

EXPOSURE AND RISK TO NON-TARGET RECEPTORS FOR AGRICULTURAL
SPRAY DRIFT OF FORMULATION TYPES AND ADJUVANTS

by

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DEDICATION

To my grandfather, Dr. Marcel J. Kniedler (Nonno).

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ABSTRACT

Agricultural applications of crop protection products can have negative economic and ecological consequences when spray drift occurs. Among the ways to reduce spray drift is to manipulate the physical properties of the spray solution with formulated products and tank additives, but further research is required to better understand their effects. By measuring spray drift under field conditions and using the results to estimate ecological risk, we characterize the effect on drift for two formulation types and two adjuvants. A field study was conducted where off-target ground deposition and droplet size were measured to indicate spray drift for different combinations of the formulations and adjuvants, accounting for environmental conditions. Each treatment combination was also sprayed in a wind tunnel set up to precisely measure droplet spectra so that these could be related to deposition in the field. Finally, an efficacy experiment was conducted to test for tradeoffs between drift reduction and pest control. Results from the field study suggest that as much as 32% drift reduction was achieved by selecting between the tested formulation types, and as much as 62% by incorporating certain spray adjuvants, but this effect depended on the formulation/adjuvant combination. Treatments with smaller droplet sizes had greater drift, and there was no tradeoff between drift reduction and pest control. We assessed ecological risk for terrestrial insects in non-target habitats using a novel approach to estimate insecticide residue on plant surfaces based on ground deposition data from the field study. Exposure concentrations were combined with a cumulative distribution of species sensitivities to statistically represent the risk of toxicity for the active ingredient that was used and the levels of drift that were observed. We found that substantial reductions in the percentage of insect species affected in an off-target area could be achieved by certain formulation types and adjuvants. This work could be useful for developing a classification scheme for formulated products and tank additives based on their potential for reducing spray drift and ecological risk to non-target receptors.

CHAPTER ONE

LITERATURE REVIEW

Pesticides and Drift

Pesticide use is often a contentious issue because of their potential to harm humans and other non-target organisms in and around the application area. However, pesticides do offer many advantages and their use in modern agriculture is an integral part of crop production. Theoretically, pathogen, weed, and arthropod management could be accomplished without the use of pesticides if the decrease in crop production due to these pests were acceptable (Norris et al. 2003). However, pesticide use makes up part of an economic balance between agricultural inputs and crop production, and pesticides allow for more consistent and predictable crop yields from one year to the next.

Residues from pesticide applications, however, have most likely been ending up in untargeted areas since their use began. Given that they are designed to kill or deter certain pest-, or “target”-, organisms, they may also pose risks to organisms in areas that are not intended for their use. These organisms or areas are referred to as “non-target receptors”, and may include human bystanders, critical habitats, or terrestrial or aquatic invertebrates. For this reason, pesticide use is often a contentious issue, and minimizing drift is a high priority for the agricultural and application technology industry, government agencies, and general public alike.

Drift is defined by the EPA as the “movement of pesticide dust or droplets through the air at the time of application or soon after, to any site other than the area

intended” (EPA 2016b). Because unintended exposure of non-target receptors to pesticide spray drift is almost inevitable (EPA 1999, Felsot et al. 2011, Salyani and Cromwell 1992), there have been many efforts to quantify that exposure, characterize its effects, and reduce its occurrence.

Droplet Size as a Predictor of Spray Drift

The rate at which a particle falls to the ground can be predicted by Stokes Law and is proportional to its radius because of gravitational forces and the viscosity of air (Hinds 1982). Droplet size is therefore a fundamentally important factor when considering drift, and indeed, has been suggested to be the most important drift-determining factor in many studies (Hoffmann et al. 2008, Knewitz et al. 2002, Qin et al. 2010, Spanoghe et al. 2007, Hobson et al. 1993, Carlsen et al. 2006). There are five standard classifications for nozzles that produce droplet sizes within a certain range in volume median diameter (VMD), designated by the American Society of Agricultural Engineers (ASAE). These classifications are very fine ($<100\ \mu\text{m}$), fine ($100\text{-}175\ \mu\text{m}$), medium ($175\text{-}250\ \mu\text{m}$), coarse ($250\text{-}375\ \mu\text{m}$), very coarse ($375\text{-}450\ \mu\text{m}$), and extremely coarse ($>450\ \mu\text{m}$). Although droplets of all sizes are capable of contributing to drift, smaller droplets spend more time in the air and are therefore more prone to off-target movement (Felsot et al. 2011, Hilz and Vermeer 2013).

The degree of drift potential has been attributed to different droplet diameters by various researchers, but typically the fraction of droplets categorized as “very fine” ($\text{VMD}<100\ \mu\text{m}$), relative to the spray volume, is used as a simplified estimate of drift

risk (Hobson et al. 1993, Miller and Ellis 2000). While this may be a useful tool, some research has suggested that this relationship does not always hold true for ground applications (Smith et al. 1982, Smith et al. 2000) produced results that suggest. Smith et al. (2000) found that neither VMD, nor the fraction of droplets $\leq 105 \mu\text{m}$ had a significant effect on deposition. They hypothesize that ground applications occur so close to the ground that evaporation and movement time are so limited that variations in droplet size have less of an effect on drift. This could be an important consideration when using models developed based on wind tunnel data to predict drift for ground applications because droplet size is often the key dependent variable in wind tunnel drift studies.

Nuyttens et al. (2010) tested the effects of different nozzle-pressure combinations in a wind tunnel and found that measuring the proportion of the total volume of droplets smaller than $75 \mu\text{m}$ not $100 \mu\text{m}$, diameter was best suited to represent the drift. Butler et al. (2002) also observed a poor correlation between spray volume contained in droplets smaller than $100 \mu\text{m}$ and spray drift. The objectives of their study was to evaluate whether droplet size could be used to predict drift with different formulation types. Their results suggest that droplet size distributions alone would not allow for accurate estimates of drift potential when considering different spray liquids.

This variability in drift-predictions based on droplet size is a reminder of the complicated nature of spray drift, and that the interaction of many factors must be considered when estimating the environmental fate of airborne particles.

Causes of Drift

There are a number of factors that influence the movement and deposition of pesticide particles both before and after they leave the spray source. Certain properties of the spray mixture have downstream effects on how a pesticide-containing droplet is formed, with implications for its size once it leaves the source. The composition of the spray solution in combination with variables like nozzle type, spray pressure, application rate, driving speed, wind speed, and boom height will ultimately determine the size distribution of the droplets that comprise the spray. Once the droplets are formed, their fate in the environment depends on interactions between their physicochemical properties and environmental factors (e.g. temperature, humidity, wind speed etc.). Local landscapes can also influence drift because droplets can impinge on, and be intercepted by, obstructions such as vegetation and landforms. These variables, which have all been studied for their effect on pesticide drift, can be divided into two broad categories. Based on whether or not they can be manipulated, drift factors can be thought of as either “operator-” or “non-operator-” controlled variables” (Felsot et al. 2011).

Operator-Controlled Variables

Formulation and Adjuvant

Droplet size spectrum can be greatly influenced by the composition of the tank mixture that is being sprayed. The formulation of the pesticide product as well as tank additives, can affect drift by changing the size distribution of the droplets (Butler et al.

2002, De Schampheleire et al. 2009, Felsot et al. 2011, Hilz and Vermeer 2013, Miller and Ellis 2000, Stainier et al. 2006).

A pesticide formulation is a mixture of chemicals designed to maximize biological efficacy given the mode of action of the active ingredient. Other considerations when formulating a pesticide are the type of target surface, drift potential, habits of the pest, application equipment, storage, handling, and safety for the applicator (Knowles 2008). Formulation types include granules, solution concentrates, emulsifiable concentrates, wettable powders, suspension concentrates, oil in water emulsions, suspoemulsions, microemulsions, water dispersible granules, microcapsules, and seed treatments (Knowles 2008). Of the most common formulation types, there are those that result in a spray liquid that either contains emulsions, micro-emulsions or particulate suspensions, or one that is a completely homogenous liquid due to the high solubility of the concentrate (Hilz and Vermeer 2013). The effect of formulation type and adjuvant on droplet size has been investigated in numerous studies, but results are variable (Butler et al. 2002, Chechetto et al. 2013, De Oliveira et al. 2013, de Ruiter et al. 2003, Dorr et al. 2013, Hoffmann et al. 2008, Miller and Ellis 2000, Qin et al. 2010, Spanoghe et al. 2007, Stainier et al. 2006).

When a formulated pesticide is sprayed from a hydraulic nozzle it is first in the form of an unbroken sheet before turning into droplets. Miller and Ellis (2000) found that droplet size was a function of certain properties of this sheet at the time it broke up into droplets. One property of the liquid sheet that influenced droplet size was its thickness at the time of breakup. They found that long liquid sheets associated with water-soluble

liquids were thinner at break-up and thus produced finer sprays. Spray liquids that were not homogenous (e.g. emulsifiable concentrate formulations) produced shorter, and thus thicker, liquid sheets at break-up resulting in coarser sprays. The time, and thus thickness, at liquid sheet break-up in this study was thought to be a result of the number of emulsion droplets (heterogeneities) in the spray liquid. Although the authors noted that the degree to which physical properties of a spray liquid can change droplet size had yet to be fully characterized, the effect of formulation type on droplet formation was highlighted in their results.

Qin et al. (2010) investigated the effects of emulsion particle size on mechanisms of droplet atomization. Their results were consistent with findings from Miller and Ellis (2000) in that the closer to the nozzle that breakup of the liquid sheet occurred, the coarser the droplets were. By creating droplet emulsions of three different sizes and testing their effect on liquid sheet breakup their results supported Miller and Ellis (2000) hypothesis that heterogeneities in the spray solution could affect liquid sheet breakup and thus droplet size.

The heterogeneity of a formulation can be due to the presence of either solid particles (e.g. suspension concentrates and wettable powders) or micro-hydrophobic globules (emulsifiable concentrates), both of which have been shown to affect spray drift. Stainier et al. (2006) tested combinations of these formulation types with four different adjuvants, an esterified vegetable oil, and three surfactants. They found that the emulsifiable concentrate (EC) formulations produced more drift-prone particles (<100

µm) than the suspension concentrate (SC) formulation regardless of which adjuvant was added.

De Schampheleire et al. (2009) also addressed the importance of considering the physicochemical properties of the complete spray mixture to characterize the drift-reducing potential of adjuvants. Their results elucidate the effects of physicochemical parameters such as evaporation rate, density, and surface tension on spray formation. Their results suggest that dynamic surface tension of the liquid pesticide is a main drift-determining factor and that increasing viscosity of the spray liquid resulted in coarser droplets. They found that spray liquids of water-dispersible granules and powders were more effective at reducing drift than those of emulsifiable and suspension formulation types.

Dexter (2001) observed an increase in droplet size with increasing emulsion concentration, but that this effect reached a point at which droplet coarsening began to decrease. This decrease was thought to be a function of the dynamic surface tension of the spray liquid being modified by the emulsion concentration.

Hilz and Vermeer (2013), on spray drift as a function of formulation type, reports that formulations which contain high concentrations of emulsifiable oil will coarsen sprays more so than water when sprayed through conventional nozzles, but that knowledge of the composition is required to evaluate the effects of other formulation types on spray characteristics.

Nozzle Type and Spray Pressure

Virtually every research study aimed at characterizing drift recognizes that spray nozzles and application systems can affect drift through the influence they have on physical characteristics of the spray droplets, such as droplet size and velocity during the atomization process. Some studies specifically address the influence of the different application systems (i.e. nozzle type, size, and application pressure) on spray drift, all of which suggest the importance of nozzle selection (Cooke et al. 1990, Dorr et al. 2013, McCartney and Obermiller 2008, Nordbo 1992, Nuyttens et al. 2007a, Nuyttens et al. 2007b, Nuyttens et al. 2009b, Vallet and Tinet 2013, Walklate et al. 2000).

Nuyttens et al. (2007a) estimated drift from multiple combinations of nozzle types and sizes and found that in general, larger nozzle sizes, lower spray pressures, lower driving speeds, and lower spray boom heights tend to reduce spray drift. Their research also suggested that air inclusion nozzles have the highest drift reduction potential, followed by the low-drift nozzles and the standard flat-fan nozzles. All of the estimates of drift in this research were based on the close link between droplet size and drift potential.

Nuyttens et al. (2009a) found there are important differences in droplet velocities depending on the size and type of nozzle being used. They found that droplet velocities were greater for flat –fan nozzles than for low-drift nozzles and air-inclusion nozzles. They also found that larger nozzle openings corresponded with faster droplets of equal sizes, thus, droplets with greater ejection velocities will reach their target faster than similar sized droplets with slower ejection velocities. This means that the types of nozzles that result in slower velocities should be more prone to drift simply due to greater

exposure time to environmental drift factors. Low drift nozzles produce a smaller fraction of small droplets than standard flat-fan nozzles, which means that fewer of the droplets produced will have the velocities prone to lower drift once they leave the nozzle orifice (Nuyttens et al. 2009a).

The effect of increasing spray pressure on droplet size has been shown to increase the risk of drift by increasing the fraction of spray volume contained in fine droplets. This effect of the elevated fraction of fine droplets on drift begins to decrease once the increased velocity of the high spray pressure becomes the dominating drift factor (Nuyttens et al. 2009a).

Driving Speed and Boom Height

Higher driving speeds, and boom heights have been associated with greater spray drift (Nuyttens et al. 2007b, Teske and Thistle 1999). Nuyttens et al. (2007b) tested the effects of three different driving speeds on spray drift in a field trial and found that by increasing driving speed more small droplets are able to escape into the atmosphere and drift from the target area. They also showed that raising boom height significantly increased spray drift. Other research has also suggested that drift could be reduced by operating at a spray boom height as close to the vegetation as possible without sacrificing uniformity of the spray pattern (Smith et al. 1982, Bode et al. 1976).

Non-Operator-Controlled Variables

The factors known to influence drift that have been discussed thus far can be thought of as operator-controlled variables. However, there are variables such as

meteorological conditions that the operator is unable to manipulate, but that can still greatly affect spray drift. Spray drift is influenced by environmental conditions such as wind speed and direction, temperature, relative humidity and atmospheric stability. Characteristics of the crop canopy are also important to consider. Canopy height, density of foliage, row spacing, growth stage and condition, can all affect downwind deposition (Felsot et al. 2011).

Wind Speed and Atmospheric Stability

A number of studies have shown a positive correlation between wind speed and drift for both ground and aerial pesticide applications (Smith et al. 2000, Teske and Thistle 1999, Endalew et al. 2010). Threadgill and Smith (1975) on the other hand, reported decreased drift at higher wind speeds but hypothesized that this was likely due to the highly unstable atmospheric conditions co-occurring with the high wind events. Unstable atmospheric conditions should result in greater drift since droplets would likely remain aloft more readily compared to more stable conditions. Yates et al. (1966) found that a stability ratio (SR) could be correlated to drift deposits following aerial applications with the following equation:

$$(SR) = [(T_2 - T_1) / \mu^2] (10^5) \quad \text{[Equation 1]}$$

where T_2 and T_1 are air temperatures ($^{\circ}\text{C}$) at different heights, μ is the average horizontal wind speed in cm/sec, and 10^5 gives the ratio an acceptable magnitude. A stability ratio is a measure of atmospheric turbulence and can be used to estimate the relative amount of vertical mixing of droplet particles. Atmospheric turbulence is a function of vertical

temperature gradients and the degree to which they affect vertical movement of air.

Unstable conditions occur when a decrease in air temperature with increasing height occurs at a greater rate than the adiabatic lapse rate of 1 °C per 100 m (Yates et al. 1966). A low SR would therefore correspond with unstable conditions, greater vertical mixing of the particle cloud, and possibly further off target drift (Yates and Akesson 1966, Yates et al. 1966, Threadgill and Smith 1975). However, Fritz (2006) was unable to determine any statistically significant effect of atmospheric stability on ground deposition following a series of aerial applications.

Evaporation of Airborne Droplets

Temperature and relative humidity can affect drift through their influence on evaporation rate and the time it takes a droplet to shrink to a more drift-prone size in a given situation. A decrease in relative humidity or an increase in temperature are both conducive situations for evaporation of airborne droplets. An evaporation variable has been integrated in many models, but assumptions on which evaporation rate is based vary because quantifying its effect on drift is not obvious (Al Heidary et al. 2014). A reasonable assumption is that, for short distances from the field edge (10-20 m), only water will evaporate when water is the solvent (Al Heidary et al. 2014). The more water that evaporates, the lighter the pesticide spray droplets will become, and the farther they will be able to move with the prevailing winds (Asman et al. 2003).

