

DEVELOPMENT OF AN ENVIRONMENTAL FATE MODEL FOR RISK  
ASSESSMENT OF ULTRA-LOW-VOLUME INSECTICIDES

by

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## ABSTRACT

One of the most effective ways of managing adult mosquitoes that vector human and animal pathogens is the use of ultra-low-volume (ULV) insecticides. The U.S. Environmental Protection Agency uses models that are not validated for ULV insecticide applications and exposure assumptions to perform their human and ecological risk assessments. Currently, there is no validated model that can accurately predict deposition of insecticides applied using ULV technology for adult mosquito management. In addition, little is known about the deposition and drift of small droplets like those used under conditions encountered during ULV applications. The objectives of my dissertation were to perform field studies to measure environmental concentrations of insecticides and to develop a validated model to predict the deposition of ULV insecticides, and use the data generated from the field study to perform refined human and aquatic ecological risk assessments. To model the field data collected during the summers of 2009-2011 a regression model selected by the Bayesian Information Criterion and *k*-fold cross validation was used to validate the selected model. *k*-fold cross validation demonstrated that the mean square error and mean square prediction error were similar indicating good predictive ability. The human-health risk assessment demonstrated that previous risk assessments used conservative exposure scenarios that overestimated risks, thus being conservative in protecting human health. Our results demonstrated a 10-fold reduction in the RQ estimates when comparing risk assessments using estimated environmental concentrations and actual environmental concentrations from the environmental fate model. Because I used a large data set to model concentrations deposited on surfaces, this variance in exposure is due to the inherent variability in deposition concentrations after ULV applications and, therefore, would not warrant further refinement to improve risk assessments. The aquatic risk assessment using actual environmental concentrations showed that the 95<sup>th</sup> percentile estimated concentration would result in less than 0.0001% of the potentially affected fraction of species reaching their respective LC50. Our results are supported by the weight of evidence that pyrethroids applied by ground-based ULV applications will not result in deleterious effects on aquatic organisms.

## CHAPTER 1

## INTRODUCTION

Mosquitoes vector many important human and animal pathogens that cause diseases that continue to inflict high morbidity and mortality, and are an important cause of poverty and underdevelopment in many countries (van den Berg and Takken 2009). Some of these diseases include western, eastern, and Venezuelan equine encephalitis, St. Louis and Japanese encephalitis, malaria, human filariasis, yellow fever, Rift Valley fever, and dengue (Harwood and James 1979). The mosquito-borne pathogen garnering the most attention in the United States is West Nile virus (WNV).

Currently, WNV is the major cause of encephalitis in North America (Davis et al. 2008). West Nile virus has become endemic to North America since its introduction in 1999, and disease cases occur throughout the virus transmission season. Since the arrival of WNV, more areas of the country have experienced large-scale insecticide applications for mosquitoes. To effectively manage infection rates, morbidity, and mortality due to mosquito-borne pathogens like WNV, there must be a reduction in contact between infected mosquitoes and humans and animals (Marfin and Gubler 2001).

### Ultra-low-Volume Pesticide Applications and Spray Drift

One of the most effective ways of managing high densities of adult mosquitoes that vector human and animal pathogens is ultra-low-volume (ULV) aerosol applications

of insecticides (Mount 1998; Mount et al. 1996). Ultra-low-volume applications utilize small droplets from 5 to 25  $\mu\text{m}$ , which are the optimum size to impinge on and knock-down flying adult mosquitoes (Haile et al. 1982; Lofgren et al. 1973; Weidhaas et al. 1970). Ultra-low-volume-applications produce aerosol clouds of droplets that disperse throughout the target area (Figure 1). Currently in the U.S. ULV applications of insecticides are registered for black fly, gnat, and mosquito management.

There are many advantages to using ULV applications as opposed to non-thermal or thermal aerosol insecticides, which were traditionally diluted in fuel oil (Mount 1998). The advantages of ULV applications include lower cost, elimination of fuel oil, increased effective payload, rapid application, increased safety by the elimination of the dense fuel oil and pesticide fog, lowered environmental impact, and lower non-target impact (Mount 1998).

Ground-based ULV applications used for adult mosquito management are very different than agricultural pesticide applications because the nozzles produce an aerosol (droplets  $<100 \mu\text{m}$ ) and are pointed at a  $+45^\circ$  angle from the horizon. Ultra-low-volume applications used for adult mosquito management are most effective when the insecticide remains airborne and moves through the target area; in contrast, applications for agricultural pests are designed to minimize the movement of droplets (Hiscox et al. 2006). Thus, pesticide spray drift is defined as the physical movement of a pesticide through air at the time of application or soon thereafter, to any site other than that intended for the application (Craig et al. 1998; Gil et al. 2008).

Little is currently known about the deposition and drift of small droplets from both ground and aerial applications of insecticides (Teske et al. 2000). Insecticides used for mosquito management are designed and applied with special sprayer equipment, so they drift over the target area with very little settling out on surfaces. Currently, data from agricultural pesticide applications suggest that the most important factor affecting spray drift is droplet spectrum (Akesson and Yates 1964; Craig et al. 1998; Teske et al. 2002; Yates et al. 1967). Droplet spectra for ULV applications used during mosquito control operations use a volume median diameter (VMD) between 8 and 30  $\mu\text{m}$  ( $\text{VMD} < 30 \mu\text{m}$ ) and 90% of the droplet spectrum should be smaller than 50  $\mu\text{m}$  ( $\text{VMD} 0.9 < 50 \mu\text{m}$ ). The droplet spectrum used for mosquito management is well below those classified as American Society of Agricultural Engineers (ASAE) “very fine” to “fine” ( $\text{VMD} < 137 \mu\text{m}$ ), which is considered to be a high drift hazard (Hewitt 2008; Teske et al. 2000). Field experiments have shown that droplets greater than VMD of 140  $\mu\text{m}$  present a lower drift hazard than smaller droplets (Threadgill and Smith 1975). Droplets smaller than 50  $\mu\text{m}$  have very low settling velocities, and have similar transport characteristics to those of gaseous mixtures (Thistle 2000). Agricultural ULV applications to cotton increase drift by about 5- to 10-fold versus conventional agricultural application techniques (Bird et al. 1996; Wilson et al. 1986; Yates et al. 1967). However, the VMD used during ULV applications to cotton is generally 80 to 100  $\mu\text{m}$ , which is about 2-fold larger than the largest recommend spray droplet used for adult mosquito management (Woods et al. 2001). Modeling droplet spectra with the Agricultural Drift model (AgDrift<sup>®</sup>) has shown that going from ASAE “very fine” to “fine” to those used for mosquito adulticides could

result in a 5-fold increase in the magnitude of deposition at distances greater than 100 m assuming the same application rate (Teske et al. 2000).

Currently there is a lack of knowledge on what influences the deposition and movement of ULV applications, despite extensive study of agriculture spray drift. Researchers have found that spray drift is independent of the active ingredient properties (molecular weight, structure, etc.), but is dependent on environmental factors and formulation properties (Klein and Johnson 2002; Majewski and Capel 1995; Reichenberger et al. 2007; SDTF 2001). Drift of pesticides occurs through gravitational settling of droplets, downwind transport by wind currents, aircraft wake turbulence, and turbulent mixing of the atmosphere. Factors that have been shown to influence the drift of agricultural pesticide applications are droplet spectrum, mean wind speed, air temperature, wet bulb depression, dew point, relative humidity, atmosphere stability, distance from spray source, boom height, nozzle type, nozzle orientation, spray pressure, and driving or flying speed (Armstrong 1979; Bird 1995; Carlsen et al. 2006; Fritz 2006; Gil et al. 2008; Hewitt 2008; Hiscox et al. 2006; Kreutzweiser and Nicholson 2007; Nuyttens et al. 2006a, b; Nuyttens et al. 2005; Padovani and Capri 2005; Reichenberger et al. 2007; Salyani and Cromwell 1992; Teske et al. 2000; Threadgill and Smith 1975; Wang and Rautmann 2008). Water-based, and to a lesser extent oil-based, sprays are affected by evaporation which is influenced by the ambient air temperature, relative humidity, and wind speed (Teske et al. 2003; Teske et al. 1998). Aerosols have a greater surface area to volume and therefore it increases the effect of evaporation and or the absorption of water from the atmosphere (Hesketh 1977). Padovani and Capri (2005)



found that wind speed contributed the largest amount of variability to the deposition of insecticides when measuring in spray drift from agricultural applications. Although winds determine the horizontal travel of pesticides in the atmosphere, turbulent mixing is thought to determine the concentration of aerosols in a given air volume (Thistle 2000).

Atmospheric turbulence (also known as atmospheric stability) influences the dispersion of finer droplets through reducing mixing as the atmosphere becomes more stable (Thistle 2000). Atmospheric stability calculations are a means of characterizing atmospheric turbulence at the time of application (Chapter 2, Eq. 1). It is hypothesized that inversions lead to better deposition on the target site resulting in less drift during agricultural applications. An inversion (stable atmospheric turbulence) occurs when the temperature of the air near the ground is lower than that of the air just above it. Since the cooler air at ground level has a greater density than the warmer air above, there is minimal vertical air displacement and airflow is generally laminar with the layers passing smoothly over each other. Pesticide applications in such conditions tend to follow the airflow: therefore remaining close to the ground with deposition at ground level being dependent on the terminal velocity of the individual droplets and the velocity of the wind. The atmospheric condition opposite to inversion is known as lapse. During lapse, a negative vertical temperature gradient prevails that is caused by the heat at the surface of the ground. The warmer air at ground level tends to rise, which causes vertical displacement of the air resulting in atmospheric turbulence.

Currently there is contradictory evidence on how atmospheric stability and inversions influence agricultural spray drift. There have been several studies that indicate

that stable atmospheric conditions increase the drift of agricultural sprays (Bird 1995; Bird et al. 1996; Miller et al. 2000; Yates et al. 1966, 1967). However, Yates et al. (1966) found that as atmospheric stability ratio increased (decreasing atmospheric stability), drift deposit increased and was greater at farther distances for aerial applications. Threadgill and Smith (1975) found that as the atmospheric stability increased, drift decreased when examining ground-based agricultural ULV applications on cotton. Unstable conditions (inversions) are atmosphere states that have the lowest atmospheric mixing and thus can result in the largest amount of drift (Fritz 2006; Thistle 2000).

Sensitivity analysis of the Agricultural Dispersion model (AGDISP) used for aerial applications showed that release height, spraying speed, wind direction, and wind speed contributed the most variability to the model outputs (Teske and Barry 1993). Bode et al. (1977) conducted a series of tests showing that wind speed influenced drift more than atmospheric stability in neutral and unstable conditions. Field studies conducted by Fritz (2006) showed that atmospheric stability did not significantly influence the drift of pesticides, however increased wind speeds resulted in increases in deposition at farther distances from the sprayer.

Current evidence shows that wind speed dominates deposition of pesticides in the near field (downwind distances less than 300 m where larger droplets are deposited by gravitational forces), while atmospheric stability is more important in the far field (downwind distances greater than 300 m where smaller droplets deposit) (Miller et al. 2000). Hoffmann and Salyani (1996) showed that downwind ground deposition was

greater for nighttime applications versus daytime applications, most likely because the most stable atmospheric conditions occur at night.

### Aerosol Movement

The behavior of aerosol particles, droplets between 0.001 and 100  $\mu\text{m}$ , like those used in ULV applications, is strongly dependent on droplet size (Baron and Willeke 2001a). The transport and deposition of aerosols in the environment is due to gravity, diffusion, inertia, and electrostatic mechanisms (Baron and Willeke 2001a, b). Although aerosol particles follow the overall gas flow, the trajectories can deviate due to external forces such as temperature and relative humidity as well as changes in wind direction and velocity (Baron and Willeke 2001b).

The density of a formulation affects how particles gravitationally settle out of the air (Baron and Willeke 2001a; Hinds 1982). The aerodynamic diameter is used to characterize aerosol particles that move by settling by incorporating both gravity and drag. The aerodynamic diameter standardizes the size of droplet based on the density of a standard-density ( $1 \text{ g/cm}^3$ ) sphere having a gravitational settling velocity as the particle being measured (Baron and Willeke 2001a). The aerodynamic diameter is determined by,

$$d_a = d_p \left( \frac{\rho_p}{\rho_0} \right)^{1/2} \quad (1)$$

where  $d_a$  is the aerodynamic diameter ( $\mu\text{m}$ ),  $d_p$  is the diameter of the measured particle ( $\mu\text{m}$ ),  $\rho_p$  is the density of measured particle, and  $\rho_0$  is the standard particle density ( $1 \text{ g/cm}^3$ ) (Baron and Willeke 2001a).

The forces acting on a settling particle are gravity and drag, which influences the particle's velocity at any instant. The aerodynamic diameter therefore influences the terminal settling velocity for of a droplet of a given size. The terminal settling velocity for a droplet of a given size is,

$$V_{TS} = 0.003(d_a)^2 \quad (2)$$

where  $V_{TS}$  is the terminal settling velocity in cm/s for particles measuring  $1 < \text{diameter} < 100 \mu\text{m}$  and  $d_a$  is the aerodynamic diameter of the particle ( $\mu\text{m}$ ) (Hinds 1982). The terminal settling velocity ignores the acceleration of the particle and only considers the balance between drag and gravity (Hinds 1982). The particle relation time (the time a particle takes to reach its final velocity in a gravitational field) is short for aerosols, so it can be neglected for most applications in aerosol physics (Baron and Willeke 2001b).

### Fluorescent Tracers

Fluorescent tracers have been used since the early 1950's for rapidly estimating spray deposition of insecticides (Davis and Elliott 1953). Traditional analytical techniques to quantify spray drift by using gas or liquid chromatography is cost prohibitive, involves extensive sample cleanup, can have low instrument sensitivity, and background contamination with residues already present in the environment (Akesson and Yates 1964). The advantages of fluorescent tracers include high sensitivities, rapid

quantification, solubility in spray mixtures, distinctive properties that are different from background substances, low cost, and low toxicity (Sharp 1974; Yates and Akesson 1963).

Experiments have shown that the addition of fluorescent tracers do not alter the formulation of the pesticide (Schleier III et al. 2010). Many studies have used fluorescent tracers to estimate the concentrations of pesticides in agricultural spray drift tests (Barber and Parkin 2003; Cadogan et al. 2005; Cai and Stark 1997; Cooke and Hislop 1993; Davis and Elliott 1953; Longley et al. 1997; Parkin and Merritt 1988; Peng et al. 2005; Pergher 2001; Sharp 1974, 1976; Staniland 1959; Sundaram and Sundaram 1992; Yates and Akesson 1963). Tracer selection is based on the following desirable characteristics: high sensitivity in the instrument, rapid extraction and quantification, solubility in the spray mixture (oil- or water-based) with minimal effects on physical characteristics of the droplets, stable under environmental conditions, and differentiation from background contaminants (Akesson and Yates 1964; Yates and Akesson 1963; Yuill and Secrest 1966a; Yuill and Secrest 1966b). The best fluorescent tracers based on the above characteristics are fluorescein, rhodamine B, rhodamine WT, uvitex OB (also known as tinopal OB), and brilliant sulfaflavine (Cai and Stark 1997; Cooke and Hislop 1993; Duan et al. 1994; Gil et al. 2008; Miller et al. 1992; Pergher 2001; Yates and Akesson 1963). The addition of tracers has been found not to change the deposition of the insecticide (Sundaram et al. 1996). Tracers do not change the droplet distribution, density, or viscosity of ULV formulations (Schleier III et al. 2010).

Fluorescent tracers have practical limitations such as photo and storage degradation. In addition pH also affects the fluorescent strength of tracers (Hall et al. 1992; Zhu et al. 2005). Light stability can greatly affect agricultural drift tests, but this is not a limitation for mosquito operations because the insecticides are applied at night or dusk and all samples are collected before daylight.

Fluorescent tracers are mixed at lower concentrations than the active ingredient (A.I.) of the formulation. After measuring the tracer in the samples, a correction factor (adjustment for the ratio of tracer to A.I.) is applied to the tracer concentration to determine the amount of insecticide present. For terrestrial deposition studies, mylar, filter papers, Petri dishes, and tin foil targets have been shown to be the most efficient sampler type for fluorescent spray drift based on degradation and extraction rates of the fluorescent materials (Dabrowski et al. 2005; Glass 2006; Pergher 2001; Preftakes et al. 2011).

To measure the concentration of fluorescent material, fluorometers expose a sample to a light source and, as it absorbs light, it fluoresces (excitation wavelength) at a longer wave length (emission wavelength) (Goering and Butler 1974; Speelman 1971). The emission filter further screens the light, and the light emitted by the tracer is measured by the detector (photomultiplier tube), and the fluorescence value is displayed on the instrument. The fluorescence value provides a measurement that is proportional to a known concentration standard, which produces quantitative measurements (Goering and Butler 1974). Thus, if the concentration of the fluorescent material is known, then the

insecticide concentration can be estimated by applying a conversion factor that corrects for the proportion of fluorescent material to insecticide present in the formulation.

### Environmental Fate and Deposition Studies

There have been few studies examining the movement and deposition of ULV applications used for adult mosquito management. Tucker et al. (1987) examined the effects of 91% malathion and 85% naled sprayed via aerial and ground-based ULV applications on copepods and juvenile fish in coastal areas. They measured the amount of insecticide deposited on boat docks to determine the amount deposited on the surface of the water. The concentrations of malathion and naled on the ground after ground-based ULV applications were 0.0793 and 0.0573  $\mu\text{g}/\text{cm}^2$  12 min after application, respectively. Water concentrations of naled after ground-based ULV applications peaked at 0.71  $\mu\text{g}/\text{l}$  about 15 minutes after spraying, but were not detectable after 9 h. No significant mortality of copepods and juvenile fish after ground-based ULV applications of malathion or naled.

For aerial applications, Tucker et al. (1987) observed concentrations of malathion and naled in the water at 5 and 20.15  $\mu\text{g}/\text{L}$ , respectively. The amount of malathion deposited on the ground 24 to 36 min after aerial ULV application was 0.381 and 0.492  $\mu\text{g}/\text{cm}^2$ , respectively.

Hennessey et al. (1992) measured terrestrial concentrations of naled at 1.5 and 6 h after post aerial ULV applications within and outside of a theoretical spray zone. The

researchers measured concentrations within the spray zone at 15, 30, and 90 m from the spray path. Concentrations ranged from 0.011 to 0.005  $\mu\text{g}/\text{cm}^2$  1.5 h post application, and at 6 h post application concentrations ranged from 0.003 to 0.007  $\mu\text{g}/\text{cm}^2$ . Outside of the theoretical spray zone, they measured concentrations at 15, 30, 90, 150, and 750 m downwind, and observed concentrations ranging from non-detectable (ND) to 0.009  $\mu\text{g}/\text{cm}^2$  1.5 h post application, and concentrations ranging from 0.004 to 0.0005  $\mu\text{g}/\text{cm}^2$  6 h post application.

Moore et al. (1993) determined the amount of malathion deposited on human targets, and at ground level at different distances. There were no significant concentration differences found in the ground-level patches at 15.2, 30.4, and 91.2 m downwind of the spray head when sprayed at 58.5 g/ha. Malathion deposition on filter paper ranged from 0.0059 to 0.075  $\mu\text{g}/\text{cm}^2$  which is 1 to 14% of the insecticide sprayed, assuming an even amount of coverage over a 100 m swath width. The amount deposited on the masks of stationary human subjects was not significantly different from a jogger running in the spray path. The amount deposited on the backs of the stationary human targets was significantly less than the front of the targets.

Knepper et al. (1996) quantified the amount of malathion and permethrin deposition on sod grass after ULV application in a suburban neighborhood in Michigan. Blocks of sod were placed at 7.6, 15.2, 30.4, and 91.4 m from the edge of the road. Malathion was detected on 19 of 32 blocks and permethrin was detected on 20 of 32 blocks. The detection of both insecticides was greatest 15 minutes post treatment at a distance of 7.6 m. The concentrations of malathion deposited ranged from ND to 9.22



$\mu\text{g}/\text{cm}^2$ . The concentration of permethrin deposited ranged from ND to  $14.3 \mu\text{g}/\text{cm}^2$ .

Regression analyses showed that residues at 7.6 m declined as a function of time.

Detection of the insecticides also declined as a negative exponential function of distance from the road.

Tietze et al. (1994) investigated deposition patterns of malathion at 5, 25, 100, and 500 m from the spray truck. The mass of malathion deposited decreased with distance from the spray source. The amount of malathion deposited at 500 m was significantly less than at 5, 25, and 100 m. The amount measured on the ground ranged from 0.3 to 3.8% of the insecticide sprayed. Average deposition at the distances listed above was 0.022, 0.017, 0.016, and  $0.002 \mu\text{g}/\text{cm}^2$ , respectively.

Tietze et al. (1996) investigated deposition rates of ground-based ULV malathion around houses, and assessed the impact on non-target species. The house cricket (*Acheta domesticus* (L.)) was used as an indicator to determine spray distribution. The concentration of malathion ranged from 0.03 to  $0.089 \mu\text{g}/\text{cm}^2$  with deposition decreasing as distance from the spray head increased. Malathion deposition did not differ significantly between the front yard, side of house, behind the house, and the back yard. Cricket mortality ranged from 5.4 to 8.9 % and also decreased as distance from the spray head increased. Stepwise regression indicated that the crickets were a good indicator of spray deposition. Amounts that were collected in the peridomestic environment were greater than those collected in the open field study done by Tietze et al. (1994). Discrepancies may have been associated with the equipment because two different

sprayers were used, or possibly because the spray truck had to slow down because of traffic.

Pierce et al. (2005) investigated deposition rates and water concentrations of permethrin sprayed via ground-based ULV and water concentrations of naled sprayed via aerial ULV in the Florida Keys National Marine Sanctuary. Deposition concentrations of permethrin 12 h post application ranged from 0.00005 to 0.005  $\mu\text{g}/\text{cm}^2$  and water concentrations ranged from 5.1 to 9.1  $\mu\text{g}/\text{L}$ . Naled water concentrations ranged from 0.1 to 0.6  $\mu\text{g}/\text{L}$  14 h after application. Distances from the spray source were not reported.

Jensen et al. (1999) found non-detectable (ND) concentrations of pyrethrins and permethrin in water sample from wetlands before and after ground-based ULV. Weston et al. (2006) examined water concentrations of pyrethrins and PBO 10 h after the second aerial ULV application of mosquito insecticides and 34 h after the third aerial ULV application of mosquito insecticides over Sacramento, CA. They observed concentrations of 0.44 to 3.92  $\mu\text{g}/\text{L}$  of PBO, but did not detect pyrethrins. Lothrop et al. (2007) measured concentrations of pyrethrins and PBO directly under the airplane through to 300 m from the flight path, to maximize efficacy while minimizing evaporation of the insecticide in a desert environment. They observed concentrations of pyrethrins ranging from ND to 0.0791  $\mu\text{g}/\text{cm}^2$ , and for PBO they observed concentrations ranging from ND to 1.07  $\mu\text{g}/\text{cm}^2$ . The researchers observed very low mortality of caged mosquitoes with an average mortality ranging from only 1.5 to 12% 1 h after application.

Schleier et al. (2008b) measured concentrations of pyrethrins and PBO deposited on the ground and in water after aerial application. There were no measurable

concentrations of pyrethrins found in either sample media. One hour after the spray event, the average ground deposition concentrations of PBO ranged from 0.0125 to 0.0199  $\mu\text{g}/\text{cm}^2$  and concentrations in the water ranged from 0.1723 to 1.274  $\mu\text{g}/\text{L}$ . Concentrations deposited on the ground decreased significantly by 36 h after application, and concentrations in the water returned to background levels by 36 h.

Concentrations of PBO in Suffolk County, New York were detected in 33% of water samples taken with concentrations ranging from ND to 59.8  $\mu\text{g}/\text{L}$  and resmethrin was detected in 11% of water samples taken with concentrations ranging from ND to 0.293  $\mu\text{g}/\text{L}$ . Concentrations of resmethrin and PBO become ND by four days after helicopter or ground-based ULV applications (Abbene et al. 2005). Zulkosky et al. (2005) measured concentrations of resmethrin ranging from ND to 0.98  $\mu\text{g}/\text{L}$  and concentrations of PBO ranging from ND to 15  $\mu\text{g}/\text{L}$  1 h after ground-based ULV application. Phenothrin was ND in all samples taken during the study (Zulkosky et al. 2005).

Schleier III and Peterson (2010) measured concentrations of permethrin and naled after ground-based ULV applications. One hour after application concentrations of permethrin on cotton dosimeters 25, 50, and 75 m from the spray source ranged from 0.0009 to 0.005  $\mu\text{g}/\text{cm}^2$ . Concentrations one hour after applications of naled 25, 50, and 75 m from the spray source ranged from 0.0009 to 0.005  $\mu\text{g}/\text{cm}^2$ . Deposition concentrations 12 h after application were not significantly different than 1 h after application for both permethrin and naled. Permethrin air concentrations ranged from 0.375 to 0.397  $\mu\text{g}/\text{m}^3$  1 h after application. Permethrin air concentrations ranged from 2.3

to  $4 \mu\text{g}/\text{m}^3$  1 h after application. There were no quantifiable air concentrations between 1 and 12 h after application in either 2007 or 2008 for both naled and permethrin. These results suggest that the insecticides moved rapidly through the sample collectors and that air exposures after ULV application may be limited to within 1 h.

The environmental fate studies that have been conducted to date have found that the amount of malathion and permethrin deposition and droplet abundance decreased with distance from the point of origin for ground-based ULV application. Malathion, permethrin, pyrethrins, PBO, and naled all rapidly degrade in the environment with residues becoming ND 9 to 72 h post application. In general, the amount of insecticide that was deposited on the ground within 200 m of the spray source was 1.4 to 30% of the insecticide sprayed. Some studies were pseudo-replicated since the treatments were not applied separately through space, time, distance, or as combinations of the three. Also, many of these studies did not obtain samples before the application of ULV insecticides to determine levels of these insecticides already present in the environment.

### Risk Assessments and Biomonitoring

Human-health and ecological risks can be described in quantitative terms as a function of toxicity and exposure (NRC 1983). Toxicity is determined by a series of studies, and from lethal concentration that kills 50% of a population (LC50) and no-observable-adverse-effect-levels (NOAEL) are chosen and represent acute and chronic toxic effects. Exposure is coming into contact with, ingesting, or inhaling the chemical of interest. Risk assessment typically utilizes a tiered approach extending from deterministic

models (Tier 1), which are based on extremely conservative assumptions, to field evaluation and probabilistic models (Tier 4), which use refined assumptions (SETAC 1994). Risk assessments use conservative assumptions in lower-tier assessments which represent overestimates of toxicity and exposure, with resulting deterministic and quantitative risk values typically being conservative and erring on the side of safety. Tier 4 risk assessments use refinements like experimentally derived environmental concentrations and probabilistic techniques to estimate exposures.

In environmental and human health risk assessments of pesticides, the risk quotient (RQ) is a method to quantitatively express risk (Peterson 2006). Risk quotients are calculated by dividing the potential exposure by its toxic endpoint value depending on whether the endpoint is oral, inhalation, or dermal. Risk quotients are compared to a level of concern (LOC) which is set by U.S. Environmental Protection Agency (USEPA) to determine if regulatory action is needed. If an RQ breaches a regulatory LOC at a lower tier, then risk managers decide to either restrict the product use or progress to higher tier risk assessments or to field-verified models (USEPA 2006g).

