The effect of fluorescent tracers on droplet spectrum, viscosity, and density of pesticide formulations

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

Keywords: Distribution modeling; droplet spectrum; fluorescein; pesticide; spray drift; Tinopal OB.

Introduction

The most important factor affecting efficacy and drift of pesticide applications is droplet size and distribution. Researchers have found that spray drift is independent of the active ingredient properties (molecular weight, structure, etc.), but is dependent on environmental factors and formulation properties.

Pesticide drift can be quantified using droplet count techniques or through traditional analytical measures of pesticide concentrations. Droplet count techniques enumerate the number and size of droplets that are present either by directly sampling from the spray cloud using laser measurement techniques or manual droplet count techniques using magnesium or Teflon coated slides. The most commonly used measurement to characterize droplet spectra is volume median diameter (VMD) (also known as the mass median diameter). The VMD is the droplet diameter in which 50% of the total volume (or mass) of liquid sprayed is comprised of droplets with diameters smaller than the VMD.
the diameter of a unit-density sphere having the same gravitational settling velocity as the particle being measured. [29,30] In addition, spray pressure also influences the size of droplets with higher pressures producing smaller droplets. However, if the addition of a tracer requires a change in the spray pressure to obtain a suitable droplet size, then direct comparisons between drift of pesticides with and without tracer cannot be made.

We examined the effect of an oil- and water-based tracer on the droplet spectrum, viscosity, and density of oil- and water-based pesticide formulations. In addition, few studies on pesticide drift or the analysis of the droplet spectrum of spray equipment have utilized modeling techniques for characterizing droplet distributions. [6] Droplet spectra are distributions of various sized droplets. Thus, determining the distribution for spray events is important for characterizing what environmental and physical processes influence the movement of droplets. [29] Therefore, we experimentally fit and demonstrate the utility of using distributions to characterize pesticide droplet spectra.

Materials and methods

We performed our study using ultra-low-volume (ULV) pesticide spray equipment used for adult mosquito management. Ultra-low-volume applications are applied as an aerosol with special spray equipment, so they drift over the target area with very little settling out onto surfaces. We chose ULV spray equipment because the movement and behavior of aerosol particles (droplets between 0.001 and 100 µm in size) are strongly dependent on droplet size and are also a higher drift hazard than larger droplets. [6,20]

The oil-soluble tracer Tinopal OB (BASF Corp., Florham Park, NJ, USA) was mixed with Permanone® 30–30 (Bayer Environmental Science, Research Triangle Park, NC, USA) at a rate of 11 g/L and the water soluble tracer Fluorescein (Aqua Solutions, Deer Park, TX, USA) was mixed with Aqua-Reslin® (Bayer Environmental Science, Research Triangle Park, NC, USA) at a rate of 11 g/L. Aqua-Reslin was mixed 1:1 with deionized (D.I.) H₂O and was applied at the maximum flow rate of 192 mL/min. Permanone 30–30 was mixed 1:2:1 with Crystal Plus 70T light mineral oil (STE Oil Company, Inc., San Marcos, TX, USA) and American Chemical Society (ACS) grade toluene (99.5 % purity, Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA) and was applied at the maximum flow rate of 193 mL/min.

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

Aqua-Reslin and Permanone 30–30 formulations with and without tracer were randomly chosen with five replicates of each formulation mixture for a total of 20 replications. Two subsamples were taken for each replication. Between each spray replication the hoses and nozzle were rinsed with 300 mL of D.I. H₂O followed by 300 mL of a 1:1 mixture of high pressure liquid chromatography acetone (99.7 % purity; EMD Chemicals, Gibbstown, NJ, USA) and ACS grade toluene. The measurement of kinematic viscosity of the different formulations was conducted using an Ostwald viscometer (VWR International Inc., West Chester, PA, USA) according to American Society for Testing and Materials (ASTM) procedures. [31,32] Formulation density was determined by weighing a 10 mL sample of each formulation on a calibrated Mettler AM100 analytical balance (Mettler Toledo AG, Switzerland). Measurement of density and viscosity was performed at 20°C. The reference standard was deionized (D.I.), H₂O which has a density of 0.998 g/mL and a viscosity of 1.004 cSt at 20°C. The experimental design for the measurement of viscosity and density was the same as stated for the droplet spectrum measurement.

Statistical Analysis System 9.2 [33] was used to run t-tests (α = 0.05) to determine differences in VMD, kinematic viscosity, and density for the respective formulations with and without tracer. Distributions were fit using MATLAB®R2009a [34] distribution fitting tool. Distributions for droplet spectra were determined based on the chi-square goodness of fit test, which tests if a sample of data came from a population with a specified distribution [13,30,35].

