Statistics of spray deposition and drift for inhomogeneous suspensions

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In agriculture, crop protection often involves spraying of chemicals or biopesticides. Many chemical formulations are suspensions or emulsions, therefore particulate by nature. Biopesticides are particulate systems as well. At relatively high concentrations such particulate systems can be considered as homogeneous solutions. However, at relatively low particle concentrations, or using an application with fine sprays, the particulate nature cannot be neglected.
This study deals with calculating the effect of particle statistics in such sprays. The effect of particle concentration and clustering behaviour are investigated. Roughly, at particle concentrations >10^{12} L^{-1} particle statistics do not need to be considered.
The particulate nature also affects sampling of spray deposits: sampling variance is enhanced with respect to homogeneous solutions. For particle concentrations <10^{11} L^{-1} and <10^{10} L^{-1}, respectively for fine and coarse sprays, the required detection area is significantly enlarged to maintain the same sampling variance.
Particle concentration appears to be more important than clustering behaviour, though the effect of clustering on sampling variance cannot be neglected.

1. Introduction

In agriculture, chemicals used for crop protection commonly are applied by spraying. Usually these chemicals are dissolved or suspended in a solvent (often water or oil) to improve overall performance. Performance refers to aspects like facilitation of the spraying process, enhancement of on-target deposition, and improving retention and uptake by the crop. Off-target deposition of spray drops and losses due to spray drift should be minimized. These losses can be quantified by field studies or simulation studies. In all cases it is assumed implicitly that the spray liquid is a homogeneous liquid throughout. While this seems reasonable for solutions, with emulsions and suspensions several problems regarding homogeneity may occur. First of all, emulsions and suspensions may slowly disintegrate due to differences in density (i.e. the heavy particles slowly sink, light particles tend to float). This requires appropriate mixing of the liquid in the spray tank not only before but also during the time of spraying.
A second source of variability in local concentration is due to stochastic processes. Since each droplet has finite volume, the number of suspended particles in the droplet is also finite. Therefore particle concentration and its variation are governed by statistical rules. Especially in liquids where the suspended particles are relatively large (individually or by aggregation) the smallest drops may contain only a few particles or even no particles at all [1]. Pesticides based on particulate systems are quite common. In biopesticides the particles are bacteria, spores or viruses; typical size range 1-5 μm (average diameter).

Table 1. Particle concentration in spray liquid and averaged diameter of a drop containing exactly one particle, as a function of intended particle dose and actual liquid dose.

Intended dose	Volumetric dose of spray application (Q)					
	10 l/ha		100 l/ha		1000 l/ha	
B	C_p [(a)]	D_1 [(b)]	C_p	D_1	C_p	D_1
[part/ha]	[part/l]	[μm]	[part/l]	[μm]	[part/l]	[μm]
10^8	10^7	576	10^6	1241	10^5	2673
10^{10}	10^9	124	10^8	267	10^7	576
10^{12}	10^{11}	26.7	10^{10}	57.6	10^9	124
10^{14}	10^{13}	5.8	10^{12}	12.4	10^{11}	26.7

(a) $C_p = B/Q$ (b) $D_1 = (6Q/\pi B)^{1/3}$

Dose rates of 10^{12}-10^{14} bioparticles per hectare resulted in effective pest control in several cases [2]. Table 1 shows that the required particle concentration in the bulk liquid not only depends on intended dose, but also on liquid dose rate: obviously low-volume applications need high initial particle concentrations to achieve the same number of particle per hectare. D_1 in Table 1 is the diameter of a drop that exactly contains one suspended particle, on average.

Most chemical pesticides are particulate as well: this applies to suspensions (e.g wettable powders: solid particles, typically <5 μm, though larger particles may occur [2]) and emulsions (e.g. small drops of oil in water, typically <10 μm [2]). Often concentration of chemicals is given as a percentage by volume or by weight. Table 2 gives the corresponding particle concentration, when the concentration by %volume is known, and all suspended particles have the same size. This shows that particle concentrations in chemical suspensions are in the same order of magnitude as with biopesticide sprays.

The size distribution of spray droplets is determined by nozzle choice, liquid pressure and physical properties of the spray liquid, and often covers a wide range of drop sizes. Optimum drop sizes, however, depend on the intended target (Table 3). This table shows that often relatively small drops are required. The occurrence and the volume of spray drift are strongly related to the amount of small drops. Consequently spray drift may be affected primarily by the statistics of suspended particles in small drops, rather than by the averaged concentration in the spray tank.