Measuring and Predicting Drift

After publication of the first comprehensive review of the drift phenomena (Akesson and Yates 1964) early research on pesticide drift was confined to aerial applications (Yates and Akesson 1966, Yates et al. 1966). More recently, deposition and drift characteristics resulting from ground applications have been studied under field conditions (Threadgill and Smith 1975, Nordby and Skuterud 1974, Grover et al. 1978, Maybank et al. 1978, Nuyttens et al. 2007b, Salyani and Cromwell 1992, Smith et al. 1982, Wolters et al. 2008). Drift can be estimated through either direct measurement of off target deposition in the field, or by indirect methods which relate drift to droplet characteristics measured in wind tunnels. Methods for collecting and quantifying the off target loss of crop protection products are highly variable, and only recently has the development of standard protocols for this purpose begun (Costa and Miller 2006, ISO22856 2008, EPA 2016, ASABE 2009). Ground collectors have included glass plates, plastic plates, filter papers, silica gel plates, Mylar sheets, and pans of water. Airborne spray particles have been measured with passive samplers such as strings or spheres at different heights, as well as mannequins for estimating risks to bystanders. Active samplers of the spray cloud have included rotating microscope slides and aspirated filters. Both passive and active methods measure either the chemical active ingredient, or a surrogate such as a fluorescent tracer.

Traditional analytical techniques to quantify spray drift, such as gas or liquid chromatography, are cost prohibitive, can have low instrument sensitivity, may contain background contamination by pre-existing environmental residues, and can involve

extensive sample cleanup (Akesson and Yates 1964). Fluorescent tracers, however, have been used in many studies to estimate pesticide concentrations in agricultural spray drift tests (Cai and Stark 1997, Cooke and Hislop 1993, Grover et al. 1978, Kjaer et al. 2014, Nordby and Skuterud 1974, Parkin and Merritt 1988, Pergher 2001, Sharp 1974, Staniland 1959), and have been shown to have little or no effect on the atomization of the spray solution (Carlsen et al. 2006, Cooke and Hislop 1993, Costa and Miller 2006, Schleier III et al. 2010).

Deposited insecticide concentrations can be quantified with the use of fluorescent dyes by measuring excitation and emission wavelengths with a fluorometer. Fluorometers expose a sample to a light source causing emission of a diagnostic photon at a certain wavelength which can be measured to quantify the proportion of dye present in the sample (Cooke and Hislop 1993). This proportion of dye can then be used to quantify insecticide concentration by applying a conversion factor which correlates fluorescent material to insecticide present in the spray solution.

More pesticides by mass are applied by ground application methods than any other type, including aerial, in the US (Teske et al. 2009, Mathews & Hilsop 1993). Spray drift from aerial applications has been studied to a greater extent than for ground applications by the Spray Drift Task Force (SDTF). The SDTF represents a joint effort among registrant companies to build a database of studies aimed at assessing spray drift in the US (Hewitt 2000). From this database, analyses of the factors affecting spray drift were used to develop a model called AgDRIFT®.

The internet available model AgDRIFT was originally developed to estimate drift from aerial applications, but now includes a module designed to model drift as a result of ground boom applications. It was based on a model called AGDISP[®] developed by the US Department of Agriculture Forest Service. AGDISP is the non-regulatory version of AgDRIFT, and both assume constant atmospheric conditions over flat terrain, free of vegetative barriers (Felsot et al. 2011). AgDRIFT is a Lagrangian model that incorporates user-defined conditions under which aerial applications might occur. It is structured such that for conservative assumptions of input variables for ground applications spray quality and boom height can be adjusted (Hewitt 2000).

These assumptions are based on the 50th percentile distribution of downwind deposition relative to the application rate. The U.S. EPA may use AgDRIFT in ecological risk assessments, or may assume that 1-5% of the applied active ingredient drifts beyond the target area (Felsot et al. 2011). AgDRIFT was originally developed for use with aerial applications and was found to over predict downwind deposition (greater than 50 m) when used for this purpose (Bird et al. 2002). Furthermore, few commercial scale applications to test the validity of AgDRIFT have been conducted with ground sprayers, and comparison with other models in use is lacking regarding their adequacy in estimating drift, especially from ground sprayers (Felsot et al. 2011).

Wind tunnels can be used to measure droplet size distributions and biophysical behavior characteristics for different liquid mixtures and application equipment in a controlled environment. Wind tunnels can be set up to measure deposition, or equipped with lasers to measure droplet size distributions. The ability to manipulate environmental

conditions such as wind speed, temperature, and humidity in a wind tunnel allows for the testing of these effects on drift systematically. Wind tunnel experiments are also much less expensive and time consuming than field experiments which allows for the collection of data on more drift factors in a shorter period of time.

Data collected in wind tunnels supports extrapolation to drift potentials expected under natural conditions, however, this requires a statistically verifiable relationship with field experimentation. This can be difficult, because the relationship between expected drift as estimated through wind tunnel experimentation and actual drift as measured through field experimentation is unclear. Eliminating environmental stochasticity in order to evaluate individual factors of drift limits the ability to estimate drift where environmental stochasticity is present. Nuyttens et al. (2010) compared indirect wind tunnel estimates of drift (deposition and droplet size distributions) to actual drift measurements in the field for different nozzle types. They concluded that indirect drift assessment methods could be valuable alternatives to field drift experiments, but that it is difficult to test the effects of driving speed, boom height, and air assistance without actual field experimentation.

Ecotoxicology and Environmental Risk Assessment for Pesticide Drift

The process of ecological risk assessment (ERA) is a means by which data can be organized and systematically evaluated to estimate the likelihood that adverse ecological effects may occur (USEPA 1998). Risk assessment is an iterative process which goes through the steps of problem formulation, hazard identification, risk analysis, and risk

characterization. A tiered approach to this process is typically taken which begins with deterministic generalizations based on conservative assumptions (tier 1) and progresses towards assessments based on more refined assumptions (tier 4).

Toxicity is the inherent ability of a toxicant to cause harm, and exposure is coming in contact with the toxicant through routes such as ingestion, dermal absorption, or inhalation. The combined effect of both toxicity and exposure is used to quantitatively express risk as the probability of an adverse outcome under specified conditions (NRC 1983). Various endpoints of toxicity are chosen to represent either acute or chronic effects. For example, laboratory bioassays may be performed to determine a concentration that is statistically shown to kill 50 % of a test population (LC_{50}). “No observable adverse effect levels” (NOAEL) or “lowest observed adverse effect levels” (LOAEL) may be used to express sub-chronic or chronic exposure effects.

Regardless of the endpoint that is chosen, the relationship between the response of the organism and the amount of the toxicant can be expressed in a dose-response curve. Dose-response curves can be used to characterize the response of an individual organism to varying concentrations of a toxicant (graded dose response), or to characterize the distribution of responses of a population (quantal dose response) (Casarett and Doull 2010). The LC_{50} (or LD_{50}) represents an estimated single dose with an associated confidence interval that is statistically derived from the quantal dose response curve. When the level of exposure is divided by a toxic endpoint such as the LC_{50} the result is a quantitative expression of risk called a risk quotient (RQ). If a RQ is shown to exceed a level of concern (LOC) set by the U.S. Environmental Protection Agency (U.S. EPA),

then risk managers can decide if regulatory action is needed. Another option would be to go through another iteration of the risk assessment process at the next level of refinement (higher tier).

As risk assessment progresses towards a higher level of refinement so as to more accurately represent risk the process may incorporate more probabilistic approaches and uncertainty analyses. Extrapolating from laboratory bioassay data to effect distributions on individuals, populations, and ecosystems in the field involves a level of uncertainty. Likewise exposure distributions are based on uncertainty analyses of environmental fate models for a given compound. The joint probability of these distributions can be used to estimate ecological risk by incorporating regression models, population demographic models, and ecosystem simulation models to extrapolate to actual environmental scenarios (Posthuma et al. 2002).

Ecotoxicological extrapolation models known as species sensitivity distributions (SSDs) can be used to derive environmental quality criteria that are protective of a desired percentage of species. Developed by the U.S. EPA, SSDs are based on the idea that susceptibility to a toxicant will differ among species, and that the variability can be described by a statistical distribution. SSDs can be used to estimate the probability that a certain percentage of species will be affected at a given concentration of a toxicant. This is the “forward” use, and is common in ecological risk assessments. The other use is to establish a cutoff percentage that is chosen so that a concentration of the toxicant considered safe for that fraction of species may be calculated. Species sensitivity distributions, therefore, can be used to either estimate the potentially affected fraction

(PAF) of species at a certain concentration of a toxicant, or to estimate the concentration that affects a particular portion of species, the HCp (Posthuma et al. 2002). The hazardous concentration at which 5% of species are affected (HC₅) has become a common regulatory threshold (Posthuma et al. 2002, Frampton et al. 2006).

Research Objectives

The U.S. EPA recently developed a voluntary verification protocol to evaluate the effectiveness of drift reduction technologies (DRTs) (EPA 2016). The protocol for evaluating DRTs, however, is limited to high- and low-speed wind tunnel testing (the protocol references ISO standards for field testing methods), and does not include methods for evaluating certain tank mixtures such as the combination of formulation type and adjuvant. Combinations of formulation types and adjuvants in the tank mix can be as substantial a factor as nozzle type on resulting spray drift (Miller and Ellis 2000). Therefore, the first part of this research is to focus on the effect of formulation type and adjuvant on drift in both field and wind tunnel experimentation to evaluate their drift reduction potential. It is not uncommon for ground deposition to be used as the only indicator for spray drift in field studies, and vertical characteristics of the drifting spray cloud are considered less frequently. Therefore, part of the evaluation of these DRTs includes measuring the droplet size distribution of the spray cloud at different heights and distances from the spray source in the field. The relationship between droplet size and drift will also be characterized by measuring droplet spectra for the different spray solutions in a wind tunnel and comparing them to ground deposition in the field. Finally,

the benefits of drift reduction must be weighed against potential losses in product efficacy. Therefore, an efficacy trial is performed to test if lower-drift treatments are any less effective at controlling a pest population.

In the second part of this research, we incorporate the actual environmental concentrations estimated from the drift trial into a non-target insect risk assessment for the drift reduction technologies evaluated. To do this, we first estimate levels of insecticide residue on different plant surfaces based on the amount of drifting material. We then use a species sensitivity distribution to estimate risk as a function of the residue levels at different distances.

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CHAPTER TWO

EFFECT OF INSECTICIDE FORMULATION AND ADJUVANT COMBINATION ON AGRICULTURAL SPRAY DRIFT

Contribution of Authors and Co-Authors

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CHAPTER TWO

EFFECT OF INSECTICIDE FORMULATION AND ADJUVANT COMBINATION
ON AGRICULTURAL SPRAY DRIFT

The following chapter has been prepared for submission to a peer-reviewed journal.

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Abstract

Losses of crop protection products through agricultural spray drift have economic and ecological consequences. In addition to decreasing the efficiency of a pesticide application, spray drift potentially can negatively affect humans and other organisms in off-target areas. Modification of the spray solution through tank additives and product formulation is an important drift reduction strategy that could mitigate these effects, but is less understood than other approaches. Therefore, the objective of this study was to evaluate spray drift resulting from agricultural ground applications of an insecticide in

two commonly used and closely related formulation types with and without spray enhancement additives. Spray drift of a suspension concentrate and wettable powder formulation, with and without two oil-based adjuvants, was measured in a three-year field study under variable meteorological conditions. Droplet sizes were also measured in a wind tunnel to determine if indirect methods could be substituted for more expensive field experimentation to quantify spray drift from these technologies. In the field study, the suspension concentrate deposited less than the wettable powder formulation by an estimated 37% over all downwind distances in an off-target area. The adjuvant with vegetable-based oil reduced ground deposition of the suspension concentrate by 52% and the wettable powder by 63%. The mineral oil-based adjuvant did not reduce downwind deposition of the suspension concentrate formulation, but did for the wettable powder by 62%. Biological efficacy was not sacrificed for drift reduction among the low drift combinations, and downwind deposition was most affected by wind speed and relative humidity. The wind tunnel data on droplet spectra showed strong agreement with field deposition trends suggesting that droplet statistics could be used to estimate drift reduction of spray solutions.

Introduction

Spray drift from agricultural applications of pesticides is almost always considered an inevitable outcome, regardless of measures to minimize its occurrence (Damalas 2015, EPA 1999, Felsot et al. 2011, Salyani and Cromwell 1992). The U.S. Environmental Protection Agency (EPA) defines drift as the “movement of pesticide dust

or droplets through the air at the time of application or soon after, to any site other than the area intended” (EPA 2016b). Loss of crop protection products by drift can result in potentially harmful human and environmental health effects, inefficient pest control, and economic losses to the product user. Therefore pesticide drift is axiomatically problematic because it compromises the objectives of integrated pest management, which are to reduce pest status through means that are effective, economically sound, and ecologically compatible (Pedigo 1989). Developments in drift reduction technologies (DRTs) and environmental policy for pesticides have progressed with increased knowledge of the drift phenomenon, but research gaps remain.

Environmental conditions can affect pesticide spray drift and must be considered when making an application, but these cannot be controlled. Operating conditions on the other hand, can be manipulated by the person making the application to mitigate spray drift. Environmental conditions such as wind speed and direction, temperature, relative humidity, atmospheric stability, and crop characteristics interact with airborne droplets and influence their deposition. Operating conditions such as boom height, driving speed, spray pressure, nozzle orientation, and application rate can also affect drift and are among the variables that may be manipulated by the equipment operator. Nozzle type, nozzle size, formulation type, and tank additives are commercially available DRTs designed to affect drift through modification of the droplet size distribution upon atomization. Other DRTs such as shielded- and air-assisted sprayers act by interrupting the interaction between airborne droplets and the surrounding air movement.

There are a number of commercially available DRTs and the EPA has recently developed a protocol for verifying and rating their drift reduction potential (EPA 2016b). The protocol provides a standard method for the application technology industry to voluntarily test their DRTs. Pesticide drift considerations are included in the registration process and registrants are encouraged by the EPA to include verified DRT options on their product labels. However, there are limitations to the protocol as it has only been evaluated for spray nozzles in low- and high-speed wind tunnels, and does not include the effect of tank mixes.

In this paper, the combination of a formulated pesticide active ingredient, with or without an adjuvant, is referred to as the spray solution. A pesticide formulation is a mixture of chemicals designed to maximize biological efficacy given the mode of action of the active ingredient. Many types of formulations have been developed and they have evolved in response to market demand and pressure from consumer groups and government authorities to minimize pesticide residues on food crops (Knowles 2008). However, physical properties of certain formulation types have been shown to influence droplet formation upon atomization from the spray nozzle. Adjuvants are tank additives that are marketed for their enhancement benefits according to the function they are designed to perform. Some adjuvants are designed to enhance the performance of the pesticide, usually through better absorption, whereas others are designed to enhance the quality of the spray by modifying the physical properties of the spray solution (De Oliveira et al. 2013, Richards et al. 2017).

Manipulating components of the spray solution as a drift reduction strategy has been reported in the scientific literature to a lesser degree than other technologies such as nozzle type, and results are variable (Butler et al. 2002, De Schampheleire et al. 2009, Miller et al. 2011, Stainier et al. 2006, Al Heidary et al. 2014). Quantification of the drift reduction due to formulation and adjuvant type is an important objective because these can have an effect that is equivalent to nozzle type on downwind deposition (Miller and Ellis 2000). Furthermore, selecting the formulation with optimal drift reduction potential could reduce the need to include drift reduction adjuvants, which may not perform consistently when employed in different combinations.

This research characterizes downwind deposition of two common formulation types and adjuvants from a ground sprayer in a three-year field study. Part of that characterization included deposition on vertical samplers to observe differences in droplet spectra between treatments and to better understand the environmental factors that contribute to that difference. An experiment was also conducted to test for differences in efficacy between the spray solutions used in the drift experiment. This was considered because manipulating the size distribution of spray droplets to achieve drift reduction could negatively affect the biological efficacy of the pesticide in certain situations.

Methods

Field experiments were conducted in California over three consecutive summers from 2014 to 2016 at the Dow AgroSciences Western U.S. Research Center near Fresno, CA. The topography at the field site was flat, and there was no vegetation because it had

been fallow the previous season, and disked before the start of the experiment. The spray swath was 145-m long by 15-m wide, and oriented with driving direction perpendicular to the wind direction. The off-target area was 110 m by 145 m and downwind from the spray source. Two sample lines 2.5 m to the left and right of the center of the off-target plot consisted of both horizontal (ground) and vertical (1 and 2 m above ground) sample locations. The sample lines were perpendicular to the spray line and approximately parallel to the wind direction. The orientation and relative lengths of the spray swath and sample lines (Figure 2.1) were designed so that spray droplets could travel toward the farthest downwind sample locations if no more than a 30° deviation angle in wind direction was allowed (ASABE 2009).