There has been greater public attention to the human-health and environmental risks associated with ULV insecticide applications since more areas of the country have been experiencing large-scale insecticide applications for WNV (Peterson et al. 2006; Reisen and Brault 2007; Roche 2002; Thier 2001). In response to concerns about the safety of ULV applications of insecticides, tier I/II (reasonable worst case) risk assessments have been performed to quantify estimates of risk. Peterson et al. (2006) performed a deterministic human-health risk assessment for acute and sub-chronic

exposures to six mosquito insecticide active ingredients, and the synergist PBO, after ground-based ULV applications. They found that the acute and subchronic risks to humans from the insecticides most likely would result in negligible risk.

Schleier III et al. (2009b) performed a probabilistic two-dimensional risk assessment of the same insecticides and population groups of Peterson et al. (2006). The probabilistic analysis showed that Peterson et al. (2006) overestimated risk by about 10-fold. The results of Schleier III et al. (2009b) supported the findings of Peterson et al. (2006) that the risks to humans from mosquito adulticides are most likely negligible. Sensitivity analysis performed by Schleier III et al. (2009b) showed that air concentrations and dermal exposure contributed the most to the model output variance.

Davis et al. (2007) conducted a deterministic ecological risk assessment and examined the same mosquito insecticides and synergist as Peterson et al. (2006) using a tier I/II assessment and found that the risks to mammals, birds, and aquatic vertebrates and invertebrates most likely are negligible after ground-based ULV applications.

Schleier III et al. (2008a) examined deterministically and probabilistically the six mosquito insecticides and the synergist as well, and found similar results, demonstrating that the equine risks from ground-based ULV applications are very low. The probabilistic analysis of Schleier III et al. (2008a) demonstrated that the deterministic analysis was sufficiently conservative, with deterministic exposures between the 85<sup>th</sup> to 95<sup>th</sup> percentile of exposures.

Macedo et al. (2007) determined that the risks to military personnel exposed to ground-based ULV applications of permethrin, resmethrin, phenothrin, or PBO are most

likely negligible. Schleier III et al. (2009a) estimated the acute and subchronic risks from resmethrin, malathion, PBO, and pyrethrins applied via ground-based ULV applications for sand fly control at Tallil Air Base, Iraq. We found that the risks from ground-based ULV applications were below the USEPA LOC. Schleier III et al. (2009a) sensitivity analysis showed that air concentrations and deposition on surfaces contributed the largest amount of variance to the output which is similar to the results of other risk assessments (Schleier III 2008; Schleier III et al. 2009b). Carr Jr. et al. (2006) found that aerial ULV applications of resmethrin above agricultural fields as a result of a public health emergency would most likely result in negligible human dietary risk. Schleier III et al. (2008b) performed a risk assessment for aquatic organisms using actual environmental concentrations after aerial ULV applications of pyrethrins and PBO. We found that the risks did not exceed the USEPA LOC for endangered aquatic organisms.

Schleier III (2008) performed a probabilistic human-health risk assessment on permethrin and naled using actual environmental concentrations that were measured in the field. Median RQs for permethrin and naled were below those calculated by previous risk assessments. Sensitivity analysis demonstrated that deposition of insecticides on surfaces contributed the largest variance to the exposure. Schleier III (2008) demonstrated that previous risk assessments used conservative exposure scenarios that overestimated risks, thus were conservative in protecting human health (Peterson et al. 2006; Schleier III et al. 2009b).

Currier et al. (2005) found no statistical differences in naled, permethrin, and phenothrin urinary metabolites in humans from areas that were treated with ground-based

ULV applications and non-treated areas at application rates of 0.045, 0.002, and 0.004 kg/ha, respectively. Kutz and Strassman (1977) and Duprey et al. (2008) demonstrated that aerial spraying of naled did not result in increased levels of naled urinary metabolites in humans. Both studies found that there were detectable levels of organophosphate metabolites before and after the aerial spraying in similar proportions. In addition to risk assessments and biomonitoring studies published in journals, epidemiological studies, reports, and regulatory assessments have concluded that risks to humans and non-target organisms from exposure to mosquito insecticides most likely are negligible (Karpati et al. 2004; NYCDOH 2005; O'Sullivan et al. 2005; Suffolk County 2006). Therefore, the current weight of evidence demonstrates that ULV insecticide exposures and risks are most likely below a regulatory LOC.

Valcke et al. (2008) and Gosselin et al. (2008) performed a probabilistic human-health risk assessment on malathion applied by ground-based and aerial ULV. They found that deposition on surfaces was the largest source of exposure for all groups assessed. In contrast to previous risk assessments, their exposure model suggested that exposure to malathion from truck-mounted and aerial ULV applications could exceed the EPA's LOC. This could be, in part, explained by the fact that they took into account the exposure to malaaxon, the primary degradation product of malathion. In addition, they found that the risks from aerial applications are greater than ground-based applications. They used AGDISP to model concentrations deposited on the ground and in the air and found concentrations were greater after aerial applications than after ground-based ULV applications, which contradict the findings of other studies (NYCDOH 2005; Schleier III



2008; Schleier III et al. 2008b). In addition to contradicting the findings of previous risk assessments and environmental fate studies, their results are not supported by biomonitoring studies which have shown no increase in urinary metabolites after ULV applications.

#### Models Used to Estimate Environmental Concentrations of Mosquito Adulticides

Models are used as tools to help explain natural processes and for predicting outcomes and behaviors in settings where empirical observations may not be available or may be impractical (Holmes et al. 2009). Model estimates and subsequent risk assessments can become the basis for a decisions making process, such as limiting the use of an insecticide (Beck et al. 1997). Without an accurate method of estimating the environmental concentrations of pesticides, researchers cannot make predictions or even reasonable assumptions about the impact of pesticides on environmental and human health (Teske et al. 1995).

The USEPA and other regulatory agencies use models to support evaluations of anthropogenic agents during the decision making process. Currently there is no model in use that has been validated or verified as an accurate means of estimating concentrations of insecticides after either ground-based or aerial ULV applications. In addition the registration documents for all of the insecticides currently used for the control of adult mosquitoes use different models and assumptions to assess risks (USEPA 2002b, 2006a, b, c, d, e, f).

To estimate the risk of malathion and naled applied by ground-based ULV to adults the USEPA uses two exposure routes, dermal and inhalation. However, for toddlers the exposures routes are dermal, incidental oral from hand-to-mouth and object-to-mouth from residues deposited on turf, and incidental ingestion of soil from treated areas (USEPA 2002b, 2005a, 2006c). In contrast, the USEPA only takes into account inhalation exposure when assessing the risk from ground-based ULV applications of permethrin, resmethrin, and pyrethrins for both adults and toddlers (USEPA 2006b, e, f). For estimating the risks from aerial applications, the USEPA used AgDrift to estimate environmental concentrations in the air and deposition on turf for malathion, but they used AGDISP to estimate the same parameters for permethrin, resmethrin, and pyrethrins (USEPA 2005a, 2006b, e, f).

The lack of knowledge with respect to the fate of ULV insecticides is reflected by the use of several different models to estimate environmental concentrations of insecticides. To predict deposition and air concentrations, previous risk assessments and environmental impact statements have used Industrial Source Complex Short Term version 3 (ISCST3) and American Environmental Regulatory Model (AERMOD), which are industrial plume models, and AGDISP and AgDrift which are designed for agricultural pesticide applications (Davis et al. 2007; Gosselin et al. 2008; Macedo et al. 2007; NYCDOH 2005; Peterson et al. 2006; Schleier III et al. 2009a; Schleier III et al. 2008a; Schleier III et al. 2009b; Valcke et al. 2008).

Gaussian plume and puff models are the basis for the above models which are the most commonly used algorithms for regulation of anthropogenic pollutants (Baetens et al.

2009; Sharan and Modani 2006; Sharan et al. 1996). These models can be used to understand the movement of pesticides in the environment and provide a useful first approximation. However, their validity for a wide range of environmental and technical parameters that are not covered by the original experimental setup has not been demonstrated (Baetens et al. 2009; Craig 2004; Smith et al. 2000). Risk assessments have used these models to estimate deposition within 50 m of the spray source, which is one major limitation of Gaussian models because they provide inaccurate estimations of deposition within that distance (Craig 2004).

The ISCST3 and AERMOD models were used to estimate the deposition and air concentrations of insecticides after ULV applications (Davis et al. 2007; Macedo et al. 2007; Peterson et al. 2006; Schleier III et al. 2009a; Schleier III et al. 2009b). The regulatory model, ISCST3, was used by the USEPA for new source review and other air permitting applications from industrial smoke stacks. However, it has since been replaced by AERMOD (USEPA 2003, 2005c, 2009a). The ISCST3 and AERMOD models are based on a steady-state Gaussian plume algorithm, and are applicable for estimating ambient impacts from point, area, and volume sources out to a distance of about 50 km. Both ISCST3 and AERMOD include algorithms for addressing building downwash influences, dry and wet deposition, and also incorporate the complex terrain screening algorithms (USEPA 1995, 2003). Both ISCST3 and AERMOD were sufficiently conservative models for conducting lower tiered risk assessments (Davis et al. 2007; Macedo et al. 2007; Peterson et al. 2006; Schleier III et al. 2009b), and overestimated

environmental concentrations by as much as 16-fold when compared to actual environmental concentrations (Schleier III 2008).

### AGDISP and AgDrift Models

For agricultural and forest health sprays the industry standard for calculating spray drift and deposition has been AGDISP and AgDrift (Bilanin et al. 1989; Teske et al. 2002). Both models use Gaussian diffusion algorithms as a simple estimation of the downwind distribution of droplets dispersing and settling from an aircraft (Craig et al. 1998; Sharan and Modani 2006). More complicated models like AGDISP and AgDrift utilize a lagrangian approach in addition to the Gaussian diffusion algorithms to calculate the swath pattern produced by the aircraft (Craig et al. 1998; Craig 2004).

AGDISP has been validated as an accurate means of estimating the drift of pesticides after aerial agricultural applications, but there has been no attempt to validate it for ground-based sprayers (Baetens et al. 2009; Bilanin et al. 1989; Duan et al. 1992b; Teske and Barry 1993). Additionally, there has been little work done on validating or calibrating other Gaussian models for the estimation of spray drift from ground-based sprayers (Baetens et al. 2009). The Spray Drift Task force later incorporated the algorithms of AGDISP into the model AgDrift with some modifications to the equations (Teske et al. 2002). AgDrift is a model used to estimate deposition of pesticides downwind in a spray block, and has been validated as accurate means of estimating the aerial agricultural spray drift pesticides, but like AGDISP there has been no attempt to validate it for ground-based applications (Bird et al. 2002; Teske et al. 2002).

To demonstrate the limitations of AGDISP and AgDrift, Schleier III (2008) used the model assumptions of Mickle et al. (2005) and Schleier et al. (2008a) to estimate concentrations 25 m from the spray source for permethrin and naled. Actual concentrations of permethrin and naled were estimated in the field 8 and 12 times greater than what AgDrift estimated (Schleier III 2008). Mickle et al. (2005) found that AGDISP accurately estimated deposition of malathion sprayed from ground-based ULV, however they performed no statistical analysis to support their findings. In addition Mickle et al. (2005) used a 400 m shift in the model results, which is an extrapolation of the model because it not has been validated for far-field estimations of pesticide drift (drift greater than 300 m) (Bilanin et al. 1989; Duan et al. 1992b). In addition, all of the AGDISP validation literature is for agricultural spray applications which use much larger droplet spectrums, and the use of smaller droplet spectrums in the model is also an extrapolation (Bilanin et al. 1989; Bird et al. 2002; Duan et al. 1992a; Duan et al. 1992b; Mickle et al. 2005; Teske and Barry 1993). Actual concentrations of permethrin and naled were estimated in the field 6 and 4 times greater than what AGDISP estimated at 25 m using the assumptions outlined by Mickle et al. (2005), and weather conditions and application rate for the sprays in 2007 and 2008 (Schleier III 2008).

AGDISP and AgDrift have never been calibrated or validated for ground-based applications of pesticides or with the droplet spectrums used during adult mosquito management. Therefore the use of either model is an extrapolation which should be interpreted with caution. Droplets smaller than 50  $\mu\text{m}$  have very low settling velocities, and have similar transport characteristics to those of gaseous mixtures which behave

much different than coarse droplet sizes used for agricultural applications (Miller et al. 1992; Thistle 2000). Modeling droplet spectra with AgDrift have shown going from ASAE very fine to fine to those used for mosquito adulticides could result in a 5-fold increase in the magnitude of deposition at distances greater than 50 m (Teske et al. 2000), but these results have never been verified. AgDrift and AGDISP are designed to model high boom, agricultural sprays where the nozzles are facing toward the ground, which is considerably different than ULV applications as outlined above.

Schleier III (2008) revealed that the primary uncertainty in the estimated risks were associated with environmental concentrations and fate of the insecticides. The environmental concentrations of permethrin and naled largely are determined by environmental conditions. Furthermore, Schleier III (2008) found that current models used by USEPA are not accurate and could be underestimating environmental concentrations of pesticides by as much as 12-fold.

### Objectives

Current environmental models for pesticides and other anthropogenic agents are not appropriate for modeling pesticide fate when applied via ULV application techniques. This includes the USEPA models, ISCST3 and AERMOD, and the pesticide drift models, AGDISP and AgDrift, which are not accurate in predicting deposition after ULV applications (Schleier III 2008; Schleier III et al. 2008b). In addition, previous risk assessments for ground-based ULV applications demonstrated the deposition and fate of

the insecticides contributed the most variance to the exposure of humans and ecological receptors.

Therefore, the first objective of my dissertation was to perform field studies to measure actual environmental concentrations of insecticides and use that data to develop a validated environmental fate model specific to ground-based ULV applications.

Because we used fluorescent tracers to measure the concentration of the insecticides we also wanted to determine if the tracers influences the droplet spectrum, density, and viscosity of the formulations which could adversely affect the movement of the aerosol.

The second objective of my dissertation research was to use the data generated to perform risk assessments for both human and aquatic organisms after ULV applications of permethrin.

## CHAPTER 2

AN ENVIRONMENTAL FATE MODEL FOR ULTRA-LOW-VOLUME  
INSECTICIDE APPLICATIONS USED FOR ADULT MOSQUITO MANAGEMENTAbstract

One of the more effective ways of managing high densities of adult mosquitoes that vector human and animal pathogens is ultra-low-volume (ULV) aerosol applications of insecticides. The U.S. Environmental Protection Agency uses models that are not validated for ULV insecticide applications and exposure assumptions to perform their human and ecological risk assessments. Currently, there is no validated model that can accurately predict deposition of insecticides applied using ULV technology for adult mosquito management. In addition, little is known about the deposition and drift of small droplets like those used under conditions encountered during ULV applications. The objective of this study was to perform field studies to measure environmental concentrations of insecticides and to develop a validated model to predict the deposition of ULV insecticides. A regression model selected by the Bayesian information criterion and  $k$ -fold cross validation was used to validate the selected model. Density of the formulation and the density and CMD interaction coefficients were the largest in the model. The results showed that as density of the formulation decreases, deposition increases. The interaction of density and CMD shows that greater density formulations and larger droplets result in greater deposition. These results are supported by the aerosol



physics literature. A  $k$ -fold cross validation demonstrated that the mean square error of the selected regression model is not biased, and the mean square error and mean square prediction error indicated good predictive ability.

### Introduction

West Nile virus (WNV) has now become endemic to North America and disease cases occur throughout the virus transmission season. Since the arrival of WNV, more areas of the country have been experiencing large-scale insecticide applications for mosquito-borne pathogens like WNV. To effectively manage infection rates, morbidity, and mortality due to mosquito-borne pathogens like WNV, there must be a reduction in contact between infected mosquitoes and humans and other virus-impacted animals (Marfin and Gubler 2001).

One of the more effective ways of managing high densities of adult mosquitoes that vector human and animal pathogens is ultra-low-volume (ULV) aerosol applications of insecticides (Mount 1998; Mount et al. 1996). Ultra-low-volume applications utilize small droplets from 5 to 25  $\mu\text{m}$ , which are the optimum size to impinge on and knock down flying adult mosquitoes (Haile et al. 1982; Lofgren et al. 1973; Weidhaas et al. 1970).

Ground-based ULV applications used for adult mosquito management are very different than agricultural pesticide applications because the nozzles produce an aerosol (droplets  $<100 \mu\text{m}$ ) and are pointed at a  $+45^\circ$  angle from the horizon. Ultra-low-volume applications used for adult mosquito management are most effective when the insecticide

remains airborne and moves through the target area; in contrast, applications for agricultural pests are designed to minimize the movement of droplets (Hiscox et al. 2006). Droplet spectra for ULV applications used during adult mosquito control operations have a volume median diameter (VMD) between 8 and 30  $\mu\text{m}$  ( $\text{VMD} < 30 \mu\text{m}$ ) and 90% of the droplet spectrum should be smaller than 50  $\mu\text{m}$  ( $\text{VMD} 0.9 < 50 \mu\text{m}$ ). The droplet spectrum used for adult mosquito management is well below those classified as “very fine” to “fine” ( $\text{VMD} < 137 \mu\text{m}$ ) by the American Society of Agricultural Engineers, which is considered to be a high drift hazard (Hewitt 2008; Teske et al. 2000).

Little is currently known about the deposition and drift of small droplets such as those used during ULV applications for adult mosquito management (Teske et al. 2000). Droplets smaller than 50  $\mu\text{m}$  have very low settling velocities, and have similar transport characteristics to those of gaseous mixtures (Thistle 2000). Currently, there is no validated model that can accurately predict deposition of insecticides applied using ULV technology for adult mosquito management.

Computer models of pesticide drift are widely used tools by regulatory agencies for predicting the deposition of spray particles beyond the intended target area (Felsot et al. 2011). The U.S. Environmental Protection Agency use different models and assumptions to assess the risks of ULV insecticides (USEPA 2002b, 2006a, b, c, d, e, f). Previous risk and regulatory assessments have used models like ISCST3 (<http://www.epa.gov/scram001/tt22.htm#screen>), AgDrift<sup>®</sup> (Stewart Agricultural Research Services, Macon, MO, USA) (Teske et al. 2002), and AGDISP (<http://www.continuum-dynamics.com/pr-agdisp.html>) (Bilanin et al. 1989) to estimate

environmental concentrations of insecticides (Davis et al. 2007; Macedo et al. 2007; Peterson et al. 2006; Schleier III et al. 2009a; Schleier III et al. 2008a; Schleier III et al. 2009b; USEPA 2008). The ISCST3, AERMOD, AgDrift, and AGDISP models use steady-state Gaussian plume algorithm, and are applicable for estimating ambient impacts from point, area, and volume sources with coarse droplet sizes and applications that are 10 to 100 m above ground level. Schleier III and Peterson (2010) demonstrated that ISCST3 over-estimates ULV insecticide deposition concentrations while AgDrift and AGDISP under-estimate concentrations.

There have been no studies that have systematically examined the fate of pesticide aerosols like those used for ULV applications. A reliable model that can predict environmental concentrations of ULV insecticides is needed because previous probabilistic risk assessments have shown that the deposition of the insecticide contributes the largest amount of variance to the estimated exposure (Schleier III et al. 2009a; Schleier III et al. 2009b). In addition, a model is needed because of the limited amount of knowledge about which environmental and physicochemical factors have the largest effect on the movement of pesticide aerosols.

Because of public concerns about the safety of adulticides used for the control of adult mosquitoes (Peterson et al. 2006; Roche 2002; Thier 2001), the lack of actual environmental concentration data (Schleier III and Peterson 2010), and uncertainties associated with the fate of the ULV insecticides, we conducted environmental fate studies during the summers of 2009 to 2011 in California, Montana, and Louisiana to generate a validated model of ULV insecticide deposition.

### Materials and Methods

Ground-based ULV field experiments were conducted near Elk Grove, California (38°27'17.27"N, 121°27'9.25"W), Bozeman, Montana (45°38'47.09"N, 111°24'8.18"W), and Baton Rouge, Louisiana (30°31'1.57"N, 91° 9'20.32"W) during the summers of 2009 to 2011. Sites with little vegetative structure and a flat topography were chosen for all experiments because vegetation affects air movement and subsequent deposition of insecticides and we were interested in high depositions for conservative estimates of exposure. Sites were 200-m long with two lines of horizontal drift collectors positioned 25 m to the left and right of the center of the plot to capture any variability of deposition within the spray plot (Figure 1). Because the two lines of deposition samplers are subsamples they were averaged together at each distance from the spray source for statistical analysis. During each spray event, 11 receptors on the two sampling lines were placed in the field at different distances from the spray source (Figure 1). Sampling occurred at distances of 5, 10, 15, 20, 30, 35, 40, 50, 60, 65, 70, 75, 80, 90, 95, 100, 110, 120, 125, 130, 135, 140, 155, 160, and 180 m from the spray source.

During all applications, the truck speed was 16.1 km/h. Applications occurred when the prevailing wind was blowing perpendicular to the collection site (Figure 1). Sprays were conducted using a Guardian 95 ES (ADAPCO, Sanford, FL, USA) in Montana and a London Fogger model 18 (London Fog Inc., Long Lake, MN, USA) in California and Louisiana. Nozzle orientation of the sprayers was +45° angle compared to the horizon which is the most commonly used angle for mosquito management. Between each spray replication the nozzle, pump, and hoses were rinsed with 300 ml of D.I. H<sub>2</sub>O

followed by 300 ml of a 1:1 mixture of high pressure liquid chromatography acetone (99.7% purity; EMD Chemicals, Gibbstown, NJ, USA) and American Chemical Society (ACS) grade toluene (99.5% purity, Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA) (Schleier III et al. 2010).

The oil-based insecticides Permanone<sup>®</sup> 30-30 (30% permethrin), Scourge<sup>®</sup> 18+54 (18% resmethrin), Permanone<sup>®</sup> 31-66 (31% permethrin) (Bayer Environmental Science, Research Triangle Park, NC, USA), Zenivex<sup>®</sup> E20 (20% etofenprox) (Central Life Sciences<sup>®</sup>, Schaumburg, IL, USA), and Pyronyl<sup>™</sup> Crop Spray (6% pyrethrins) (Prentiss Inc., Alpharetta, GA, USA) were used. The water-based formulations Aqua-Reslin<sup>®</sup> (20% permethrin) (Bayer Environmental Science, Research Triangle Park, NC, USA) and Aqua-Kontrol (20% permethrin) (Univar<sup>®</sup>, Redmond, WA, USA) were used. The active ingredients were applied at the maximum rate of 7.85 g/ha of active ingredient according to label for all insecticides, except for Pyronyl Crop Spray which was applied at the maximum rate of 2.8 g/ha of active ingredient.

Between June 21 and 26, 2009 a total of nine and eight sprays of Aqua-Reslin and Permanone 31-66 occurred in California, respectively. Aqua-Reslin was mixed 1:1.5 with deionized (D.I.) H<sub>2</sub>O and applied at the flow rate of 240 ml/min. Permanone 31-66 was mixed 1:0.25 with ACS grade toluene and applied at a flow rate of 74 ml/min.

Between July 16 and August 5, 2009, a total of 13, 12, and four sprays of Aqua-Reslin, Permanone 30-30, and Scourge 18+54 occurred in Montana, respectively. Aqua-Reslin was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. Permanone 30-30 was mixed 1:2:1 with Crystal Plus 70T light mineral oil (STE Oil Company, Inc.,

San Marcos, TX, USA) and ACS grade toluene and applied at a flow rate of 192 ml/min. Scourge 18+54 was mixed at 1:0.4:0.4 with Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min.

Between June 7 and 22, 2010 a total of seven sprays of Aqua-Reslin and Pyronyl Crop Spray occurred in California, respectively. Aqua-Reslin was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. Pyronyl Crop Spray was mixed at 1:0.2 with ACS grade toluene and applied at a flow rate of 163 ml/min.

Between July 19 and August 12, 2010, a total of eight, seven, two, seven, and six sprays of Aqua-Reslin, Permanone 30-30, Scourge 18+54, Zenivex E20, and Aqua-Kontrol occurred in Montana, respectively. Aqua-Reslin was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. Permanone 30-30 was mixed 1:2:1 with Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min. Scourge 18+54 mixed at 1:0.4:0.4 to Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min. Zenivex E20 was mixed 1:0.4:0.4 with Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min. Aqua-Kontrol was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. A total of 13, 12, and four sprays of Aqua-Reslin, Permanone 30-30, Scourge 18+54, Zenivex E20, and Aqua-Kontrol occurred, respectively.

Between July 17 and 28, 2011, a total of two and five sprays of Aqua-Reslin and Permanone 30-30 occurred in Louisiana, respectively. Aqua-Reslin was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. Permanone 30-30 was mixed 1:2:1

with Crystal Plus 70T light mineral oil and ACS grade toluene and was applied at a flow rate of 192 ml/min.

Between July 19 and August 12, 2011, a total of two, two, one, and four sprays of Aqua-Reslin, Permanone 30-30, Permanone 31-66, Zenivex E20 occurred in Montana, respectively. Aqua-Reslin was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. Permanone 30-30 was mixed 1:2:1 with Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min. Permanone 31-66 mixed 1:2.25:1 to Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min. Zenivex E20 was mixed 1:0.4:0.4 with Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min.

The experimental design was completely randomized with each formulation randomly selected for the order it was sprayed. Replications were performed over time within the same night and over different nights with a total of 96 spray events occurring during the three field seasons. Applications began no earlier than 18:00 h at all locations, but most applications occurred after 20:00 h.

Collection of deposition at ground level was with 15-cm diameter glass Petri dishes (Sundaram et al. 1987). Cardboard was staked to the ground to provide a level surface for the glass Petri dishes. One glass Petri dish was placed on each piece of cardboard at ground level and collected 10 minutes after the application. Fluorescent tracers were used to determine the concentrations of insecticide and have been commonly used in agricultural spray drift tests (Barber and Parkin 2003; Cadogan et al. 2005; Cai and Stark 1997; Cooke and Hislop 1993; Davis and Elliott 1953; Longley et al. 1997;

Parkin and Merritt 1988; Peng et al. 2005; Pergher 2001; Sharp 1974, 1976; Staniland 1959; Sundaram and Sundaram 1992; Yates and Akesson 1963). The oil-soluble tracer Tinopal OB (BASF Corp., Florham Park, NJ, USA) was mixed with all oil-based formulations at a rate of 11 g/L and the water-soluble tracer Fluorescein (Aqua Solutions, Deer Park, TX, USA) was mixed with all water-based formulations at a rate of 14 g/L. Previous research has shown that the addition of fluorescent tracers to ULV pesticide formulations does not alter the density, viscosity, or droplet spectrum of ULV insecticides (Schleier III et al. 2010). For all applications, a maximum of 1-L of formulation was mixed with the tracer in a Nalgene 1-L narrow mouth high density polyethylene bottle (Fischer Scientific, Pittsburgh, PA, USA) to ensure that the tracer was adequately mixed into the formulation.