Results

There was no significant difference in VMD for Aqua-Reslin with and without tracer (t = −0.21, p = 0.83). The mean VMD for Aqua-Reslin with and without tracer was 21.29 and 21.74 µm, respectively (Table 1). There was no significant difference in VMD for Permanone 30–30 with and without tracer (t = 0.19, p = 0.85). The average VMD for Permanone 30–30 with and without tracer was 19.48 and 19.15 µm, respectively (Table 1). Lognormal distributions provided the best fit for Aqua-Reslin and Permanone with 

Schleier III et al.
Fluorescent tracers and pesticide formulations

Table 1. Mean volume median diameter (VMD), viscosity, and density for Aqua-Reslin®, Aqua-Reslin with tracer, Permanone® 30–30, and Permanone 30–30 with tracer formulations.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>VMD (µm)</th>
<th>Viscosity (cSt)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqua-Reslin</td>
<td>21.29 (±1.14)*</td>
<td>8.72 (±0.28)</td>
<td>0.98 (±0.011)</td>
</tr>
<tr>
<td>Aqua-Reslin with tracer</td>
<td>21.74 (±1.87)</td>
<td>8.88 (±0.43)</td>
<td>0.99 (±0.015)</td>
</tr>
<tr>
<td>Permanone 30–30</td>
<td>19.48 (±1.47)</td>
<td>4.87 (±0.025)</td>
<td>0.93 (±0.003)</td>
</tr>
<tr>
<td>Permanone 30–30 with tracer</td>
<td>19.15 (±0.89)</td>
<td>4.91 (±0.11)</td>
<td>0.93 (±0.0005)</td>
</tr>
</tbody>
</table>

*Standard error.

Table 2. Mean, variance, scale (σ), and location (µ) parameters, for the lognormal distributions and the respective chi-square value (χ²) for Aqua-Reslin®, Aqua-Reslin with tracer, Permanone® 30–30, and Permanone 30–30 with tracer formulations.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Mean</th>
<th>Variance</th>
<th>σ</th>
<th>µ</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqua-Reslin</td>
<td>3.82</td>
<td>29.71</td>
<td>0.78 (±0.009)*</td>
<td>1.05 (±0.006)</td>
<td>5524</td>
</tr>
<tr>
<td>Aqua-Reslin with tracer</td>
<td>2.93</td>
<td>12.81</td>
<td>0.62 (±0.009)</td>
<td>0.95 (±0.006)</td>
<td>9998</td>
</tr>
<tr>
<td>Permanone 30–30</td>
<td>3.57</td>
<td>17.82</td>
<td>0.83 (±0.01)</td>
<td>0.94 (±0.007)</td>
<td>6708</td>
</tr>
<tr>
<td>Permanone 30–30 with tracer</td>
<td>3.84</td>
<td>22.94</td>
<td>0.88 (±0.009)</td>
<td>0.97 (±0.007)</td>
<td>8367</td>
</tr>
</tbody>
</table>

*Standard error.

Discussion and conclusion

The droplet spectrum of an application system is one of the more important variables that influence the drift of pesticides.[5,6] Although aerosol particles follow the overall gas flow, the trajectories can deviate due to external forces such as changes in wind direction and velocity. These deviations are dependent on the size of the droplets, which are in turn influenced by formulation properties. Dynamic viscosity (which is directly related to kinematic viscosity) is the strength of molecular forces of attraction in a liquid and therefore can significantly alter the droplet spectrum through the resistance of forming smaller droplets at higher...
viscosities. Our study demonstrated that the addition of tracers to both water- and oil-based formulations did not significantly alter the VMD, viscosity, and density. The results of the viscosity experiment support our finding that the addition of tracers should not significantly alter the VMD. The density of droplets is important for determining the aerodynamic diameter, which is used to estimate the terminal settling velocity. 

There are several potential problems with in situ sampling of droplet spectra, such as precision, accuracy, instrument sensitivity, and the instrument’s size. Precision and accuracy can be increased with multiple sampling events, but the instrument sensitivity may bias the estimates of smaller droplets. For example, the DC-III groups any particle less than one μm in diameter into a bin of size one μm, so our estimated distribution may have been shifted toward larger droplet sizes.

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

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

The utility of fitting a lognormal distribution is that any type of mean or median diameters (i.e. VMD and Number Median Diameter [NMD]) and the 95% confidence intervals can be calculated easily using the Hatch-Choate conversion equations. The lognormal distribution is a special case of the normal distribution which can be transformed to normalize the data for use in other modeling exercises. In addition, fitting a cumulative distribution function to the data (Fig. 1 and 2), provides both a simple visual and quantitative method for determining the percentage of droplets between a size range that is optimal for the control method.

Droplet size distributions provide both a visual and quantitative tool for understanding the mechanisms that underlie the deposition and movement of droplets in the environment. The distribution can be used to estimate the proportion of droplets that are influenced by various mechanisms like gravitational settling. In addition, it can be used to estimate the efficiency of collection filters by determining the proportion of droplets that will deposit via Brownian diffusion, interception, inertial impact, and gravitational settling which can be used to determine the optimal diameter of a filter for sampling air concentrations.

Studies of pesticide drift and spray equipment only report deterministic values such as the VMD or do not measure the droplet spectrum, and often do not report the distribution of droplets. The distribution of spray droplets is important for modeling pesticide drift because it can be used to determine the error around the point estimates like VMD. By fitting a distribution to the data, the variance around the deterministic value can be determined and used in probabilistic spray drift models.

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

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References

Fluorescent tracers and pesticide formulations


