, so the active ingredient and water are subject to equal evaporation (Barry, personal communication). The FSCBG was developed to predict droplet drift and deposition of active ingredient within the spray swathe and immediately downwind; it was not designed to predict evaporative loss of active ingredient that could be subject to long-range transport.

The model proposed in this paper is simpler in some respects than the FSCBG because it does not account for droplet size reduction due to evaporation, meteorological characteristics other than temperature, forest characteristics such as topography, or target characteristics (e.g. leaf shape). It is designed primarily to provide a rough estimate of pesticide active ingredient loss during droplet flight under still conditions. Despite these limitations, the proposed model may prove useful for refining existing models for predicting pesticide spray drift by including a method for predicting evaporative loss of active ingredient from spray drops based on empirical data.

The droplet size distribution produced in an aerial pesticide application depends on the sprayed formulation and the nature of application equipment, including spray nozzle type,

flow rate, and the nozzle angle relative to the airstream. For example, a D8 jet nozzle spraying Garlon® 4 simulant at 0 degrees azimuth and 50 mph flight speed produced a droplet VMD of 1,130 μm (Yates et al., 1985). A complete droplet size distribution, obtained from wind tunnel data by Yates et al. (1985), was included in the model (Table 4.2). The model accounts for droplet settling velocity for each class of droplets in the size distribution, but not the change in settling velocity with time due to evaporation and reduction in droplet size. Droplet settling velocities are presented in Table 4.2 as approximate fall times in sec/m based on the nearest size class fall times from Table 1.2.

The average droplet diameter produced in the usable data points in this experiment was approximately 1,600 μm, giving an approximate volume of 2.0 μl. As discussed above, at constant temperature, pressure, and exposure time, the rate of evaporative flux of active ingredient from spray droplets is a function of droplet surface area. Because only one droplet size class was examined in this experiment, no empirical relationship between droplet size and rate of evaporative flux could be determined. If one assumes that the rate of evaporative flux is a function of surface area and the relationship is not affected by decreasing droplet size, an estimate of the average flux for smaller droplets can be made simply by calculating the surface area of the droplet of interest and using the empirical data or the model to estimate flux/droplet. If the total surface area of all the droplets produced in a given volume of spray is known, the estimated loss per droplet can be used to calculate the mass of active ingredient lost to volatilization for that volume of spray.

The model estimated the surface area of the entire spray application and calculated the total mass active ingredient volatilized using the following methods:

1. Droplets were segregated into size bins (column 1) and the percent volume of the spray composed of droplets of that size was given in column 2 (based on wind tunnel data for Garlon® 4 simulant collected by Yates et al., (1985)).
2. The droplet volume in μL for each size class (column 3) was calculated using Eq. 26.

3. The droplet surface area in cm^2 for each size class (column 4) was calculated using Eq. 33.

TABLE 4.2
PREDICTED TOTAL VOLATILIZATION OF 3% AQUEOUS GARLON-4 SPRAY, D8-JET NOZZLE, 0 DEGREES AZIMUTH, 50 MPH FLIGHT SPEED