A statistical analysis of particulate spray systems may therefore be relevant with respect to spray deposits and drift, especially when small drops and low dose rates are involved. This study describes such an analysis, the relevant parameters, and the consequences for sampling spray deposits.

Table 2. Estimated particle concentrations in chemical pesticides of particulate nature

Volumetric concentration	Particle concentration C_p [l^{-1}]	
[%v/v]	part. diam. 5 μm	part. diam. 10 μm
0.1	$1.5 \cdot 10^{10}$	$1.9 \cdot 10^9$
1.0	$1.5 \cdot 10^{11}$	$1.9 \cdot 10^{10}$

Table 3. Estimated optimum droplet size for various targets [2]

Target	Droplet diameter [μm]
Flying insects	10 – 50
Insects on foliage	30 – 50
Foliage	40 – 100
Soil	> 200

2. Particle distribution in monosized spray

Assume the bulk liquid contains monosized particles at concentration C_p. Suppose a droplet with diameter D is formed. If the particle size is much smaller than the size of the droplet in which it may be suspended, and if the total volume of the bulk liquid is much larger than the volume of the droplet to be formed (i.e. average bulk concentration does not change due to droplet formation), then the number of particles suspended in the droplet is well described by a Poisson distribution. According to this distribution, the probability of having exactly k particles in the droplet is given by:

$$P\{k;\lambda\} = \frac{\lambda^k}{k!} \cdot e^{-\lambda} \tag{1}$$

where λ is the average number of particles in the droplet, which depends on drop size and particle concentration, and is given by the product of bulk concentration and droplet volume:

$$\lambda = \pi C_p D^3 / 6 \tag{2}$$

The expectation value of k and its variance are given by:

$$\langle k \rangle = \lambda \qquad Var(k) = \lambda \tag{3}$$

The coefficient of variation equals:

$$CV_k = \sqrt{Var(k)} / \langle k \rangle = 1 / \sqrt{\lambda} \tag{4}$$

Since, according to Eq.(2), λ is proportional to D^3, the average number of particles in a droplet increases rapidly for increased drop sizes (Figure 1), and the coefficient of variation decreases. For large values of λ the Poisson distribution approaches a normal distribution, with mean λ and standard deviation $\sqrt{\lambda}$.

For $\lambda > 10^4$, CV_k is less than 1% (Eq.(4)). In that case the actual particle concentration in the droplet is almost equal to the average concentration in the bulk liquid, and there is no significant difference from a homogeneous solution.

The fraction of droplets without suspended particles is found from Eq.(1) by setting $k = 0$:

$$P\{0;\lambda\} = e^{-\lambda} \tag{5}$$

In Figure 2 this equation is shown graphically for various particle concentrations and droplet sizes. Due to the strong dependence on drop size ($\lambda \sim D^3$) the transition from a situation with almost all drops empty to a situation without empty drops occurs relatively rapidly: within one decade of droplet diameters.

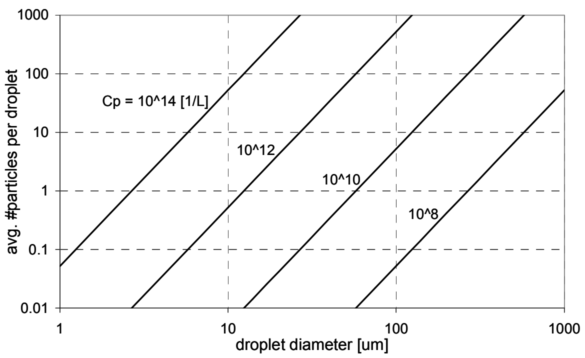

Figure 1. Average number of particles per droplet as a function of drop size, for various particle concentrations C_p.

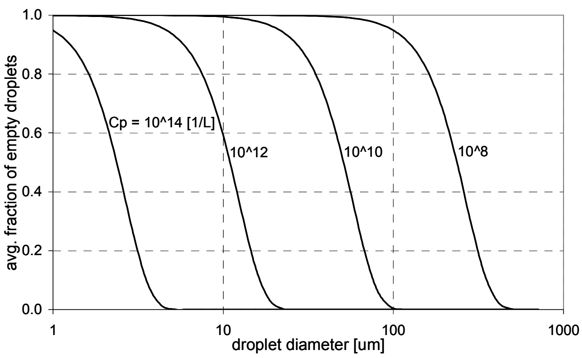

Figure 2. Average fraction of 'empty' droplets, as a function of drop size, for various particle concentrations C_p.