Downwind insecticide ground deposition was collected with 14-cm diameter plastic Petri dishes (Fisher Scientific Cat. No. FB0875714). Petri dishes were horizontally placed on plywood at 8 distances of 1, 2, 4, 8, 16, 32, 64, and 110 m from the field edge, along each of the two sample lines. The downwind samplers along the two lines were subsamples, so for statistical analysis the deposition data were averaged for each distance. Plywood was placed on the ground to provide a level surface for the dishes. Also, along the two sample lines (averaged for statistical analysis) at 2, 8, 32, 64, and 110 m, vertical samplers were positioned 1 and 2 m above the ground to sample the size distribution of the spray droplets at different heights and distances. Each vertical sampler (spinner) consisted of two rotating microscope slides with a spin rate of 600 rpm, designed to impinge on airborne droplets (Leading Edge Associates, Inc., Fletcher, North Carolina). The microscope slides were coated with a magnesium oxide (MgO) powder so

that analysis could be done at a later date. This is made possible by the MgO-coating because measurements are made on the droplet impressions instead of the droplets themselves, which are prone to evaporation (Chaskopoulou et al. 2013).

An untreated area located 15-m upwind from the spray swath contained negative controls for both horizontal and vertical samplers, and a weather station to monitor environmental conditions. The weather station consisted of a Hobo Micro Station Data Logger (Onset Computer Corporation, Bourne, Massachusetts) 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. The Hobo wind speed smart sensor (S-WSA-M003) had a starting threshold of ≤ 1 m/sec and the logger was set to measure wind speed every 20 seconds. The average wind speed was calculated over the first 10 minutes of each treatment replication to characterize wind speeds before, during, and after each application.

Hobo temperature and relative humidity data loggers were also used at different heights (2.5 and 9.2 m) to monitor atmospheric stability. Atmospheric stability was categorized by first calculating the stability ratio with the following equation from Fritz (Fritz 2006):

$$SR = [(TZ2 - Tz1/\mu_w2] \cdot 10^5 \quad (1)$$

where SR is the stability ratio, TZ2 and Tz1 is the air temperature (°C) at 9.2 m and 2.5 m respectively, μ_w is the mean wind velocity (cm/s) at 2.5 m, and 10^5 gives the ratio acceptable units. The SR for each treatment application was calculated from the average

wind speed and temperatures and were assigned to 4 categorical variables, “unstable”, “neutral”, “stable”, and “very stable” (Fritz 2006).

Treatments consisted of two formulation types, two adjuvants, and a water only. Each of the formulation types and adjuvants were applied individually (4 treatments), and each formulation type was also applied with each of the adjuvants (4 treatments). Including the water only treatment results in 9 treatments from a 3x3 factorial design. We used the active ingredient spinosad (a mixture of spinosyn A and spinosyn D) formulated as a wettable powder (WP) and a suspension concentrate (SC) under the product names Entrust[®] and Entrust[®]SC containing 80 and 22.5% active ingredient, respectively (Dow AgroSciences, LLC, Indianapolis, Indiana). The two adjuvant products were Maximizer[®] (Loveland Products, Inc., Loveland, Colorado) and Powerlock[®] (Winfield Solutions, LLC, St. Paul, Minnesota). Maximizer is composed of paraffin based petroleum oil (83%) and nonionic surfactant (16.3%), whereas Powerlock contains modified vegetable oil (63%) and nonionic surfactant (32%). The water-soluble fluorescent dye Rhodamine-WT (CAS No: 37299-86-8) was mixed with the spray solution of each treatment (0.2% v/v) to allow for the quantification of spray deposition (Smart and Laidlaw 1977).

Petri dishes and spinners were placed within the control area at the beginning of each replication and the treatment solution was sampled immediately before application to measure the actual fluorescent dye concentration in the tank. From the tank sample, two control dishes were loaded with 0.1 mL to quantify potential tracer degradation and recovery for each replication. Eight Petri dishes were also placed within the spray swath

before application to estimate deposition within the targeted area. These samplers were evenly spaced 29.3 m apart along the middle of each of the two spray lines.

Treatments were selected in random order and applications were made with a ground rig boom sprayer (Avenger high clearance tractor by Lee, Lubbock, Texas). The boom length was 7.62 m and all applications were made with a boom height above the ground of 58 cm. For this study, 15 XR11002 flat fan broadcast nozzles with a 110° spray angle, and a size 50 mesh, were evenly spaced 50.8 cm apart, along the length of the boom (TeeJet®, Glendale Height, Illinois). Spray pressure was measured at the end of the spray boom and driving speed was monitored by an onboard GPS system; these were held at 2.07 bar and 6.8 km/h (4.2 mph), respectively. Two spray passes per application were made so as to simulate a single pass with a 15 m spray boom.

Following each treatment replication (spray application) horizontal and vertical samples were collected from all locations (off-target, on-target, and untreated). Sample collection began three minutes after the sprayer had been turned off at the end of the spray swath to allow for deposition to occur at the farthest samplers. Exposed Petri dishes and microscope slides were placed in dark containers to minimize photo-degradation of any insecticide or fluorescent material, and control samples were the last to be collected. Replications were performed over time within the same day or over multiple days with 9 replications of each of the 9 treatments, totaling 81 spray events in the months of July (2014), and May (2015, 2016).

Insecticide deposition on Petri dishes was extracted with 15 ml of D.I. H₂O and decanted into 20-ml scintillation vials (Thermo Fisher Scientific, Rockwood, Tennessee).

Analysis vials were wiped with KimWipes (Kimberly-Clark, LLC, Roswell, Georgia) to remove exterior moisture, and were inspected for clarity before being analyzed. Light absorption at a specific wavelength, representing the amount of dye present in each sample, was quantified and recorded using a GFL-1A fluorometer (Opti-Sciences, Inc., Hudson, New Hampshire). The source and detection filters that were used for the excitation and detection of Rhodamine-WT were 530 and 590 nm, respectively (manufacturer recommendation). Standard curves were prepared using serial dilutions prepared in D.I. H₂O and the detection limit (DL) of Rhodamine-WT, given the sensitivity of the fluorometer, was estimated by adding three standard deviations of a known low concentration measured 20 times to the mean of a blank sample (Armbruster and Pry 2008). After extraction and analysis, Petri dishes were discarded and scintillation vials were triple rinsed with D.I. H₂O before reuse. Less than 10% of the ground samples consisted of concentrations below the DL so one half of the DL was substituted for non-detectable concentrations (Lubin et al. 2004, Helsel 2005, Schleier III et al. 2012).

Statistical analysis for ground deposition was done using the amount of Rhodamine-WT deposited per unit area ($\mu\text{g}/\text{cm}^2$) for each distance, averaged over the two sample lines. Tank mixes for each treatment were analyzed for actual dye mixing rates following the procedure above. Based on the actual amount of dye in the tank, the estimated volume on the spiked control plates was compared to the actual volume of the spike (0.1 mL) to estimate recovery rates for each treatment. To represent deposition as a percentage of the total material applied, first the area for each sample location was calculated, as one-half the distance between two sample locations multiplied by the

diameter of the Petri dish (Table 2.1). The application rate of the dye for each treatment was then estimated by multiplying the actual dye mixing rates by the application rate (Table 2.2). Multiplying the application rate of the dye by the total area of the sample locations returned the total mass of dye applied. The area for each sample location was then multiplied by the deposition data, averaged over the two sample lines, for each distance, to return mass of dye per sample location. Finally, the mass of dye per sample location was divided by the total dye applied to express deposition as a percentage of applied material. Deposition data for both in swath and downwind samples were calculated in this way.

Due to minimal ground deposition beyond 32 m, only 6 downwind distances were included in the statistical analysis. This resulted in a total of 486 data points (9 treatments, 6 distances, 9 reps) for ground deposition which were analyzed using multiple linear regression in the statistical software package R, version 3.3.2 (RCoreTeam 2016b). Exploratory data analysis was done to identify outliers, potential interactions, linearity, and normality, among dependent and independent variables. Table 2.3 lists summary statistics for numerical variables considered in this data set.

Log transformations on the deposition of Rhodamine-WT ($\mu\text{g}/\text{cm}^2$) and the independent variable, distance (m), were required before parametric statistics could be used. Correlation coefficients between independent variables was used to eliminate those with a correlation greater than 0.5 to avoid collinearity. This resulted in the exclusion of temperature and relative humidity (RH) at the upper height (9.2 m), as well as temperature measured at the lower height (2.5 m). Temperature, instead of RH, at 2.5 m

was removed because RH resulted in a better fit for the regression model, and because 2.5 m is a more practical measurement height. Model selection with Akaike's information criterion (AIC) was used to select between candidate models, which were based on specific hypotheses about pesticide drift. Full and reduced models were compared using an extra sums of squares (ESS) F-test to determine the contribution of certain independent variables in explaining variability in the response variable. The model with the lowest AIC was selected and diagnostic plots were used to check that the requirements for linear regression were met regarding statistical assumptions. The data were centered by subtracting the average RH so that the main term coefficients for treatment could be interpreted as the estimates at average, instead of zero, RH.

Droplet spectra resulting from deposition on vertically positioned microscope slides were recorded with a DropVision[®] measurement system (Leading Edge Associates, Inc., Fletcher, North Carolina). The DropVision[®] system integrates a compound microscope and image processing software to recognize, count, and measure droplets while eliminating background objects. A calibration slide containing circles of known diameters was used to calibrate the system at 10X magnification. This is achieved by relating the number of pixels contained in the calibration circle to its diameter. Microscope slides for all three years (4,221 slides) were scanned by a single person following a specific protocol to minimize user error. A specific viewing pattern was designed to sample a representative number of droplet impressions from an evenly distributed area of the slide surface. A minimum of 100 droplets or 200 pictures were required before moving to the second slide from a given field location (each spinner

contains two slides). Once 200 droplets were counted, or the entire surface area of both slides was viewed, the droplet statistics were compiled into a report produced by the software. The diameter at which half of the volume was contained in droplets smaller than the median (VMD) was recorded for all slide sets containing 30 or more droplets, which limited the farthest downwind distance from the spray source to 32 m, resulting in 273 data points for statistical analysis.

The same statistical approach for ground deposition was used to analyze the droplet data. Correlated independent variables that were excluded above were also excluded here. Exploratory analysis suggested a log transformation of the response (VMD) was required to meet assumptions of normality and AIC model selection was used to choose the final model. The predictor variable for height was analyzed as a categorical variable at 1 and 2 m above the ground. Linear model assumptions were assessed using residual plots and the global validation package, *gvlma*, in R (Slate 2014). These data were centered by subtracting the average wind speed so that the main term coefficients for treatment could be interpreted as estimates at average wind speed.

The droplet spectra of all treatments were also measured in a wind tunnel so that general trends in droplet size could be compared to differences in ground deposition from the field study. Using the same application system as in the field study (i.e. nozzle set up, application rate, and spray pressure) three replications of each treatment were sprayed in a wind tunnel at the University of Nebraska West Central Research & Extension Center in North Platte, Nebraska. A Sympatec laser diffraction particle size analyzer (Sympatec Inc., Clausthal, Germany) positioned near the spray nozzle was used to measure droplet

spectra for each of the treatments in the wind tunnel. Droplet sizing data measured for each treatment included VMD, the 10% and 90% diameters, the relative span, and the percent spray volume contained in droplets less than 141 μm . This percentage represents the fraction of spray droplets within the “fine” classification (100-175 μm) for droplet sizes (ASABE 2009b), and was used as an indicator for spray drift. The treatments were ranked according to the percentage of droplets within this size range and compared to the ranks for ground deposition (Table 2.8).

An insecticide efficacy experiment was also conducted to test differences in insect control between the treatments used in the drift study. The study was conducted August 2016 at the same experimental station in Fresno, California. The experimental setup was a randomized complete block design with 7 treatments (treatments consisting of only adjuvant were excluded) and 4 replications (blocks) of each treatment. Each plot was 3.05 m long and 2.03 m wide, and contained two rows of newly planted broccoli (Green Magic variety of Brassicaceae sp., 16 plants per plot). Plots were 1.5 m apart, and two empty rows (2.03 m) were left between blocks so as to avoid contamination from adjacent plots. Before spraying on application day a pre-count was conducted to record cabbage looper larvae (*Trichoplusia ni*) on broccoli plants in the study area which had been infested by endemic populations. Applications were made with a handheld boom sprayer at the same rate, and with the same nozzle type, as in the drift study. All treatments were applied in random order and *Trichoplusia ni* larvae on the broccoli plants were counted to estimate percentage mortality at 1, 3, and 7 days after application.

Efficacy data were represented and analyzed as count data, and as a fraction of the untreated control plots at each time-step after application. Count data and percent mortality data were analyzed using ANOVA fit to a linear model for a randomized block design in R, version 3.3.2 (RCoreTeam 2016a). The hypothesis that was tested with the count data was that there would be no differences in the number of *Trichoplusia ni* larvae between treated and untreated plots. For the percent mortality data the tested hypothesis was that there would be at least one difference in percent mortality between treatments.

Results

Ground Deposition

The recovery rates of Rhodamine-WT for each treatment (Supplementary Table 2.1) were within the recommended range of 80 to 120% (EPA 2016, ASABE 2009a). The high recovery rate of the dye from the control plates suggests that degradation of the fluorescent dye in samples was negligible due to the short exposure time to sunlight. In some cases, more material deposited on the swath plates than was expected given the application rate of the dye (Supplementary Table 2.2). Various sources of error could have contributed to an inaccurate estimation of recovery, such as fluctuations in the actual driving speed, spray pressure, flow rate, or errors in the analysis on the fluorometer (Arvidsson et al. 2011).

Coefficient estimates and standard errors for the selected model for ground deposition, centered on average relative humidity, are listed in Table 2.4. Treatment, log of distance (m), wind speed (m/s), relative humidity (%), and a term for the interaction

between treatment and relative humidity were included in the final model. Year, stability ratio, and stability category were excluded because they had no effect on deposition, and did not significantly change the error sums of squares when compared to the final model (ESS F-test, $F=1.46$, $p=0.2004$, on 461 and 466 degrees of freedom). Diagnostic plots of the model residuals suggested that the assumptions of normality, linearity, and homoscedasticity were reasonably met. The selected regression model for the ground deposition data was shown to explain 89.3% of the variability in the response variable (adjusted R-squared of 0.8934 for overall model). The regression equation centered on relative humidity with water as the reference level for treatment is:

$$\begin{aligned} LT = & -5.43 + 0.305*WP + 0.162*SC - 0.660*WPM_{\text{ax}} - 0.683*WPPL - 0.491*SCM_{\text{ax}} \\ & - 0.894*SCPL - 0.543*Max - 1.058*PL - 1.662*LD + 0.456*Wind - 0.019*RH \\ & + 0.006(WP*RH) - 0.038(Max*RH) + 0.034(PL*RH) + 0.0176(SCM_{\text{ax}}*RH) \\ & + 0.003(SCPL*RH) - 0.033(SC*RH) + 0.034(WPM_{\text{ax}}*RH) - 0.001(WPPL*RH) \end{aligned} \quad (2)$$

where LT is the log of the Rhodamine-WT deposition ($\mu\text{g}/\text{cm}^2$), WP= Entrust WP, Max=Maximizer, SCPL=Entrust SC with PowerLock, WPM_{ax}=Entrust (WP) with Maximizer®, WPPL=Entrust (WP) with PowerLock, LD is the log of the distance (m), Wind is wind speed (m/s), and RH is the relative humidity (%) at 2.5m above the ground.

Deposition of Rhodamine-WT ($\mu\text{g}/\text{cm}^2$) for all treatments decreased with increasing distance from the field edge as indicated by the negative coefficient for logged

distance in the overall regression model ($p < 0.0001$, Table 2.4). After controlling for wind speed and RH, this decrease in deposition was estimated to be 68.4% with an associated 95% confidence interval from 67.19 to 69.57% for every doubling of distance (e.g. going from one ground sample to the next in this study, Figure 2.2). The treatments with the highest and lowest amounts of active ingredient observed at the farthest downwind distance were Entrust SC with Maximizer and Entrust (WP) with PowerLock, respectively (Supplementary Tables S2.3 and 2.4).

All treatments also exhibited more deposition in higher wind conditions as indicated by the negative coefficient for wind speed in the overall regression ($p < 0.0001$, Table 2.4), with every additional 1-unit increase in wind speed (m/s) resulting in an estimated 36.59% increase in deposition after controlling for distance and RH (95% CI from 28.13 to 44.06%) (Figure 2.3).