Petri dishes were extracted with 15 ml of toluene or D.I. H<sub>2</sub>O for Tinopal OB and Fluorescence, respectively. The liquid was decanted into analysis vials which were wiped with KimWipes (Kimberly-Clark<sup>®</sup> Global Sales, LLC, Roswell, GA, USA) to remove fingerprints and dry the vials before analysis. After extraction, Petri dishes were rinsed with toluene or D.I. H<sub>2</sub>O depending on the tracer used then rinsed with high pressure liquid chromatography acetone.

A GFL-1A fluorometer (Opti-Sciences, Inc., Hudson, NH, USA) was used to detect the amount of light absorbed at a specific wavelength which represented the amount of tracer present in the sample. For the detection of Fluorescence, the source filter was 465 nm and the detection filter was 530 nm. For the detection of Tinopal OB, the source filter was 370 nm and the detection filter was 430 nm. Standard curves were



prepared using serial dilutions prepared in toluene and D.I. H<sub>2</sub>O for Tinopal OB and fluorescence, respectively. Absorbance was recorded for each sample representing the concentration of the insecticide. The detection limit for Tinopal OB and Fluorescence is 0.00012 and 0.000015  $\mu\text{g}/\text{cm}^2$ , respectively. Therefore the detection limit for water- and oil-based insecticides was 0.00076 and 0.0002  $\mu\text{g}/\text{cm}^2$ , respectively. For non-detectable (ND) concentrations in the data, I substituted half of the detection limit because the number of NDs was less than 10% of the data points (Lubin et al. 2004).

On August 4, 2010 in Montana we sprayed Aqua-Reslin and Permanone 30-30 three consecutive times over the collectors to determine if our technique was correctly measuring the fluorescent tracers. The three sprays were applied back-to-back-to-back by spraying the 200-m block turning the truck around and spraying the site again using the same application parameters used during 2010 listed above. These results demonstrated that the concentration of the tracers was three times greater than a single spray in similar environmental conditions.

A DC-III portable droplet measurement system (KLD Labs, Inc., Huntington Station, NY, USA) was used to measure droplet spectra of each formulation at all locations. The DC-III probe was held 2 m from the nozzle in the center of the spray plume and sampling was terminated at 15 seconds or when 10,000 droplets were sampled (Schleier III et al. 2010). Two subsamples were taken for each spray formulation and combined. Distributions were fit using MATLAB<sup>®</sup> R2010a distribution fitting tool to determine the count median diameter (CMD;  $\mu\text{m}$ ) and the volume median diameter (VMD;  $\mu\text{m}$ ) using the Hatch-Choate conversion equations (Cooper 2001; Hinds 1982).

Distributions for droplet spectra were determined based on the chi-square goodness of fit test, which tests if a sample of data came from a population with a specified distribution (Cooper 2001; Hinds 1982; Neter et al. 1996). The log-normal distribution fit all spectra obtained, which is consistent with previous studies of droplet distributions for ULV sprays and aerosols other than ULV (Hinds 1982; Schleier III et al. 2010). Volume and count median diameters by year, location, and formulation mixture are listed in table 1.

Wind speed, air temperature, wet-bulb depression, and relative humidity were measured with a Hobo Micro Station Data Logger (Onset Computer Corporation, Bourne, MA) attached to 12-bit temperature and relative humidity sensors with a solar radiation shield and a wind speed and direction smart sensor positioned 2.5 m above the ground. Temperature and relative humidity readings were also taken 10 m above the ground using a Hobo temperature and relative humidity data logger (Model H08-032-08, Onset Computer Corporation, Bourne, MA). Meteorological measurements were taken upwind of the spray site. Wind speed, wet bulb depression, temperature, and relative humidity at both 2.5 and 10 m above the ground were averaged over a 5 minute interval.

Temperature readings taken 2.5 and 10 m and the mean wind speed at 2.5 m above the ground was used to calculate the stability ratio. The stability ratio is defined as:

$$SR = \frac{T_{10} - T_{2.5}}{\mu_w} \times 10^5 \quad (1)$$

where SR is the stability ratio,  $T_{10}$  and  $T_{2.5}$  is air temperature ( $^{\circ}\text{C}$ ) at 10 and 2.5 m respectively and  $\mu_w$  is the mean wind velocity (cm/s) at 2.5 m (Armstrong 1979; Yates et al. 1981). A stable atmospheric condition (termed an inversion) is defined as a warm air layer overlying a cold air layer. An unstable atmosphere condition (termed a lapse) is

defined as a cold air layer overlying a warm air layer. For model development, atmospheric stability was categorized into four categories as defined by Yates et al. (1981) (Table 2). A categorical variable was used to simplify the model inputs and because the continuous stability ratio variable did not substantially increase the predictive ability of the selected model.

Formulation density was determined by averaging the weight of five 1 ml samples of each formulation on a calibrated Mettler AM100 analytical balance (Mettler Toledo AG, Switzerland). The density of Aqua-Reslin mixed 1:1 with D.I. H<sub>2</sub>O, Aqua-Reslin mixed 1:0.75 with D.I. H<sub>2</sub>O, Aqua-Reslin mixed 1:1.5 with D.I. H<sub>2</sub>O, Permanone 30-30, Permanone 31-66, Scourge, Aqua-Kontrol, Zenivex E20, and Pyronyl Crop Spray was 0.99, 0.99, 1.02, 0.88, 1.01, 0.93, 1.02, 0.88, and 0.89 g/L, respectively.

Linear regression analysis and analysis of variance (ANOVA) were run using R Statistical Package version 2.12.2 (The R Foundation for Statistical Computing, Vienna, Austria). Diagnostic plots of the selected model showed that concentrations required log transformation to meet the assumptions of normality and constant variance. Correlation analysis between predictor variables was assessed, and correlation values greater than 0.5 were excluded because collinearity inflates the standard errors. Variables that were excluded were temperate and relative humidity measured at 10 m above the ground, wet bulb depression, and dew point was correlated with 2.5 m above the ground temperature and relative humidity.

Linear regression variables that were incorporated into the model were wind speed (cm/s), air temperature (°C), relative humidity (%), stability category, distance

from spray source (m), application rate (g/L), flow rate (ml/min), density (g/ml), CMD ( $\mu\text{m}$ ), and VMD ( $\mu\text{m}$ ). Interactions were allowed based on aerosol physics and included: distance \* CMD, distance \* density, distance \* wind speed, distance \* temperature, distance \* relative humidity, distance \* stability category, distance \* CMD, distance \* VMD, distance \* flow rate, density \* CMD, density \* VMD, density \* wind speed, density \* stability category, CMD \* wind speed, CMD \* temperature, CMD \* relative humidity, CMD \* stability category, CMD \* VMD, VMD \* wind speed, VMD \* temperature, VMD \* relative humidity, VMD \* stability category, wind speed \* temperature, wind speed \* relative humidity, wind speed \* stability category, temperature \* relative humidity. These interactions were included because they indirectly take into account variables that cannot be directly measured. For example the temperature \* relative humidity can indirectly estimate the effects evaporation. In addition, multicollinearity with interactions variables does not affect the predictive ability of multiple linear regression models (Neter et al. 1996).

Model selection was performed using the Bayesian information criterion (BIC) with the R library MASS because of the higher penalization for the number of coefficients which is appropriate for large sample sizes (Hastie et al. 2009). Analysis of variance was performed to determine if there were significant differences in mean concentrations between years and location ( $\alpha = 0.05$ ). Extra sums of squares *F*-test was carried out to determine if there is a reduction in the error sums of squares between the model selected with BIC and the full model with all interactions listed above ( $\alpha = 0.05$ ).

In addition, we performed extra sums of squares  $F$ -test to determine if adding location to the selected model would reduce the error sums of squares.

Model validation and estimation of mean square prediction error was performed using  $k$ -fold cross validation using the R library DAAG.  $k$ -fold cross validation was used because it reduces the bias associated with other model validation techniques (Olson and Delen 2008).  $k$ -fold works by splitting the complete data set into  $k$  mutually exclusive subsets of approximately equal size with the model being trained  $k$  times and compared to the held out set of data (Olson and Delen 2008). The data were split into 10 data sets ( $k$ ), which is the most commonly used number of data sets for  $k$ -fold cross validation (Olson and Delen 2008).

### Results

A total of 1,067 data points were used over the three years for the linear regression model and ANOVA. Analysis of variance showed that there was no significant effect of year ( $F = 1.72, p = 0.19$ ), but there were significant differences in concentrations measured between Montana, California, and Louisiana ( $F = 11.18, p = 0.0009$ ). However, the extra sums of squares  $F$ -test showed that adding location to the model selected with BIC did not significantly reduce the error sums of squares ( $F = 0.37, p = 0.54$ ) and location was not a significant coefficient within the selected model ( $t = -0.89, p = 0.38$ ). In addition, figure 2 shows significant overlap for the three locations and demonstrates that the significant difference may be due to outliers and the larger number of samples and the greater variety of formulations in Montana. Therefore, because there was no difference

between years, and location did not significantly improve the selected model we pooled all of the data together to use the largest data set for generating the predictive model so that it has the largest range of environmental and application scenarios (Table 3).

The selected model variables by the BIC algorithm along with coefficient estimates and standard errors are listed in table 4. The extra sums of squares  $F$ -test showed the selected model with BIC was not different from the full model with all interactions ( $F=1.01, p=0.43$ ) indicating that the model is parsimonious and fits as well as the full model. Diagnostic plots for the selected model demonstrate that there were no significant outliers and the residuals were consistent with the assumption of normality (Figure 5). The selected model adjusted  $R^2$  is 0.4 and the model BIC estimate was -140. The full model with all interactions has an adjusted  $R^2$  of 0.42 and BIC estimate of 2919. The regression model mean square error was 0.904 which was similar to the average mean square prediction error of 1.24 (range of mean square prediction errors was 1 - 1.4 for the 10 folds) estimated by the  $k$ -fold cross validation, indicating that the selected regression model was not seriously biased, with both measures show good predictive ability (Figure 7) (Neter et al. 1996).

The regression model that was selected is,

$$\begin{aligned}
 C = & -3.71 + 0.008 * D - 1.15 * AR - 0.005 * FR - 24.57 * DEN + 3.95 * \\
 & CMD + 1.13 * VMD - 0.014 * WS + 0.34 * T + 0.15 * RH + 1.44 * SC - \\
 & 0.007(D * CMD) - 0.00002(D * WS) + 18.95 (DEN * CMD) - 0.007(DEN * WS) - \\
 & 1.66(DEN * SC) - 0.16(CMD * T) - 0.064(CMD * RH) - 0.32 (CMD * SC) - \\
 & 0.78(CMD * VMD) - 0.004(VMD * T) + 0.034(VMD * SC) + 0.001(WS * T) + \\
 & 0.0001(WS * RH) + 0.0004(WS * SC) - \\
 & 0.003(T * RH)
 \end{aligned} \tag{2}$$

where C is the log of the concentration ( $\mu\text{g}/\text{cm}^2$ ), WS is wind speed (cm/s), T is temperature ( $^{\circ}\text{C}$ ), RH is relative humidity (%), SC is stability category, D is distance from spray source (m), AR is application rate (g/L), FR is flow rate (ml/min), DEN is density (g/ml), CMD is count median diameter ( $\mu\text{m}$ ), and VMD is volume median diameter ( $\mu\text{m}$ ).

Figure 4 shows the estimated prediction line and the 95% prediction interval using equation 2 for the log of concentration ( $\mu\text{g}/\text{cm}^2$ ) using application rate, flow rate, density, count median diameter, volume median diameter, wind speed, temperature, relative humidity, and stability category of 7.85, 192, 0.996, 2.2, 19.76, 215.06, 24.86, 29.68, 1, respectively. The input parameters represent the explanatory factors for the data points from one trial randomly selected from the entire data set to demonstrate the predictive ability of the model. Figure 4 demonstrates that the predictive accuracy of the model is good with all data points falling between the 95% prediction interval. The model is robust with respect to a wide range of applications (flow rate, density of formulation etc.) and environmental explanatory factors used for its development (Table 3). In addition, because we grouped over years and locations it shows the model is robust with respect to different environments and explanatory factors.

Density of the formulation and the density and CMD interaction coefficients were the largest in the model (Table 4). The results showed that as density of the formulation decreases, deposition increases. A 0.1 g/ml decrease in density results in a 2.46 times greater concentration over all distances when all other variables are held constant. This is most likely because greater density formulations have greater deposition within 75 m of

the spray source while lower density formulations have greater deposition beyond 75 m. Schleier III and Peterson (2010) observed the same pattern with an increase in concentration between 25 and 50 m and a subsequent decrease in the concentration. Therefore because we fit a linear model to the data it resulted in a negative density coefficient. Larger CMD results in greater deposition of the insecticide. The interaction of density and CMD shows that greater density formulations and larger droplets result in greater deposition.

Distance did not have a large influence on the deposition of ULV insecticides, which is most likely due to the large number of droplets between 1 and 10  $\mu\text{m}$  which have low settling velocities and therefore settle out uniformly across the spray area. However, figure 4 shows that the model predicts decreasing concentrations of insecticide with increasing distance from the spray source. Higher temperatures and relative humidity lead to greater deposition most likely because these conditions lead to less dense air allowing the droplets to settle out faster (Davis 1992). Higher wind speeds resulted in lower deposition of ULV insecticides because higher wind speeds push the aerosol through the spray area allowing less to settle out. Stable atmospheric conditions resulted in greater deposition than unstable conditions. During unstable atmospheric conditions thermal currents from the warmer ground keep the aerosol in the air column longer thus leading to lower deposition of the insecticides.



## Discussion

Previous studies of ground-based ULV applications using both pyrethroid and organophosphate insecticides have found 1 to 30% of the insecticide sprayed deposits on the ground within 100 m of the spray source (Knepper et al. 1996; Moore et al. 1993; Schleier III and Peterson 2010; Tietze et al. 1994). We observed an average of 10.4% (SE = 0.4%) of the insecticides sprayed settled out within 180 m of the spray source. Concentrations of insecticide measured in the present study are similar to concentrations measured by previous studies that used gas chromatography to quantify concentrations (Knepper et al. 1996; Moore et al. 1993; Schleier III and Peterson 2010; Tietze et al. 1994).

The transport and deposition of aerosols in the environment is due to gravity, diffusion, inertia, and electrostatic mechanisms (Baron and Willeke 2001a, b). Although aerosol particles follow the overall wind direction, the trajectories can deviate due to external forces such as wind direction and velocity (Baron and Willeke 2001b). The density of a formulation affects how particles gravitationally settle out of the air column (Baron and Willeke 2001a; Hinds 1982). To describe the gravitational settling of aerosols, the aerodynamic diameter is used to characterize particles that move primarily by settling as opposed to diffusion in still air (Hinds 1982). The aerodynamic diameter therefore characterizes the terminal settling velocity of a droplet of a given size which determines the distance a droplet travels. Therefore, the settling velocity modeled by the CMD and density interaction confirms the distance a droplet travels is significantly influenced by the settling velocity of the droplets.

A statistical approach to modeling aerosols like those used for ULV applications is more appropriate for model development than physics based modeling techniques because of the difficulties in estimating the evaporation of droplets within the aerosol cloud and the large spectrum of droplet sizes produced within the cloud (Teske et al. 2003). Physics based models for pesticide drift use wet-bulb depression to estimate droplet evaporation (Teske et al. 2003). We excluded wet-bulb depression from the model because it is highly correlated with both temperature and relative humidity. This is because temperature and relative humidity are used to determine the wet-bulb depression. However, our statistical approach allows the model to indirectly take into account the evaporation of droplets through temperature and relative humidity and the interaction term, thus overcoming the complexities of droplet evaporation within the spray cloud.

Studies of agricultural spray drift have found that the deposition of insecticides is independent of the active ingredient properties (molecular weight, structure, etc.), but is dependent on environmental factors and formulation properties (Klein and Johnson 2002; Majewski and Capel 1995; Reichenberger et al. 2007; SDTF 2001). Our results similarly showed significant overlap of concentrations for each formulation used (Figure 5); therefore, the model developed can be applied to classes of insecticides other than pyrethroids.

The model can also be used to estimate bystander exposure because Preftakes et al. (2011) observed similar concentrations of permethrin depositing on manikins within the spray zone using the formulations Aqua-Reslin and Permanone 30-30 at the application rates, flow rates, droplet spectrum, and dilutions that were used in the current

study. In addition to human-health risk assessment, the model can be applied to ecological risk assessment including exposure to aquatic organisms. Therefore, the model can be used by regulatory agencies and researchers to standardize their estimation of human-health and ecological exposures associated with ULV technology.

We have created a validated model for predicting deposition concentrations of insecticides applied with ground-based ULV technology for adult mosquito management using, to our knowledge, the largest data set yet generated to develop and validate a spray drift model. The under or over prediction by the models ISCST3, AgDrift, and AGDISP is because they were designed for larger droplets which settle out closer to the spray source. Because of the inherent differences between coarse and fine droplet sizes, these models are not appropriate for ULV applications because smaller droplets travel farther from the spray source. The model that we developed is robust with respect to environmental and application scenarios and demonstrates a good predictive performance. The model coefficients of the selected model reported here are supported by the aerosol physics literature showing that the density of the formulation and diameter of the droplets are the most important determinants of the movement and subsequent deposition of ULV insecticides. Because the model has been validated and is specific to ULV applications used for mosquito management, regulatory agencies such as the USEPA could use it to improve and standardize their risk assessments for registration and re-registration of relevant insecticides.

The model may be useful for mosquito control districts to mitigate risk because they are now required to obtain National Pollutant Discharge Elimination System permits

for insecticide applications which require the monitoring of insecticide concentrations in aquatic environments. The model can be used to predict concentrations in water bodies and can allow users to predict when the greatest amount of deposition will occur, thus allowing them to determine if applications should occur.

Table 1. Volume median diameter (VMD), count median diameter (CMD), and number of each formulations and number of replications for each year, location, and formulation

Year	Location	Formulation	VMD ( $\mu\text{m}$ )	CMD ( $\mu\text{m}$ )	Number of Replications
2009	California	Aqua-Reslin	21.3	1.3	9
2009	California	Permanone 31-66	24.56	1.36	8
2009	Montana	Aqua-Reslin	21.19	2.2	13
2009	Montana	Permanone 30-30	18.72	2.3	12
2009	Montana	Scourge	11.63	1.43	4
2010	California	Aqua-Reslin	22.56	1.75	7
2010	California	Pyronyl Crop Spray	31.3	2.1	7
2010	Montana	Aqua-Reslin	19.76	1.25	8
2010	Montana	Permanone 30-30	13.4	1.3	7
2010	Montana	Zenivex E20	13.96	1.3	7
2010	Montana	Aqua-Kontrol	24.75	1.2	6
2010	Montana	Scourge	12.37	1.25	2
2011	Louisiana	Aqua-Reslin	6.99	1.19	2
2011	Louisiana	Permanone 30-30	8.79	1.24	5
2011	Montana	Permanone 31-66	20.8	1.57	1
2011	Montana	Permanone 30-30	16.1	1.43	2
2011	Montana	Zenivex E20	12.6	1.47	4
2011	Montana	Aqua-Reslin	22.95	1.36	2

Table 2. Atmospheric turbulence, stability ratio calculation as defined by equation 1, as defined by Yates et al. (1981), and the linear regression category

Atmospheric Turbulence	Stability Ratio (SR)	Linear Regression Category
Unstable	-1.7 to -0.1	1
Neutral	-0.1 to 0.1	2
Stable	0.1 to 1.2	3
Very Stable	1.2 to 7.0	4

Table 3. Minimum and maximum values for explanatory variables used for model selection

Response	Minimum	Maximum
Distance (m)	5	180
Application Rate (g/L)	2.8	7.85
Flow Rate (ml/min)	74	240
Density (g/ml)	0.88	1.02
CMD ( $\mu\text{m}$ )	1.19	2.3
VMD ( $\mu\text{m}$ )	6.99	31.3
Wind Speed (cm/s)	31.76	1267.24
Temperature ( $^{\circ}\text{C}$ )	13.94	32.17
Relative Humidity (%)	13.06	77.97
Stability Category	1	4

Table 4. Coefficients, coefficient estimates, standard error of the coefficient estimates (SE),  $t$ -values, and  $p$ -values for the selected model using the Bayesian Information Criterion

Coefficients:	Coefficient Estimate	SE	$t$ -value	$p$ -value
Intercept	-3.71	3.71	-1.0	0.32
Distance	0.008	0.003	3.01	0.003
Application Rate	-1.15	0.18	-6.45	< 0.0001
Flow Rate	-0.005	0.001	-5.46	< 0.0001
Density	-24.57	4.73	-5.2	< 0.0001
CMD <sup>a</sup>	3.95	1.59	2.48	0.013
VMD <sup>b</sup>	1.13	0.13	8.54	< 0.0001
Wind Speed	-0.014	0.004	-3.7	< 0.0001
Temperature	0.34	0.058	5.79	< 0.0001
Relative Humidity	0.15	0.026	5.57	< 0.0001
Stability Category	1.44	0.63	2.3	0.022
Distance * CMD	-0.007	0.001	-5.09	< 0.0001
Distance * Wind Speed	-0.00002	0.000004	-3.67	0.0003
Density * CMD	18.95	2.64	7.18	< 0.0001
Density * Wind Speed	-0.007	0.003	-2.11	0.035
Density * Stability Category	-1.66	0.65	-2.58	0.010
CMD * Temperature	-0.16	0.031	-5.06	< 0.0001
CMD * Relative Humidity	-0.064	0.009	-6.89	< 0.0001
CMD * Stability Category	-0.32	0.10	-3.11	0.002
CMD * VMD	-0.78	0.088	-8.78	< 0.0001
VMD * Temperature	-0.004	0.002	-2.38	0.018
VMD * Stability Category	0.034	0.007	4.73	< 0.0001
Wind Speed * Temperature	0.001	0.0001	8.28	< 0.0001
Wind Speed * Relative Humidity	0.0001	0.00002	7.90	< 0.0001
Wind Speed * Stability Category	0.0004	0.0002	2.03	< 0.0001
Temperature * Relative Humidity	-0.003	0.001	-3.83	< 0.0001

<sup>a</sup> CMD is count median diameter

<sup>b</sup> VMD is volume median diameter

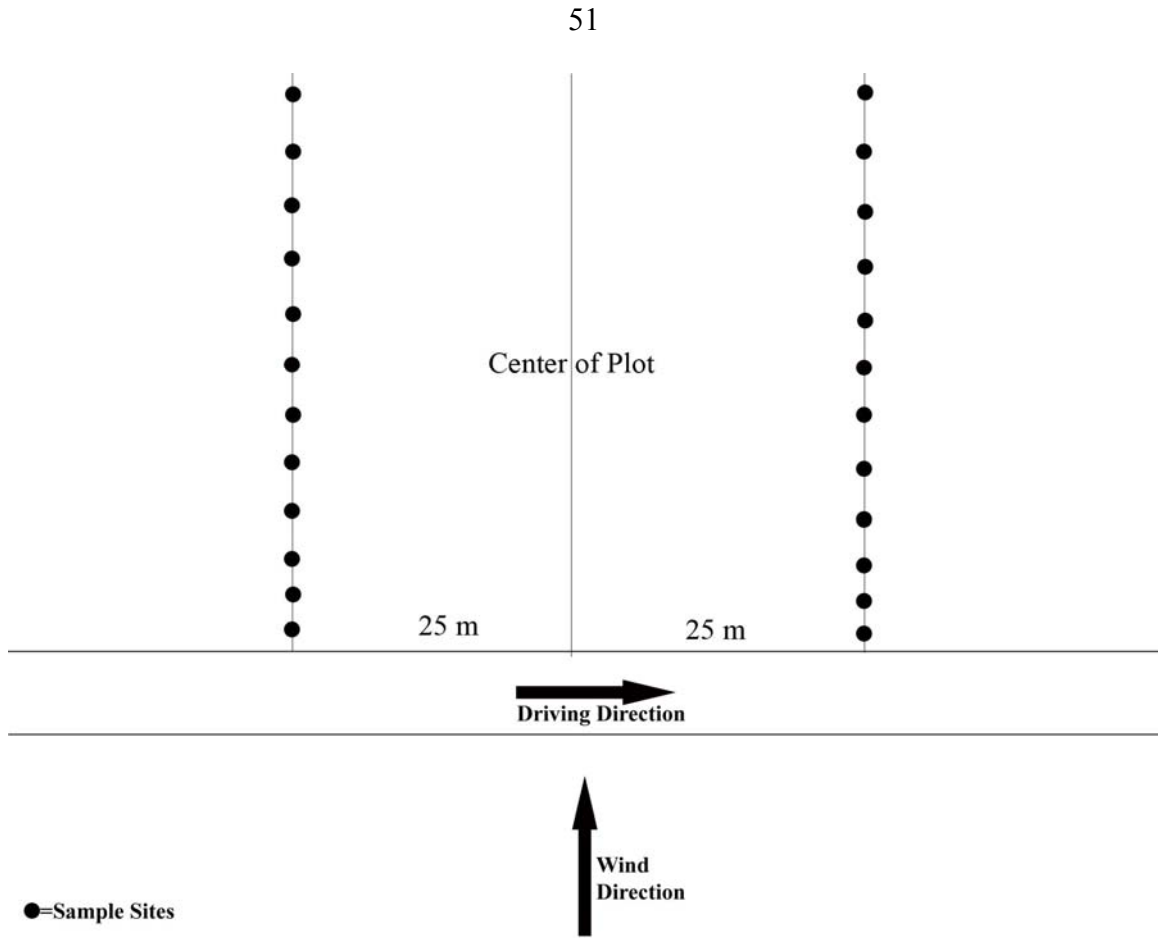


Figure 1. Site layout for the 11 receptors that were selected from distances of 5, 10, 15, 20, 30, 35, 40, 50, 60, 65, 70, 75, 80, 90, 95, 100, 110, 120, 125, 130, 135, 140, 155, 160, and 180 m from the spray source