When most drops are empty, the few non-empty drops are most likely to contain just one particle: $P\{1,\lambda\} \approx \lambda$ (<<1). Note that, since the average concentration λ is much smaller than unity, the equivalent concentration of one particle in a droplet is much higher than the average concentration.

4. Multidisperse spray containing clustered particles

Assume the bulk liquid contains monosized particles, which may agglomerate into clusters of particles acting as single objects in the suspension. The relative frequency distribution of clusters sizes is given by γ_k (index $k = 1, 2, ..$ is the number of individual particles inside a cluster). Suppose a droplet in size class j contains x_j clusters, x_j being a stochastic quantity with Poisson distribution, thus $\langle x_j \rangle = \lambda_j$ and $Var(x_j) = \lambda_j$. Each of these clusters may have relative size $u_k = k$, with probability γ_k and $\langle u \rangle = q$ is average cluster size. The total number K_j of individual particles in the given droplet is characterized by its average and variance, which can be shown to be given by:

$$\langle K_j \rangle = \langle u \rangle \langle x_j \rangle = \lambda_j \, q \tag{6}$$

$$Var(K_j) = \langle x_j \rangle Var(u) + \langle u \rangle^2 \, Var(x_j) = \lambda_j \left(Var(u) + q^2 \right) \tag{7}$$

Note that $\langle K_j \rangle$ simply is the product of average number of clusters in the droplet and average cluster size (i.e. average number of particles in a cluster). Since the probability of selecting a droplet in size class j is related to the drop size spectrum, which is characterized by spectral values β_j, the spectral average of K is the weighed sum over all size classes:

$$\langle K \rangle = \sum_{j=1}^{m} \beta_j \langle K_j \rangle = \sum_{j=1}^{m} \beta_j \, \lambda_j \, q \tag{8}$$

On the other hand, with particle concentration C_p and droplet volume V_j, the average number of particles in a droplet equals $C_p V_j$ resulting in the following obvious relation:

$$\langle K \rangle = C_p \sum_{j=1}^{m} \beta_j \, V_j = C_p \, V_0 \tag{9}$$

where $V_0 = \pi D_{30}^3/6$ is the mean volume of a drop.
It can be shown that the variance of K equals:

$$Var(K) = \sum_{j=1}^{m} \beta_j \, Var(K_j) + \Psi_{<K>} \tag{10}$$

where $\Psi_{<K>}$ is the 'spectrally induced variance', which represents the contribution to the variance due to variance in the drop size spectrum itself:

$$\begin{aligned} \Psi_{<K>} &= \sum_{j=1}^{m} \beta_j \langle K_j \rangle^2 - \left(\sum_{j=1}^{m} \beta_j \langle K_j \rangle \right)^2 \\ &= C_p^{\,2} \sum_{j=1}^{m} \beta_j \, V_j^{\,2} - C_p^{\,2} \left(\sum_{j=1}^{m} \beta_j \, V_j \right)^2 = C_p^{\,2} \, V_0^{\,2} \left(\Phi^2 - 1 \right) \end{aligned} \tag{11}$$

using $K_j = C_p V_j$ and the following spectral characteristic Φ defined by:

Table 4. BCPC threshold nozzles [5,6,7] and spectral parameters derived from PDA measurements.

BCPC threshold	Description	Pressure [bar]	$D_{V0.5}$ [μm]	D_{30} [μm]	Φ	ρ_a [b] [m^{-2}]	Q [b] [L/ha]
VF/F	Delavan LF-110-01	4.5	135	82.2	2.89	$34{\cdot}10^6$	100
F/M	Lurmark 31-03-F110	3.0	221	111	4.11	$33{\cdot}10^6$	240
M/C	Lechler LU 120-06S	2.0	311	138	4.59	$28{\cdot}10^6$	390
C/VC	Teejet 8008 VS	2.5	404	167	5.31	$23{\cdot}10^6$	580
VC/XC [a]	Teejet 8015 SS	2.0	477	191	5.46	$26{\cdot}10^6$	970