The interaction between RH and treatment suggests that the effect of RH on deposition depends on treatment type. The estimated slope coefficients are listed in Table 2.5, and can be interpreted as the percent change in deposition associated with a 1-unit increase in RH (%). Neither Entrust SC nor Entrust (WP) were affected by RH, but water alone, as well as all treatments which included adjuvant, exhibited higher deposition with increasing RH over the range of RH measured in this study.

Relative humidity had a larger positive effect on deposition of Entrust SC with Maximizer compared to the SC treatment alone ($P = 0.041$). However, deposition of the SC with PowerLock combination was not affected by RH differently than deposition of SC alone ($P = 0.10$). The same trend was observed when comparing the effect of RH on

deposition between the WP formulation and WP plus the two adjuvants. Deposition of WP with Maximizer was more affected by RH than WP alone ($P=0.010$), but WP with PowerLock was not affected differently than WP alone ($P=0.623$).

At the average RH (58.55%) recorded in this study, deposition of the SC formulation was lower than for the WP formulation after controlling for distance and wind speed ($p=0.0045$). The estimated difference in deposition between SC and WP was 32.27% with an associated 95% confidence interval from 13.54 to 54.48%. With the exception of the WP and SC treatments, deposition of the water only treatment was greater than for all other treatments at the average RH, and fixed distance and wind speed ($\alpha=0.05$).

The difference in deposition between the formulated product with and without the adjuvant can be thought of as the effect on drift caused by the adjuvant. When comparing deposition of the SC treatment to deposition of this formulation with each of the two adjuvants, PowerLock reduced deposition, but Maximizer did not ($P<0.001$ & $P=0.0594$, respectively). The estimated reduction in deposition caused by the addition of PowerLock to the SC formulation was 51.94% at average RH, and after controlling for distance and wind (95% CI from 33.33 to 65.35%).

Deposition of the WP formulation was reduced with the addition of both the PowerLock and the Maximizer adjuvants by roughly the same amount, at average RH ($p<0.0001$). After controlling for distance and wind speed, this reduction was an estimated 62.75% (95% CI from 50.34 to 72.06%) and 61.88% (95% CI from 48.46 to 71.80%) for PowerLock and Maximizer, respectively.

Vertical Deposition

Coefficient estimates and standard errors for the selected model for VMD, centered on average wind speed, are listed in table 2.6. Treatment, log of VMD (μm), wind speed (m/s), and relative humidity (%), were included in the final model for vertical deposition. Year, stability ratio, and stability category were excluded because they had no effect on deposition, and did not significantly change the error sums of squares when compared to the final model (ESS F-test, $F=1.204$, $p=0.3079$, on 247 and 252 d.f.). Diagnostic plots of the model residuals suggested that the assumptions of normality, linearity, and homoscedasticity were reasonably met. The selected regression model for the VMD data was shown to explain 41.9% of the variability in the response variable (Adjusted R-squared of 0.4187 for overall model). The estimated regression equation for logVMD from the selected model centered on wind speed and with water as the reference level for treatment is:

$$\begin{aligned} \text{IVMD} = & 3.941 + 0.133 \cdot \text{WP} + 0.119 \cdot \text{SC} + 0.109 \cdot \text{WPMax} + 0.093 \cdot \text{WPPL} + 0.089 \cdot \text{SCMax} \\ & + 0.149 \cdot \text{SCPL} + 0.073 \cdot \text{Max} + 0.135 \cdot \text{PL} - 6.9\text{E-}4 \cdot \text{D} - 0.005 \cdot \text{RH} - 0.070 \cdot \text{Height} \\ & + 0.101 \cdot \text{Wind} + 0.125(\text{WP} \cdot \text{Wind}) + 0.094(\text{SC} \cdot \text{Wind}) + 0.018(\text{WPMax} \cdot \text{Wind}) \\ & - 0.030(\text{WPPL} \cdot \text{Wind}) + 0.081(\text{SCMax} \cdot \text{Wind}) + 0.085(\text{SCPL} \cdot \text{Wind}) \\ & - 0.044(\text{Max} \cdot \text{Wind}) + 0.072(\text{PL} \cdot \text{Wind}) \end{aligned} \quad (3)$$

Where IVMD is the log of the VMD (μm), D is the distance from the field edge (m), and Height is the vertical distance above the ground from 1 to 2 m, at which the rotating

microscope slides were positioned. All other variables are defined the same as in equation (2).

The VMD was not significantly affected by distance after controlling for height, wind speed, and RH ($P=0.3087$). Elevated RH led to smaller VMD values for all treatments at fixed height and wind speed as indicated by a negative coefficient from the overall regression model ($P<0.0001$). The estimated rate at which VMD decreased was 0.544% for every 1-unit increase in RH (%) with an associated 95% CI from 0.411 to 0.677%. The results also suggest that larger droplets were collected on spinners at the lower height (1 m) compared with the upper heights (2 m) for all treatments and distances ($P<0.0001$). Droplets collected at 1m were an estimated 6.7% larger than droplets collected at 2 m with an associated 95% CI from 4.35 to 9.15% (figure 2.4).

The interaction between treatment and wind speed suggests that the effect of wind speed on droplet size differs between treatments (figure 2.5). The estimated slope coefficients are listed in table 2.7, and can be interpreted as the percentage change in VMD associated with a 1-unit increase in wind speed (m/s). Of the treatments that were affected by wind speed, the effect was such that higher wind speed resulted in larger VMD values (positive slope). The effect of wind speed on VMD was not different between Entrust SC and Entrust (WP) ($P=0.568$). When the SC formulation was combined with either of the adjuvants the degree to which wind affected VMD was not changed ($P=0.861$ and $P=0.714$ for SC with PowerLock and SC with Maximizer, respectively). When the two adjuvants were added to the WP formulation the addition of PowerLock resulted in a lesser influence of wind speed on VMD ($P=0.011$), but the effect

on VMD was not different between WP with Maximizer and Entrust (WP) alone ($P=0.058$). The effect of wind speed on VMD for water was significantly lower than for either formulations alone ($P=0.024$ and $P=0.044$, for Entrust SC and WP, respectively).

The order in which treatments had the largest to smallest VMD on the field samplers can be viewed in Figure 2.5. At the average wind speed (2.38 m/s), and after controlling for RH, distance, and height, there was not difference in VMD between the two formulations ($P=0.666$), or between either formulation in combination with either of the adjuvants ($P=0.283$; 0.272; 0.606; 0.175 for PowerLock and Maximizer combined with SC and WP, respectively). The VMD of water was significantly lower than all other treatment combinations at average wind speed and fixed values for RH, height, and distance. The VMD of water was an estimated 8.43% smaller than the treatment with the next largest VMD (SC with Maximizer), with an associated 95% CI from 2.74 to 13.79%. At the average wind speed there was no difference in VMD between either formulation with PowerLock or either formulation with Maximizer ($p=0.110$ and 0.451, respectively).

The fraction of spray volume containing droplets less than 141 μm , measured in the wind tunnel, can be viewed in Table 2.8. The order in which treatments had the highest to lowest fraction of fine droplets ($<141 \mu\text{m}$), measured in a wind tunnel was the same for treatments ordered by ground deposition.

Biological Efficacy Study

There were statistically fewer *Trichoplusia ni* larvae in the treated plots than in the untreated plots at 3 and 7 days after application, suggesting that all treatments were

effective at reducing the pest population ($p < 0.05$, ANOVA on 18 d.f.). Furthermore, no difference in percentage mortality was observed between treatments at either 3 or 7 days after application, suggesting that all treatments were similarly effective ($p > 0.05$, ANOVA on 15 d.f.).

Discussion

This study aimed to ascertain how differences in formulation type, with and without the addition of two adjuvants, would behave under variable weather conditions. Because treatment replications were independent, and applied in random order, it is reasonable to infer the differences in deposition were caused by the various predictor variables that were considered.

Our findings support previous studies in that formulation type can affect spray drift, and should be considered when evaluating a given spray system for its drift potential. Specifically, our results differentiate between two formulations that are typically categorized together with regard to their drift potential. Both wettable powders and suspension concentrates are formulations of solid crystalline active ingredients which form non-deformable dispersions throughout the spray solution (Knowles 2008). These formulations are thought to share a common mechanism for affecting spray atomization on the basis of this physical property (Hilz and Vermeer 2013). However, the scientific literature is inconclusive regarding the effect of solid dispersions on droplet size, and therefore drift (Stainier et al. 2006, Qin et al. 2010, Dexter 2001, Hilz and Vermeer 2012, De Schampheleire et al. 2009). This study provides evidence that spray solutions of

formulations with solid particles do influence drift, and that drift of the WP formulation was greater than for sprays of water alone. Results from the efficacy study suggest that pest control was not sacrificed for drift reduction and further support the apparent advantages of the SC over the WP formulation as a DRT. Differentiating the drift potential of these closely related formulations could help inform DRT manufacturing decisions, although generalizations are premature.

The greater drift reduction of PowerLock compared to Maximizer in this study is consistent with results from Western et al. (1999), who found that adjuvants of vegetable oil, rather than mineral oils, were more effective at reducing drift, but others have found the effect of these adjuvant types on VMD to be small (Ellis et al. 1997). Given the many interactions between certain properties of the spray solution and other components of the system, it could be advantageous if no additional tank additives were required to improve drift reduction. Both of the adjuvants tested in this study were shown to effectively reduce deposition without any apparent tradeoffs with biological efficacy, but their effect depended on the formulation type with which they were combined. This demonstrates the additional level of uncertainty introduced by incorporating adjuvants marketed for drift reduction into spray solutions.

Deposition on the vertical samplers was used to characterize the size distribution of spray droplets throughout the off-target area. Over the distances that were sampled in this study, there was more of a vertical, rather than horizontal, stratification of droplet sizes, with larger droplets collected below 2 m heights. The discrepancy between droplet size and ground deposition with increasing distance could be explained by the fact that

the total number of droplets at each distance was not quantified. It is plausible that at the farther distances fewer droplets were contributing to both ground deposition and droplet size on the spinners. At average RH and wind speed, the treatment containing only water and Rhodamine-WT had the second highest ground deposition, and the smallest VMD. This suggests that smaller droplets resulted in greater drift, but this cannot be conclusively stated. To test the well supported assumption that smaller droplet sizes lead to greater drift (Threadgill and Smith 1975, Al Heidary et al. 2014, Nuyttens et al. 2010, Miller et al. 2011, Carlsen et al. 2006, Hilz and Vermeer 2013, Felsot et al. 2011), we analyzed the droplet spectra of our treatments in a wind tunnel. We found that treatments with smaller droplets correlated with greater off-target deposition in the field, providing further support for this relationship.

Meteorological factors that affected deposition were wind speed and relative humidity. The observed effect of wind speed on drift is consistent with previous studies (Fritz 2006, Felsot et al. 2011, Maybank et al. 1978, Smith et al. 1982, FOCUS 2007), and is further supported by the presence of larger droplets on the vertical samplers during higher wind conditions. The positive correlation between relative humidity and deposition for some treatments in this study is also reasonable given the relatively short sampling distance from the field edge. Conditions with higher relative humidity are less conducive to evaporation of spray droplets, which may have led to larger droplets and greater deposition over the distances sampled. This may still be true even though the relationship between RH and VMD observed in this study would suggest otherwise. The effect of RH was small relative to the effect of wind speed on VMD, with $< 0.1\%$

decrease in droplet size for every 10% increase in RH, whereas a 10% increase in wind speed led to an estimated 1.3% increase in VMD.

This paper provides information on deposition and environmental factors related to agricultural spray drift of two of the most commonly used formulation types (Knowles 2008) under realistic application scenarios, including the use of enhancement additives. Overall, ground deposition values were within the range of EPA assumptions for drift (1-5%) for estimating pesticide exposure to adjacent areas when models are not used (Felsot et al. 2011). The fraction of applied material, and the estimated 68% decrease in ground deposition for every doubling of distance from the field edge, are comparable to findings from other drift experiments (Asman et al. 2003). Quantification of exposure and risk to non-target organisms using actual environmental concentrations from this, and similar studies, is needed to fully characterize the benefits of drift reduction technologies.

This work demonstrates an effective method for testing the effects of formulation type and adjuvant on spray drift, which showed strong agreement between droplet size data from the wind tunnel and actual spray drift in the field. The EPA verification protocol currently stipulates that when the combined effect of nozzle design and formulated product is evaluated, the drift reduction rating is only valid for that specific combination (EPA 2016a). Our results suggest that droplet size data could be used to demonstrate drift reduction regardless of the formulated product being sprayed, but more spray mixtures need to be tested before reference sprays can be defined for comparing and rating spray mixtures as DRTs.

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Table 2.1. Sample areas for in-swath and downwind ground deposition samplers.

Swath			Downwind		
Sample Location (m)	Range (m)	Sample Area (given a sampler diameter of 14 cm) (cm ²)	Sample Location (m)	Range (m)	Sample Area (given a sampler diameter of 14 cm) (cm ²)
18.13	0 to 36.25	50750	1	0 to 1.5	2100
54.38	36.25 to 72.5	50750	2	1.5 to 3	2100
90.63	72.5 to 108.75	50750	4	3 to 6	4200
126.88	108.75 to 145	50750	8	6 to 12	8400
			16	12 to 24	16800
			32	24 to 32	11200

Table 2.2. Application rates of Rhodamine-WT (RWT) for each treatment

	Dye Mixing Rate ($\mu\text{g/mL}$)	Flow Rate (L/ha)	RWT Application Rate ($\mu\text{g/cm}^2$)
Entrust SC (SC)	80.06	123.47	0.0988
Entrust WP (WP)	96.46	127.21	0.1227
SC & PowerLock	103.15	127.21	0.1312
SC & Maximizer	72.35	128.15	0.0927
WP & PowerLock	93.26	130.02	0.1213
WP & Maximizer	83.38	127.21	0.1061
PowerLock	93.69	124.41	0.1165
Maximizer	80.41	124.41	0.1000
Water	82.07	127.21	0.1044

Table 2.3. Summary statistics for numerical variables

Variable	Units	Mean	SD	Range	
				Minimum	Maximum
Rhodamine-WT	$\mu\text{g}/\text{cm}^2$	2.88E-03	6.27E-03	2.60E-07	5.08E-02
Active Ingredient	$\mu\text{g}/\text{cm}^2$	0.0236	0.0619	6.05E-07	0.6938
Tank Solution	$\mu\text{L}/\text{plate}$	5.025	0.0109	4.50E-04	88.52
VMD	μm	36.7	5.08	26.08	52.54
Wind Speed	m/s	2.27	0.6865	0.3	3.82
Temp @2.5 m	$^{\circ}\text{C}$	20.39	4.14	13.38	30.14
Temp @9.5 m	$^{\circ}\text{C}$	21.2	4.56	12.96	31.08
RH @2.5 m	%	58.55	12.23	26.94	82.08
RH @9.5 m	%	55.03	13.68	22.67	86.16
Stability Ratio		2.11	5.83	-27.22	32.56
Distance	m			1	32

Table 2.4. Coefficient estimates and SEs for selected ground deposition model with an adjusted R-squared of 0.8934 for the overall model. Data centered on average RH. Centering data on RH allows the estimates of the main term effects to be interpreted at average RH instead of a RH of zero.

Ref. = Water	Estimate	Std.Error	t value	Pr(> t)
(Intercept)	-5.42587	0.20664	-26.258	< 0.0001*
Entrust WP	0.304542	0.146499	2.079	0.038*
Entrust SC	-0.16177	0.166646	-0.971	0.332
Maximizer	-0.54323	0.150797	-3.602	0.0003*
PowerLock	-1.05842	0.148866	-7.11	< 0.0001*
SC Maximizer	-0.49139	0.153832	-3.194	0.001*
SC PowerLock	-0.89444	0.146654	-6.099	< 0.0001*
WP Maximizer	-0.65979	0.160134	-4.12	< 0.0001*
WP PowerLock	-0.68294	0.159084	-4.293	< 0.0001*
log Distance (m)	-1.66215	0.02758	-60.267	< 0.0001*
Wind Speed (m/s)	0.455592	0.063746	7.147	< 0.0001*
RH (%)	0.019221	0.006816	2.82	0.005*
Entrust WP*RH	-0.00602	0.01066	-0.565	0.572
Entrust SC*RH	-0.03335	0.021728	-1.535	0.125
Maximizer*RH	-0.03756	0.014681	-2.558	0.010*
PowerLock*RH	0.034091	0.010877	3.134	0.001*
SC Maximizer*RH	0.017643	0.016531	1.067	0.286
SC PowerLock*RH	0.002819	0.009565	0.295	0.768
WP Maximizer*RH	0.03434	0.014663	2.342	0.019*
WP PowerLock*RH	-0.00109	0.009062	-0.121	0.904*

* Statistically significant at $\alpha=0.05$

Table 2.5. Slope coefficients for interaction terms in regression models for ground deposition and volume median diameter (VMD). Slopes interpreted as a percent change in the response for every 1 unit increase in the independent variable.