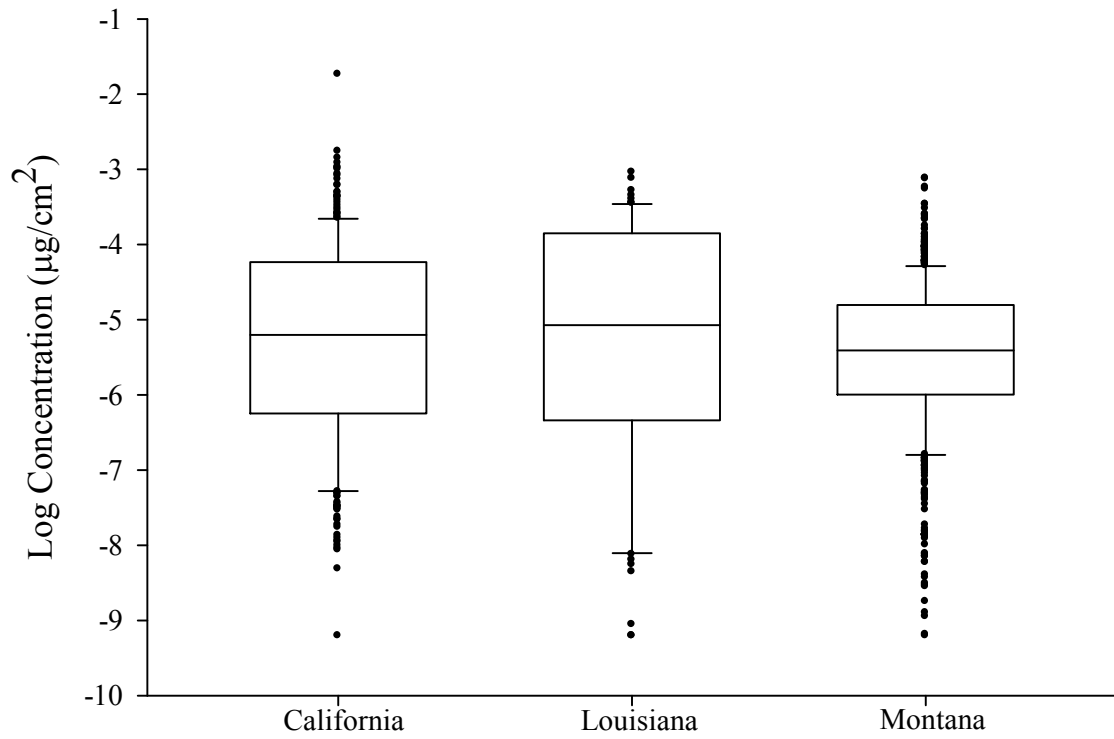


Figure 2. Boxplot of log concentrations ( $\mu\text{g}/\text{cm}^2$ ) in California, Louisiana, and Montana



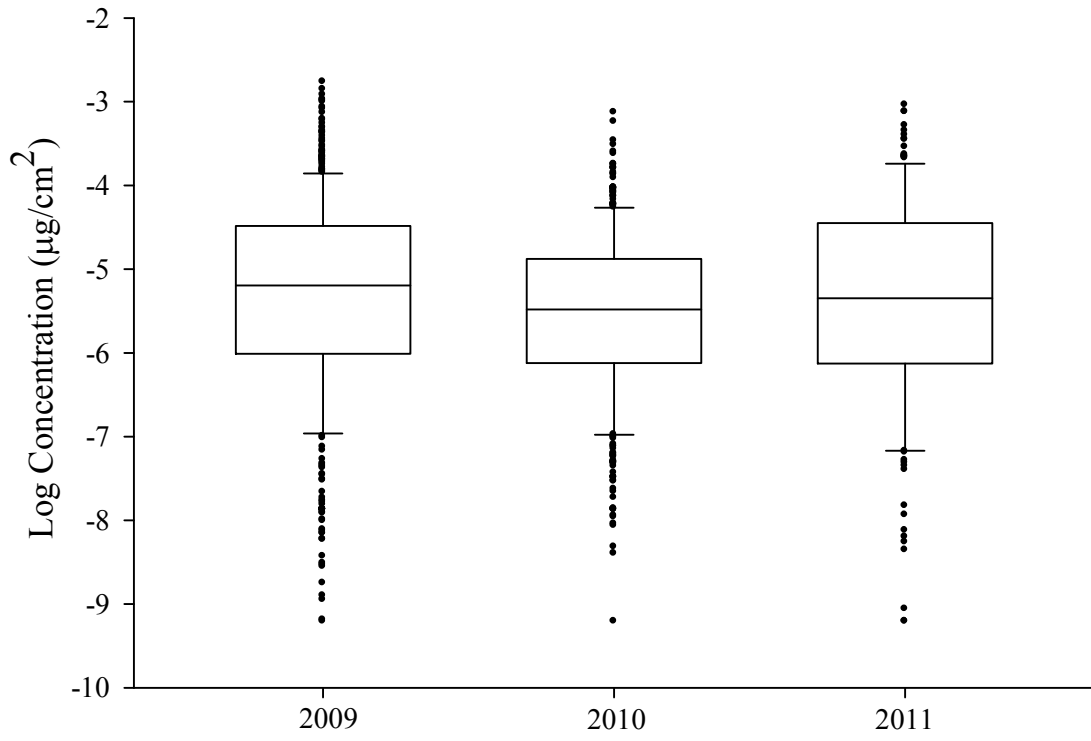


Figure 3. Boxplot of log concentrations ( $\mu\text{g}/\text{cm}^2$ ) in 2009, 2010, and 2011

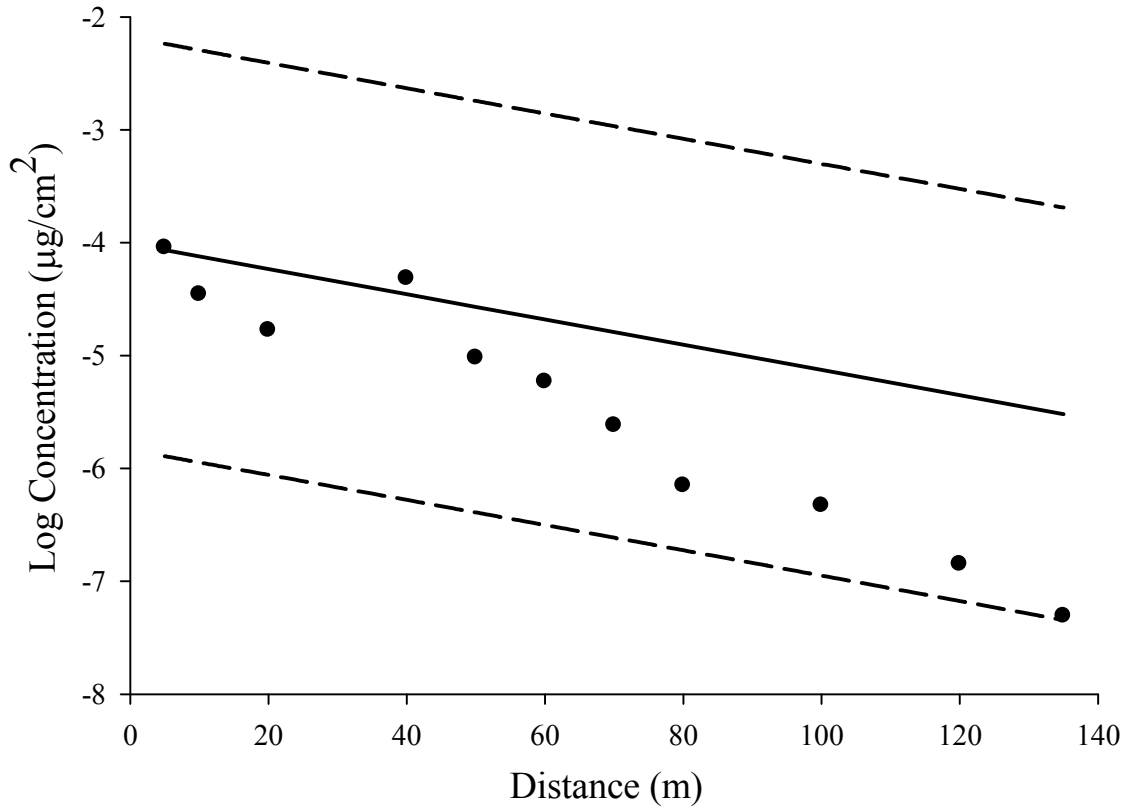


Figure 4. The prediction line (solid line) and 95% prediction interval (dashed lines) using equation 2 for the log of concentration ( $\mu\text{g}/\text{cm}^2$ ) with a application rate, flow rate, density, count median diameter, volume median diameter, wind speed, temperature, relative humidity, and stability category of 7.85, 192, 0.996, 2.2, 19.76, 215.06, 24.86, 29.68, 1, respectively. The input parameters represent the explanatory factors for the data points from one trial randomly selected from the entire data set to demonstrate the predictive ability of the model.

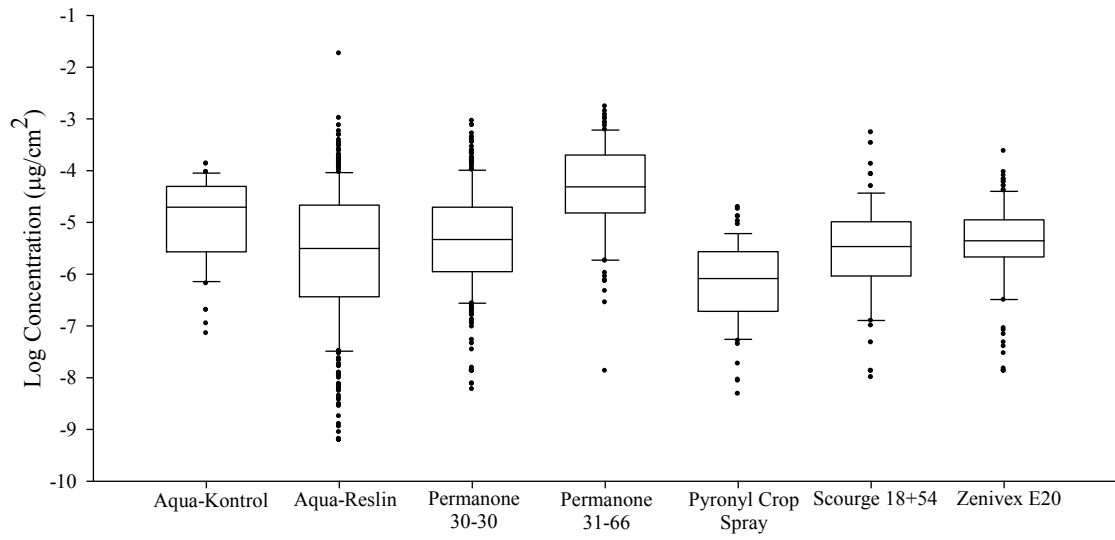


Figure 5. Boxplots of log concentrations ( $\mu\text{g}/\text{cm}^2$ ) for each formulation

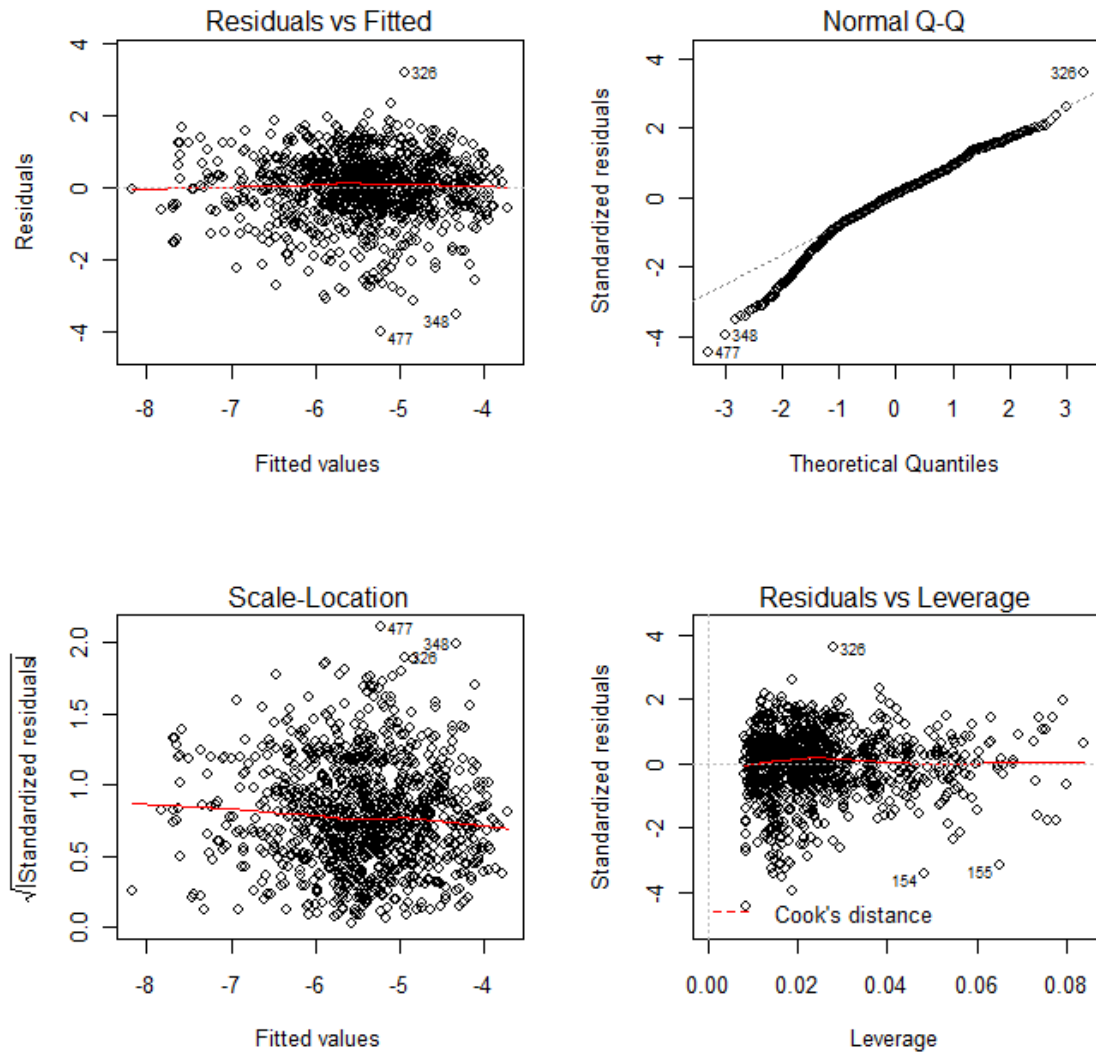


Figure 6. Diagnostic plots for the selected predictive model

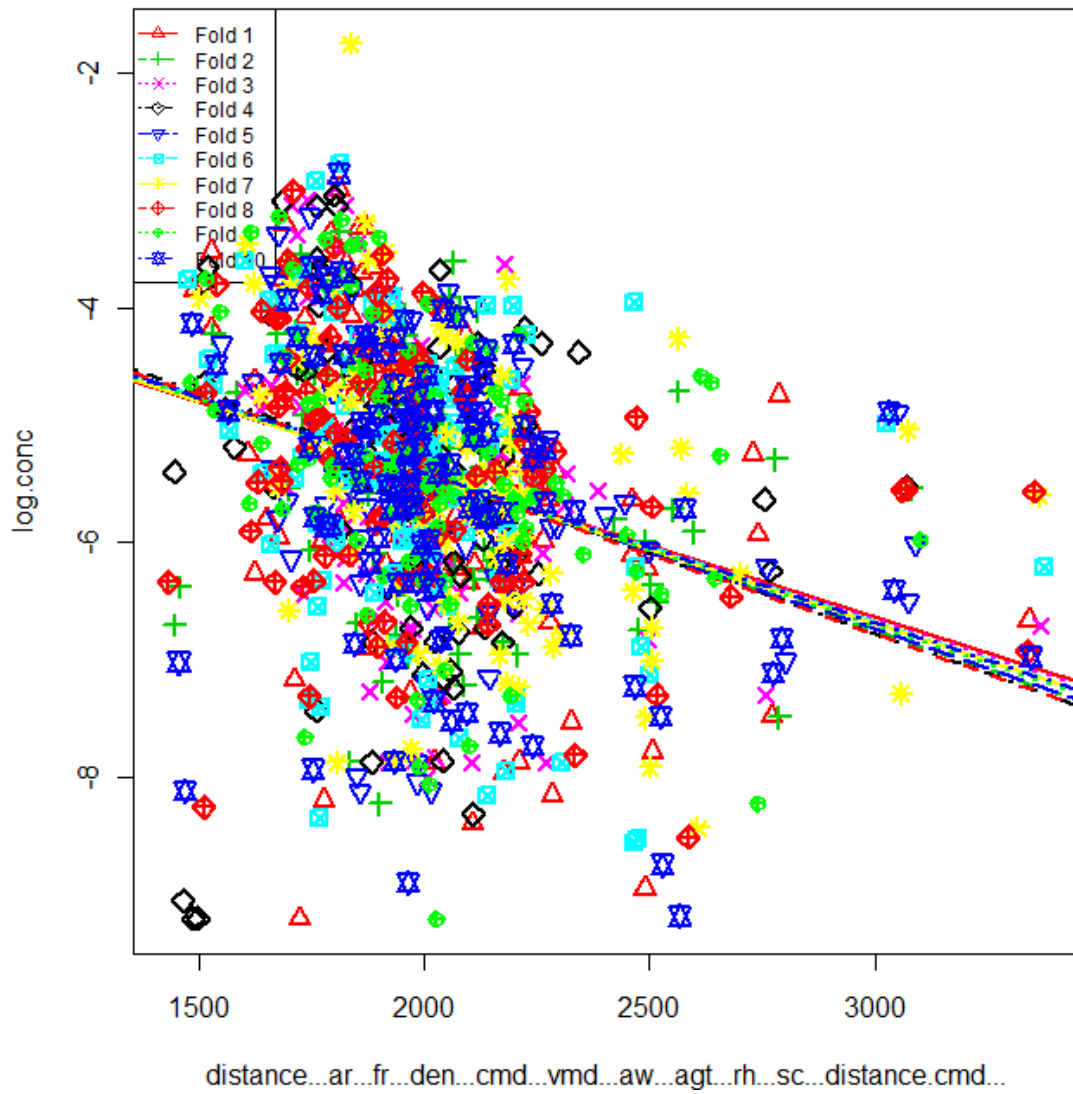


Figure 7. The k-fold cross validation figure showing the distance between the predicted concentrations (lines) and the held out concentration which was used to determine the prediction mean square error

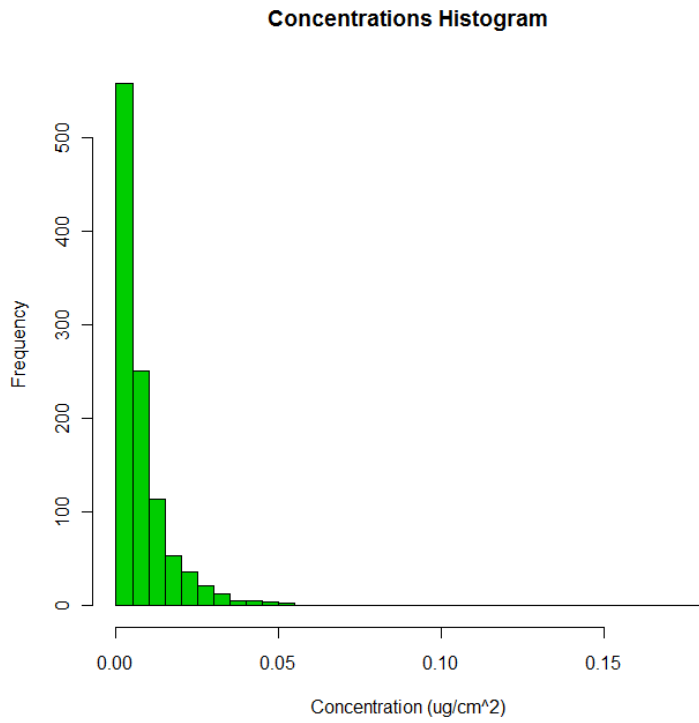
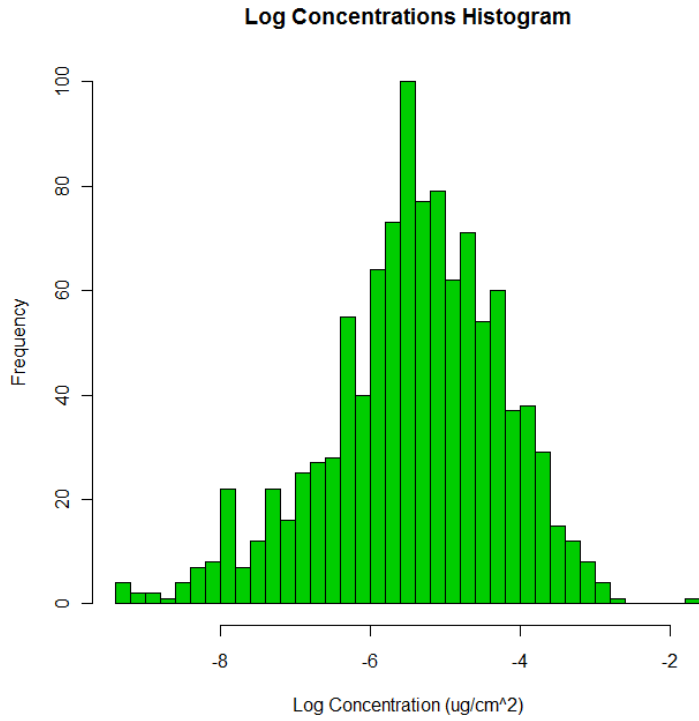


Figure 8. Histograms for log transformed and non-log transformed concentrations

## CHAPTER 3

A REFINED HUMAN-HEALTH RISK ASSESSMENT USING ACTUAL  
ENVIRONMENTAL CONCENTRATIONS OF AN INSECTICIDE FOR ADULT  
MOSQUITO MANAGEMENT

Abstract

Risk assessment often uses a tiered approach extending from deterministic models (Tier I), which are based on extremely conservative assumptions, to field evaluation and probabilistic models (Tier IV), which use refined assumptions. Surprisingly, few studies have been conducted that quantitatively demonstrate the change in risk for pesticides when higher-tiered assessments are performed, particularly with respect to human health. Therefore, we chose a case study with ultra-low-volume (ULV) aerosol applications of the insecticide permethrin to characterize the change in risk estimates when higher tiered risk assessments are performed and to refine previous risk assessments using estimated environmental concentrations (EECs) by incorporating actual environmental concentrations (AECs). We used the risk quotient (RQ) method, which is calculated by dividing the total potential exposure for each group and chemical by its ingestion toxic endpoint value (RfD). Risks to toddlers and infants were highest while risks to adult males were lowest risk. Median total acute exposures for permethrin ranged from 0.00002 to 0.0001 mg/kg body weight (BW)/day. Median RQs for permethrin ranged

from 0.00009 to 0.0004 for all groups. Our results show that previous lower tiered risk assessments used conservative exposure scenarios that overestimated risks, thus being conservative in protecting human health. Our results demonstrated a 10-fold reduction in the RQ estimates when comparing risk assessments using EECs and AECs. Because we used a large data set to model concentrations deposited on surfaces, this variance in exposure is due to the inherent variability in deposition concentrations after ULV applications and, therefore, would not warrant further refinement to improve risk assessments.

### Introduction

Risk assessment often uses a tiered approach extending from deterministic models (Tier I), which are based on extremely conservative assumptions, to field evaluation and probabilistic models (Tier IV), which use refined assumptions (SETAC 1994). Lower-tier risk assessments use conservative assumptions and models to estimate concentrations of insecticide which represent overestimates of toxicity and exposure, with resulting quantitative risk estimates typically being conservative and erring on the side of safety. Higher-tier (Tier III and IV) risk assessments use refinements such as experimentally derived environmental concentrations and probabilistic methods. Despite the well-known risk assessment approaches of tiers, recursiveness, and refinement (NRC 1983; SETAC 1994), surprisingly few studies, with the majority focused on ecological risk assessment, have been conducted and published that quantitatively characterize the change in risk from lower to higher tiered assessments (Boon et al. 2003; Giddings et al. 2001; Hendley



et al. 2001; Lunchick 2001; Maund et al. 2001; Peterson 2006; Schleier III et al. 2008b; Travis and Hendley 2001).

Since the introduction of West Nile virus (WNV) into the United States more than a decade ago, more areas of the country have been experiencing large-scale insecticide applications for mosquitoes. Currently, the majority of Americans are not concerned about contracting WNV (Ho et al. 2007); consequently, there has been greater public attention to the human-health and environmental risks associated with ULV insecticide applications (Peterson et al. 2006; Roche 2002; Thier 2001). In response to concerns about the safety of ULV insecticides, tier I/II (reasonable worst case) risk assessments have been performed to estimate risk. Peterson et al. (2006) performed a deterministic human-health risk assessment for acute and sub-chronic exposures to six mosquito insecticide active ingredients, and the synergist piperonyl butoxide (PBO), after ground-based ULV applications. They found that acute and subchronic risks to humans from the insecticides were well below regulatory levels of concern.

Schleier III et al. (2009b) performed a lower tiered acute probabilistic risk assessment of the same insecticides and population groups as Peterson et al. (2006). The results of Schleier III et al. (2009b) supported the previous findings that the risks to humans from mosquito adulticides would most likely not exceed regulatory levels of concern. Both Peterson et al. (2006) and Schleier III et al. (2009b) used Industrial Source Complex Short Term version 3 (ISCST3) and American Environmental Regulatory Model (AERMOD) to estimate environmental deposition and air concentrations of insecticides, respectively (USEPA 1995, 2003). Although the majority of deterministic

and probabilistic risk assessments conducted to date using estimated environmental concentrations (EECs) have not suggested unacceptable exposures, they have relied on models that are designed for industrial plumes and agricultural applications, which greatly differ from ULV applications, to estimate environmental concentrations after ground-based ULV applications. Schleier III and Peterson (2010) demonstrated that ISCST3 overestimated environmental concentrations by as much as 16-fold when compared to AECs. Additionally, Schleier III and Peterson (2010) demonstrated that the models currently utilized for ULV applications are either over- or under-estimating environmental concentrations, which adds to the uncertainty of previous risk assessments.

Probabilistic risk assessments have suggested that the estimated air concentrations and deposition of insecticides contribute the largest amount of variance to the potential exposure (Schleier III et al. 2009a; Schleier III et al. 2009b). To address the lack of a model specific to ULV applications for adult mosquito management in chapter 2, a validated model was developed for predicting deposition concentrations of insecticides applied with ground-based ULV technology for adult mosquito management. This model uses the largest data set yet generated to develop and validate a spray drift model. The data set and model are robust with respect to environmental and application scenarios (i.e. formulation type, flow rate, etc.).

Because of the uncertainties associated with environmental concentrations of the insecticides used during mosquito management and the fact that no previous assessments have used AECs, we conducted a risk assessment using AECs for permethrin. Here, we report the results of a human-health risk assessment for permethrin used in a ground-

based ULV application. In addition, we examine the difference in exposure estimates between risk assessments that use EECs and AECs.

## Materials and Methods

### Problem Formulation

We performed a probabilistic risk assessment of acute human exposure to permethrin used during ground-based ULV applications. Chronic exposures were not considered because environmental fate studies have demonstrated that exposures are most likely limited to 24 h after application (Schleier III and Peterson 2010; Schleier III et al. 2008b). Acute exposures were defined in this study as single-day exposures after a single insecticide application.

Exposures were estimated for several population groups to account for age related differences in exposure. The groups included adult males and adult females (18-65 years of age), youth (10-12 years of age), children (5-6 years of age), toddlers (2-3 years of age), and infants (0.5-1.5 years of age).

### Hazard Identification

Permethrin, a type I pyrethroid insecticide which is a neurotoxin that acts on the sodium channels of mammals, was assessed. Permethrin is currently registered by the U.S. Environmental Protection Agency (USEPA) for use in adult mosquito management in the U.S. (USEPA 2006b).

### Toxicity and Dose-response Relationships

Dose-response information for permethrin was reviewed and the toxicity endpoint chosen for this assessment was the ingestion reference dose (RfD). The RfD is based on the no-observed-adverse-effect-level in mammals with inclusion of appropriate safety factors, which are determined by the USEPA. The acute oral RfD for permethrin is 0.25 mg/kg body weight (BW)/day (USEPA 2006b, 2009c).