		Flux (pg/cm2 sec)			107.8		
		Volume Sprayed (gallons):			50.0		
		Volume Sprayed (L):			189.27		
		Height Sprayed (m):			12.0		
		Total Mass Active Ingredient Volatilized (mg):			**8.23**		
Upper Limit Drop Diameter (μm)	**Percent Volume**	**Drop Volume μL**	**Drop Surface Area (cm^2)**	**Drops/Liter Sprayed**	**Drop Size Class Surface Area (cm^2)**	**Approx. Fall Rate (sec/m)**	**Mass Volatilized (μg)**
56	0.10	9.20e-05	9.85e-05	1.09e+07	1,071	3.70	9.71e+05
89	0.10	3.69e-04	2.49e-04	2.71e+06	674	3.70	6.11e+05
122	0.18	9.51e-04	4.68e-04	1.89e+06	885	3.70	8.02e+05
154	0.31	1.91e-03	7.45e-04	1.62e+06	1,208	1.39	4.11e+05
187	0.29	3.42e-03	1.10e-03	8.47e+05	930	1.39	3.17e+05
219	0.28	5.50e-03	1.51e-03	5.09e+05	767	1.39	2.61e+05
252	0.36	8.38e-03	2.00e-03	4.30e+05	857	0.83	1.74e+05
284	0.44	1.20e-02	2.53e-03	3.67e+05	930	0.83	1.89e+05
318	0.50	1.68e-02	3.18e-03	2.97e+05	943	0.83	1.92e+05
351	0.72	2.26e-02	3.87e-03	3.18e+05	1,231	0.63	1.90e+05
382	0.80	2.92e-02	4.58e-03	2.74e+05	1,257	0.63	1.94e+05
414	0.93	3.72e-02	5.38e-03	2.50e+05	1,348	0.63	2.08e+05
447	1.00	4.68e-02	6.28e-03	2.14e+05	1,342	0.63	2.07e+05
479	1.21	5.75e-02	7.21e-03	2.10e+05	1,516	0.48	1.78e+05
512	1.11	7.03e-02	8.24e-03	1.58e+05	1,301	0.48	1.53e+05
545	1.43	8.48e-02	9.33e-03	1.69e+05	1,574	0.48	1.85e+05
578	1.54	1.01e-01	1.05e-02	1.52e+05	1,599	0.40	1.57e+05
611	1.74	1.19e-01	1.17e-02	1.46e+05	1,709	0.40	1.67e+05
644	1.52	1.40e-01	1.30e-02	1.09e+05	1,416	0.40	1.39e+05
677	1.54	1.62e-01	1.44e-02	9.48e+04	1,365	0.34	1.14e+05
710	2.13	1.87e-01	1.58e-02	1.14e+05	1,800	0.34	1.50e+05
743	1.99	2.15e-01	1.73e-02	9.27e+04	1,607	0.34	1.34e+05
776	2.29	2.45e-01	1.89e-02	9.36e+04	1,771	0.30	1.30e+05
809	2.42	2.77e-01	2.06e-02	8.73e+04	1,795	0.30	1.32e+05

TABLE 4.2 (continued)