Treatment	Ground Deposition/RH		VMD/Wind Speed	
	Slope (%)	C.I. (95%)	Slope (%)	C.I. (95%)
Entrust SC	-1.41	(-5.49, 2.67)	10.07*	(5.83, 14.31)
Entrust WP	1.32	(-0.29, 2.93)	13.2*	(3.3, 23.1)
SC with PowerLock	2.2*	(0.9, 3.51)	9.18*	(0.12, 18.23)
SC with Maximizer	3.69*	(0.7, 6.67)	8.84*	(3.63, 14.04)
WP with PowerLock	1.81*	(0.66, 2.96)	-2.33	(-9.27, 4.61)
WP with Maximizer	5.36*	(2.78, 7.93)	2.50	(-2.39, 7.39)
PowerLock	5.33*	(3.64, 7.03)	7.90*	(0.61, 15.19)
Maximizer	-1.83	(-4.39, 0.73)	-3.66	(-11.7, 4.39)
Water	1.92*	(0.58, 3.26)	0.71	(-6.28, 7.69)

* Slope statistically different from zero at $\alpha=0.05$

Table 2.6. Coefficient estimates and SEs for selected VMD model with an adjusted R-squared of 0.4187 for the overall model. Data centered on average wind speed. Centering data on wind speed allows the estimates of the main term effects to be interpreted at average wind speed instead of a wind speed of zero.

Ref. = Water	Estimate	Std.Error	tvalue	Pr(> t)
(Intercept)	3.94112	0.049635	79.402	< 0.0001*
Entrust WP	0.13277	0.03384	3.923	0.0001*
Entrust SC	0.118991	0.029544	4.028	< 0.0001*
Maximizer	0.073092	0.031878	2.293	0.023*
PowerLock	0.134597	0.031834	4.228	< 0.0001*
SC Maximizer	0.088095	0.030629	2.876	0.004*
SC PowerLock	0.149319	0.030304	4.927	< 0.0001*
WP Maximizer	0.108916	0.029193	3.731	0.0002*
WP PowerLock	0.093255	0.037198	2.507	0.013*
Distance (m)	-0.00069	0.00068	-1.02	0.309
RH (%)	-0.00546	0.000679	-8.042	< 0.0001*
Height (m)	-0.07025	0.013066	-5.377	< 0.0001*
Wind Speed (m/s)	0.007064	0.035475	0.199	0.842
Entrust WP*Wind	0.124947	0.061732	2.024	0.044*
Entrust SC*Wind	0.093626	0.041187	2.273	0.024*
Maximizer*Wind	-0.04367	0.053981	-0.809	0.419
PowerLock*Wind	0.071954	0.050305	1.43	0.154
SC Maximizer*Wind	0.081286	0.04373	1.859	0.064
SC PowerLock*Wind	0.084699	0.058615	1.445	0.149
WP Maximizer*Wind	0.01789	0.042898	0.417	0.677
WP PowerLock*Wind	-0.03036	0.050863	-0.597	0.551

* Statistically significant at $\alpha=0.05$

Table 2.7. Slope coefficients for interaction terms in regression models for ground deposition and volume median diameter (VMD). Slopes interpreted as a percent change in the response for every 1 unit increase in the independent variable.

Treatment	Ground Deposition/RH		VMD/Wind Speed	
	Slope (%)	C.I. (95%)	Slope (%)	C.I. (95%)
Entrust SC	-1.41	(-5.49, 2.67)	10.07*	(5.83, 14.31)
Entrust WP	1.32	(-0.29, 2.93)	13.2*	(3.3, 23.1)
SC with PowerLock	2.2*	(0.9, 3.51)	9.18*	(0.12, 18.23)
SC with Maximizer	3.69*	(0.7, 6.67)	8.84*	(3.63, 14.04)
WP with PowerLock	1.81*	(0.66, 2.96)	-2.33	(-9.27, 4.61)
WP with Maximizer	5.36*	(2.78, 7.93)	2.50	(-2.39, 7.39)
PowerLock	5.33*	(3.64, 7.03)	7.90*	(0.61, 15.19)
Maximizer	-1.83	(-4.39, 0.73)	-3.66	(-11.7, 4.39)
Water	1.92*	(0.58, 3.26)	0.71	(-6.28, 7.69)

* Slope statistically different from zero at $\alpha=0.05$

Table 2.8. Droplet size data from wind tunnel test with treatments ordered by ground deposition from the field study. The treatments with the largest fraction of “fine” droplets (100-175 μm) measured in the wind tunnel had the highest downwind ground deposition in the field study at any downwind distance.

Treatments containing A.I. Sprayed in Wind Tunnel	% Spray Volume Containing Droplets $\leq 141 \mu\text{m}$ (SD)	Treatments Ordered by Ground Deposition (Highest to Lowest)	Droplet Size is Indication of Spray Drift
Entrust WP	19.98 (0.61)	Entrust WP	Yes
Entrust SC	15.30 (0.28)	Entrust SC	Yes
SC & Maximizer	13.62 (0.03)	SC & Maximizer	Yes
WP & Maximizer	13.33 (0.08)	WP & Maximizer	Yes
WP & PowerLock	12.18 (0.23)	WP & PowerLock	Yes
SC and PowerLock	11.69 (0.08)	SC and PowerLock	Yes

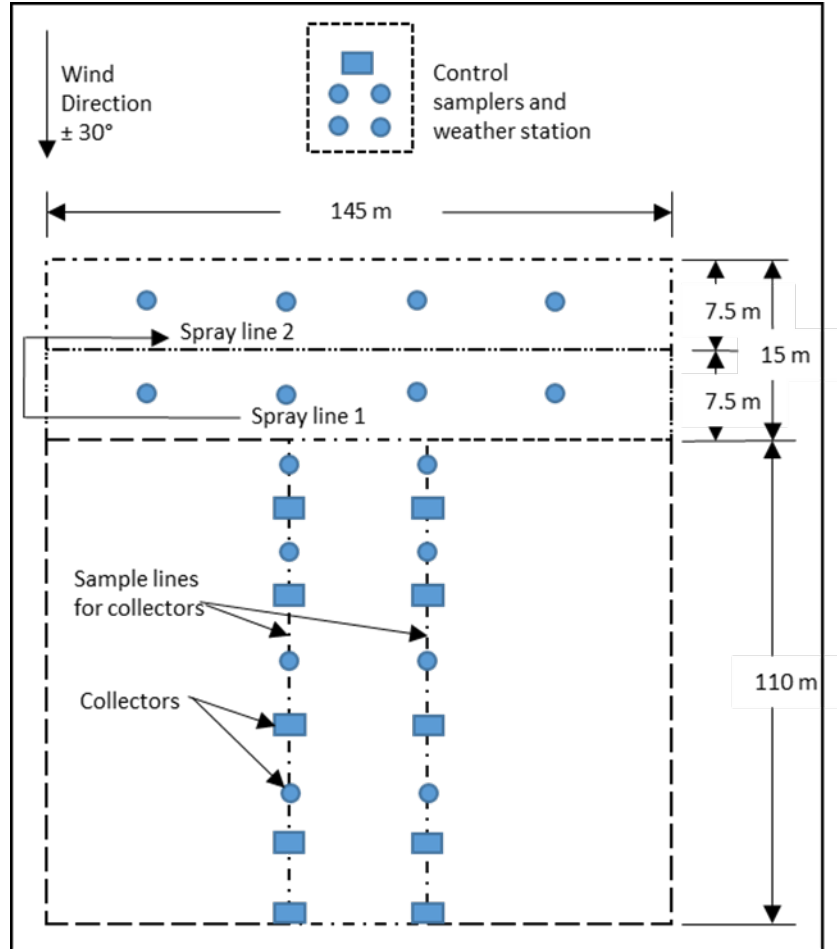


Figure 2.1. Field layout for drift experiment in Fresno, California. Blue circles represent locations where only horizontal ground samplers (14-cm diameter Petri dishes) were placed. Blue triangles represent locations where ground samplers and 2-m vertical samplers (rotating impingers) were placed. Blue rectangles represent locations where ground samplers and 1- and 2-m vertical samplers were placed. Black rectangles (located at farthest downwind distance from spray source) represent locations where only 1- and 2-m vertical samplers were placed, no ground samplers were placed there in 2015 and 2016. The control area was located 15 m from the farthest upwind edge of spray line 2. Collector locations in diagram are not representative of actual distances in the field.

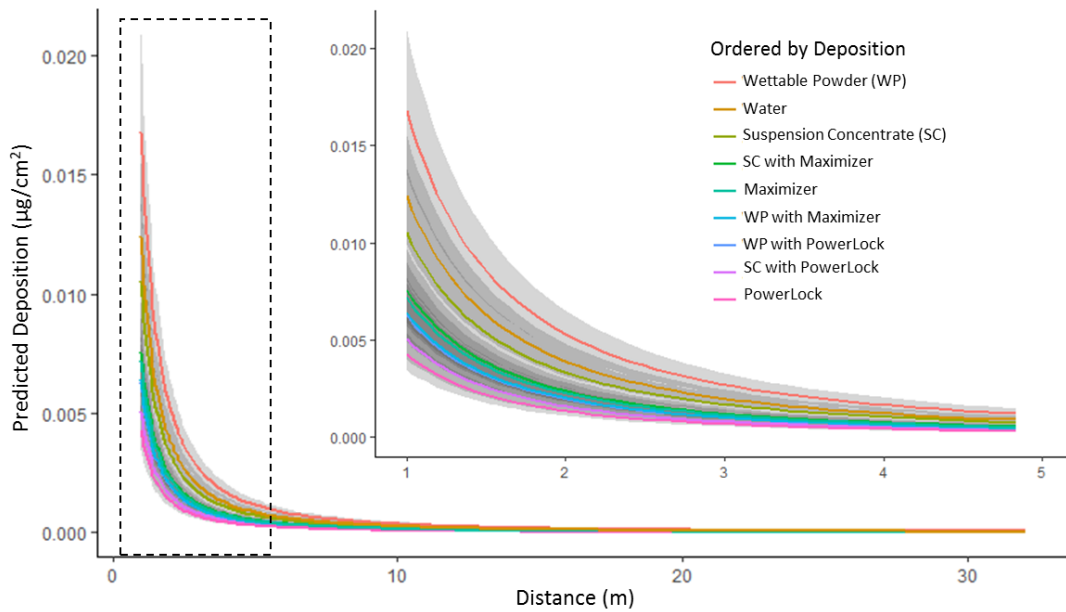


Figure 2.2. Predicted deposition of Rhodamine-WT as a function of distance at average RH and wind speed. After controlling for wind speed and RH, this decrease in deposition was estimated to be 68.4% with an associated 95% confidence interval from 67.19 to 69.57% for every doubling of distance (i.e. going from one ground sample to the next in this study). Adjusted R-squared of 0.8934 from overall model and gray bands represent the 95% C.I.

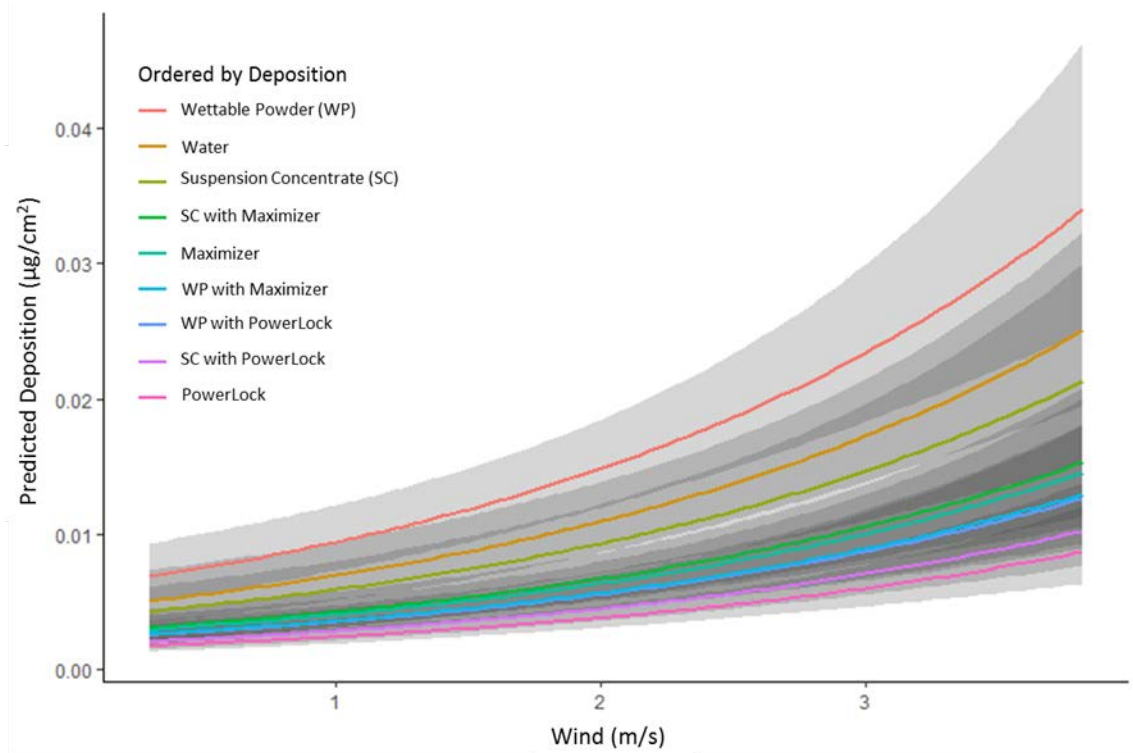


Figure 2.3. Predicted deposition of Rhodamine-WT as a function of wind speed at average RH and a distance of 1 meter. All treatments exhibited more deposition in higher wind conditions with every additional 1-unit increase in wind speed (m/s) resulting in an estimated 36.59% increase in deposition after controlling for distance and RH (95%CI from 28.13 to 44.06%). Adjusted R-squared of 0.8934 from overall model and gray bands represent the 95% C.I.

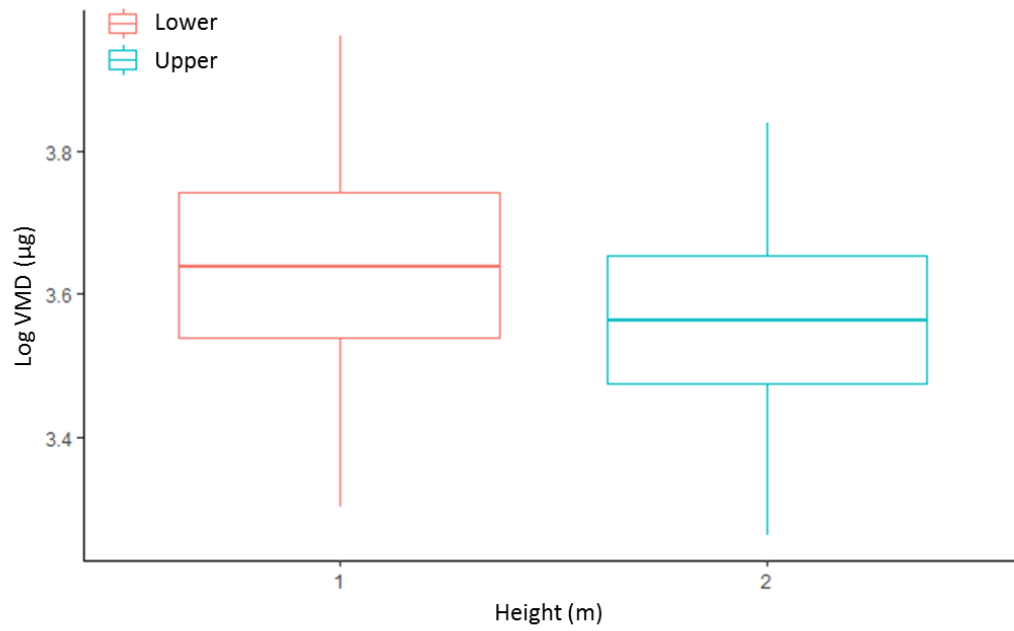


Figure 2.4. Droplet size by height.