### Environmental Concentrations

We used the environmental fate data for ground deposition concentrations from chapter 2. The data were collected using a ground-based ULV field experiments were conducted near Elk Grove, California (38°27'17.27"N, 121°27'9.25"W), Bozeman, Montana (45°38'47.09"N, 111°24'8.18"W), and Baton Rouge, Louisiana (30°31'1.57"N, 91° 9'20.32"W) during the summers of 2009 to 2011. Sites with little vegetative structure and a flat topography were chosen for all experiments because vegetation affects air movement and subsequent deposition of insecticides and we were interested in high depositions for conservative estimates of exposure. The ground deposition concentrations for the formulations Permanone<sup>®</sup> 30-30 (30% permethrin), Permanone<sup>®</sup> 31-66 (31% permethrin), Aqua-Reslin<sup>®</sup> (20% permethrin) (Bayer Environmental Science, Research Triangle Park, NC, USA), and Aqua-Kontrol (20% permethrin) (Univar<sup>®</sup>, Redmond, WA, USA) between the distances of 5 to 180 m was used to model the environmental concentrations. Chapter 2 shows that the densities of the formulations were most important for predicting the fate and concentration of insecticide deposition; therefore,

we modeled all concentrations of permethrin using the different formulations to reflect the variability of formulation density. Permethrin was applied at the maximum application rates of 7.85 g active ingredient/ha as listed on the label. Formulations and the order in which the formulations were sprayed were randomly selected. The experimental design was an incomplete block design with each spray (block) occurring in the order that it was randomly selected. Replications were performed over time within the same night and over different nights with a total of 826 deposition data points taken over 82 spray events. Ground deposition concentration values were used for all exposure pathways and routes, except inhalation, because Preftakes et al. (2011) showed that the amount settling on different body parts was similar to the ground deposition using similar formulations as chapter 2.

Air concentrations were estimated using roto-slide samplers positioned 1.5 meters above the ground. To determine the amount of air volume sampled by the roto-slide samplers I used the following,

$$V = 2\pi * H * W * D * R, \quad (1)$$

where V is the volume sampled in l/min, H is the height of the slide (5.6 cm), W is the width of the slide (2.5 cm), D is the distance between slides (10.3 cm), and R is the rotation velocity (330 revolutions/min); therefore based on the above equation the air sampled was 298.9 l/min (Miller et al. 1996). DropVision<sup>®</sup> (Leading Edge Associates, LLC, Waynesville, NC) was used to quantify the diameter of the droplets deposited on the Teflon<sup>®</sup> slides. The DropVision system takes pictures of the slide through a compound microscope and using the provided software determines the size of the

droplets. To sample the slide, a picture was taken and the slide was moved 5 mm horizontally along the slide, when the edge of the slide was reached we moved laterally over 5 mm to begin sampling again so we did not sample the same droplets twice. The majority of the total slide area was sampled by taking 50 pictures from the slide resulting in a total surface area of 131.48 mm<sup>2</sup> sampled, which is due to the small surface area the objective could see. To account for not sampling from the entire surface area of the slide, we multiplied the volume of droplets obtained by 10.65 to reflect the remaining area not sampled. Droplet distribution analysis using a DC-III portable droplet measurement system (KLD Labs, Inc., Huntington Station, NY, USA) which obtains a more representative sample of the droplets produced by ULV machines shows that  $\geq 50\%$  of the total count of droplets from ULV applications are below 10  $\mu\text{m}$  (Schleier III et al. 2010). Roto-slide samples under-sample droplets below 10  $\mu\text{m}$ , so we doubled the volume of the sample to account for the fraction of droplets not adequately sampled (Miller et al. 1996).

Roto-slide field experiments were conducted near Williston, North Dakota (48°16'30.00"N, 103°43'43.11"W) and Baton Rouge, Louisiana (30°31'1.57"N, 91°9'20.32"W) during the summer of 2011. Sites with little vegetative structure and a flat topography were chosen for all experiments because vegetation affects air movement and subsequent movement of the insecticides through the environment. Sites were 200-m long with the roto-slide samplers positioned in the middle of the field plot. During each spray event, three roto-slide samplers were placed in the field at different distances from the spray source. Sampling occurred at distances of 40, 60, 100, 120, and 160 m from the

spray source. The roto-slide samplers were 1.5 m above the ground to mimic where humans would be breathing.

Between June 17 and July 19, 2011, Aqua-Reslin, Permanone 30-30, and Permanone 31-66 were applied. Aqua-Reslin was mixed 1:1 with D.I. H<sub>2</sub>O and applied at a flow rate of 192 ml/min. Permanone 30-30 was mixed 1:2:1 with Crystal Plus 70T light mineral oil (STE Oil Company, Inc., San Marcos, TX, USA) and ACS grade toluene (99.5% purity, Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA) and applied at a flow rate of 192 ml/min. Permanone 31-66 mixed 1:2.25:1 to Crystal Plus 70T light mineral oil and ACS grade toluene and applied at a flow rate of 192 ml/min. Formulations and the order in which the formulations were sprayed were randomly selected. The experimental design was an incomplete block design with each spray occurring in the order that was randomly selected. Replications were performed over time within the same night and over different nights with a total of 17 spray events. Applications began no earlier than 17:00 h, but most applications occurred after 20:00 h.

The distributions for deposition on surfaces and air concentrations was chosen based on the Anderson-Darling goodness of fit test, which for non-normalized data, weights the differences between two distributions at their tails (Oracle 2007; Pettitt 1977; Table 1).

### Acute Exposure

We assumed that multi-route exposures immediately after a single-spray event were limited to 24 h (Figure 6). Routes of insecticide exposure to each group were

inhalation, dermal, and dietary and non-dietary ingestion. Assumptions of body weight, respiration rate, and frequency of hand-to-mouth activity are presented in table 6.

Inhalation exposures were limited to 10 mins due to the rapid dispersion of the ULV aerosol after application. For all other exposure routes, we assumed that each group would be outside when the spray truck passed and the duration of the exposure was for 6 h. The exposure modeling assumptions follow Schleier III et al. (2009b), which are reviewed here.

Inhalation exposure was estimated by

$$PE_{\text{Inhalation}} = (\text{AAEC} * \text{RR} * \text{D}) / \text{BW}, \quad (2)$$

where  $PE_{\text{Inhalation}}$  is potential exposure from inhalation (mg/kg BW), AAEC is actual environmental air concentrations ( $\mu\text{g}/\text{m}^3$ ; Table 5), RR is respiratory rate for each group ( $\text{m}^3/\text{h}$ ; Table 6), D is duration of exposure (10 mins), and BW is body weight for each group (kg; Table 6).

Dermal exposure from spray deposition was estimated by

$$PE_{\text{Dermal}} = (\text{DAEC} * \text{CF} * \text{SA} * \text{PSE} * \text{AR}) / \text{BW}, \quad (3)$$

where  $PE_{\text{Dermal}}$  is potential exposure from dermal contact (mg/kg BW), DAEC is the estimated environmental concentrations of insecticide that would settle on surfaces ( $\mu\text{g}/\text{cm}^2$ ; Table 5), CF is the conversion from  $\mu\text{g}/\text{cm}^2$  to  $\text{mg}/\text{m}^2$ , SA is the surface area ( $\text{m}^2$ ) of an individual in each group as estimated by equation 4, AR is dermal absorption rate for permethrin which is which was a uniform distribution between 1.2 and 3.3% (Reifenrath et al. 2011; Ross et al. 2011), and BW is body weight (kg). To estimate the percent body surface area exposed to the spray (PSE), we assumed a triangular



distribution with the maximum being the surface area of a person wearing only shorts (82.3%), minimum being a person wearing single layer of clothing with only head, hands, and feet exposed (20%), and the most likely being a person wearing a tee-shirt and shorts with their head, forearms, hands, lower legs, and feet exposed (38.7%) (Schleier III et al. 2009b; USEPA 1997b).

Surface area for all groups was estimated using

$$SA = 4BW + 7 / BW + 90, \quad (4)$$

where SA is surface area (m<sup>2</sup>), and BW is body weight (kg) (USEPA 1997b, 2002a).

For infants and toddlers, hand-to-mouth exposure from insecticide settling on their hand was estimated by

$$PE_{\text{Hand-to-mouth skin}} = [(DAEC * CF * AR * HSA) * PC * SEF] / BW, \quad (5)$$

where  $PE_{\text{Hand-to-mouth skin}}$  is potential exposure from hand-to-mouth activity from the insecticide settling on the skin (mg/kg BW), DAEC is the actual environmental concentration of insecticide that would settle on the skin ( $\mu\text{g}/\text{cm}^2$ ), CF is the conversion from  $\mu\text{g}/\text{cm}^2$  to  $\text{mg}/\text{m}^2$ , HSA is hand surface area for each group as calculated by equation 6 (m<sup>2</sup>), PC is percent of the hand contacted with the mouth which we assumed to be 50%, SEF is saliva extraction factor of 50% (USEPA 2005a), and BW is body weight (kg).

Child hand surface area (HSA) was estimated by

$$HSA = (SA * PH) / 2, \quad (6)$$

where SA is the surface area as calculated by equation 4 and PH is the percent surface area of two hands. PH for infants had a triangular distribution with a mean of 5.3% and a

minimum value of 5.21% and a maximum value of 5.39% and for toddlers we used a triangular distribution with a mean of 5.68% a minimum of 5.57% and a maximum of 5.78% (USEPA 2002a).

Exposure from hand-to-mouth activity from turf dislodgeable residue was estimated by,

$$PE_{\text{Hand-to-mouth turf}} = [(DAEC * CF * CSA * DR) * PC * AR * FA * SEF * D] / BW, \quad (7)$$

where  $PE_{\text{Hand-to-mouth turf}}$  is potential exposure from hand-to-mouth turf dislodgeable residue (mg/kg BW), DAEC is the actual environmental concentration of insecticide that settled on surfaces ( $\mu\text{g}/\text{cm}^2$ ), CF is the conversion from  $\mu\text{g}/\text{cm}^2$  to  $\text{mg}/\text{m}^2$ , CSA is child hand surface area as estimated by equation 6 ( $\text{m}^2$ ), DR is the dislodgeable residue, which we assumed to be 20% (USEPA 1997a, 2011), PC is percent of the hand contacted with the mouth which we assumed to be 50% per event, FA is frequency of hand-to-mouth activity (events/hour; Table 6), SEF is saliva extraction factor of 50% (USEPA 2005a), D is duration of exposure which we assumed to be 6 h, and BW is body weight (kg).

For acute ingestion exposure from tomatoes that were exposed to the pesticide, we assumed that all foods containing tomatoes eaten per day were consumed from tomatoes grown in a home garden without being washed. In addition, we assumed there would be no degradation in the preparation process. Acute ingestion was estimated by,

$$PE_{\text{Ingestion}} = [(DAEC * CF) * SAT] / BW, \quad (8)$$

where  $PE_{\text{Ingestion}}$  is potential exposure from consuming exposed produce (mg/kg BW), DAEC is the actual environmental concentration of insecticide that settles on surfaces

( $\mu\text{g}/\text{cm}^2$ ), CF is the conversion from  $\mu\text{g}/\text{cm}^2$  to  $\text{mg}/\text{m}^2$ , SAT is the surface area of tomatoes consumed as estimated by equation 9 ( $\text{m}^2$ ), and BW is body weight (kg).

The surface area of tomatoes consumed was estimated by

$$\text{SAT} = 69 + [0.57 + (\text{WT} * \text{BW})]/1000, \quad (9)$$

where SAT is the surface area of tomatoes consumed (Eifert et al. 2006) ( $\text{m}^2$ ), and WT is the average weight of tomatoes consumed per day by each group (g/kg BW), and BW is body weight (kg). The average amount of tomatoes consumed per day by adult males and females, youth, children, toddlers, and infants is 0.804, 0.804, 0.874, 1.19, 1.77, and 1.21 (g dry weight/kg BW), respectively (USEPA 1997c).

Total acute exposure to permethrin for each group was estimated by

$$\text{PE}_{\text{acute}} = \text{PE}_{\text{Inhalation}} + \text{PE}_{\text{Dermal}} + \text{PE}_{\text{Hand-to-mouth skin}} + \text{PE}_{\text{Hand-to-mouth turf}} + \text{PE}_{\text{Ingestion}} \quad (10)$$

### Risk Characterization

We used the risk quotient (RQ) method for the risk assessment, which is calculated by dividing the total potential exposure as estimated by equation 9 for each group and chemical by its respective ingestion toxic endpoint value (RfD). The multi-route exposure in our assessment was compared to the ingestion RfD because it provides a conservative endpoint, which is based on the most sensitive NOAEL. Estimated RQs are compared to a RQ level of concern (LOC) which is set by the USEPA or another regulatory agency to determine if regulatory action is needed. The RQ LOC used in the assessment was 1.0. An  $\text{RQ} > 1.0$  means that the estimated exposure is greater than the relevant RfD.

### Probabilistic Analysis

To perform the probabilistic risk assessment, we used Monte Carlo simulation (Crystal Ball<sup>®</sup> 7.3; Oracle<sup>®</sup>, Denver, CO, USA) to estimate the exposures and RQs using 20,000 iterations. Probabilities of occurrence of RQ values were determined by incorporating sampling from the statistical distribution of each input variable used to calculate the RQs. Sensitivity analysis was performed using 20,000 iterations on all parameters to determine percent contribution of the input variable to the output variance of the model for each group and chemical. Respiratory rate, body weight, percent surface area of two hands, air concentrations, and deposition on surfaces were truncated at zero because it is not possible for these quantities to have negative values.

### Results

Risk quotients for permethrin did not exceed the RQ LOC of 1. Toddlers and infants were the highest risk groups and adult males were the lowest risk group assessed in this study (Tables 7 and 8). Median total acute exposure for permethrin ranged from 0.00002 to 0.0001 mg/kg BW/day (Table 7). Median RQs for permethrin ranged from 0.00009 to 0.0001 and 95<sup>th</sup> percentile RQs ranged from 0.001 to 0.0004 for all groups (Table 8). Consequently, this tier IV risk assessment using AECs suggests that exposures would be well below regulatory LOCs.

Not surprisingly, the estimates of risks for ground-based ULV applications show the reduction in risks when higher-tiered probabilistic risk assessments utilize AECs. The

deterministic risk estimates of Peterson et al. (2006) using EECs were 10 times greater than the results at the 95<sup>th</sup> percentile (Table 8). The most interesting finding is that the exposures and RQs estimated in the current study were similar to the estimates of Schleier III et al. (2009b) (Table 8), who conducted a probabilistic risk assessment using EECs. I observed only a small decrease in the RQs for adult males and females, youth, and children compared to Schleier III et al. (2009b), but as much as a 90% decrease in RQs for infants and toddlers.

Dermal exposure contributed > 43% to the total exposure for adult males and females, youth, and children but only accounted for about 24% of the total exposure for toddlers and infants. Tomato consumption contributed an average of 47% to the total exposure for all groups assessed. Turf dislodgeable residue and hand-to-mouth activities contributed an average of 28% to estimated total exposure to toddlers and infants. Inhalation exposure contributed < 0.00001% to the exposure for all groups assessed. Sensitivity analysis demonstrated that deposition of the insecticide on surfaces contributed > 95% of the variance to the exposure for all groups.

### Discussion

In this assessment, we estimated the risks from a multi-pathway and multi-route exposure after a ground-based ULV insecticide application. The most interesting result was that the RQs at the 50<sup>th</sup> and 95<sup>th</sup> percentile of exposure were similar to those of Schleier III et al. (2009b), who used EECs based on the models ISCST3, default flagger scenario in the USEPA Pesticide Handler Exposure Database (PHED), and AERMOD

rather than AECs based on ground deposition concentrations and air concentrations measured in the field. Using AECs, we found that dermal exposure and tomato consumption contributed the most to the estimated total exposure for all groups. In contrast, Schleier III et al. (2009b) reported that inhalation exposure contributed the majority of the exposure for adult males and females, youth, and children and 7 and 9% to the total exposure of toddlers and infants. However, we found that inhalation exposure contributed  $< 0.00001\%$  for all groups when exposure was based on AECs. Therefore, based on the current analysis using field-measured air concentrations, inhalation exposure can be assumed to be negligible.

It is assumed that there will be a reduction in the risk when AECs are used. To estimate dermal exposure, Peterson et al. (2006) and Schleier III et al. (2009b) used the default flagger scenario in the USEPA PHED. Our results show that when using actual deposition data, PHED may underestimate the dermal exposure. However, even though dermal exposures may have been underestimated, the RQs were still lower than Peterson et al. (2006) because of the reduction in exposure from other routes such as inhalation. Preftakes et al. (2011) used mannequins to estimate dermal exposure to ULV applications of permethrin and calculated exposures ranging from 0.00009 and 0.00005 mg/kg BW, which is similar to the present study's estimates using ground deposition data.

Our results are important because in its reregistration eligibility decision documents for pyrethrins, permethrin, resmethrin, and d-phenothrin the U.S. Environmental Protection Agency (USEPA) only estimated exposure from inhalation after ground-based ULV applications (USEPA 2006b, e, f, 2008). In contrast, for adults

the USEPA used two exposure routes, dermal and inhalation, to estimate the risk of malathion and naled applied with a ground-based ULV applicator. However, for toddlers the exposures routes used were dermal, incidental oral from hand-to-mouth and object-to-mouth from residues deposited on turf, and incidental ingestion of soil from treated areas for both malathion and naled (USEPA 2002b, 2005a, 2006c). Our results demonstrate that inhalation exposures are negligible, which was the only exposure route assessed for pyrethrins and pyrethroids in the USEPA risk assessments; therefore, the USEPA should incorporate a multi-route exposure scenario.

Our results demonstrate that when the uncertainties associated with models that are not validated for ULV applications are addressed certain exposures either increase (dermal and oral exposure) or decrease (inhalation), thus leading to a more accurate estimation of the risks. To estimate deposition and air concentrations, previous risk assessments have used Industrial Source Complex Short Term version 3 (ISCST3) and American Environmental Regulatory Model (AERMOD), which are industrial plume models, and AGDISP and AgDrift, which are designed for agricultural pesticide applications (Davis et al. 2007; Macedo et al. 2007; Peterson et al. 2006; Schleier III et al. 2009a; Schleier III et al. 2008a; Schleier III et al. 2009b; Valcke et al. 2008). The ISCST3 and AERMOD models are based on a steady-state Gaussian plume algorithm, and are applicable for estimating ambient impacts from point, area, and volume sources out to a distance of about 50 km (USEPA 1995, 2003). Because of the inherent differences between coarse (used for agricultural pesticide applications) and fine droplet sizes (used for ULV pesticide applications), these models are not appropriate for ULV

applications because smaller droplets travel farther from the spray source. Therefore, future risk assessments should use the validated model developed in chapter 2 to estimate exposures to ULV insecticides.

Although we used AECs, the exposure scenarios were still conservative and therefore overestimated exposure. For example, we assumed that all groups would be outside for 6 hours following a ULV application. Applications of ULV insecticides for mosquito management typically take place at dusk when mosquitoes are actively seeking a blood-meal. In addition, we assumed that each group's total consumption each day from tomatoes and food products containing tomatoes was from tomatoes from their garden and was consumed without washing or processing. Based on the conservative assumptions of the model, the risks to humans are likely much lower than our estimates.

We did not perform a chronic risk assessment because of the attributes of both the ULV application method and pyrethroids. The exposure to ULV applications would be a pulsed event with applications only occurring, at most, two times per week in the same area. Pyrethroids have a low toxicity to mammals which is attributed to the rapid metabolism in the blood and liver with greater than 90% of pyrethroids being excreted as metabolites in urine within 24 hours after exposure (Eadsforth and Baldwin 1983; Eadsforth et al. 1988; Leng et al. 1997). Results of previous biomonitoring and epidemiology studies for permethrin, resmethrin, d-phenothrin, malathion, and naled showed no increase in urinary metabolites or increases in asthma related visits to hospitals after ULV applications (Currier et al. 2005; Duprey et al. 2008; Karpati et al.



2004; Kutz and Strassman 1977; O'Sullivan et al. 2005), adding support to the current risk assessment findings.

Previous risk assessments have shown that deposition on surfaces contributes the most variance to human exposure; therefore, in chapter 2 we developed a model that can more accurately estimate deposition concentrations so that more refined risk assessments can be conducted on current and future insecticide active ingredients for both human-health and ecological risks. For the current study, the sensitivity analysis demonstrated that > 95% of the variance to the exposure was from deposition on surfaces. Because we used a large data set to model concentrations deposited on surfaces, this variance in exposure is due to the inherent variability in deposition concentrations after ULV applications and, therefore, would not warrant further refinement to improve risk assessments.

Table 5. Custom input distributions for deposition on surfaces and aerial concentrations for permethrin as measured in the current study and chapter 2

Input	Distribution Type	Parameter	Concentration	Units
Deposition on Surfaces	Gamma (Truncated)	Location	0.0001	$\mu\text{g}/\text{cm}^2$
		Scale	0.01	
		Shape	0.82	
Air Concentration	Weibull (Truncated)	Location	4.25E-13	$\mu\text{g}/\text{m}^3$
		Scale	1.12E-10	
		Shape	0.81	

Table 6. Assumptions for body weight, respiration rate, and frequency of hand-to-mouth activity for each group assessed

Input Variables	Group	Parameter	Values	Units	Distribution	Source
Body Weight	Adult Males <sup>b</sup>	Mean	78.65	kg	Log-normal (Truncated)	Portier et al. (2007)
		SD*	13.23			
	Adult Females <sup>c</sup>	Mean	65.47	kg		
		SD	13.77			
	Youth <sup>d</sup>	Mean	36.16	kg		
		SD	7.12			
	Children <sup>e</sup>	Mean	19.67	kg		
		SD	2.81			
	Toddlers <sup>f</sup>	Mean	13.27	kg		
		SD	1.62			
Infants <sup>g</sup>	Mean	9.1	kg			
	SD	1.24				
Respiration Rate	Adult Males	Mean	17.53	m <sup>3</sup> /day	Log-normal (Truncated)	Brochu et al. (2006)
		SD	2.8			
	Adult Females	Mean	13.78	m <sup>3</sup> /day		
		SD	2.1			
	Youth	Mean	11.3	m <sup>3</sup> /day		
		SD	2.14			
	Children	Mean	7.74	m <sup>3</sup> /day		
		SD	1.04			
	Toddlers	Mean	5.03	m <sup>3</sup> /day		
		SD	0.94			
	Infants	Mean	3.72	m <sup>3</sup> /day		
		SD	0.81			
Hand-to-Mouth Frequency	Toddlers	Location	5.3	events/h	Weibull (Truncated)	Xue et al. (2007)
		Scale	3.41			
	Infants	Location	14.5	events/h		
		Scale	15.98			
		Shape	1.39			

<sup>a</sup> SD= Standard Deviation, <sup>b</sup> 18-65 years of age, <sup>c</sup> 18-65 years of age, <sup>d</sup> 10-12 years of age, <sup>e</sup> 5-6 years of age, <sup>f</sup> 2-3 years of age, <sup>g</sup> 0.5-1.5 years of age

Table 7. Acute total potential exposure (PE) at the 50<sup>th</sup> and 95<sup>th</sup> percentile for each group

PE <sup>a</sup>	Adult Males	Adult Females	Youth	Children	Toddlers	Infants
	18-65 years of age	18-65 years of age	10-12 years of age	5-6 years of age	2-3 years of age	0.5-1.5 years of age
50th	0.00002	0.00002	0.00003	0.00004	0.00008	0.0001
95th	0.0001	0.0001	0.0001	0.0002	0.0004	0.0005

<sup>a</sup> Total potential acute exposure as estimated by equation 10 (mg/kg BW/day)

Table 8. Acute risk quotients (RQ) for permethrin from Peterson et al. (2006) and the 50<sup>th</sup> and 95<sup>th</sup> percentile RQ from Schleier III *et al.* (2009b), and the present study for each group

Study	RQ <sup>a</sup>	Adult Males	Adult Females	Youth	Children	Toddlers	Infants
		18-65 years of age	18-65 years of age	10-12 years of age	5-6 years of age	2-3 years of age	0.5-1.5 years of age
Peterson et al. (2006)		0.002	0.0021	0.0029	0.0049	0.0063	0.0058
Schleier III et al. (2009b)	50th	0.0003	0.0003	0.0003	0.0004	0.003	0.004
	95th	0.0004	0.0004	0.0005	0.0005	0.006	0.007
Present Study	50th	0.00009	0.0001	0.0001	0.0001	0.0003	0.0004
	95th	0.0004	0.0005	0.0007	0.001	0.001	0.002

<sup>a</sup> Risk Quotient

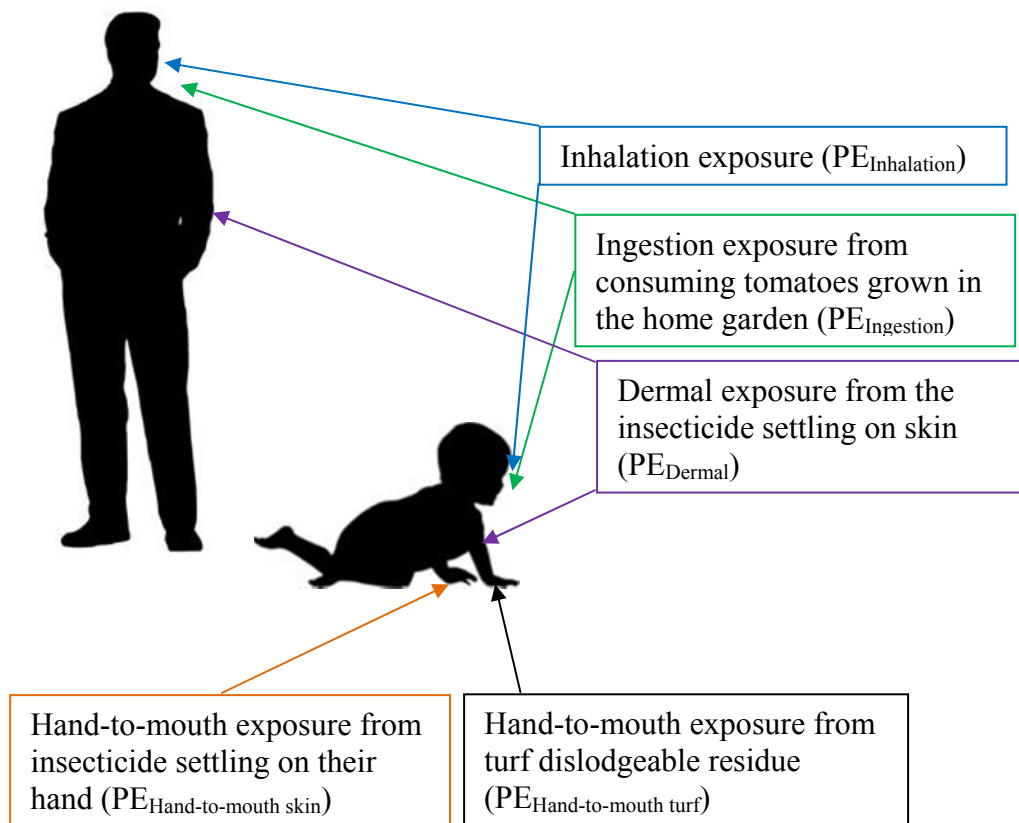


Figure 9. Exposure routes for all groups assessed and was taken from Schleier III (2008)

## CHAPTER 4

A REFINED AQUATIC ECOLOGICAL RISK ASSESSMENT FOR A PYRETHROID  
INSECTICIDE USED FOR ADULT MOSQUITO MANAGEMENTAbstract

The use of pyrethroid insecticides has increased substantially throughout the world over the past few decades as organophosphate, carbamate, and organochlorine insecticides are being phased out of use. Pyrethroids are the most common class of insecticides for ultra-low-volume (ULV) aerosol applications used to manage high densities of adult mosquitoes. Pyrethroids are highly toxic to non-target organisms such as certain aquatic organisms, and there have been concerns about the effect of ULV insecticide applications on these organisms. To address the uncertainties associated with the risks of ULV applications and the contradictory findings of other ecological risk assessments, we performed a probabilistic aquatic ecological risk assessment for permethrin using actual environmental concentrations deposited on surfaces to estimate water concentrations. In addition, this is the first ecological risk assessment for pyrethroids to quantitatively integrate the reduction in bioavailability due to the presence of dissolved organic matter. As part of the risk assessment, we incorporated a species sensitivity distribution to take into account the differences in toxicity for different species. The 95<sup>th</sup> percentile estimated concentration would result in less than 0.0001% of

the potentially affected fraction of species reaching their respective LC50. Our results are supported by the weight of evidence that pyrethroids applied by ground-based ULV applications will not result in deleterious effects on aquatic organisms.