842	2.58	3.13e-01	2.23e-02	8.25e+04	1,838	0.30	1.35e+05
875	2.41	3.51e-01	2.41e-02	6.87e+04	1,653	0.27	1.09e+05
908	2.06	3.92e-01	2.59e-02	5.26e+04	1,361	0.27	9.00e+04
941	2.18	4.36e-01	2.78e-02	5.00e+04	1,390	0.27	9.19e+04
974	3.23	4.84e-01	2.98e-02	6.68e+04	1,990	0.25	1.22e+05
1007	1.90	5.35e-01	3.19e-02	3.55e+04	1,132	0.25	6.93e+04
1040	3.45	5.89e-01	3.40e-02	5.86e+04	1,990	0.25	1.22e+05
1073	1.96	6.47e-01	3.62e-02	3.03e+04	1,096	0.25	6.71e+04
1106	2.62	7.08e-01	3.84e-02	3.70e+04	1,421	0.22	7.66e+04
1139	3.63	7.74e-01	4.08e-02	4.69e+04	1,912	0.22	1.03e+05
1172	1.76	8.43e-01	4.32e-02	2.09e+04	901	0.22	4.85e+04
1205	3.37	9.16e-01	4.56e-02	3.68e+04	1,678	0.22	9.04e+04
1238	1.69	9.93e-01	4.81e-02	1.70e+04	819	0.22	4.41e+04
1271	2.55	1.08e+00	5.08e-02	2.37e+04	1,204	0.22	6.48e+04
1304	2.03	1.16e+00	5.34e-02	1.75e+04	934	0.22	5.03e+04
1337	2.15	1.25e+00	5.62e-02	1.72e+04	965	0.19	4.49e+04
1370	2.20	1.35e+00	5.90e-02	1.63e+04	964	0.19	4.48e+04
1403	1.49	1.45e+00	6.18e-02	1.03e+04	637	0.19	2.96e+04
1436	1.65	1.55e+00	6.48e-02	1.06e+04	689	0.19	3.21e+04
1469	0.65	1.66e+00	6.78e-02	3.92e+03	265	0.19	1.24e+04
1502	1.20	1.77e+00	7.09e-02	6.76e+03	479	0.19	2.23e+04
1535	3.61	1.89e+00	7.40e-02	1.91e+04	1,411	0.18	6.22e+04
1568	2.61	2.02e+00	7.72e-02	1.29e+04	999	0.18	4.40e+04
1601	2.37	2.15e+00	8.05e-02	1.10e+04	888	0.18	3.91e+04
1634	2.41	2.28e+00	8.39e-02	1.06e+04	885	0.18	3.90e+04
1667	0.70	2.43e+00	8.73e-02	2.89e+03	252	0.18	1.11e+04
1700	2.26	2.57e+00	9.08e-02	8.79e+03	798	0.18	3.52e+04
1733	0.00	2.73e+00	9.44e-02	0.00e+00	0	0.18	0.00e+00
1766	0.00	2.88e+00	9.80e-02	0.00e+00	0	0.16	0.00e+00
1799	0.00	3.05e+00	1.02e-01	0.00e+00	0	0.16	0.00e+00
1832	1.52	3.22e+00	1.05e-01	4.72e+03	498	0.16	1.95e+04
1865	0.00	3.40e+00	1.09e-01	0.00e+00	0	0.16	0.00e+00
1898	0.00	3.58e+00	1.13e-01	0.00e+00	0	0.16	0.00e+00
1931	0.00	3.77e+00	1.17e-01	0.00e+00	0	0.15	0.00e+00
1964	0.00	3.97e+00	1.21e-01	0.00e+00	0	0.15	0.00e+00
1997	12.87	4.17e+00	1.25e-01	3.09e+04	3,867	0.15	1.42e+05
2030	0.00	4.38e+00	1.29e-01	0.00e+00	0	0.15	0.00e+00
Total:	**100.04**				**65,812**		**8.23e+06**

4. The number of drops in a given size class sprayed per liter of spray mix was calculated (column 5) using the following equation:

$$\frac{\%\ volume}{100} \times \frac{1\ drop}{drop\ volume\ (\mu L)} \times \frac{10^6\ \mu L}{L} \quad \textbf{(43)}.$$

5. The surface area of all droplets in each size class in cm^2 (column 6) was calculated by multiplying column 4 by column 5.
6. The approximate fall rate in sec/m for each droplet size class was input into column 7. These values were taken from Table 1.2 from the nearest size class available in the table and are therefore rough approximations of fall rates.
7. The mass volatilized in μg (column 8) for each droplet size class per liter of spray mix was calculated by multiplying the droplet size class surface area in column 6 by the volume sprayed (user input at the top of the spreadsheet) by the flux (user input) by the height sprayed (user input) by the fall rate in column 7. Volume sprayed was input in gallons, which was converted to liters by the spreadsheet for use in the calculations.

For the example flux calculation given in Table 4.2, the experimental mean flux of 107.8 $pg/cm^2 \cdot sec$ was selected. The height of the spray application was input as 12 m, and the volume of the spray application was set at 50 gallons. The model output using the listed parameters was 8.23 mg total mass active ingredient volatilized.

The model can be used for estimating downwind exposure of nontarget receptors to sprayed chemicals. Alternatively, for persistent pesticides, the model can be used to estimate the mass of sprayed chemical lost to volatilization during spray application for use in global dispersion models.

4.4 Project Objectives and Hypotheses

The objectives of this project and the associated hypotheses (Section 1.3) are discussed below. They are listed here in italics before the experimental findings for each.

Objective 1. *Develop a protocol for measurement of herbicide volatilization rates from aqueous Garlon® 4 emulsion droplets in airstreams of different temperatures and humidities.*

Result: The PVC was designed to simulate falling pesticide droplets in a temperature and humidity controlled environment and collect volatilized active ingredient on the column walls and in the PUF trap at the head of the column.