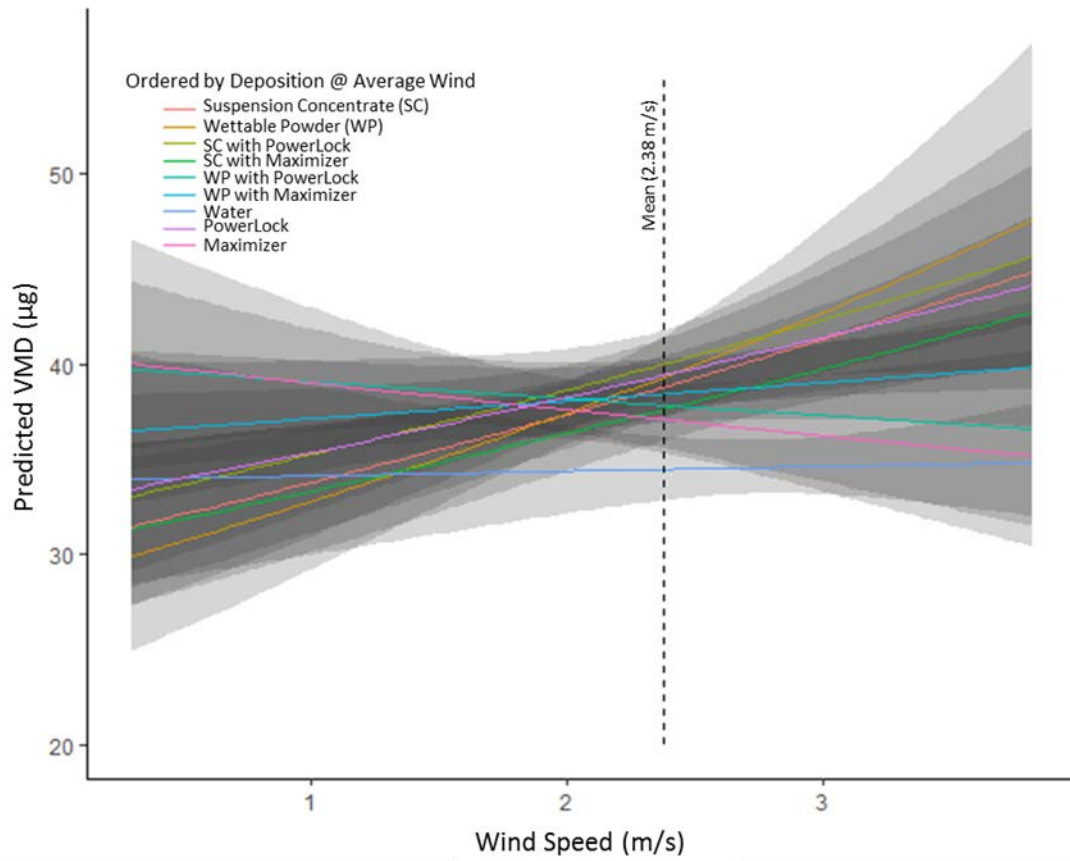


Figure 2.5. Interaction between VMD and Wind speed. Treatments are ordered by decreasing VMD at 1 m height, and at average wind speed.

Supplemental Material

Table S2.1. Recovery rate of Rhodamine-WT for drift study.

Treatment	Recovery (%)
Entrust SC	103.6
Entrust WP	109.1
SC & PowerLock	108.7
SC & Maximizer	107.0
WP & PowerLock	100.9
WP & Maximizer	106.2
PowerLock	108.5
Maximizer	109.1
Water	89.9

Table S2.2. Mean Rhodamine-WT deposition on swath plates represented as a percentage of amount applied.

Treatment	Swath Deposition (% Applied)
Entrust SC	114.90
Entrust WP	81.65
SC & PowerLock	80.62
SC & Maximizer	120.05
WP & PowerLock	86.68
WP & Maximizer	110.74
PowerLock	88.31
Maximizer	105.67
Water	100.19

Table S2.3. Ground deposition with increasing distance from the field edge as a percentage of Rhodamine-WT or a.i. applied. The ratio between Rhodamine-WT and a.i. is constant, so values represent both.

	Mean (%)	95th percentile (%)	Mean (%)	95th percentile (%)	Mean (%)	95th percentile (%)
	<u>1 m</u>		<u>2 m</u>		<u>4 m</u>	
Entrust SC	0.756	1.369	0.171	0.281	0.125	0.203
Entrust WP	0.856	1.796	0.202	0.357	0.161	0.308
SC & PowerLock	0.301	0.692	0.042	0.092	0.035	0.071
SC & Maximizer	0.707	1.234	0.150	0.241	0.132	0.214
WP & PowerLock	0.338	0.973	0.056	0.114	0.039	0.070
WP & Maximizer	0.592	0.302	0.146	0.302	0.118	0.193
PowerLock	0.307	0.654	0.050	0.174	0.041	0.190
Maximizer	0.517	1.007	0.092	0.150	0.064	0.109
Water	0.683	1.606	0.202	0.454	0.191	0.521
	<u>8 m</u>		<u>16 m</u>		<u>32 m</u>	
Entrust SC	0.094	0.162	0.042	0.095	0.007	0.020
Entrust WP	0.117	0.191	0.036	0.061	0.006	0.015
SC & PowerLock	0.028	0.059	0.017	0.047	0.003	0.018
SC & Maximizer	0.101	0.265	0.060	0.132	0.009	0.031
WP & PowerLock	0.030	0.055	0.014	0.037	0.003	0.011
WP & Maximizer	0.082	0.184	0.027	0.052	0.004	0.005
PowerLock	0.044	0.142	0.015	0.039	0.001	0.005
Maximizer	0.045	0.078	0.020	0.032	0.002	0.005
Water	0.152	0.443	0.091	0.166	0.011	0.032

Table S2.4. Ground deposition of active ingredient with increasing distance from the field edge.

	Mean (ng/cm ²)	95th percentile (ng /cm ²)	Mean (ng/cm ²)	95th percentile (ng/cm ²)	Mean (ng/cm ²)	95th percentile (ng/cm ²)
	<u>1 m</u>		<u>2 m</u>		<u>4 m</u>	
Entrust SC	72.91	132.04	16.51	27.11	6.33	10.29
Entrust WP	104.54	219.20	24.61	43.63	10.37	19.80
SC & PowerLock	37.86	88.55	5.26	10.88	2.26	4.54
SC & Maximizer	63.96	111.62	13.58	21.48	6.27	10.07
WP & PowerLock	40.75	117.37	6.80	13.15	2.47	4.37
WP & Maximizer	62.43	115.97	15.39	25.84	6.56	9.94
	<u>8 m</u>		<u>16 m</u>		<u>32 m</u>	
Entrust SC	2.31	4.01	0.51	1.16	0.13	0.36
Entrust WP	3.67	5.97	0.55	0.94	0.14	0.35
SC & PowerLock	0.90	1.77	0.27	0.61	0.09	0.28
SC & Maximizer	2.34	4.88	0.69	1.47	0.15	0.42
WP & PowerLock	0.92	1.62	0.21	0.49	0.06	0.20
WP & Maximizer	2.21	4.21	0.37	0.65	0.08	0.16

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CHAPTER THREE

NON-TARGET INSECT RISK ASSESSMENT OF DRIFT REDUCTION
INSECTICIDE FORMULATIONS AND SPRAY ADJUVANTS

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CHAPTER THREE

NON-TARGET INSECT RISK ASSESSMENT OF DRIFT REDUCTION
INSECTICIDE FORMULATIONS AND SPRAY ADJUVANTS

The following chapter has been prepared for submission to a peer-reviewed journal.

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Abstract

Agricultural field margins and adjacent natural habitats can experience pesticide spray drift. Drift reduction technologies offer a partial solution to this issue, but the degree to which reductions in drift correlate with pesticide risk requires further research. Therefore, ground deposition data from a field drift study were used with the EPA food-chain (Kenaga) nomogram to estimate insecticide residue on plant surfaces for the purpose of relating drift reduction to risk levels for terrestrial insects in agricultural field margins. Statistical differences in drift reduction of the active ingredient spinosad were observed through application of different combinations of formulation types and adjuvants. These differences were quantified in terms of ecological risk by comparing exposure levels to effect concentrations estimated with a species sensitivity distribution.

Reductions in the percentage of species potentially affected when exposed to spinosad at 5 m in a short-grass field margin ranged from 21.3 to 43.6% for the drift reduction technologies tested in this study. When formulated as a suspension concentrate, rather than a wettable powder, spinosad posed lower risk to non-target insects through exposure to spray drift. Regardless of formulation type, spray drift was reduced when combined with either of the adjuvants, but there were differences in the magnitude of this effect. A novel, conservative approach for quantitatively estimating pesticide residues on plant surfaces in an off-target area based on spray drift is proposed, and suggestions for future research to validate and refine this approach are discussed.

Introduction

Agricultural spray applications of crop protection products almost always result in some amount of exposure to adjacent, untargeted areas (Salyani and Cromwell 1992, EPA 2016, Felsot et al. 2011, Damalas 2015). Because field margins provide important habitat for wildlife and insect natural enemies, it is important to understand the degree to which pesticide spray drift affects these areas (Schmitz et al. 2014).

There is a growing body of scientific knowledge regarding spray formation and the factors that lead to its off target movement, but the risk associated with pesticide spray drift is often difficult to characterize. Innovations in drift reduction technologies (DRTs) continue to develop based on our understanding of the drift phenomenon, and currently there is a standard protocol for evaluating their drift reduction potential (EPA 2016). However, the relationship between spray drift and actual exposure and risk to non-

target organisms needs further refinement before DRTs can be evaluated in the context of pesticide risk.

There are several factors that make it difficult to accurately estimate terrestrial insect exposure to agrochemicals based on traditional methods for predicting and measuring spray drift in field margins. Passive sampling techniques are among the most common methods for measuring spray drift and underpin the development of drift models used in ecological risk assessments (Hewitt 2000). In spray drift models, such as AgDRIFT® (Teske et al. 2002), the amount of downwind ground deposition is estimated based on input variables such as application rate, wind speed, nozzle type, and a roughness factor for representing canopy structure and ground surface characteristics. However, the amount of off-target movement is not typically related to actual residue levels on plant surfaces because the relationship between deposits on ground samplers compared to three-dimensional plant structures is difficult to characterize.

The USEPA uses a linear model known as the Kenaga nomogram (Fletcher et al. 1994) to estimate residue levels on directly sprayed plant surfaces in its Terrestrial Residue Exposure (T-REX) model (EPA 2012). The Kenaga nomogram was developed to predict pesticide residue levels on plant surfaces directly sprayed at any application rate, and has been shown to achieve this with reasonable accuracy (Fletcher et al. 1994, Pfleeger et al. 1996). Assuming application rate could be reasonably represented by sample deposits, the Kenaga nomogram may also provide a way to estimate pesticide residue on off-target plant tissue based on ground deposition in an area exposed to spray

drift, but we are unaware of any previous implementations of the Kenaga nomogram for this purpose.

Because risk is a function of both exposure and effect, the toxicity of the stressor to the species of concern must also be characterized. Ecotoxicological extrapolation models known as species sensitivity distributions (SSDs) are statistical representations of the variability among species in their response to a particular toxicant (Posthuma et al. 2002). Species sensitivity distributions visualized as a cumulative distribution function of species effect concentrations such as LC_{50} values and no-observed-effect concentrations derived from acute or chronic toxicity tests, respectively. SSDs are sometimes used in the so-called “Forward” way, in which the fraction of species affected is estimated for a given toxicant concentration. They may also be used to estimate an environmental concentration that protects a certain percentage of species (Posthuma et al. 2002).

By using ground deposition to represent concentrations on plant residue, exposure can be compared to toxicity to characterize risk as a function of spray drift resulting from different DRTs. Among the DRTs that are now commercially available, the drift reduction potential of formulation types and tank additives is of particular interest. This is because the drift reduction from other technologies results from an interaction with the physical properties of the spray solution (Butler et al. 2002, Miller and Ellis 2000, Spanoghe et al. 2007). In a three-year field study, we showed that formulation and adjuvant types differed in their potential for drifting beyond the target area (Chapter 2), but the importance of these differences in terms of risk is unclear. The goal of this study therefore is to use the ground deposition data from our previous field study to

characterize the drift reduction in terms of differences in risk by using the Kenaga nomogram to estimate exposure and a species sensitivity distribution to estimate effect for non-target insects in an agricultural field margin. Recommendations for future work are provided to test some of the assumptions that were made in this approach.

Methods

A three-year drift experiment was conducted in which ground deposition of the active ingredient spinosad (mixture of spinosyn A and spinosyn D) was quantified on horizontally positioned Petri dishes located in an off-target area (see Chapter 2 for a detailed description of this study). The drift experiment was designed to test for differences in deposition resulting from the application of a wettable powder (Entrust) and a suspension concentrate (EntrustSC) formulation, with and without two oil-based adjuvants. Entrust® and EntrustSC (Dow AgroSciences, LLC, Indianapolis, Indiana) contain 80 and 22.5% spinosad, respectively, which exhibits its highest toxicity when insects are exposed through ingestion. The two adjuvant products were Maximizer® (Loveland Products, Inc., Loveland, Colorado) and Powerlock® (Winfield Solutions, LLC, St. Paul, Minnesota). Maximizer is a paraffin based petroleum oil containing 16.3% nonionic surfactant and PowerLock consists of a modified vegetable oil that contains 32% nonionic surfactant. The water-soluble fluorescent tracer Rhodamine-WT (CAS No: 37299-86-8) was mixed with the spray solution of each treatment (0.2% v/v) to allow for the quantification of spray deposition.

Spray applications were made with a tractor sprayer (Avenger high clearance tractor, Lee, Lubbock, Texas) over a 145 m by 15 m swath of bare ground that had been disked before the experiment. The height of the spray boom was held at 58 cm above the ground, and 15 flat-fan broadcast nozzles (TeeJet® XR11002, Glendale Height, Illinois) with a 110° spray angle were evenly spaced along its length. All treatment replications were applied at 2.07 bar spray pressure, at a driving speed of 6.8 km/h. A weather station containing a Hobo Micro Station Data Logger (Onset Computer Corporation, Bourne, Massachusetts) was located upwind of the treated area to monitor environmental conditions throughout the experiment.

Petri dishes (14-cm diameter polystyrene) were geometrically spaced, beginning at 1 and progressing to 110 m downwind from the edge of the sprayed area along two sample lines perpendicular to the driving direction of the sprayer. The ground surface in the off-target area was the same as in the spray swath (disked before experiment), which resulted in the entire study site having a flat topography free of vegetation. Three treatment, and three experimental, replications were performed over the summers of 2014-2016 resulting in 9 replications of each treatment.

After each treatment replication, Petri dishes were rinsed with 15 ml of deionized H₂O and decanted into 20-ml scintillation vials (Thermo Fisher Scientific, Rockwood, Tennessee). The samples were then analyzed using a GFL-1A fluorometer (Opti-Sciences, Inc., Hudson, New Hampshire) to quantify the amount of Rhodamine-WT in each vial. The amount of Rhodamine-WT could then be related to the deposition of active ingredient at each sample location (see Chapter 2 for a detailed description of this study).

The next step was to extrapolate to actual insect exposure by estimating spinosad residue on plant surfaces using ground deposition data and the Kenaga nomogram (Hoerger & Kenaga 1972; Fletcher et al. 1994). The 90th percentile ground deposition values at each downwind distance were estimated at average wind speed (2.38 m/s) and relative humidity (58.55%) from the regression model developed previously (see Chapter 2). Deposition was only measured up to 32 m in the drift study so residue values were estimated up to that distance for different plant categories defined by Hoerger and Kenaga (1972) and modified by Fletcher et al. (1994). Upper-bound residue levels on plant surfaces (mg/kg) were calculated by multiplying the predicted 90th percentile ground deposition (converted to lb/acre) by empirically derived multipliers from the Kenaga nomogram for each plant category. These multipliers were 240 for short grass, 110 for tall grass, 135 for broad-leafed plants, 15 for fruits/pods/seeds, and 94 for arthropods. Pesticide residues on arthropods are based on the assumption that amounts will be in the same order of magnitude as those on plants with similar surface area to mass ratios (EPA 2012) and will be referred to as a plant category throughout this paper. The upper bound multipliers for residue levels were used instead of those for deriving mean residue values as recommended for risk assessment purposes (EPA 2012).