[a] additional threshold nozzle in the Netherlands [7]

[b] for field sprayer, with 0.5 m nozzle distance and driving speed 1.67 m/s (= 6 km/h)

$$\Phi = \left(\sqrt{\sum_{j=1}^{m} \beta_j V_j^{\,2}} \right) \Bigg/ \sum_{j=1}^{m} \beta_j V_j = \left(D_{60} / D_{30} \right)^3 \tag{12}$$

where common mean diameter notation is used in the latter equality [4]. For a wide range of hydraulic pressure nozzles $\Phi \approx 4$ [3] (also see Table 4). Finally, using Eq.(7)-(9) and (11), Eq.(10) returns:

$$Var(K) = q\left(1 + CV_u^{\,2}\right) \cdot C_p V_0 + C_p^{\,2} V_0^{\,2} \left(\Phi^2 - 1\right) \tag{13}$$

where CV_u (= $\sqrt{Var(u)} / q$) is the coefficient of variation of possible cluster sizes. The first part of the variance of K reflects the Poisson-like variance ($q\, C_p\, V_0$), corrected for varying cluster sizes; the second part obviously is the spectrally induced variance. Note that only the first part is affected by clustering of particles. Clustering enhances variance through average cluster size (q) and variation of cluster sizes (CV_u). For suspensions without clustering, $q = 1$ and $CV_u = 0$, and $Var(K)$ has a minimum value (provided that neither C_p nor the drop size spectrum have changed):

$$Var(K)_{\min} = C_p V_0 + C_p^{\,2} V_0^{\,2} \left(\Phi^2 - 1\right) \tag{14}$$

The effect of clustering on variance can be assessed using the ratio $\chi \equiv Var(K) / Var(K)_{\min}$. Clearly, $\chi = 1$ when no clustering occurs, and $\chi > 1$ in all other cases. In a simple clustering model, the probability of finding clusters of a certain size may decrease exponentially with increasing cluster size: $\gamma_{k+1} = \alpha\, \gamma_k$, ($0 < \alpha < 1$) and $\gamma_1 = 1 - \alpha$ (required for normalization). Then it can be shown that:

$$q = \frac{1}{1-\alpha} \qquad Var(u) = \frac{\alpha}{(1-\alpha)^2} \tag{15}$$

from which follows $CV_u^{\,2} = \alpha$. This results in:

$$\chi = 1 + \frac{2\alpha / (1-\alpha)}{1 + C_p V_0 \left(\Phi^2 - 1\right)} \tag{16}$$

Indeed, for $\alpha = 0$ no clustering occurs and $\chi = 1$. The largest effect of clustering occurs when $C_p V_0 << 1$. Figure 3 shows χ as a function of α and C_p, for a fine spray. Apparently moderate clustering may affect variance considerably. For this spray, if $C_p < 10^7$ [L^{-1}] concentration has little effect and $Var(K)$ is completely governed by clustering. With higher particle concentrations, the effect of clustering on variance is less pronounced since the spectrally induced variance is becoming more important.

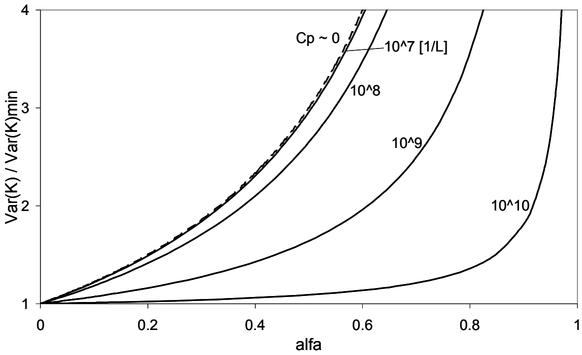

Figure 3. Ratio representing effect of clustering on variance, as a function of cluster parameter α, for various values of particle concentration C_p (Eq.(16)). Spray: BCPC threshold nozzle VF/F; $D_{30} = 82$ μm, $\Phi = 2.89$.