Objective 2. *Quantify the loss by evaporation of triclopyr ester from falling droplets of Garlon® 4 aqueous emulsions.*

Result: Volatilized pesticide was quantified by analyzing rinsate of the column walls and PUF extract. The methods for analyzing triclopyr ester in the rinsate, freezer vessel, and PUF were developed specifically for this experiment. The majority of experimental runs did not produce useable data due to droplet impact on the column walls (Tables 3.2 and 3.3). However, three of the runs produced results with no known bias. Therefore, it appears that the PVC can be used to quantify the evaporative flux of triclopyr ester from falling droplets of Garlon® 4 aqueous emulsions. Based on the method validation results, it appears that the methods developed for collecting and analyzing the samples were reasonably accurate and precise.

Objective 3: *Determine the effects of varying temperature and humidity on the volatilization rate of triclopyr ester from the falling droplets.*

Result: Only three experimental runs resulted in data useful for estimating the evaporative flux of triclopyr ester from falling droplets (Tables 3.2 and 3.3).

All of the experiments producing useful data were conducted at 35°C and 15 percent relative humidity. Therefore, the relationship between the evaporative flux of the pesticide and temperature or humidity could not be assessed from the available data.

Objective 4: *Evaluate the relationship between triclopyr ester volatilization and droplet time-of-flight.*

Result: The time-of-flight of the pesticide droplets in this experiment was estimated to be approximately 0.45 secs. When the time for the droplet to form and fall off the needle was added, the total exposure time was approximately 1.45 secs. Based on the total amount of pesticide volatilized in an experimental run and the number of droplets delivered to the system, the relationship between droplet time-of-flight and the evaporative flux of the pesticide can be estimated (Section 4.3).

Objective 5: *Determine the effect of varying droplet size on the volatilization rate of triclopyr ester.*

Result: Due to the problem of droplet impact on the column walls, only one droplet size class was evaluated in this experiment. However, the data from the successful runs can be used to make volatilization rate predictions based on droplet surface area, expressed as flux (Section 4.2).

Objective 6: *Develop a predictive model of triclopyr ester loss from droplets under different environmental conditions based on experimental data.*

Result: The data was collected from a single temperature/humidity regime; therefore, it was not useful for predicting triclopyr ester loss under differing conditions. However, temperature effects can be estimated using the STF model because temperature affects the Henry's Law constant of a chemical.

A compound's Henry's Law constant can also be expressed as the ratio of its vapor pressure P_v to its water solubility S:

$$H = \frac{P_v}{S} \qquad (44)$$

where P_v is in atm, S is in mol/m^3, and H is in atm-m^3/mol. Both vapor pressure and solubility are temperature dependent and can be estimated for organic compounds when empirical data are unavailable (Lyman, 1982).

Hypothesis 1: *Sufficient amounts of triclopyr ester volatilizes from falling droplets during aerial applications of Garlon® 4 to be of environmental consequence.*

Conclusion: The spreadsheet model was used to estimate the amount of triclopyr ester volatilized from a spray application of 50 gallons of 3 percent Garlon® 4 aqueous emulsion sprayed from 12 m at 50 mph wind speed using a D8-jet nozzle at 0 degrees azimuth (Table 4.2). The output is based on a number of assumptions and is probably conservative because it does not account for decreasing droplet size due to evaporation of the carrier. The estimated loss to volatilization of active ingredient is less than 8 mg, a not-surprisingly small amount given the low vapor pressure of triclopyr ester. However, during large spraying operations involving multiple applications, this quantity of chemical in the vapor phase could have a significant effect on non-target receptors, particularly under adverse meteorological conditions such as stable temperature inversions where little mixing of the atmosphere occurs. For other, longer-lived pesticides, evaporative loss during spraying operations may be a significant contributor to long range transport and global dispersion of these chemicals.