After estimating spinosad residue on different plant types, a database of species sensitivities to spinosad was compiled (Table 3.1) which included only bioassays meeting pre-defined criteria. Only studies that provided acute mortality LC_{50} values of terrestrial insect populations through ingestion of spinosad were included. Only studies that assessed acute mortality for terrestrial insect populations exposed to spinosad through

ingestion were included. Also, only LC_{50} values with reported units in milligrams per kilogram diet were accepted as the toxic endpoint. In some cases, toxicity values that could be converted to these standard units were also included. Nine of the 32 selected observations required unit conversion, which was done by making conservative assumptions about water content and consumption rate of the treated diet (see Table 3.1). The pesticide effect literature relevant to this study was located by searching the U.S. Environmental Protection Agency ECOTOX (Duluth, MN, USA) database, Institute for Scientific Information Web of Knowledge (Thomson Scientific), and Google Scholar. All of the species, except one, included in the dataset are considered target species and would be expected to exhibit high toxicity (i.e., low LC_{50} values) to spinosad through ingestion.

The 12 different insect species and 32 effect concentrations (multiple toxicity results for some species) included in the dataset were considered to be representative of an actual community of non-target insect species in a field margin. The species sensitivity data were compiled in Microsoft Excel and imported into R version 3.3.2 (RCoreTeam 2016) for analysis. To construct the SSD the LC_{50} for each species population was ordered from smallest to largest and assigned percentiles based on rank. These percentiles were plotted against the concentration of spinosad (mg/kg) resulting in a cumulative distribution function (CDF) of species sensitivities. Then the 2.5, 50, and 97.5% confidence bounds around the toxicity values in the distribution were estimated using a parametric bootstrap method which has been shown to safeguard against distributional ambiguity of the response data, as well as smaller sample sizes (Posthuma et al. 2000, Wheeler et al. 2002, Newman et al. 2000).

To perform the bootstrap regression, first the observed toxicity endpoints (LC_{50}) were fit to a lognormal distribution and checked for goodness of fit (Anderson-Darling test). Then resampling from the distribution was done to create a data set of 1000 observations. This resampling was repeated 1000 times to produce 1,000,000 estimates of each LC_{50} value from the fitted distribution. The 95% confidence interval around the fitted toxicity values could then be used to more adequately represent uncertainty in the point estimates in the distribution. The percentage affected fraction (PAF) by distance was then estimated by comparing the lower 95% confidence bound around the LC_{50} data to the upper-bound residue levels of the different treatments. The lower limit of the 95% bootstrap confidence interval was used to provide a more conservative estimate of PAF for each treatment because lower LC_{50} values represent more sensitive species. The PAF associated with the residue levels at 5 meters was estimated for each treatment. Also, the PAF associated with the residue levels at all distances (1-32 m) was estimated for each treatment and plotted against distance.

For specific treatment comparisons, the percentage reduction in risk (PRR) was calculated using the PAF at 5 m and only treatments that exhibited significant differences in deposition in the drift study were compared. The two formulations without adjuvants were compared to calculate the PRR when going from a wettable powder to a suspension concentrate at 5 meters. Also, the effect of adjuvants was characterized by calculating PRR when going from the formulated products without adjuvant to the formulated product with each of the two adjuvants. The PRR was calculated with the following equation:

$$PRR_5 = \frac{PAF_{GDT,5} - PAF_{LDT,5}}{PAF_{GDT,5}} 100 \quad (\text{Eq.1})$$

Where PRR_5 is the percent reduction in risk at 5 m, PAF_{GDT} is the PAF (%) for the treatment exhibiting greater deposition at 5 m, and $PAF_{LDT,x}$ is the PAF (%) for the treatment exhibiting lower deposition at 5 m.

Results & Discussion

Figure 3.1 shows the species sensitivity distribution with the upper and lower bootstrapped 95% confidence limits around the fitted sensitivity data. The LC_{50} data for each species population in the SSD followed a lognormal distribution (Anderson-Darling goodness of fit test, $p=0.519$), with greater than 4 orders of magnitude variation in sensitivity. The lesser grain borer (*Rhyzopertha dominica*) and the Indianmeal moth (*Plodia interpunctella*) were the most sensitive species to ingestion of spinosad and the red flour beetle (*Tribolium castaneum*) and beet armyworm (*Spodoptera exigua*) were the least sensitive. This SSD can be considered a conservative representation of an actual insect community's susceptibility to spinosad because it consists almost entirely of target species, which would be expected to experience high toxicity.

The species sensitivity distribution superimposed on the plant residue by distance data can be viewed for each plant category in Figures 3.2 and 3.3. As a result of the residue multipliers, the short grass category contained the highest residue levels followed by broadleaf plants, tall grasses, arthropods (exposure assumed to be through ingestion of other arthropods), and seeds/fruits/pods. Deposition of the wettable powder formulation without adjuvant resulted in the highest levels of plant residue (mg/kg) across all

distances and plant categories. The suspension concentrate deposited the next highest levels of plant residue, followed by the wettable powder with either adjuvant (both Maximizer and PowerLock had the same effect on deposition of this formulation type), and lastly, the suspension concentrate with PowerLock. The percentage of species potentially affected by residue levels at 5 m is labeled for each of the treatments that exhibited significantly different deposition in the drift study (Figure 3.2).

The following results are estimated for insects that would be exposed 5 m into an off-target area consisting of a short grass environment. In this scenario, the potential reduction in risk to non-target insects by spraying a suspension concentrate instead of a wettable powder was an estimated 21.3%. When either Maximizer or PowerLock was added to the wettable powder formulation, 43.6% fewer species were expected to encounter residue levels high enough to cause 50% mortality. The addition of adjuvant to the wettable powder resulted in a greater reduction in risk than when added to the suspension concentrate formulation. Maximizer did not reduce deposition of the suspension concentrate and therefore did not reduce risk. However, when PowerLock was added to the suspension concentrate the reduction in deposition resulted in a 38.6% reduction in species potentially affected. The different fractions of affected species between the plant categories arises from the different residue levels estimated from the Kenaga nomogram. Therefore, the same general trends in risk will be exhibited across plant categories, but the magnitude of affect will differ.

Another way to characterize the drift reduction in terms of risk can be viewed in Figure 3.4. Here, the PAF is plotted over distance, whereas before the PAF was only

calculated at 5 m for each treatment. The same method for calculating the PAFs was used (upper-bound residue levels with lower-bound LC_{50} data), and only the short grass plant category is represented to provide the most conservative estimates of risk. The distance at which residue levels would be low enough to affect fewer than 5% of species are marked for each treatment and can be thought of as the point at which 95% of species are considered unaffected.

By setting the level of protection to the commonly used 5% threshold (Posthuma et al. 2000, Frampton et al. 2006), the distance at which 95% of species can be considered unaffected was calculated for each treatment. The effect on drift reduction exhibited by adding either of the adjuvants to a spray solution containing spinosad formulated as a wettable powder was that the distance at which 95% protection is achieved was reduced from 29.9 m to 15.7 m from the spray source. PowerLock reduced this distance from 22.7 to 13.6 m when added to the suspension concentrate formulation.

Using the approach discussed above, differences in spray drift were evaluated in the context of ecological risk. The ground deposition data from the drift study suggest that between the two formulations of spinosad, suspension concentrates resulted in lower spray drift than wettable powders, and between the two adjuvants, PowerLock reduced drift more than Maximizer for suspension concentrates but not for wettable powders. The current analysis extrapolates from these differences in deposition to environmental risk, and suggests that substantial reductions in risk to non-target insects can be achieved when spinosad formulations and adjuvant combinations are applied.

As with any extrapolation practice for ecotoxicological effect characterization, there is a level of uncertainty in the current approach, so it is important to provide transparency in the assumptions that were made so that conclusions can be interpreted appropriately. Caution was taken to build conservatism into the assumptions which likely led to overestimates of risk. For example, by using the 90th percentile for deposition with the upper bound Kenaga multipliers and the lower 95% confidence limit of effect, the PAFs were between 2 and 6 times greater than if the means/medians had been used for these parameters. For example, the PAF for the suspension concentrate with PowerLock treatment was an estimated 18.6% at 5 m in a short grass environment (SCPL, Figure 3.2). However, if the mean deposition, effect, and Kenaga multipliers were used this PAF reduces to an estimated 3.0%.

The greatest source of uncertainty arguably arises from the extrapolation from ground deposition to insecticide residue on three-dimensional plant structures in an off-target area. These residue levels were likely overestimated by ground deposition due to the nature in which the data were collected and the unaccounted filtering effect of upper aerial plant structures. The ground deposition data were collected from horizontally positioned Petri dishes exposed to spray drift over bare soil. However, in an actual environment containing vertical plant structures, some fraction of the spray drift will be intercepted before reaching the distance at which exposure is estimated. Therefore, in substituting ground deposition on the Petri dishes for application rate in the Kenaga nomogram, the residue levels in an actual environment would likely be lower than predicted in the current study. As mentioned above, additional conservatism was

incorporated by using the 90th percentile deposition values from the drift study and upper-bound Kenaga multipliers to estimate residues.

In an experimental field study, Schmitz, Hahn et al. (2014) assessed the effect of spray drift on plant communities in agricultural field margins. They sprayed plant communities at application rates equivalent to the fractions of the field rate that would be expected to drift into the first meter of a field margin. Their research provides an example where similar assumptions about exposure and risk were made for the relationship between pesticide effect and spray drift, but does not relate spray drift to the residue levels on plant surfaces. Sometimes bioassays are conducted to estimate buffer zone width based on the effects of spray drift. For example, Marrs et al. (1993) tested the effect of surrounding vegetation on seedling mortality exposed to spray drift and found that mortality was lower when the surrounding vegetation was taller. This supports our assumption that ground deposition led to conservative estimates of plant residues, but again, provided no quantification of the actual residue levels that the drifting spray caused. Other research has demonstrated the importance of vertical structures in influencing pesticide exposure to spray drift (Longley and Sotherton 1997, Miller et al. 2011), but there is a dearth of information on the amount of pesticide residues on plant surfaces that result from spray drift.

The SSD approach for environmental risk assessment has been scrutinized because of the assumptions behind the theory, and those required to put the theory into practice (Forbes and Calow 2002). Although the goal of this analysis was not to determine absolute values of risk, or to set regulatory thresholds for exposure to spray

drift of spinosad, the SSD that was constructed for the purposes of this paper was done with these assumptions in mind. In theory, the species that are selected for the construction of a SSD should be a representative random sample of the target species of concern. However, given that the species used for the current SSD were chosen from the available literature, there was a bias toward pest species that might be expected to exhibit greater sensitivity to spinosad. Also, by parsing the data to include only bioassays in which ingestion toxicity was measured the SSD represented sensitivities to the most effective exposure pathway for spinosad. The number of species and model choice are additional considerations that are important for the purposes of SSD approaches to risk assessment. The use of the parametric bootstrap method to estimate confidence intervals has been shown to safeguard against ambiguity in the distribution type and is suggested for smaller data sets (Wheeler et al. 2002). The current SSD included 32 observations of 12 different species that followed a lognormal distribution and was constructed using a parametric bootstrap method. A complete and detailed description of the assumptions behind SSDs has been outlined by others (Newman et al. 2000, Posthuma et al. 2000, Forbes and Calow 2002, Solomon et al. 2008).

Extrapolating from laboratory to field sensitivities of species depends on the assumption that exposure is comparable for the two scenarios (Solomon et al. 2008) and the SSDs that are used for this should be constructed with conservatism and transparency. For the purposes of this study, the current SSD was considered sufficient, but uncertainty regarding the purposed use of the Kenaga nomogram remains. The Kenaga nomogram was designed to estimate pesticide residue on plants from application rates of sprays

made directly to the plants. However, in this study, residue levels were estimated for plants that would be exposed to spray drift instead of a direct application. Therefore, future research should focus on quantifying plant residue based on spray drift so that the Kenaga nomogram can be evaluated for its utility in bridging between estimates of drift and exposure for the purpose of environmental risk assessment.

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Table 3.1. Acute sensitivity of terrestrial insects to spinosad from published ingestion bioassays.

Species	LC ₅₀ (reported units)	Life stage	Bioassay	LC ₅₀ (mg/kg)	Reference
<i>Rhyzopertha dominica</i> (lesser grain borer)		Adults	Treated wheat	0.005	Huang et al. 2004
<i>Rhyzopertha dominica</i> (lesser grain borer)		Adults	Treated wheat	0.009	Huang et al. 2004
<i>Rhyzopertha dominica</i> (lesser grain borer)		Adults	Treated wheat	0.009	Huang et al. 2004
<i>Plodia interpunctella</i> (Indianmeal moth)		Eggs	Treated wheat	0.04	Huang et al. 2004
<i>Plodia interpunctella</i> (Indianmeal moth)		Eggs	Treated wheat	0.07	Huang et al. 2004
<i>Plodia interpunctella</i> (Indianmeal moth)		Eggs	Treated wheat	0.07	Huang et al. 2004
<i>Cryptolestes ferrugineus</i> (rusty grain beetle)		Adults	Treated wheat	0.07	Huang et al. 2004
<i>Cryptolestes ferrugineus</i> (rusty grain beetle)		Adults	Treated wheat	0.12	Huang et al. 2004
<i>Choristoneura rosaceana</i> (obliquebanded leafroller)	4.99 (mg/L)	2nd instar larvae	Diet overlay	0.208 ^a	Ahmad et al. 2002
<i>Cydia pomonella</i> (codling moth)	4.69 (mg/L)	Neonate larvae	Diet overlay	0.235 ^b	Reyes & Sauphanor 2008
<i>Pandemis heparana</i> (dark fruit-tree tortrix moth)		Neonate larvae	Diet incorporation	0.24	Ioriatti et al. 2006
<i>Choristoneura rosaceana</i> (obliquebanded leafroller)	6.0 (mg/L)	2nd instar larvae	Diet overlay	0.25 ^a	Ahmad et al. 2002
<i>Cydia pomonella</i> (codling moth)	6.06 (mg/L)	Neonate larvae	Diet overlay	0.303 ^b	Reyes & Sauphanor 2008

Table 3.1. Continued

Species	LC ₅₀ (reported units)	Life stage	Bioassay	LC ₅₀ (mg/kg)	Reference
<i>Cydia pomonella</i> (codling moth)	9.7 (mg/L)	Neonate larvae	Diet overlay	0.485 ^b	Reyes & Sauphanor 2008
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	0.51	Kristensen et al. 2004
<i>Tribolium</i> <i>castaneum</i> (red flour beetle)		Adults	Treated wheat	0.6	Fang et al. 2002
<i>Cydia pomonella</i> (codling moth)	12.04 (mg/L)	Neonate larvae	Diet overlay	0.602 ^b	Reyes & Sauphanor 2008
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	0.74	Kristensen et al. 2004
<i>Melipona</i> <i>quadrifasciata</i> (Neotropical stingless bee)	12.07 (ng/bee)	Adult (workers)	ad libitum	0.966 ^c	Tome et al. 2015
<i>Tribolium</i> <i>castaneum</i> (red flour beetle)		Adults	Treated wheat	1.1	Huang et al. 2004
<i>Pandemis heparana</i> (dark fruit-tree tortrix moth)		12-day old larvae	Diet incorporation	1.17	Ioriatti et al. 2006
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	1.7	Kristensen et al. 2004
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	1.8	Kristensen et al. 2004
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	1.85	Burgess & King 2015
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	2.1	Kristensen et al. 2004
<i>Spodoptera</i> <i>littoralis</i> (egyptian cotton leafworm)		3rd instar larvae	Diet incorporation	2.11	Pineda et al. 2004
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	2.8	Kristensen et al. 2004

Table 3.1. Continued

Species	LC ₅₀ (reported units)	Life stage	Bioassay	LC ₅₀ (mg/kg)	Reference
<i>Musca domestica</i> (house fly)		Adults	Diet incorporation	2.8	Kristensen et al. 2004
<i>Spodoptera exigua</i> (beet armyworm)	71.6 (ppm)	3rd instar larvae	Diet overlay	2.98 ^a	Mascarenhas et al. 1998
<i>Spodoptera</i> <i>frugiperda</i> (fall armyworm)		3rd instar larvae	Diet overlay	4.4	Adamczyk et al. 1999
<i>Tribolium</i> <i>castaneum</i> (red flour beetle)		Adults	Treated wheat	5.31	Huang et al. 2004
<i>Spodoptera exigua</i> (beet armyworm)	164.7 (ppm)	3rd instar larvae	Diet overlay	6.863 ^a	Mascarenhas et al. 1998
<i>Tribolium</i> <i>castaneum</i> (red flour beetle)		Adults	Treated wheat	8.33	Huang et al. 2004

* Assumptions used for converting from units reported in study to mg/kg were (a) the diet contained 80% water, (b) the diet contained 80% water and 100% of the diet was consumed by the insect, and (c) a leaf contains 80% water.