### Introduction

The use of pyrethroid insecticides has increased substantially throughout the world over the past few decades as organophosphate, carbamate, and organochlorine insecticides are being phased out of use (Spurlock and Lee 2008; USDHHS 2007; USEPA 2010b). Pyrethroids are the most common class of insecticides for ultra-low-volume (ULV) aerosol applications that are used to manage high densities of adult mosquitoes (Mount 1998; Mount et al. 1996).

Pyrethroids are highly toxic to non-target organisms such as invertebrates and aquatic organisms, and there have been concerns about the effect of ULV insecticide applications on these organisms (Amweg et al. 2006a; Amweg et al. 2006b; Paul and Simonin 2006; Paul et al. 2005; Schleier III and Peterson 2012; Weston et al. 2006). Pyrethrins and pyrethroids are highly nonpolar chemicals that have low water solubility and volatility, high octanol:water partition coefficients, and a high affinity to bind to sediment dissolved organic matter (Laskowski 2002). Studies have shown that the presence of dissolved organic material significantly decreases the bioavailable concentration of pyrethroids and the toxicity to aquatic organisms that are not sediment dwelling (Burkhard 2000; Leahey 1985; Maund et al. 2002; Schleier III and Peterson

2011; Sharom and Solomon 1981; Yang et al. 2007a; Yang et al. 2006a; Yang et al. 2007b; Yang et al. 2006c).

Davis et al. (2007) performed a Tier 1 deterministic risk assessment on ground-based ULV applications using the Pesticide Root Zone Model and the Exposure Analysis Modeling System (PRZM EXAMS) (USEPA 2005b) to estimate water concentrations for pyrethrins, permethrin, resmethrin, and phenothrin. They found that acute and chronic risks to aquatic vertebrates and invertebrates most likely would not result in deleterious impacts on populations after ground-based ULV applications.

To assess the risks of ground-based ULV applications of permethrin, the U.S. Environmental Protection Agency (USEPA) used the Agricultural Dispersion model (AGDISP) (Bilanin et al. 1989) to estimate water concentrations of permethrin in a standard farm pond of 2 m deep (USEPA 2009c). The USEPA estimated that acute risk to freshwater and estuarine/marine fish would be below regulatory levels of concern (USEPA 2009c). However, the USEPA found that acute risks to freshwater and estuarine/marine invertebrates would exceed regulatory levels of concern (USEPA 2009c). However, the USEPA did not refine its Tier 1 assessment.

Schleier III and Peterson (2010) demonstrated that the models currently used to estimate environmental concentrations of insecticide from ground-based ULV are not appropriate and either over- or under-estimate concentrations. This is because ground-based ULV applications used for adult mosquito management are very different than agricultural pesticide applications and industrial point-source pollutants because the



nozzles produce an aerosol (droplets  $<100\ \mu\text{m}$ ) and are pointed at a  $+45^\circ$  angle compared to the horizon (Chapter 2).

Ultra-low-volume applications used for adult mosquito management are most effective when the insecticide remains airborne and moves through the target area; in contrast, applications for agricultural pests are designed to minimize the movement of droplets (Hiscox et al. 2006). To address the lack of a model specific to ULV applications for adult mosquito management in chapter 2, a validated model was developed for predicting deposition concentrations of insecticides applied with ground-based ULV technology for adult mosquito management using the largest data set of actual environmental concentrations yet generated. The data set and model are robust with respect to environmental and application.

To date, only deterministic ecological risk assessments have been conducted for insecticides used for adult mosquito management, and these have used inappropriate models to estimate environmental concentrations (Davis et al. 2007; NYCDOH 2005; Suffolk County 2006; USEPA 2006a, d, e, f, 2009b, c). To address the uncertainties associated with the risks of ULV applications and the contradictory findings of other ecological risk assessments, we performed a probabilistic aquatic ecological risk assessment for permethrin using actual environmental concentrations from chapter 2. In addition, this is the first ecological risk assessment for pyrethroids to quantitatively integrate the reduction in bioavailability due to the presence of dissolved organic matter. As part of the risk assessment, we incorporated a species sensitivity distribution to take into account the differences in toxicity for different species.

## Materials and Methods

### Problem Formulation

We performed a probabilistic acute ecological risk assessment using actual environmental concentrations of permethrin depositing on surfaces after ground-based ULV applications. We chose an acute risk assessment because the presence of suspended sediment substantially reduces the freely dissolved concentration of pyrethroids, thereby greatly reducing the bioavailability (Burkhard 2000; Leahey 1985; Maund et al. 2002; Schleier III and Peterson 2011; Sharom and Solomon 1981; Yang et al. 2007a; Yang et al. 2006a; Yang et al. 2007b; Yang et al. 2006c). Acute exposures were defined in this study as a single-day exposure after a single insecticide application.

### Hazard Identification

Permethrin and pyrethroids, in general, are highly nonpolar chemicals that have low water solubility and volatility, high octanol:water partition coefficients, and a high affinity to bind to soil and sediment particles (Laskowski 2002; Schleier III and Peterson 2011). Pyrethroids are broad-spectrum insecticides, and so they may have impacts on non-target organisms (Naumann 1990). Pyrethroids are highly toxic to certain aquatic organisms which typically are much more susceptible to pyrethroids than terrestrial organisms (Bradbury and Coats 1989; Siegfried 1993). We performed a risk assessment using permethrin because it is one of the more widely used insecticides for adult

mosquito management and has similar toxicity to the other pyrethroids used for mosquito management.

### Toxicity and Dose-Response

To estimate the risk to aquatic organisms, we created a species sensitivity distribution using the USEPA's Ecotox Database (USEPA 2010a) for permethrin with 40 aquatic species based on the 96-hr lethal concentration that kills 50% of a population values (LC50; Table 9). We used both freshwater and saltwater receptors to construct a species sensitivity distribution to reflect the diversity of habitats where ULV insecticides may be applied (Table 9). Species sensitivity distributions are used to estimate the concentrations at which a specified fraction or proportion of species could be affected (also known as the potentially affected fraction). Species sensitivity distributions can also estimate the concentration that may result in p (%) of species reaching their respective LC50, which is referred to as the hazardous concentration (HCp) (Newman et al. 2000). The HCp typically used for regulatory purposes is the HC5 which represents 5% of the potentially affected fraction of species reaching their respective LC50 (Newman et al. 2000).

The species sensitivity distribution was fit using MATLAB<sup>®</sup> R2010a (The MathWorks, Natick, MA, USA) distribution fitting tool (Newman et al. 2000). The distribution was estimated based on the chi-square goodness of fit test (Cooper 2001; Hinds 1982; Neter et al. 1996). The parameters for the species sensitivity distribution are shown in table 10.

## Exposure Assessment

We used the environmental fate data for ground deposition concentrations from chapter 2. The data were collected using ground-based ULV field experiments conducted near Elk Grove, California (38°27'17.27"N, 121°27'9.25"W), Bozeman, Montana (45°38'47.09"N, 111°24'8.18"W), and Baton Rouge, Louisiana (30°31'1.57"N, 91°9'20.32"W) during the summers of 2009 to 2011. Sites with little vegetative structure and a flat topography were chosen for all experiments because vegetation affects air movement and subsequent deposition of insecticides and we were interested in the greatest depositions for conservative estimates of exposure. The ground deposition concentrations for the formulations Permanone<sup>®</sup> 30-30 (30% permethrin), Permanone<sup>®</sup> 31-66 (31% permethrin), Aqua-Reslin<sup>®</sup> (20% permethrin) (Bayer Environmental Science, Research Triangle Park, NC, USA), and Aqua-Kontrol (20% permethrin) (Univar<sup>®</sup>, Redmond, WA, USA) between the distances of 5 to 180 m were used to model the environmental concentrations. Chapter 2 shows that the densities of the formulations had the largest effect on the predicted concentration of insecticide depositing on surfaces; therefore, we modeled all concentrations of permethrin using the different formulations to reflect the variability of formulation density. All formulations of permethrin were applied at the maximum application rate of 7.85 g active ingredient/ha as listed on the label. Formulations and the order in which the formulations were sprayed were randomly selected. The experimental design was an incomplete block design with each spray application (block) occurring in the order in which it was randomly selected. Replications were performed over time within the same night and over different nights with a total of

826 deposition data points taken over 82 spray events were modeled as a distribution of concentrations. MATLAB R2010a was used to fit a distribution to all concentrations measured 5 to 180 m from the spray source (Table 10).

To estimate the water concentrations of the insecticide, a static pond (no in-flow or out-flow of water) 2-m deep was used (USEPA 2001). We used the following equation to estimate the concentration of insecticide in the water,

$$WC = D * WD * CF \quad (1)$$

where WC is the water concentration  $\mu\text{g/l}$ , D is the deposition on the water surface ( $\mu\text{g}/\text{cm}^2$ ), WD is the water depth (2 m), and CF is the conversion from  $\mu\text{g}/\text{m}^3$  to  $\mu\text{g}/\text{l}$ .

Schulz et al. (2001) demonstrated that the above conversion produces similar concentrations to actual measured water concentrations.

For chemicals that have similar lipophilicity as pyrethroids, such as organochlorine insecticides, the dissolved organic content in water is the most significant factor influencing partitioning of the chemicals (Hoke et al. 1994; Hoke et al. 1995). To model the bioavailable fraction of permethrin in the presence of dissolved organic matter, I used the equation experimentally derived by Yang et al. (2007b),

$$C_w = \frac{C_t}{1 + K_{doc} (DOC)} \quad (2)$$

where  $C_w$  is the bioavailable concentration of permethrin ( $\mu\text{g}/\text{l}$ ),  $C_t$  is the total aqueous concentration of permethrin ( $\mu\text{g}/\text{l}$ ) from equation 1,  $K_{doc}$  is the partition coefficient for dissolved organic carbon (Yang et al. 2007b), and DOC is the dissolved organic content (Di Toro et al. 1991; Maund et al. 2002; Yang et al. 2007b). The  $K_{doc}$  values obtained from Yang et al. (2007b) and were modeled using a uniform distribution 16000 to 79000

to incorporate the differences in measured values. We used uniform distribution from 3 to 20 mg/l to model the dissolved organic carbon content which is representative of ponds, lakes, streams, and rivers (Yang et al. 2006a; Yang et al. 2007b; Yang et al. 2006b).

The model for estimating concentrations of permethrin in water is conservative because of the following four key assumptions: (1) when the insecticide deposits on the water, it will disperse instantly into the 2 m water column; (2) there will be no dilution due to water movement; (3) the application will occur immediately adjacent to the pond and the prevailing wind direction will be over the pond; and (4) the insecticide will be applied at the maximum application rate of 7.846 g/ha.

#### Probabilistic Risk Assessment

To generate the percentiles of water concentrations, we used Monte Carlo simulation (Crystal Ball<sup>®</sup> 7.3; Oracle<sup>®</sup>, Denver, CO, USA) with 20,000 iterations using equation 1 and 2 and the distribution for deposition in table 10. We compared the modeled percentile concentrations to the species sensitivity distribution to determine the potentially affected fraction of species.

#### Results and Discussion

The percentiles of estimated water concentrations of permethrin are presented in table 11. The concentration that could potentially affect 5% (HC5) of the species is 0.05µg/l. The 95<sup>th</sup> percentile estimated concentration would result in less than 0.0001% of the potentially affected fraction of species reaching their respective LC50 (Table 11;

Figure 7). If the concentrations were not modeled with the incorporation of dissolved organic content, the estimated concentrations at the 50<sup>th</sup> and 95<sup>th</sup> percentile would be 0.03 and 0.14 µg/l, which would result in less than 3 and 13% of the potentially affected fraction species reaching their respective LC50, respectively.

Our results can also be used for a semiaquatic habitat because the range of dissolved organic content used to model adsorption of permethrin were similar to those observed in the Florida Everglades (Aiken et al. 2011). In addition, semiaquatic habitats are modeled with a water depth of 0.15 m which would not appreciably change our results (USEPA 2007).

The National Marine Fisheries Service (NMFS) is currently examining the direct and indirect effects of pesticides on endangered salmonids (NMFS 2010). The NMFS found that aerial applications of ULV could adversely affect salmonid prey species (NMFS 2010). However, Bogen and Reiss (2012) showed that the NMFS estimate of risk was overestimated because flowing water in a riparian-aquatic scenario reduced the concentration of insecticide between 50 and 300-fold depending on the water depth and flow rate. Therefore, the concentration incorporating dilution without incorporating the effect of DOC at the 95<sup>th</sup> percentile would be between 0.003 and 0.0005 µg/l, which would result in less than 0.1 and 0.009% of the potentially affected fraction of species reaching their LC50, respectively.

Davis et al. (2007) estimated that the water concentration for permethrin was approximately 0.0004 µg/l using PRZM EXAMS. The concentration estimated by Davis et al. (2007) is greater than the 95<sup>th</sup> percentile concentration in the current study.

Therefore, the risk estimate of Davis et al. (2007) is most likely conservative based on our results.

Although pyrethroids display very high acute toxicities to certain aquatic organisms when in the aqueous phase, the presence of suspended sediment substantially reduces the freely dissolved concentration of pyrethroids, and therefore, their bioavailability (Leahey 1985; Schleier III and Peterson 2011; Sharom and Solomon 1981). Pyrethroids have little mobility in soils and are associated with sediments in natural water; consequently, they will only be in the water phase for a relatively short time, limiting the exposure to many organisms (Yang et al. 2006a; Yang et al. 2007b; Yang et al. 2006c). In addition, the half-life of many pyrethroids in aquatic systems that are not bound to sediment is one to five days (Laskowski 2002; Schleier III and Peterson 2011). Therefore, chronic exposures to organisms that do not have a benthic component in their life cycle most likely will not result in observed effects because pyrethroids dissipate rapidly (dissipation half-life in the water column is generally less than one day) (Laskowski 2002). Our results suggest that the bioavailable permethrin after ground-based ULV applications would not result in concentrations above the detection limit in aquatic systems. Furthermore, the rapid dissipation of pyrethroids makes it difficult to reconcile field exposures with those used in laboratory studies that maintain constant concentrations without dissolved organic content.

Experiments have shown that the toxicity of cypermethrin to *Daphnia magna* and *Chironomus tentans* decreased as the dissolved organic carbon content of the water increased (Maund et al. 2002). Acute pyrethroid toxicity decreases 56 to 92% depending



on the concentration of suspended sediments (Yang et al. 2006a; Yang et al. 2006b).

Yang et al. (2006c) found that pyrethroids adsorbed on suspended sediment or dissolved organic matter were completely unavailable for uptake by *D. galeata mendotae* after a 24-hr exposure period. Therefore, because of the physicochemical properties and the use of the 96-hr LC50 values for permethrin, the estimated species sensitivity distribution most likely overestimates the toxicity (Burkhard 2000; Maund et al. 2002; Wheelock et al. 2005; Yang et al. 2006a; Yang et al. 2007b; Yang et al. 2006b, c).

In measurements of actual water concentrations of pyrethrins and permethrin, Jensen et al. (1999) found no detectable concentrations in wetlands before and after ground-based ULV applications. Weston et al. (2006) found no detectable concentrations of pyrethrins in suburban streams 10 and 34 hrs after aerial ULV applications over Sacramento, California, USA. Schleier III et al. (2008b) found no detectable concentrations of pyrethrins one hour after aerial ULV applications over irrigation ditches and static ponds. Concentrations of ULV resmethrin in Suffolk County, New York, USA after ground-based applications were below the limit of detection (Abbene et al. 2005). These studies support our findings that the concentrations would be below the detection limit in water, which is approximately 5 ng/l (Abbene et al. 2005).

There have been several studies on the effects of both aerial and ground-based ULV applications on aquatic organisms. Davis and Peterson (2008) demonstrated that there was little to no significant impact on sampled aquatic and terrestrial invertebrates after single and multiple ground-based ULV applications. Lawler et al. (2008) found that ground-based ULV applications of pyrethrins synergized with PBO did not cause

significant mortality of the aquatic invertebrates, *D. magna* and *Callibaetis californicus*. Ground-based applications of ULV permethrin had no significant impact on aquatic macroinvertebrates and *Gambusia affinis* when used above wetlands (Jensen et al. 1999).

After agricultural applications of pyrethroids, reductions of populations in aquatic communities have been observed at concentrations of 5 to 10 µg/l of pyrethroid in the water with recovery occurring within two weeks (Bloomquist 1993; Cole and Casida 1983; Giddings et al. 2001; Schleier III and Peterson 2011). Agricultural applications use as much as 100-fold greater concentrations of active ingredient compared to ULV applications for mosquito management. Hill (1989) reviewed approximately 70 freshwater field studies in natural ponds, farm ponds, streams, rivers, rice paddies, and microcosms and mesocosms and found that there were few to no acute effects of pyrethroids on fish and aquatic invertebrates. Aerial agricultural applications of cypermethrin adjacent to a farm pond showed that dipterans were the most affected in the water, but the populations quickly recovered after the application (Kedwards et al. 1999). Sediment-dwelling invertebrates in the families Gammaridae and Asellidae were adversely affected by direct agricultural sprays of cypermethrin and lambda-cyhalothrin in experimental ponds, but increases in the families Planorbidae, Chironomidae, and Lymnaeidae were also observed (Walker 2009). The effects on sediment-dwelling invertebrates can also be accounted for because type II pyrethroids like cypermethrin and lambda-cyhalothrin have a greater toxicity than type I pyrethroids (permethrin) to both aquatic and terrestrial invertebrates (Mokry and Hoagland 1990; Schleier III and Peterson 2012; Siegfried 1993).

Our exposure model is most likely conservative because most mosquito control districts typically apply the insecticides at one-half or one-quarter of the maximum application rate (Mount 1998), which would reduce the exposure because we modeled the concentrations based on the maximum application rate of 7.845 g/ha. We also assumed there would be no buffer, the prevailing wind direction would be over the water body, the truck would travel along the water's edge, and the insecticide would instantly disperse into the water column. In addition Bogen and Reiss (2012) incorporated the flow of water to estimate the exposure to insecticides after pesticide applications and found that dilution reduced the exposure by about 50- to 300-fold from the initial concentration depending on the water depth and flow rate.

Supporting our exposure model are field studies on the effects of both ground-based and aerial applications of ULV insecticides which showed no significant effects on aquatic organisms. In addition, agricultural applications, which often use 100-fold greater concentrations of pyrethroids and greater toxicity type II pyrethroids, do not have significant effects on aquatic communities until the concentrations reach substantially greater concentrations than the estimated 95<sup>th</sup> percentile concentration in the current study.

Our study is the first to estimate the aquatic risks from ground-based ULV applications for adult mosquito management using a species sensitivity distribution and actual environmental concentrations deposited on surfaces. It is also the first study to integrate the effect of dissolved organic matter to estimate the bioavailable concentration of pyrethroids in the environment into a risk assessment framework. The data used to

estimate the deposition of ULV insecticides on water were obtained from the data set used to generate the validated model developed in chapter 2, which more accurately represents environment concentrations. We found that the estimated 95<sup>th</sup> percentile concentration of permethrin would result in less than 0.0001% of the potentially affected fraction of species would reach their respective LC50 when the physiochemical properties of pyrethroids are incorporated. Our results are supported by the weight of evidence that pyrethroids disseminated by ground-based ULV applications will not result in detectable concentrations of insecticides or deleterious effects on aquatic organisms.

Because our exposure model estimates concentrations of permethrin in water based on ground deposition data and dissolved organic matter, further research is needed to systematically measure actual concentrations in water after ground-based ULV applications. This research would not only test the conservatism of our assessment, but it also could be used to refine our exposure model by incorporating actual water concentrations.

Table 9. Values for 96-hour lethal concentration of permethrin that kills 50% of a population (LC50) for both vertebrate and invertebrate species used to develop the species sensitivity distribution

Species	Vertebrate or Invertebrate	LC50 ( $\mu\text{g/L}$ )
<i>Menippe mercenaria</i>	Invertebrate	0.018
<i>Hyalella azteca</i>	Invertebrate	0.021
<i>Palaemonetes pugio</i>	Invertebrate	0.05
<i>Chironomus dilutus</i>	Invertebrate	0.059
<i>Americamysis bahia</i>	Invertebrate	0.075
<i>Crangon septemspinosa</i>	Invertebrate	0.13
<i>Gammarus pseudolimnaeus</i>	Invertebrate	0.17
<i>Penaeus duorarum</i>	Invertebrate	0.22
<i>Procambarus clarkii</i>	Invertebrate	0.28
<i>Daphnia magna</i>	Invertebrate	0.3
<i>Penaeus aztecus</i>	Invertebrate	0.34
<i>Gammarus pulex</i>	Invertebrate	0.44
<i>Ceriodaphnia dubia</i>	Invertebrate	0.57
<i>Nitocra spinipes</i>	Invertebrate	0.6
<i>Homarus americanus</i>	Invertebrate	0.73
<i>Salmo salar</i>	Vertebrate	1.5
<i>Oncorhynchus clarki ssp. henshawi</i>	Vertebrate	1.58
<i>Erimonax monachus</i>	Vertebrate	1.7
<i>Oncorhynchus gilae ssp. apache</i>	Vertebrate	1.71
<i>Salvelinus fontinalis</i>	Vertebrate	2.3
<i>Uca pugilator</i>	Invertebrate	2.39
<i>Etheostoma lepidum</i>	Vertebrate	2.71
<i>Chironomus riparius</i>	Invertebrate	2.89
<i>Oncorhynchus mykiss</i>	Vertebrate	2.9
<i>Pimephales promelas</i>	Vertebrate	3
<i>Etheostoma fonticola</i>	Vertebrate	3.34
<i>Notropis mekistocholas</i>	Vertebrate	4.16
<i>Xyrauchen texanus</i>	Vertebrate	5.95
<i>Ictalurus punctatus</i>	Vertebrate	7.2
<i>Micropterus salmoides</i>	Vertebrate	8.5
<i>Micropterus sp.</i>	Vertebrate	8.5
<i>Chironomus tentans</i>	Invertebrate	10.45
<i>Gambusia affinis</i>	Vertebrate	12
<i>Lepomis macrochirus</i>	Vertebrate	13
<i>Cyprinodon variegatus</i>	Vertebrate	17
<i>Cyprinodon bovinus</i>	Vertebrate	21
<i>Ptychocheilus lucius</i>	Vertebrate	24
<i>Atherinops affinis</i>	Vertebrate	25.3
<i>Menidia beryllina</i>	Vertebrate	27.5

Table 10. Distributions for deposition on surfaces to estimate water concentrations using equation 1 and the species sensitivity distribution for permethrin

Input	Distribution Type	Parameter	Concentration	Units
Deposition on Water	Gamma (Truncated)	Location	0.00009	$\mu\text{g}/\text{cm}^2$
		Scale	0.01	
		Shape	0.81	
Species Sensitivity Distribution	Log-Normal (Truncated)	Mean	11.56	$\mu\text{g}/\text{l}$
		SD*	92.19	

\*Standard Deviation

Table 11. Percentiles of water concentrations of permethrin modeled using equations 1 and 2

Percentiles	Water Concentration ( $\mu\text{g}/\text{L}$ )
5%	3.3E-09
10%	6.7E-09
15%	1.1E-08
20%	1.5E-08
25%	2.0E-08
30%	2.6E-08
35%	3.3E-08
40%	4.0E-08
45%	4.9E-08
50%	5.9E-08
55%	7.0E-08
60%	8.3E-08
65%	9.9E-08
70%	1.2E-07
75%	1.4E-07
80%	1.8E-07
85%	2.2E-07
90%	2.9E-07
95%	4.5E-07

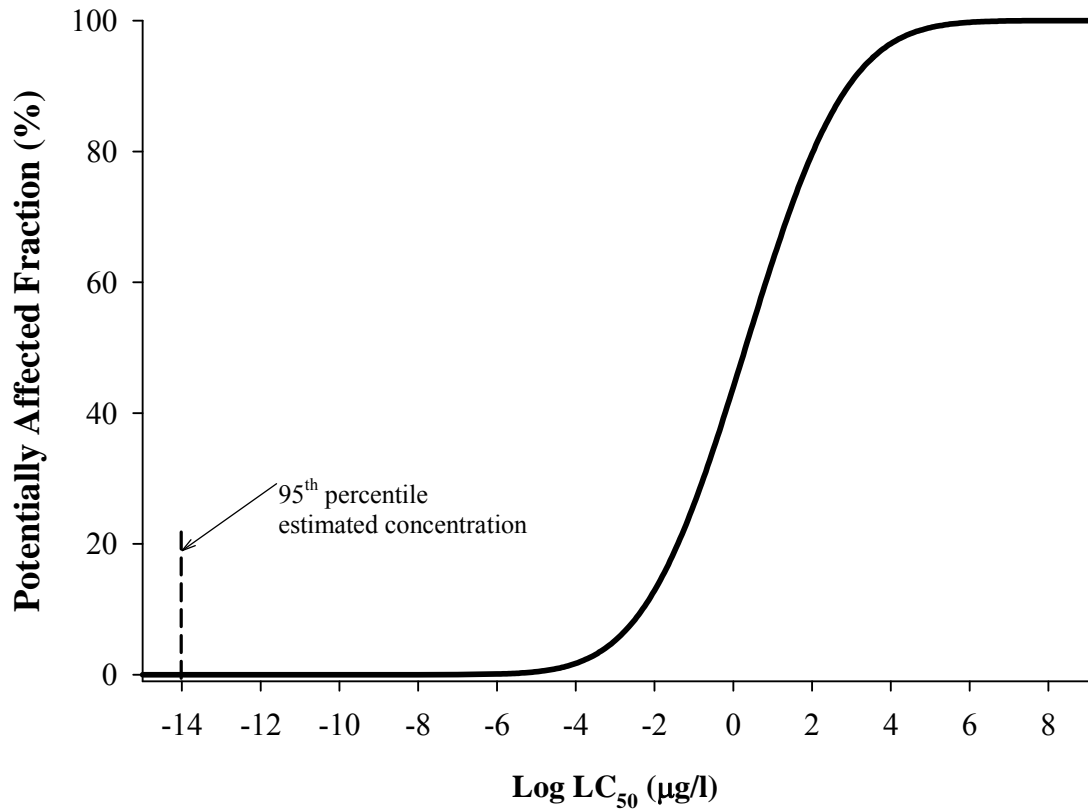


Figure 10. Acute species sensitivity distribution constructed from the 96-hour log of the lethal concentrations of permethrin that kill 50% of a population (LC50), demonstrating the proportion of species affected for aquatic organisms at each concentration.