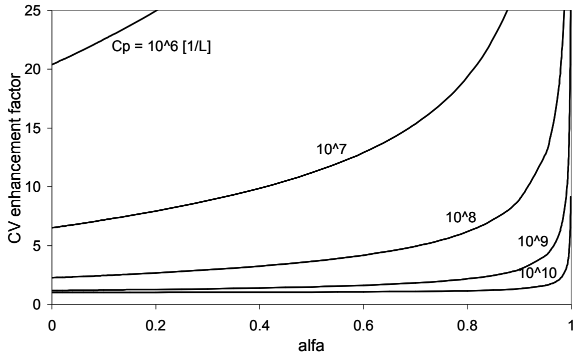

Figure 4. *CV* enhancement factor (Eq.(21)) as a function of clustering parameter α and bulk particle concentration C_p. Spray: BCPC threshold nozzle VF/F; $D_{30} = 82$ μm. $\Phi = 2.89$.

5. Sampling a spray containing clustered particles

The previous section dealt with average and variance of selecting at random a single drop from a given spray. In practice spray samples will involve a large number of drops, though that number itself may be undetermined. The average number of particles in the whole sample (S) is equal to the product of average sample size N_S (i.e. number of sampled drops) and average number of particles in a droplet (K, whether or not clustered):

$$\langle S \rangle = \langle N \rangle \langle K \rangle = N_S \, C_p \, V_0 \tag{17}$$

Note that this average is not affected by clustering that may occur after the suspension has been made. However, the variance of S should reflect clustering. If on average N_S drops are sampled from a total number N_0 of produced drops, $Var(N) = N_S(1 - N_S/N_0)$ [3], and $Var(S)$ is:

$$\begin{aligned} Var(S) &= \langle N \rangle Var(K) + \langle K \rangle^2 Var(N) \\ &= C_p V_0 N_S \left\{ q\left(1 + CV_u^{\,2}\right) + C_p V_0 \left(\Phi^2 - N_S/N_0\right) \right\} \end{aligned} \tag{18}$$

Further, in practice $N_S \ll N_0$, which reduces the variance of the sample to:

$$Var(S) = C_p V_0 N_S \left\{ q\left(1 + CV_u^{\,2}\right) + C_p V_0 \Phi^2 \right\} \tag{19}$$

The coefficient of variation is:

$$CV_S = \frac{\sqrt{Var(S)}}{\langle S \rangle} = \frac{\Phi}{\sqrt{N_S}} \cdot \sqrt{1 + \frac{q\left(1 + CV_u^{\,2}\right)}{\Phi^2 C_p V_0}} = CV_V \cdot f_p \tag{20}$$

where $CV_V = \Phi/\sqrt{N_S}$ is the coefficient of variation of spray volume in the sample [3], and the enhancement factor f_p is defined by the second root. This enhancement factor reflects the particulate nature (through $C_p V_0$) and clustering properties (through q and CV_u) of the suspension. For homogeneous solutions $f_p = 1$ (mathematically equivalent to $C_p \to \infty$, irrespective of clustering behaviour), in all other cases $f_p > 1$. Note that CV_S is proportional to $1/\sqrt{N_S}$, supporting the well-known 'law of large numbers'. Assuming the previously mentioned exponential clustering model, with parameter α (between 0 and 1), the enhancement factor is:

$$f_p = \sqrt{1 + \frac{1+\alpha}{\Phi^2 C_p V_0 (1-\alpha)}} \tag{21}$$

This factor is a function of spray quality (through V_0 and Φ), particle concentration C_p and clustering (α). Figure 4 shows the enhancement factor for a fine spray (BCPC threshold nozzle VF/F), for various particle concentrations.

6. Downwind spray deposits

The drop size distribution in the spray of a hydraulic nozzle changes rapidly: large drops will impact below or near the nozzle, while small drops may drift a considerable distance downwind before settling to the ground. For all deposits this will affect both average drop size and span of drop sizes. Average drop size for downwind deposits obviously is smaller than that of the original spectrum. Typically, the ratio ζ of local and global D_{30} is about 0.65 for downwind deposits [3]. Additionally, since a downwind spray lacks large drops, the local drop size spectrum is significantly narrower than the original spectrum. Typically, for downwind deposits $\Phi \approx 2$ [3]. Using the relation between detection area, detectable dose and coefficient of variation, as given by [3], the following equation can be derived to calculate the required collector area (A_{det}) to sample a certain deposit rate (η) with an accuracy given by the coefficient of variation CV_S.

$$A_{\mathrm{det}} = \frac{f_{p,loc}^{\;2}\, \Phi_{loc}^{\;2}\, \zeta^3}{\rho_a\, \eta\, CV_S^{\;2}} \tag{22}$$

where ρ_a is the average number of drops per unit of sprayed area in the original spectrum. Note that the enhancement factor has a local value, based on the local parameters Φ_{loc} and $V_{0,loc} = \zeta^3 V_0$. The average number of drops per unit of sprayed area is calculated from:

$$\rho_a = \frac{6Q}{\pi D_{30}^{\;3}} \qquad [\mathrm{m}^{-2}] \tag{23}$$

where Q is the spray application rate. Typical values of ρ_a are given in Table 4.