Hypothesis 2: *The volatilization rate of triclopyr ester from droplets is a function of air temperature during aerial spray applications.*

Conclusion: Due to the lack of useful experimental data at different temperatures, this hypothesis could not be evaluated. However, as mentioned previously, temperature affects a chemical's Henry's Law constant. If a given chemical's vapor pressure increase is greater than its increase in solubility with rising temperature, its Henry's Law constant would increase. Chemical diffusivities, which depend on Brownian motion, also increase with increasing temperature. Recalling Eq. 14 of the STF model shows that both terms would tend to increase with larger diffusivities and K_H, giving a greater flux:

$$F = \left(\frac{1}{(Z_w/D_w) + (Z_a/(D_a K'_H))} \right) \left(C_w - \frac{C_a}{K'_H} \right).$$

Therefore, the volatilization rate or flux of triclopyr ester would be expected to increase with increasing temperature.

Hypothesis 3: *The volatilization rate of triclopyr ester from droplets is not a function of humidity.*

Result: Due to the lack of experimental data at different humidities, this hypothesis could not be evaluated. Theoretically, however, humidity should have no effect on the loss of active ingredient from the spray droplet. Changes in humidity can affect the rate of loss of water from the droplet and thus the rate of change of droplet size. Since evaporative flux is a function of surface area, changes in humidity could thereby affect flux. The fall rate of a given droplet would also be affected, changing its exposure time. It is difficult to predict whether an increase in humidity would increase or decrease the evaporative flux of active ingredient as droplets would tend to stay larger (maintaining a higher surface area) and fall more rapidly

(decreasing exposure time). Data at differing humidities would prove useful in evaluating this question more fully.

Hypothesis 4: *The volatilization rate of triclopyr ester is a function of droplet diameter.*

Result: Due to the lack of experimental data for differing droplet sizes, this hypothesis could not be evaluated. However, data for three experiments conducted on droplets of approximately 2.0 μL were similar and an average flux was calculated. Because the droplet surface area is a function of the diameter and flux is a function of the surface area available for molecular transport, the volatilization rate can be correlated to droplet diameter (Section 4.2).

4.5 Sources of Experimental Error

Other than routine sources of experimental error associated with chemical analysis of pesticide residue samples, there are several sources of error unique to this experiment. They include the following:

1. As mentioned in Section 1.2.1, macroemulsions are inherently unstable. The length of time a given emulsion will maintain its structure as micelles depends on the chemical nature of the emulsion, its temperature, and the amount of energy input into the system by stirring. Once the herbicide used in this experiment left the stirred reservoir or the body of the pressure pump, it was no longer being stirred. At the very low liquid flow rates necessary to produce discrete droplets that would fall as evenly as possible off the needle tip, the residence time in the transfer lines sometimes exceeded the length of time the emulsion would remain stable. Thus, phase separation often occurred in the transfer lines. This caused two known problems with the experiment:

- Discrete droplets were not chemically equivalent. That is, some contained more aqueous phase and less oil, or vice versa. Thus, the exact quantity of triclopyr ester in a given droplet could not be predicted. The evaporative flux estimates from the data are therefore average values for all droplets produced in a given run.

- Droplets containing more aqueous phase and less oil have a higher surface tension than droplets composed mostly of oil. This contributed to droplet "shake" on the end of the needle. The higher the surface tension of the droplet, the more kinetic energy that was imparted to it when the droplet broke away from the adhesive forces holding it to the needle tip, and the greater distance towards the column walls the droplet would travel. The column used in this experiment was the widest commercially available at the time. Unfortunately the data produced in the majority of experiments was likely biased by droplets impacting the column walls. A great deal of time and effort was expended to remedy this problem; however, little could be done to eliminate droplet impact on the column walls. The only certain solution to the problem is to custom design a column of sufficient width to eliminate wall impacts.

2. Temperature and humidity control inside the column could be fairly tightly controlled. However, the instrumentation utilized for this experiment was accurate to only ±2.5 percent of actual conditions when properly calibrated. Thus, the actual conditions of a given experiment might have varied as much as 5 percent. This error, although likely to have only a slight effect on the data, should be kept in mind when the data is interpreted.

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