## CHAPTER 5

THE EFFECT OF FLUORESCENT TRACERS ON DROPLET SPECTRUM,  
VISCOSITY, AND DENSITY OF PESTICIDE FORMULATIONSAbstract

The most important factor affecting efficacy and drift of pesticide applications is the droplet spectrum. To measure pesticide drift, researchers utilize fluorescent tracers to rapidly quantifying spray deposition. Despite the fact that fluorescent tracers have been used for more than 50 years, no experiments have been performed on the effect they have on the properties of pesticide formulations (density and viscosity) or droplet spectrum, which affect the drift of pesticides. Therefore, we examined the effect of an oil- and water-based tracer on the volume median diameter (VMD), viscosity, and density of oil- and water-based pesticide formulations. In addition, we experimentally fit and demonstrate the utility of using distributions to characterize pesticide droplet spectra. The addition of tracers to both water- and oil-based formulations did not significantly alter the VMD, viscosity, and density. Lognormal distributions provided the best fit for the water- and oil-based formulations with and without tracer. Our results demonstrated that the addition of oil- and water-based tracers do not significantly alter pesticide formulations properties and droplet spectrum, and most likely do not alter the movement of pesticide droplets in the environment.



## Introduction

The most important factor affecting efficacy and drift of pesticide applications is droplet size and distribution (Akesson and Yates 1964; Craig et al. 1998; De Schampheleire et al. 2009; Hewitt 2008; Miller and Butler Ellis 2000; Teske et al. 2002; Yates et al. 1967). Researchers have found that spray drift is independent of the active ingredient properties (molecular weight, structure, etc.), but is dependent on environmental factors and formulation properties (Klein and Johnson 2002; Majewski and Capel 1995; Reichenberger et al. 2007).

Pesticide drift can be quantified using droplet count techniques or through traditional analytical measures of pesticide concentrations. Droplet count techniques enumerate the number and size of droplets that are present either by directly sampling from the spray cloud using laser measurement techniques or manual droplet count techniques using magnesium or Teflon<sup>®</sup>-coated slides (Walter 2001). The most commonly used measurement to characterize droplet spectra is volume median diameter (VMD) (also known as the mass median diameter) (Parkin 1993). The VMD is the droplet diameter in which 50% of the total volume (or mass) of liquid sprayed is comprised of droplets with diameters smaller than the VMD (Cooper 2001; John 2001).

The measurement of pesticide concentrations in the environment with traditional analytical techniques like gas or liquid chromatography is time and cost prohibitive, involves extensive sample cleanup, can have low instrument sensitivity, and may be confounded by background contamination (Akesson and Yates 1964). Fluorescent tracers can overcome the limitations of traditional analytical techniques and thus be used

to rapidly quantify spray deposition. Their advantages include high sensitivities, rapid quantification, solubility in spray mixtures, low cost, low toxicity, and distinctive properties that are different from background substances (Davis and Elliott 1953; Sharp 1974; Yates and Akesson 1963). Fluorescent tracers have been used to estimate the concentrations of pesticides in spray drift and efficacy studies, and for determining the amount of pesticide that settles onto the target area (Barber and Parkin 2003; Cadogan et al. 2005; Cai and Stark 1997; Cooke and Hislop 1993; Longley et al. 1997; Parkin and Merritt 1988; Peng et al. 2005; Pergher 2001; Sharp 1974, 1976; Sundaram and Sundaram 1992; Yates and Akesson 1963).

Despite the fact that fluorescent tracers have been extensively used for more than 50 years, no experiments have been performed on the effect they have on the properties of pesticide formulations (density and viscosity) or droplet spectrum. This is surprising because formulation properties and droplet spectra are important for quantifying and statistically modeling pesticide drift. Formulation viscosity and density can significantly influence the droplet spectrum of pesticide applications (De Schampheleire et al. 2009; Sundaram and Retnakaran 1987). Viscosity affects the droplet spectrum through the resistance of forming smaller droplets at higher viscosities (De Schampheleire et al. 2009; Sundaram and Retnakaran 1987). The density of droplets is used to determine the aerodynamic diameter, which is the diameter of a unit-density sphere having the same gravitational settling velocity as the particle being measured (Baron and Willeke 2001a; Hinds 1982). In addition, spray pressure also influences the size of droplets with higher pressures producing smaller droplets. However, if the addition of a tracer requires a

change in the spray pressure to obtain a suitable droplet size, then direct comparisons between drift of pesticides with and without tracer cannot be made.

We examined the effect of an oil- and water-based tracer on the droplet spectrum, viscosity, and density of oil- and water-based pesticide formulations. In addition, few studies on pesticide drift or the analysis of the droplet spectrum of spray equipment have utilized modeling techniques for characterizing droplet distributions (Hewitt 2008). Droplet spectra are distributions of various sized droplets. Thus, determining the distribution for spray events is important for characterizing what environmental and physical processes influence the movement of droplets (Baron and Willeke 2001a). Therefore, we experimentally fit and demonstrate the utility of using distributions to characterize pesticide droplet spectra.

### Materials and Methods

We performed our study using ultra-low-volume (ULV) pesticide spray equipment used for adult mosquito management. Ultra-low-volume applications are applied as an aerosol with special spray equipment, so they drift over the target area with very little settling out onto surfaces. We chose ULV spray equipment because the movement and behavior of aerosol particles (droplets between 0.001 and 100  $\mu\text{m}$  in size) are strongly dependent on droplet size and are also a higher drift hazard than larger droplets (Baron and Willeke 2001a; Hewitt 2008).

The oil-soluble tracer Tinopal OB (BASF Corp., Florham Park, NJ, USA) was mixed with Permanone<sup>®</sup> 30-30 (Bayer Environmental Science, Research Triangle Park,

NC, USA) at a rate of 11 g/L and the water soluble tracer Fluorescein (Aqua Solutions, Deer Park, TX, USA) was mixed with Aqua-Reslin<sup>®</sup> (Bayer Environmental Science, Research Triangle Park, NC, USA) at a rate of 14 g/L. Aqua-Reslin was mixed 1:1 with deionized (D.I.) H<sub>2</sub>O and was applied at the maximum flow rate of 192 mL/min. Permanone 30-30 was mixed 1:2:1 with Crystal Plus 70T light mineral oil (STE Oil Company, Inc., San Marcos, TX, USA) and American Chemical Society (ACS) grade toluene (99.5% purity, Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA) and was applied at the maximum flow rate of 193 mL/min.

Sprays were conducted outdoors at Montana State University in Bozeman, MT, USA. A DC-III portable droplet measurement system (KLD Labs, Inc., Huntington Station, NY, USA) was used to measure droplet spectra and volume median diameter (VMD) of each spray event. The DC-III probe was held 2 m from the nozzle in the center of the spray plume and sampling was terminated at 15 seconds or when 10,000 droplets were sampled. Sprays were conducted using a Guardian 95 ES ultra-low-volume sprayer (ADAPCO, Sanford, FL, USA) cold fogger with a spray pressure of 10 Kpa and a nozzle orientation of 135° with respect to the ground. The mean temperature and relative humidity during the tests were 26.83 (±0.39)°C and 35.31 (± 0.74)%, respectively.

Aqua-Reslin and Permanone 30-30 formulations with and without tracer were randomly chosen with five replicates of each formulation mixture for a total of 20 replications. Two subsamples were taken for each replication. Between each spray replication the hoses and nozzle were rinsed with 300 mL of D.I. H<sub>2</sub>O followed by 300

mL of a 1:1 mixture of high pressure liquid chromatography acetone (99.7% purity; EMD Chemicals, Gibbstown, NJ, USA) and ACS grade toluene.

The measurement of kinematic viscosity of the different formulations was conducted using an Ostwald viscometer (VWR International Inc., West Chester, PA, USA) according to American Society for Testing and Materials (ASTM) procedures (ASTM 2007a, b). Formulation density was determined by weighing a 10 mL sample of each formulation on a calibrated Mettler AM100 analytical balance (Mettler Toledo AG, Switzerland). Measurement of density and viscosity was performed at 20°C. The reference standard was deionized (D.I.), H<sub>2</sub>O which has a density of 0.998 g/mL and a viscosity of 1.004 cSt at 20°C. The experimental design for the measurement of viscosity and density was the same as stated for the droplet spectrum measurement.

Statistical Analysis System 9.2 was used to run t-tests ( $\alpha = 0.05$ ) to determine differences in VMD, kinematic viscosity, and density for the respective formulations with and without tracer. Distributions were fit using MATLAB<sup>®</sup> R2009a distribution fitting tool. Distributions for droplet spectra were determined based on the chi-square goodness of fit test, which tests if a sample of data came from a population with a specified distribution (Cooper 2001; Hinds 1982; Neter et al. 1996).

## Results

There was no significant difference in VMD for Aqua-Reslin with and without tracer ( $t=-0.21$ ,  $p=0.83$ ). The mean VMD for Aqua-Reslin with and without tracer was 21.29 and 21.74  $\mu\text{m}$ , respectively (Table 12). There was no significant difference in

VMD for Permanone 30-30 with and without tracer ( $t=0.19$ ,  $p=0.85$ ). The average VMD for Permanone 30-30 with and without tracer was 19.48 and 19.15  $\mu\text{m}$ , respectively (Table 12). Lognormal distributions provided the best fit for Aqua-Reslin and Permanone 30-30 with and without tracer (Table 13; Figures 11 and 12). In addition, the 95% confidence intervals for Aqua-Reslin with and without tracer and Permanone 30-30 with and without tracer overlapped.

Mean kinematic viscosity and density for Aqua-Reslin and Permanone 30-30 with and without tracer are presented in table 12. No significant difference in kinematic viscosity or density was observed for Aqua-Reslin with and without tracer ( $t=-0.31$ ,  $p=0.77$ ;  $t=-0.57$ ,  $p=0.59$ , respectively). No significant difference in kinematic viscosity or density was observed for Permanone 30-30 with and without tracer ( $t=-0.29$ ,  $p=0.77$ ;  $t=0.039$ ,  $p=0.97$ , respectively).

## Discussion

The droplet spectrum of an application system is one of the more important variables that influence the drift of pesticides (De Schampheleire et al. 2009; Hewitt 2008). Although aerosol particles follow the overall gas flow, the trajectories can deviate due to external forces such as changes in wind direction and velocity (Baron and Willeke 2001b). These deviations are dependent on the size of the droplets, which are in turn influence by formulation properties. Dynamic viscosity (which is directly related to kinematic viscosity) is the strength of molecular forces of attraction in a liquid and therefore can significantly alter the droplet spectrum through the resistance of forming

smaller droplets at higher viscosities (De Schampheleire et al. 2009; Sundaram and Retnakaran 1987). Our study demonstrated that the addition of tracers to both water- and oil-based formulations did not significantly alter the VMD, viscosity, and density. The results of the viscosity experiment support our finding that the addition of tracers should not significantly alter the VMD. The density of droplets is important for determining the aerodynamic diameter, which is used to estimate the terminal settling velocity (Baron and Willeke 2001a; Hinds 1982).

There are several potential problems with *in situ* sampling of droplet spectra, such as precision, accuracy, instrument sensitivity, and the instrument's size (Rader and O'Hern 2001). Precision and accuracy can be increased with multiple sampling events, but the instrument sensitivity may bias the estimates of smaller droplets. For example, the DC-III groups any particle less than one  $\mu\text{m}$  in diameter into a bin of size one  $\mu\text{m}$ , so our estimated distribution may have been shifted toward larger droplets sizes.

No two spray events produce the same droplet spectra; therefore, sampling multiple times and fitting a distribution to the data can reduce error and give a better estimate of the various statistics such as the VMD. The log-normal distribution is the most common distribution describing aerosols distributions because it is skewed toward smaller droplets which often have standard deviations that are large in comparison to the mean (Cooper 2001; John 2001). The lognormal distribution has been shown to result from the proportional breakup of large droplets into smaller sizes or it can occur with the agglomeration of smaller droplets (Cooper 2001).

The VMD is the most widely used statistic for describing droplet size, and because it is related to other statistics like the number median diameter it provides a good surrogate for testing if droplet spectra are significantly affected by the addition of chemicals like tracers. However, statistics like the VMD are centered at the tail of the distribution, and must be interpreted carefully because small increases in the standard deviation can have a large impact on values at the tail (Hinds 1982).

The utility of fitting a lognormal distribution is that any type of mean or median diameters (i.e. VMD and NMD) and the 95% confidence intervals can be calculated easily using the Hatch-Choate conversion equations (Cooper 2001; Hinds 1982). The lognormal distribution is a special case of the normal distribution which can be transformed to normalize the data for use in other modeling exercises. In addition, fitting a cumulative distribution function to the data (Figures 11 and 12), provides both a simple visual and quantitative method for determining the percentage of droplets between a size range that is optimal for the control method.

Droplet size distributions provide both a visual and quantitative tool for understanding the mechanisms that underlie the deposition and movement of droplets in the environment (Rader and O'Hern 2001). The distribution can be used to estimate the proportion of droplets that are influenced by various mechanisms like gravitational settling (Baron and Willeke 2001b). In addition, it can be used to estimate the efficiency of collection filters by determining the proportion of droplets that will deposit via Brownian diffusion, interception, inertial impact, and gravitational settling which can be used to



determine the optimal diameter of a filter for sampling air concentrations (Brockmann 2001; Lee and Mukund 2001) .

Studies of pesticide drift and spray equipment only report deterministic values such as the VMD or do not measure the droplet spectrum, and often do not report the distribution of droplets (De Schampheleire et al. 2008; Hoffmann et al. 2009; Nuyttens et al. 2006a, b; Nuyttens et al. 2005; Smith et al. 2000). The distribution of spray droplets is important for modeling pesticide drift because it can be used to determine the error around the point estimates like VMD. By fitting a distribution to the data, the variance around the deterministic value can be determined and used in probabilistic spray drift models.

Our results demonstrate that the addition of both Fluorescein and Tinopal OB do not significantly alter pesticide formulations properties and droplet spectrum, and most likely do not alter the movement of pesticide droplets in the environment. Future pesticide drift studies should estimate the droplet distribution because deterministic statistics like the VMD could be biased depending on the shape and parameters of the distribution. Fitting a distribution to the droplet spectrum also provides an estimate of the error around point measurements like the VMD, which can be used in probabilistic pesticide drift models.

Table 12. Mean volume median diameter (VMD), viscosity, and density for Aqua-Reslin<sup>®</sup>, Aqua-Reslin with tracer, Permanone<sup>®</sup> 30-30, and Permanone 30-30 with tracer formulations

Formulation	VMD ( $\mu\text{m}$ )	Viscosity (cSt)	Density (g/mL)
Aqua-Reslin	21.29 ( $\pm 1.14$ ) <sup>a</sup>	8.72 ( $\pm 0.28$ )	0.98 ( $\pm 0.011$ )
Aqua-Reslin with tracer	21.74 ( $\pm 1.87$ )	8.88 ( $\pm 0.43$ )	0.99 ( $\pm 0.015$ )
Permanone 30-30	19.48 ( $\pm 1.47$ )	4.87 ( $\pm 0.025$ )	0.93 ( $\pm 0.003$ )
Permanone 30-30 with tracer	19.15 ( $\pm 0.89$ )	4.91 ( $\pm 0.11$ )	0.93 ( $\pm 0.0005$ )

<sup>a</sup> Standard error

Table 13. Mean, variance, scale ( $\sigma$ ), and location ( $\mu$ ) parameters, and the lognormal distributions for Aqua-Reslin<sup>®</sup>, Aqua-Reslin with tracer, Permanone<sup>®</sup> 30-30, and Permanone 30-30 with tracer formulations

Formulation	mean	variance	$\sigma$	$\mu$
Aqua-Reslin	3.82	29.71	0.78 ( $\pm 0.009$ ) <sup>a</sup>	1.05 ( $\pm 0.006$ )
Aqua-Reslin with tracer	2.93	12.81	0.62 ( $\pm 0.009$ )	0.95 ( $\pm 0.006$ )
Permanone 30-30	3.57	17.82	0.83 ( $\pm 0.01$ )	0.94 ( $\pm 0.007$ )
Permanone 30-30 with tracer	3.84	22.94	0.88 ( $\pm 0.009$ )	0.97 ( $\pm 0.007$ )

<sup>a</sup> Standard error

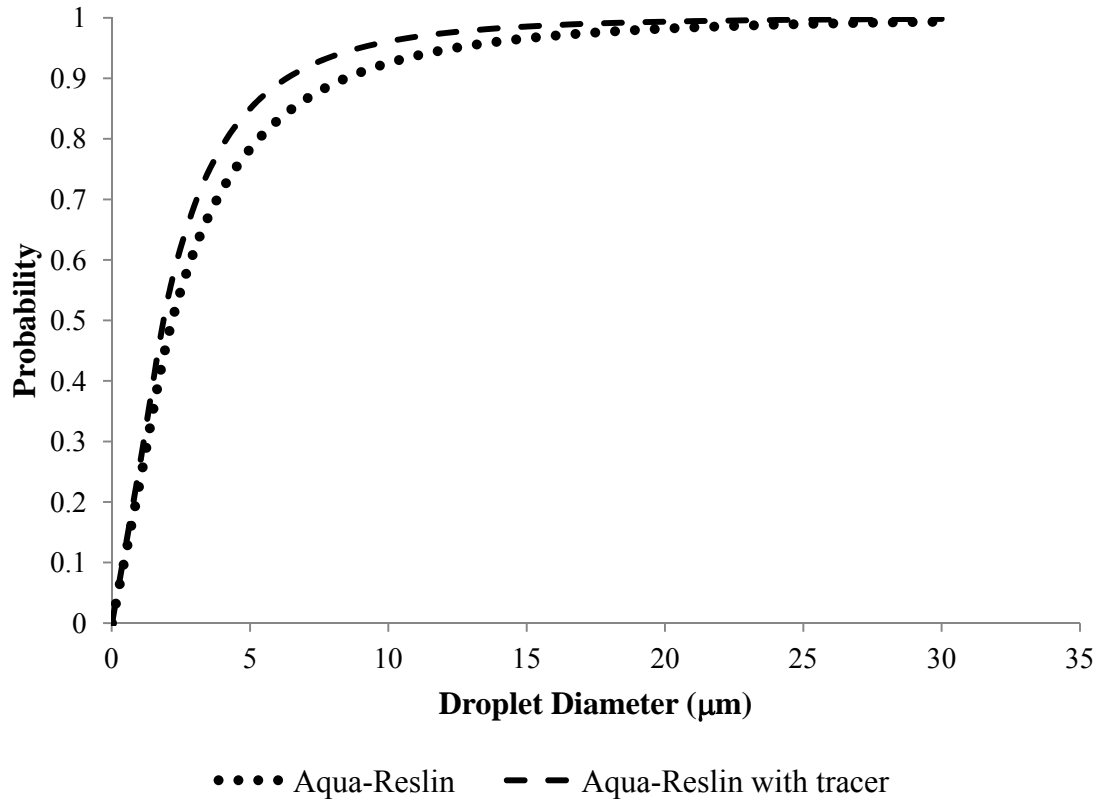


Figure 11. Lognormal cumulative distribution function for Aqua-Reslin<sup>®</sup> and Aqua-Reslin with tracer formulations

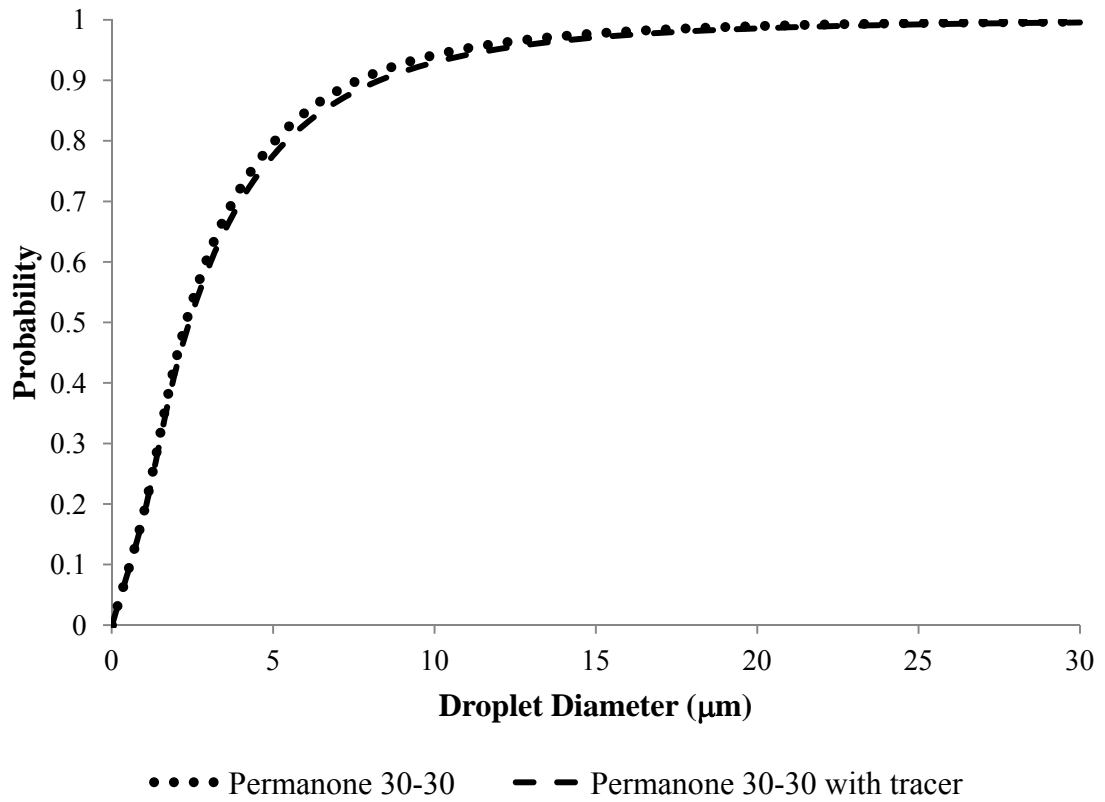


Figure 12. Lognormal cumulative distribution function for the Permanone<sup>®</sup> 30-30 and Permanone 30-30 with tracer formulations

## CHAPTER 6

## CONCLUSION

One of the more effective ways of managing high densities of adult mosquitoes that vector human and animal pathogens is ultra-low-volume (ULV) aerosol applications of insecticides. However, the U.S. Environmental Protection Agency and other regulatory agencies use models that are not validated for ULV insecticide applications. Currently, there is no validated model that can accurately predict deposition of insecticides applied using ULV technology for adult mosquito management. In addition, little is known about the deposition and drift of small droplets like those used under conditions encountered during ground-based ULV applications.

To address the lack of a validated model we perform field studies in Montana, California, and Louisiana during the summers of 2009-2011 measuring deposition concentrations of insecticides. A regression model was fit to the data to develop a model for predicting environmental concentrations of insecticides after ULV applications. The regression model selected by the Bayesian Information Criterion showed that the density of the formulation and the density and count median diameter (CMD) interaction coefficients were the largest in the model. The results showed that as density of the formulation decreases, deposition increases. The interaction of density and CMD shows that greater density formulations and larger droplets result in greater deposition. These results are supported by current understanding of aerosol physics. A  $k$ -fold cross validation demonstrated that the mean square error of the selected regression model is not

biased, and the mean square error and mean square prediction error indicated good predictive ability.

The data generated during the field studies were used to refine previous risk assessments for ground-based ULV applications. Risk assessment often uses a tiered approach extending from deterministic models (Tier I), which are based on extremely conservative assumptions, to field evaluation and probabilistic models (Tier IV), which use refined assumptions. Surprisingly, few studies have been conducted that quantitatively demonstrate the change in risk for pesticides when higher-tiered assessments are performed, particularly with respect to human health. Therefore, we chose a case study with ULV aerosol applications of the insecticide permethrin to characterize the change in risk estimates when higher tiered risk assessments are performed and to refine previous risk assessments using estimated environmental concentrations (EECs) by incorporating actual environmental concentrations (AECs). We used the risk quotient (RQ) method, which is calculated by dividing the total potential exposure for each group and chemical by its ingestion toxic endpoint value (RfD).

Risks to toddlers and infants were highest while risks to adult males were lowest risk. Median total acute exposures for permethrin ranged from 0.00002 to 0.0001 mg/kg body weight (BW)/day. Median RQs for permethrin ranged from 0.00009 to 0.0004 for all groups. Our results show that previous lower tiered risk assessments used conservative exposure scenarios that overestimated risks, thus being conservative in protecting human health. Our results demonstrated a 10-fold reduction in the RQ estimates when comparing risk assessments using EECs and AECs. Because we used a large data set to model

concentrations deposited on surfaces, this variance in exposure is due to the inherent variability in deposition concentrations after ULV applications and, therefore, would not warrant further refinement to improve risk assessments.

Pyrethroids are highly toxic to non-target organisms such as certain aquatic organisms, and there have been concerns about the effect of ULV insecticide applications on these organisms. To address the uncertainties associated with the risks of ULV applications and the contradictory findings of other ecological risk assessments, we performed a probabilistic aquatic ecological risk assessment for permethrin using actual environmental concentrations deposited on surfaces to estimate water concentrations. In addition, this is the first ecological risk assessment for pyrethroids to quantitatively integrate the reduction in bioavailability due to the presence of dissolved organic matter. As part of the risk assessment, we incorporated a species sensitivity distribution to take into account the differences in toxicity for different species. The 95<sup>th</sup> percentile estimated concentration would result in less than 0.0001% of the potentially affected fraction of species reaching their respective LC50. Our results are supported by the weight of evidence that pyrethroids applied by ground-based ULV applications will not result in deleterious effects on aquatic organisms.

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APPENDICES

APPENDIX A:

R STATISICAL PACKAGE CODE USED FOR THE DEVELOPMENT FOR THE  
DEVELOPMENT OF THE ENVIRONMENTAL FATE MODEL IN CHAPTER 2

Below is the code for the R Statistical Package (The R Foundation for Statistical Computing, Vienna, Austria) which was used to select the model developed in chapter 2, extra sums of squares *F*-tests, diagnostic plots, *k*-fold cross validation, linear regression prediction line and 95% confidence interval and prediction interval, linear regression prediction plots, boxplots, and histograms.