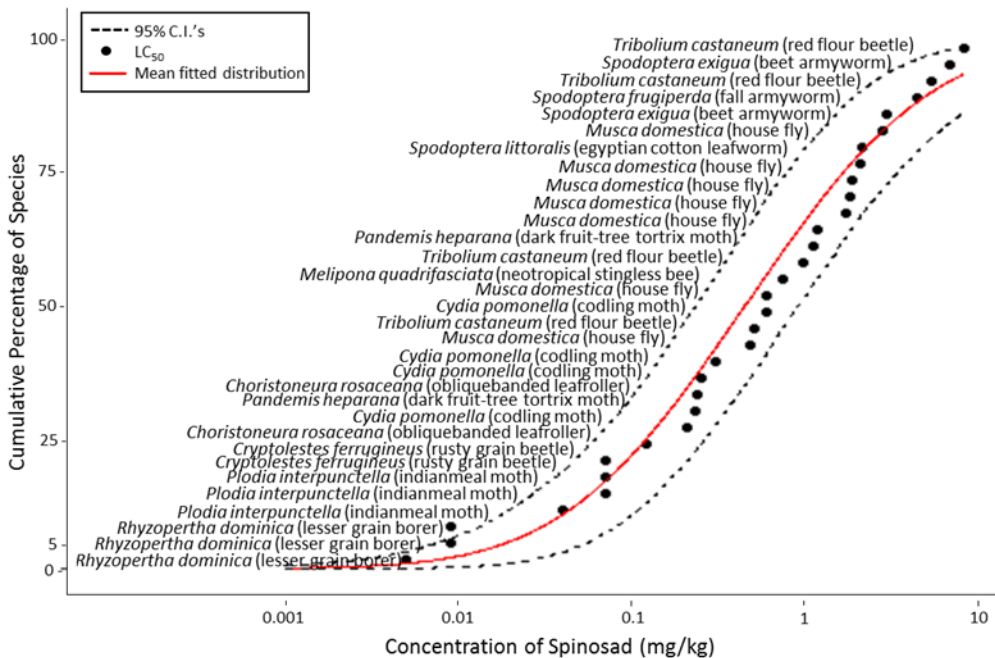


Figure 3.1. Species sensitivity distribution of acute mortality (LC₅₀) for terrestrial insect species exposed to spinosad through ingestion.

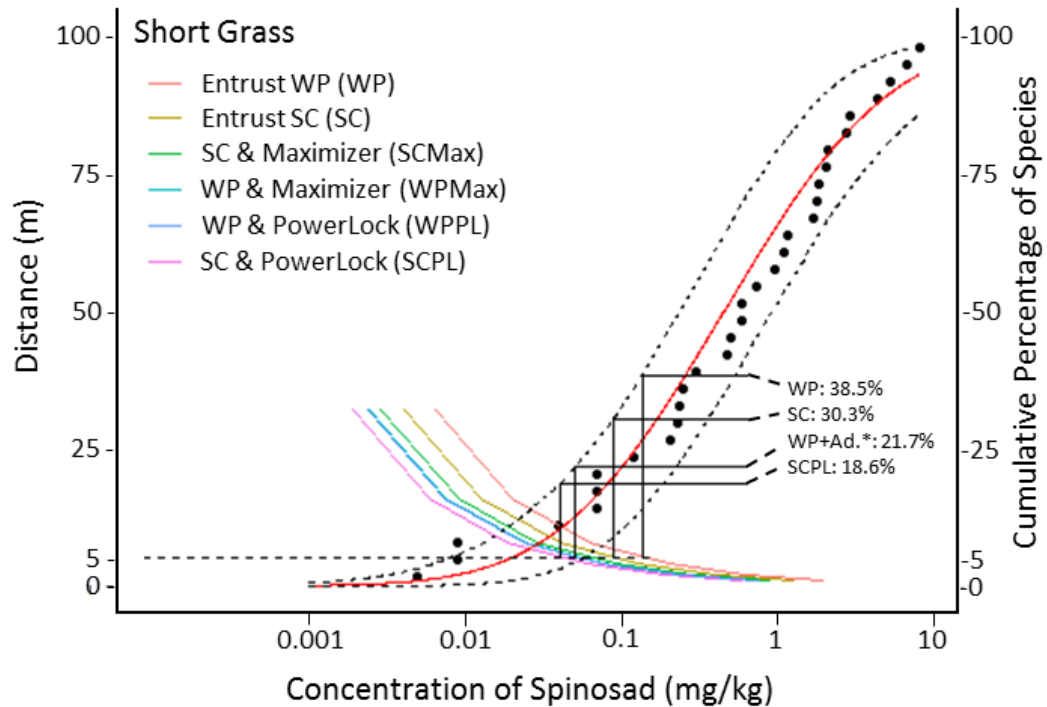


Figure 3.2. Residue by distance data superimposed on SSD to show PAF for treatments at 5 m in a short grass environment. The percent affected fraction (PAF) is labeled only for statistically different treatments based on deposition. The short-grass category had the highest residue levels and leads to conservative estimates of risk. At 5 m, the residue on the short grass for the wettable powder (WP) formulation is 0.138 mg/kg spinosad, and 38.5% of the species in the distribution have an LC_{50} lower than that concentration. Only 30.3% of species have an LC_{50} lower than the residue concentration for the suspension concentrate (SC) formulation at that distance. This suggests a 21.3% reduction in risk at 5 m from a field edge by spraying an SC instead of a WP formulation of spinosad. A greater reduction in risk is achieved (43.6%) by incorporating adjuvant with the WP formulation. The PAF for the SC formulation was reduced by PowerLock (38.6%), but not by Maximizer.

* “Ad.” Stands for “Adjuvant”. Both adjuvants had the same effect on WP so they are combined here for simplicity.

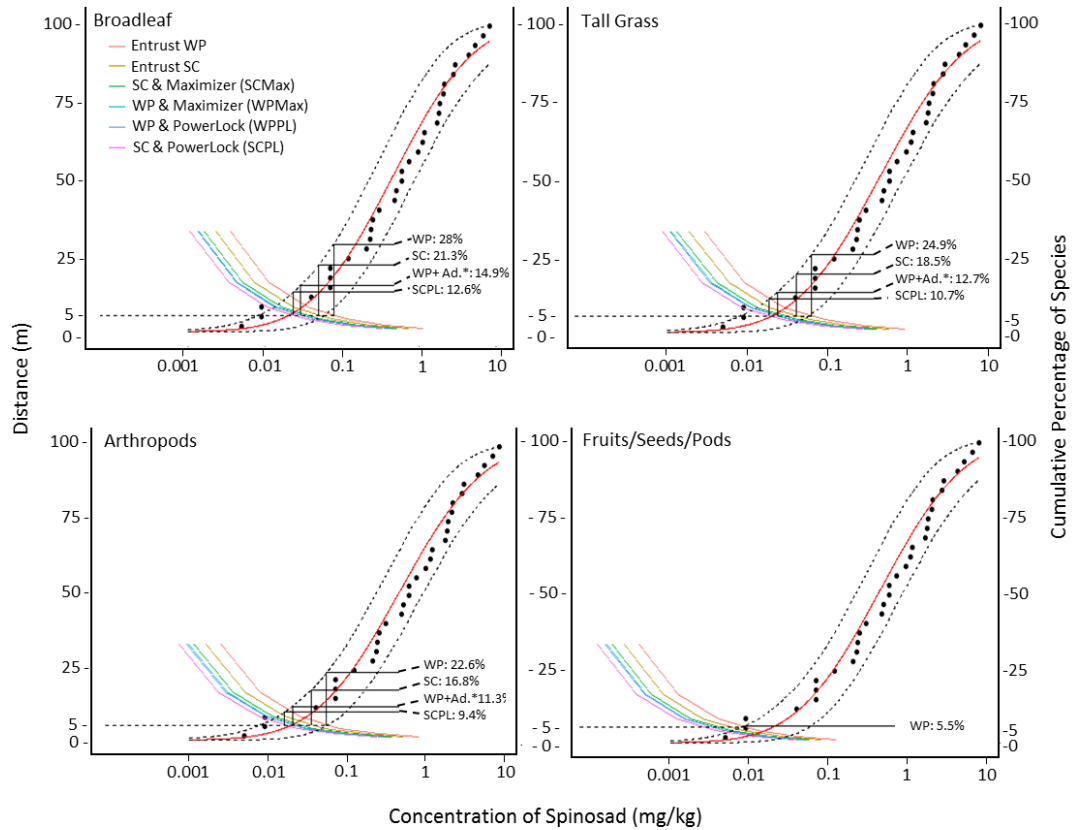


Figure 3.3. Residue by distance data superimposed on SSD to show PAF for treatments at 5 m in 4 plant categories. The percent affected fraction (PAF) is labeled only for statistically different treatments based on deposition. Four out of five categories from the Kenaga nomogram are represented here. For arthropods the exposure is assumed to be through ingestion of other arthropods. Because the Kenaga nomogram is a linear model for estimating residue (USACHPPM), the same general trends in risk can be expected for each of the categories.

* “Ad.” Stands for “Adjuvant”. Both adjuvants had the same effect on WP so they are combined here for simplicity.

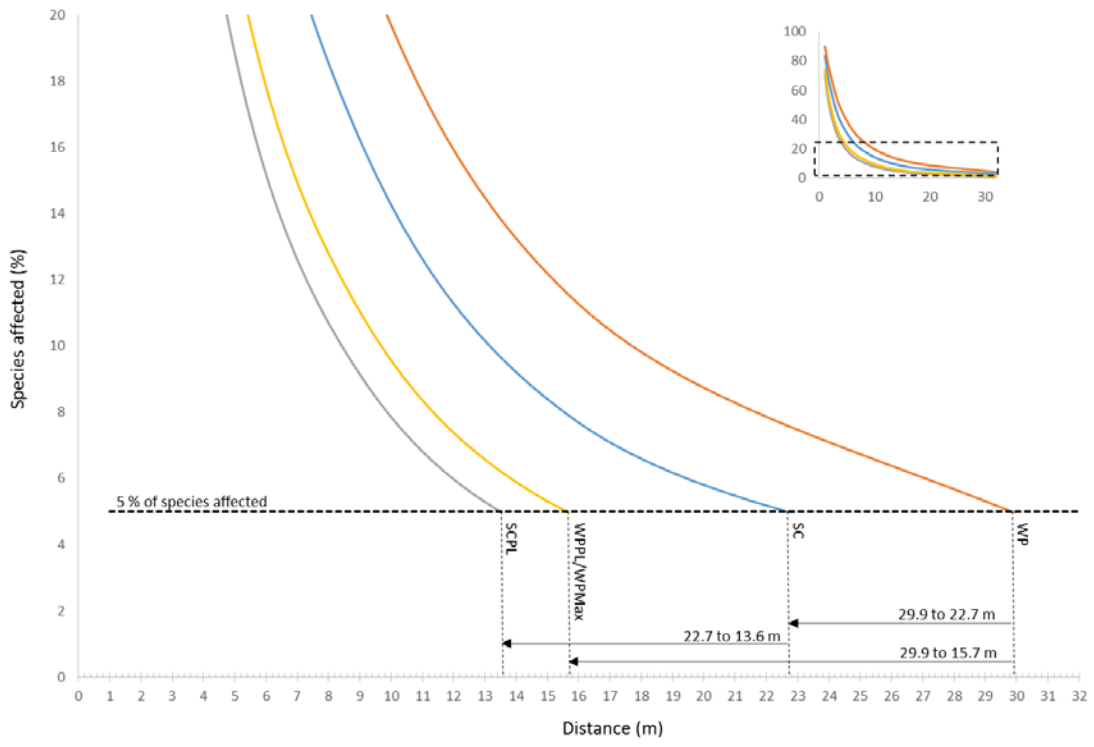


Figure 3.4. PAF plotted by distance to show distance at which HC_5 is met for each treatment combination. The distance at which 95% of species are considered unaffected is 29.9, 22.7, 15.7, and 13.6 m for the wettable powder (WP) formulation, suspension concentrate (SC) formulation, WP with PowerLock or Maximizer (WPPL/WPMax), and SC with PowerLock (SCPL), respectively.

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CHAPTER FOUR

CONCLUSION

Physical properties of an agricultural spray liquid are known to influence spray drift by interacting with other components of the application system. Therefore, one reason to formulate plant protection products in a particular way is to modify these properties to mitigate pesticide spray drift. Certain formulation types have been shown to affect the fraction of drift-prone droplets when sprayed through certain nozzles, but characterizing these effects requires further research. Spray enhancement additives (adjuvants) that are marketed for drift reduction also function by changing the physical properties of the liquid spray mixture. However, agricultural spray adjuvants may not behave the same when mixed with different formulated products, placing higher demand on formulation types that have drift reduction properties built in directly.

The primary motivation behind minimizing spray drift is largely based on concerns for nearby organisms and habitats that might be unintentionally exposed. However, quantitative estimates of drift do not necessarily represent exposure, so drift reduction is difficult to accurately express in terms of risk to non-target receptors. Our research attempts to fill certain knowledge gaps regarding the effect of formulation type and adjuvant on spray drift, as well as implications of those effects for environmental risk.

For chapter 2, we conducted a three-year field study to characterize spray drift of two formulated insecticide products with and without two oil-based adjuvants. Part of

this characterization involved an efficacy study to test for tradeoffs between drift reduction and pest control. Drift for the different spray mixtures was indicated by deposition at the ground level as well as on vertical samplers for information about the spray cloud. Environmental variables were also monitored and evaluated for their effect on drift. Finally, each treatment was sprayed in a wind tunnel to measure the droplet spectrum and test the relationship between droplet size and spray drift. For chapter 3, we used the results from chapter 2 to extrapolate from ground deposition to ecological risk for non-target insects in different habitat types in close proximity to agricultural fields.

As shown in chapter 2, differences in drift were observed for the two formulation types and adjuvants that were tested, and the magnitude of drift depended on environmental conditions. The active ingredient spinosad formulated as a suspension concentrate caused less drift compared to a wettable powder formulation and neither of the two adjuvants had the same effect on drift when combined with the two formulations. Lower drift did not result in lower pest control for the levels of drift reduction that were observed, and the wind tunnel data suggested that droplet size and spray drift were correlated.

Wettable powders and suspension concentrates are similar formulation types in that they both contain non-deformable solid particles. Increases and decreases in spray drift have been attributed to this physical property in the scientific literature, but typically these formulations are expected to have the same effect in one direction or the other. Our research suggests that these closely related formulations can differ in their effect on spray drift and illustrates a limitation in the current state of knowledge regarding these drift

reduction technologies. With respect to the adjuvants, the variability in their drift reduction for the different formulations demonstrates the difficulty in making generalizations about their effectiveness, as mentioned earlier. The characterization of spray drift in this study is limited to specific spray mixtures with a single active ingredient applied with particular equipment. However, the strong agreement between droplet spectra and spray drift suggests that other mixtures with similar droplet spectra might exhibit similar drift in the field. Other formulated active ingredients should be evaluated in this way to validate the conclusions from this work.

Chapter 3 addresses the second goal of this research, which is to evaluate drift reduction technologies in the context of environmental risk. The Kenaga nomogram was developed from pesticide residue data on plants directly sprayed at different application rates. It is a useful tool for estimating residue levels on food crops and target plants, but has not been used to estimate residues on non-target plants based on spray drift measurements. Ground deposition on drift samplers is often not related to residue levels on three-dimensional plant structures so the Kenaga nomogram represents a potential tool for refining exposure assessments for pesticide spray drift. Chapter 3 provides an example of how the Kenaga nomogram might be used in this way and discusses the uncertainties involved in doing so. By relating exposure to effect concentrations in a species sensitivity distribution, the relative risk to non-target insects for the different spray mixtures was evaluated.

This represents a novel approach for estimating ecological risk based on pesticide deposits on ground samplers, but future research should scrutinize the assumptions

required to bridge this gap. For example, wind tunnel studies could investigate the relationship between deposition onto samplers and onto plant surfaces of different plant types. This could allow the use of previously published deposition data to more accurately represent risk during re-registration for plant protection products. Models for predicting drift could be updated with this type of information as well. For example, the fraction of a spray application predicted at a certain off-target distance could be used to more accurately assess risk if that fraction were more precisely related to exposure.

Physical properties of the spray solution can change the effect of other application equipment on spray drift and the EPA verification protocol for testing drift reduction technologies has not been evaluated for testing formulation types and adjuvants as DRTs. This work demonstrates that droplet size data could be used to differentiate drift potentials between spray mixtures and suggests that formulation type and adjuvant testing could be incorporated into the EPA protocol based on this parameter. Understanding how application equipment can be further optimized for drift reduction by physical properties of the spray solution is of broad interest, and this work contributes to that effort.

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