The abbreviations for the variables are:

ar = application rate (g/ha)  
 fr = flow rate (ml/min)  
 den = density of the formulation (g/ml)  
 cmd = count median diameter ( $\mu\text{m}$ )  
 vmd = volume median diameter ( $\mu\text{m}$ )  
 aw = wind speed (cm/s)  
 agt = ground temperature ( $^{\circ}\text{C}$ )  
 rh = relative humidity (%)  
 sc = stability category, 1 = unstable, 2 = neutral, 3 = stable, and 4 = very stable as determined by equation 1 and table 2 in chapter 2

####How to Read the Data into the R Statistical Program####

```
mt<-read.table("combinedavg09-11.csv",sep=',',header=T)
names(mt)
attach(mt)
```

####Transformation of Concentration to the Log Scale####

```
log.conc<- log(conc)
```

####Full Model with no Interactions####

```
out1<-lm(log.conc~distance+ar+fr+den+cmd+vmd+aw+agt+rh+sc)
summary(out1)
```

####ANOVA of Location, Active, Year effects####

```
ana2<-lm(log.conc~year+location)
anova(ana2)
```

####Full Model with Interactions####

```
out2<-lm(log.conc~distance+ar+fr+den+cmd+vmd+aw+agt+rh+sc+
distance:cmd+distance:vmd+distance:den+distance:aw+distance:agt+
```

```

distance:rh+distance:sc+distance:fr+den:cmd+den:vmd+den:aw+den:sc+
cmd:aw+cmd:agt+cmd:rh+cmd:sc+ cmd:vmd+vmd:aw+vmd:agt+vmd:rh+vmd:sc+
aw:agt+aw:rh+aw:sc+agt:rh)
summary(out2)

```

```

####BIC Model Selection####

```

```

library(MASS)
stepAIC(out2,direction='both',scope=list(lower=~1,upper=~.),k=log(49))

```

```

####The BIC Value for the Full Model with all Interactions using Out2####

```

```

library(MASS)
AIC(out2,k=log(49))

```

```

####BIC Selected Model with interactions####

```

```

out2a<-lm(log.conc~ distance + ar + fr + den + cmd + vmd +
aw + agt + rh + sc + distance:cmd + distance:aw + den:cmd +
den:aw + den:sc + cmd:agt + cmd:rh + cmd:sc + cmd:vmd + vmd:agt +
vmd:sc + aw:agt + aw:rh + aw:sc + agt:rh)
summary(out2a)

```

```

####Obtain Full Coefficient Estimates for all Variables####

```

```

coefficients(out2a)

```

```

####BIC Selected Model with Interactions and Location Included####

```

```

out3a<-lm(log.conc~ location + distance + ar + fr + den + cmd + vmd + aw + agt + rh +
sc + distance:cmd + distance:aw + den:cmd + den:aw + den:sc + cmd:agt + cmd:rh +
cmd:sc + cmd:vmd + vmd:agt + vmd:sc + aw:agt + aw:rh + aw:sc + agt:rh)
summary(out3a)

```

```

####Extra sums of Squares F-Test for the Comparison between the Full Model and
Selected Model####

```

```

anova(out2,out2a)

```

```

####Extra Sums of Squares F-Test for the Comparison between the Selected Model and
Selected Model with Location ####

```

```

anova(out3a,out2a)

```

```

####k-fold Validation Code####

```

```

library(DAAG)
responses <- data.frame(log.conc)
predictors <- data.frame(distance + ar + fr + den + cmd + vmd +
aw + agt + rh + sc + distance:cmd + distance:vmd + distance:den +
distance:aw + distance:fr + den:vmd + cmd:agt + cmd:rh +

```



```
cmd:sc + fr:cmd + vmd:rh + vmd:sc + fr:vmd + aw:agt + aw:rh +
agt:rh + den:sc)
mymodel <- lm(log.conc~.,data=predictors)
mymodel2 <- step(mymodel)
cv_mymodel2 <- CVlm(df = cbind(responses["log.conc"],predictors),mymodel2,m = 10)
```

```
####Diagnostic Plots for the Model Selected Using BIC####
```

```
par(mfrow=c(2,2))
plot(out2a)
```

```
####How to Predict Values####
```

```
neww <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110, 115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.996, cmd=1.36, vmd=22, aw=300, agt=22, rh=50, sc=1)
prediction<-predict(out2a, newdata=neww, interval="confidence")
prediction
```

```
####The Prediction Line, Confidence Interval, and Prediction Interval for Figure 4 in
Chapter 2####
```

```
neww <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110,115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.996, cmd=2.2, vmd=19.76, aw=215.06, agt=24.86, rh=29.68, sc=1)
prediction<-predict(out2a, newdata=neww, interval="confidence")
predictw<- predict(out2a, newdata=neww, interval="prediction")
prediction
predictw
```

```
####Plot Regression Line and 95% Confidence and Prediction Intervals for Aqua-Reslin
with Points for all Aqua-Reslin Data####
```

```
neww <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110, 115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.996, cmd=1.36, vmd=22, aw=300, agt=22, rh=50, sc=2)
confidw<-predict(out2a, newdata=neww, interval="confidence")
predictw<- predict(out2a, newdata=neww, interval="prediction")
plot(distance,log.conc,type='n',xlab='Distance (m)',ylab='Log Concentration (ug/cm^2)')
points(distance[form==1],log.conc[form==1])
lines(neww$distance, confidw[,1], lty=1, lwd=3)
lines(neww$distance, confidw[,2], lty=2, lwd=3, col=2) #Confidence intervals
lines(neww$distance, confidw[,3], lty=2, lwd=3, col=2)
lines(neww$distance, predictw[,2], lty=3, lwd=3, col=4) #Prediction Intervals
lines(neww$distance, predictw[,3], lty=3, lwd=3, col=4)
```

```

####Plot Regression Line and 95% Confidence and Prediction Intervals for Aqua-Reslin
with Points for Average Application and Environmental Conditions for Aqua-Reslin####
neww <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110,115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=197,
den=0.996, cmd=1.66, vmd=20, aw=316, agt=23, rh=43, sc=2)
confidw<-predict(out2a, newdata=neww, interval="confidence")
predictw<- predict(out2a, newdata=neww, interval="prediction")
plot(distance,log.conc,type='n',xlab='Distance (m)',ylab='Log Concentration (ug/cm^2)')
points(distance[form==1],log.conc[form==1])
lines(neww$distance, confidw[,1], lty=1, lwd=3)
lines(neww$distance, confidw[,2], lty=2, lwd=3, col=2) #Confidence intervals
lines(neww$distance, confidw[,3], lty=2, lwd=3, col=2)
lines(neww$distance, predictw[,2], lty=3, lwd=3, col=4) #Prediction Intervals
lines(neww$distance, predictw[,3], lty=3, lwd=3, col=4)

####Plot Regression Line for Differing Density####
neww <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110,115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.99, cmd=1.36, vmd=22, aw=300, agt=22, rh=50, sc=2)
newo <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110,115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.89, cmd=1.36, vmd=22, aw=300, agt=22, rh=50, sc=2)
confidw<-predict(out2a, newdata=neww, interval="confidence")
predictw<- predict(out2a, newdata=neww, interval="prediction")
plot(distance,log.conc,type='n',xlab='Distance (m)',ylab='Log Concentration (ug/cm^2)')
lines(neww$distance, confidw[,1], col=1, lwd=3)
confido<-predict(out2a, newdata=newo, interval="confidence")
predicto<- predict(out2a, newdata=newo, interval="prediction")
lines(newo$distance, confido[,1], col=2, lwd=3)
legend('topright',col=c(1,2),lty=1, legend=c('0.99 g/ml','0.89 g/ml'))

####Plot Regression Line for Differing CMD####
neww <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110,115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.996, cmd=1, vmd=22, aw=300, agt=22, rh=50, sc=2)
newo <-
data.frame(distance=c(5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,
110,115,120,125,130,135,140,145,150,155,160,165,170,175,180), ar=7.846, fr=192,
den=0.996, cmd=2, vmd=22, aw=300, agt=22, rh=50, sc=2)

```

```

confidw<-predict(out2a, newdata=neww, interval="confidence")
predictw<- predict(out2a, newdata=neww, interval="prediction")
plot(distance,log.conc,type='n',xlab='Distance (m)',ylab='Log Concentration (ug/cm^2)')
lines(neww$distance, confidw[,1], col=1, lwd=3)
confido<-predict(out2a, newdata=newo, interval="confidence")
predicto<- predict(out2a, newdata=newo, interval="prediction")
lines(newo$distance, confido[,1], col=2, lwd=3)
legend('topright',col=c(1,2),lty=1, legend=c('1 um','2 um'))

####Boxplots of Concentrations Measured for the Three Locations####
boxplot(log.conc~Location,ylab='Log Concentration (ug/cm^2)',xlab=")

####Boxplots of Concentrations Measured for the Three Years####
boxplot(log.conc~Year,ylab='Log Concentration (ug/cm^2)',xlab=")

####Boxplots of Concentrations Measured for all the Formulations####
boxplot(log.conc~Formulation,ylab='Log Concentration (ug/cm^2)',xlab=")

####Histogram of Wind Speed####
hist(aw, col=3, nclass=10, main="Wind Speed Histogram")

####Histogram of Distance####
hist(distance, col=3, nclass=10, main="Distance histogram")

####Histogram of Concentrations####
hist(conc, col=3, nclass=30, main="Concentrations Histogram", xlab='Concentration
(ug/cm^2)')

####Histogram of Log Concentrations####
hist(log.conc, col=3, nclass=30, main="Log Concentrations Histogram", xlab='Log
Concentration (ug/cm^2)')

####Histogram of Temperature####
hist(agt, col=3, nclass=10, main="Average Temperature Histogram")

####Histogram of Relative Humidity####
hist(rh, col=3, nclass=10, main="Average Relative Humidity Histogram")

```

APPENDIX B:

DATA USED FOR THE DEVELOPMENT OF THE ENVIRONMENTAL FATE  
MODEL IN CHAPTER 2 AND THE HUMAN-HEALTH AND AQUATIC  
ECOLOGICAL RISK ASSESSMENTS

The abbreviations are:

site = there were multiple sites within each location

year = the year that the spray occurred listing each variable as a categorical where 1 = 2009, 2 = 2010, and 3 = 2011

Year = the year that the spray occurred

distance = distance from the spray source in m

form = categorical variable for each formulation where 1 = Aqua-Reslin, 2 = Permanone 30-30, 3 = Permanone 31-66, 4 = Scourge 18+54, 6 = Aqua-Kontrol, 7 = Zenivex E20, and 8 = Pyronyl Crop Spray

Formulation = the name of the formulations sprayed

Active = is the active ingredient within the formulation where 1 = permethrin, 2 = resmethrin, 4 = etofenprox, and 5 = pyrethrins

ar = application rate (g/ha)

wo = categorical variable for weather the formulation was water- (1) or oil-based (2) formulation

location = categorical variable for location where 1 = Montana, 2 = California, and 3 = Louisiana

Location = the names of the location where the samples were taken

fr = flow rate (ml/min)

den = density of the formulation (g/ml)

cmd = count median diameter ( $\mu\text{m}$ )

vmd = volume median diameter ( $\mu\text{m}$ )

aw = average wind speed over 10 mins (cm/s)

maxw = maximum wind speed over 10 mins (cm/s)

minw = minimum wind speed over 10 mins (cm/s)

agt = ground temperature ( $^{\circ}\text{C}$ )

rh = relative humidity (%)

wb = web bulb depression

aat = temperature measured 10 m above the ground ( $^{\circ}\text{C}$ )

rh = relative humidity measured 10 m above the ground (%)

sr = stability ratio determined by equation 1 in chapter 2

sc = stability category, 1 = unstable, 2 = neutral, 3 = stable, and 4 = very stable as determined by equation 1 and table 2 in chapter 2

site	year	Year	distance	form	Formulation	active	ar	w	lo	location	Location	conc	fr	den	vmd	cmd	aw	maxw	minw	agt	rh	wb	aat	arh	sr	sc
1	1	2009	5	1	Aqua-Reslin	1	7.846	1	1	Montana	0.014118	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	10	1	Aqua-Reslin	1	7.846	1	1	Montana	0.005523	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	15	1	Aqua-Reslin	1	7.846	1	1	Montana	0.003284	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	20	1	Aqua-Reslin	1	7.846	1	1	Montana	0.003759	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	30	1	Aqua-Reslin	1	7.846	1	1	Montana	0.002704	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	40	1	Aqua-Reslin	1	7.846	1	1	Montana	0.010203	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	60	1	Aqua-Reslin	1	7.846	1	1	Montana	0.009751	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	80	1	Aqua-Reslin	1	7.846	1	1	Montana	0.005169	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	100	1	Aqua-Reslin	1	7.846	1	1	Montana	0.001558	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	120	1	Aqua-Reslin	1	7.846	1	1	Montana	0.001899	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
1	1	2009	160	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000266	192	0.9996	21.188	2.2	596.4211	539	622	24.56	33.64	14.08	28.474	16.92	1.10031	3	
2	1	2009	5	1	Aqua-Reslin	1	7.846	1	1	Montana	0.019323	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	10	1	Aqua-Reslin	1	7.846	1	1	Montana	0.007166	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	15	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000192	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	20	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000196	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	30	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000129	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	40	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000364	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	60	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000415	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	80	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000158	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	100	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000102	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	120	1	Aqua-Reslin	1	7.846	1	1	Montana	0.0002	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
2	1	2009	160	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000217	192	0.9996	21.188	2.2	476.3158	208	582	24.5	32.14	13.74	28.37	16.9	1.70572	3	
1	1	2009	10	2	Permanone 30-30	1	7.846	2	1	Montana	0.003729	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	15	2	Permanone 30-30	1	7.846	2	1	Montana	0.018806	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	20	2	Permanone 30-30	1	7.846	2	1	Montana	0.003515	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	30	2	Permanone 30-30	1	7.846	2	1	Montana	0.002548	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	40	2	Permanone 30-30	1	7.846	2	1	Montana	0.01082	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	50	2	Permanone 30-30	1	7.846	2	1	Montana	0.00442	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	60	2	Permanone 30-30	1	7.846	2	1	Montana	0.003682	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	80	2	Permanone 30-30	1	7.846	2	1	Montana	0.0014	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	100	2	Permanone 30-30	1	7.846	2	1	Montana	0.001461	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	120	2	Permanone 30-30	1	7.846	2	1	Montana	0.001132	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
1	1	2009	180	2	Permanone 30-30	1	7.846	2	1	Montana	0.000403	192	0.879	18.719	2.3	225.1145	203.113	253.1789	18.28	46.22	11.38	21.634	28.82	6.61845	3	
2	1	2009	10	2	Permanone 30-30	1	7.846	2	1	Montana	0.00095	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	15	2	Permanone 30-30	1	7.846	2	1	Montana	0.008935	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	20	2	Permanone 30-30	1	7.846	2	1	Montana	0.005306	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	30	2	Permanone 30-30	1	7.846	2	1	Montana	0.005134	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	40	2	Permanone 30-30	1	7.846	2	1	Montana	0.009961	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	50	2	Permanone 30-30	1	7.846	2	1	Montana	0.005618	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	60	2	Permanone 30-30	1	7.846	2	1	Montana	0.00282	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	80	2	Permanone 30-30	1	7.846	2	1	Montana	0.005008	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	100	2	Permanone 30-30	1	7.846	2	1	Montana	0.002272	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	120	2	Permanone 30-30	1	7.846	2	1	Montana	0.00215	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
2	1	2009	180	2	Permanone 30-30	1	7.846	2	1	Montana	0.001115	192	0.879	18.719	2.3	225.8429	219.3946	270.2746	17.94	45.22	10.98	21.728	28.2	7.426719	3	
1	1	2009	10	2	Permanone 30-30	1	7.846	2	1	Montana	0.01861	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1	2009	15	2	Permanone 30-30	1	7.846	2	1	Montana	0.0091	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1	2009	20	2	Permanone 30-30	1	7.846	2	1	Montana	0.009723	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1	2009	30	2	Permanone 30-30	1	7.846	2	1	Montana	0.00566	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1	2009	40	2	Permanone 30-30	1	7.846	2	1	Montana	0.004582	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1	2009	50	2	Permanone 30-30	1	7.846	2	1	Montana	0.002484	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1	2009	60	2	Permanone 30-30	1	7.846	2	1	Montana	0.001695	192	0.879	18.719	2.3	209.9684	203.113	253.1789	22.54	40.9	13.9	24.512	26.26	4.473003	3	
1	1																									













2	2	2010	75	8 Ppyronyl Crop Spray	5	2.802	2	2 California	0.001409	162.65	0.89988	31.303	2.1	583.3529	416	747	26.86667	38.71667	11.635	27.05333	37.68333	0.054853	2
2	2	2010	80	8 Ppyronyl Crop Spray	5	2.802	2	2 California	0.001731	162.65	0.89996	31.303	2.1	583.3529	416	747	26.86667	38.71667	11.635	27.05333	37.68333	0.054853	2
1	2	2010	5	2 Permanone 30-30	1	7.846	2	1 Montana	0.006001	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	10	2 Permanone 30-30	1	7.846	2	1 Montana	0.004017	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	20	2 Permanone 30-30	1	7.846	2	1 Montana	0.006608	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	40	2 Permanone 30-30	1	7.846	2	1 Montana	0.003302	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	50	2 Permanone 30-30	1	7.846	2	1 Montana	0.002664	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	60	2 Permanone 30-30	1	7.846	2	1 Montana	0.002101	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	70	2 Permanone 30-30	1	7.846	2	1 Montana	0.003646	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	80	2 Permanone 30-30	1	7.846	2	1 Montana	0.002521	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	100	2 Permanone 30-30	1	7.846	2	1 Montana	0.001515	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	120	2 Permanone 30-30	1	7.846	2	1 Montana	0.005667	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	135	2 Permanone 30-30	1	7.846	2	1 Montana	0.002184	192	0.879	13.4	1.3	252.1765	167	334	24.88959	25.75294	3.95824	25.26167	21.73333	-0.58509	1
1	2	2010	5	1 Aqua-Reslin	1	7.846	1	1 Montana	0.001743	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	10	1 Aqua-Reslin	1	7.846	1	1 Montana	0.005881	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	20	1 Aqua-Reslin	1	7.846	1	1 Montana	0.00448	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	40	1 Aqua-Reslin	1	7.846	1	1 Montana	0.002621	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	50	1 Aqua-Reslin	1	7.846	1	1 Montana	0.003911	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	60	1 Aqua-Reslin	1	7.846	1	1 Montana	0.006189	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	70	1 Aqua-Reslin	1	7.846	1	1 Montana	0.002107	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	80	1 Aqua-Reslin	1	7.846	1	1 Montana	0.004138	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	100	1 Aqua-Reslin	1	7.846	1	1 Montana	0.005571	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	120	1 Aqua-Reslin	1	7.846	1	1 Montana	0.002394	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	135	1 Aqua-Reslin	1	7.846	1	1 Montana	0.004139	192	0.9996	19.757	1.25	168.0588	111	241	23.88859	30.17059	5.347059	24.625	23.93333	-2.67815	1
1	2	2010	5	7 Zenivex E20	4	7.846	2	1 Montana	0.005799	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	10	7 Zenivex E20	4	7.846	2	1 Montana	0.007845	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	20	7 Zenivex E20	4	7.846	2	1 Montana	0.005759	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	40	7 Zenivex E20	4	7.846	2	1 Montana	0.008765	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	50	7 Zenivex E20	4	7.846	2	1 Montana	0.006092	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	60	7 Zenivex E20	4	7.846	2	1 Montana	0.004918	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	70	7 Zenivex E20	4	7.846	2	1 Montana	0.004192	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	80	7 Zenivex E20	4	7.846	2	1 Montana	0.004687	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	100	7 Zenivex E20	4	7.846	2	1 Montana	0.004003	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	120	7 Zenivex E20	4	7.846	2	1 Montana	0.003834	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	135	7 Zenivex E20	4	7.846	2	1 Montana	0.004163	192	0.8776	13.963	1.3	149.2941	130	167	22.67071	35.40588	6.611765	24.02833	24.83333	-6.09109	1
1	2	2010	5	7 Zenivex E20	4	7.846	2	1 Montana	0.000658	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	10	7 Zenivex E20	4	7.846	2	1 Montana	0.002489	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	20	7 Zenivex E20	4	7.846	2	1 Montana	0.003963	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	40	7 Zenivex E20	4	7.846	2	1 Montana	0.006683	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	50	7 Zenivex E20	4	7.846	2	1 Montana	0.008525	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	60	7 Zenivex E20	4	7.846	2	1 Montana	0.008072	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	70	7 Zenivex E20	4	7.846	2	1 Montana	0.016575	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	80	7 Zenivex E20	4	7.846	2	1 Montana	0.012409	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	100	7 Zenivex E20	4	7.846	2	1 Montana	0.006417	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	120	7 Zenivex E20	4	7.846	2	1 Montana	0.003799	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	135	7 Zenivex E20	4	7.846	2	1 Montana	0.004358	192	0.8776	13.963	1.3	137.4118	111	186	21.90229	36.87059	6.511765	23.70667	24.36667	-9.55605	1
1	2	2010	5	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.005237	192	1.018	24.75	1.2	95.11765	93	111	21.75324	36.74706	6.341176	23.01833	27.41667	-13.9831	1
1	2	2010	10	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.001234	192	1.018	24.75	1.2	95.11765	93	111	21.75324	36.74706	6.341176	23.01833	27.41667	-13.9831	1
1	2	2010	20	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.013539	192	1.018	24.75	1.2	95.11765	93	111	21.75324	36.74706	6.341176	23.01833	27.41667	-13.9831	1
1	2	2010	40	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.017479	192	1.018	24.75	1.2	95.11765	93	111	21.75324	36.74706	6.341176	23.01833	27.41667	-13.9831	1
1	2	2010	50	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.010557	192	1.018	24.75	1.2	95.11765	93	111	21.75324	36.74706	6.341176	23.01833	27.41667	-13.9831	1
1	2	2010	60	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.020834	192	1.018	24.75	1.2	95.11765	93	111	21.75324	36.74706	6.341176	23.01833	27.41667	-13.9831	1
1	2	2010	70	6 Aqua-Kontrol	1	7.846	1	1 Montana	0.017715	192	1.018	24.75	1.2										

1	2	2010	135	2	Permanone 30-30	1	7.846	2	1	Montana	0.002227	192	0.879	13.4	1.3	379.8824	241	482	22.76555	41.96471	9.2	24.375	26.6	-1.1154	1
1	2	2010	5	7	Zenivex E20	4	7.846	2	1	Montana	0.003653	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	10	7	Zenivex E20	4	7.846	2	1	Montana	0.006658	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	20	7	Zenivex E20	4	7.846	2	1	Montana	0.007042	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	40	7	Zenivex E20	4	7.846	2	1	Montana	0.004872	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	50	7	Zenivex E20	4	7.846	2	1	Montana	0.004314	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	60	7	Zenivex E20	4	7.846	2	1	Montana	0.013551	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	70	7	Zenivex E20	4	7.846	2	1	Montana	0.00038	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	100	7	Zenivex E20	4	7.846	2	1	Montana	0.000534	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	120	7	Zenivex E20	4	7.846	2	1	Montana	0.000534	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	135	7	Zenivex E20	4	7.846	2	1	Montana	0.01252	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
1	2	2010	5	7	Zenivex E20	4	7.846	2	1	Montana	0.00038	192	0.876	13.963	1.3	375.4706	260	464	22.32288	42.12353	8.852941	23.88333	24.13333	-1.10687	1
2	2	2010	5	2	Permanone 30-30	1	7.846	2	1	Montana	0.004363	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	10	2	Permanone 30-30	1	7.846	2	1	Montana	0.005797	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	20	2	Permanone 30-30	1	7.846	2	1	Montana	0.006941	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	40	2	Permanone 30-30	1	7.846	2	1	Montana	0.00325	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	50	2	Permanone 30-30	1	7.846	2	1	Montana	0.00323	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	60	2	Permanone 30-30	1	7.846	2	1	Montana	0.002057	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	70	2	Permanone 30-30	1	7.846	2	1	Montana	0.00472	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	80	2	Permanone 30-30	1	7.846	2	1	Montana	0.010935	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	100	2	Permanone 30-30	1	7.846	2	1	Montana	0.001828	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	120	2	Permanone 30-30	1	7.846	2	1	Montana	0.004196	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
2	2	2010	135	2	Permanone 30-30	1	7.846	2	1	Montana	0.005748	192	0.879	13.4	1.3	297.8824	241	353	26.96929	19.21765	1.564706	26.85333	16.45	13.06884	3
1	2	2010	5	1	Aqua-Reslin	1	7.846	1	1	Montana	0.017458	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	10	1	Aqua-Reslin	1	7.846	1	1	Montana	0.011533	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	20	1	Aqua-Reslin	1	7.846	1	1	Montana	0.008406	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	40	1	Aqua-Reslin	1	7.846	1	1	Montana	0.013303	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	50	1	Aqua-Reslin	1	7.846	1	1	Montana	0.005388	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	60	1	Aqua-Reslin	1	7.846	1	1	Montana	0.005326	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	70	1	Aqua-Reslin	1	7.846	1	1	Montana	0.003614	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	80	1	Aqua-Reslin	1	7.846	1	1	Montana	0.00212	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	100	1	Aqua-Reslin	1	7.846	1	1	Montana	0.001779	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	120	1	Aqua-Reslin	1	7.846	1	1	Montana	0.001057	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
1	2	2010	135	1	Aqua-Reslin	1	7.846	1	1	Montana	0.000668	192	0.9996	19.757	1.25	278.2941	241	315	25.89888	21.97059	2.517647	25.755	19.13333	13.54243	3
2	2	2010	5	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.010571	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	10	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.013516	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	20	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.00952	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	40	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.00899	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	50	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.008666	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	60	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.014522	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	70	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.014047	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	80	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.010559	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	100	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.008094	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	120	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.00886	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
2	2	2010	135	6	Aqua-Kontrol	1	7.846	1	1	Montana	0.011272	192	1.018	24.75	1.2	138.4118	93	167	25.62124	22.44706	2.623529	25.27333	19.85	1.815979	4
1	2	2010	5	1	Aqua-Reslin	1	7.846	1	1	Montana	0.010284	192	0.9996	19.757	1.25	441	353	520	29.85371	13.05882	-1.41176	29.17	10.5	35.1554	3
1	2	2010	10	1	Aqua-Reslin	1	7.846	1	1	Montana	0.023323	192	0.9996	19.757	1.25	441	353	520	29.85371	13.05882	-1.41176	29.17	10.5	35.1554	3
1	2	2010	20	1	Aqua-Reslin	1	7.846	1	1	Montana	0.013417	192	0.9996	19.757	1.25	441	353	520	29.85371	13.05882	-1.41176	29.17	10.5	35.1554	3
1	2	2010	40	1	Aqua-Reslin	1	7.846	1	1	Montana	0.007054	192	0.9996	19.757	1.25	441	353	520	29.85371	13.05882	-1.41176	29.17	10.5	35.1554	3
1	2	2010	50	1	Aqua-Reslin	1	7.846	1	1	Montana	0.002251	192	0.9996	19.757	1.25	441	353	520	29.85371	13.05882	-1.41176	29.17	10.5	35.15	