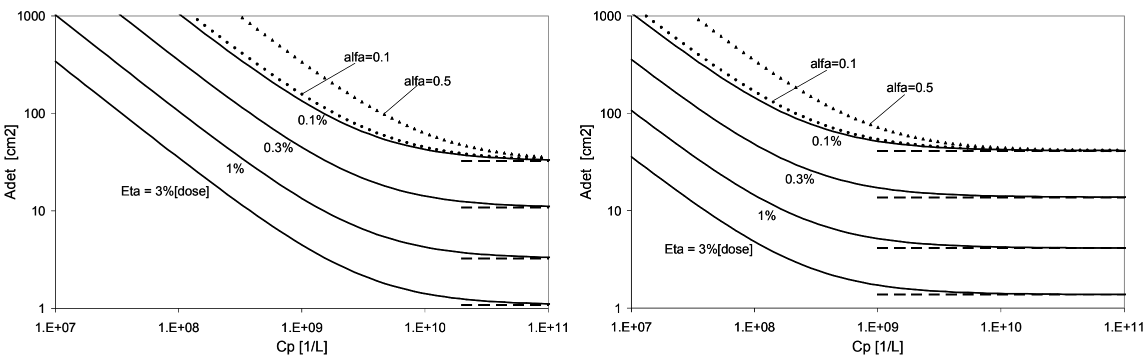

Figure 5. Required downwind detection area as a function of particle concentration and expected deposit rate (η), to obtain accuracy $CV_S = 10\%$. Constraints: $\zeta = 0.65$, $\Phi_{\mathrm{loc}} \approx 2$. *Solid lines*: unclustered suspensions; *horizontal dashed lines*: limit for homogeneous solutions; *dotted lines*: clustered suspensions belonging to $\eta = 0.1\%$, with cluster parameter $\alpha = 0.1$ and 0.5 respectively. *Left*: threshold nozzle VF/F; *right*: threshold nozzle VC/XC.

As an example, Figure 5 shows the required detection area as a function of particle concentration C_p and dose rate η, provided that sampling variance does not exceed $CV_S = 10\%$. The graph on the left belongs to the 'very fine/fine' (VF/F) threshold nozzle, the graph on the right belongs to the 'very coarse/extra course' (VC/XC) threshold nozzle (see Table 4). For high particle concentrations, $f_p \sim 1$ and the detection area approaches a minimum, depending on dose rate (and local spectrum). In the graphs this is represented by the short dashed lines near the right side. For relatively low particle concentrations ($C_p < 10^{10}\,\mathrm{l}^{-1}$ for fine sprays, $C_p < 10^{9}\,\mathrm{l}^{-1}$ for coarse sprays), particle distribution statistics appear to increase variance, implicating the need for a larger detection area. Furthermore, the graphs show that particle concentration probably is more important than clustering, with respect to their effect on sampling variance.

Conclusions

In crop protection, biopesticide and many chemical sprays are particulate systems (suspensions or emulsions). For high particle concentration ($>10^{12}\,\mathrm{L}^{-1}$) the suspensions effectively do not differ from homogeneous solutions, regarding composition of individual drops and spray deposits. For relatively low particle concentrations ($<10^{10}$-$10^{11}\,\mathrm{L}^{-1}$, depending on spray quality), variance in spray deposits may increase significantly. Also clustering of individual particles enhances variance. In general, low particle concentration, low application dose, fine sprays, and unstable suspensions may increase sampling variance.
The occurrence of small 'empty' drops does not decrease the dangers of spray drift, since such drops are completely compensated by the few non-empty drops, which have an effective concentration much higher than the average concentration in the bulk liquid.
Often small drops are required for effective pest control. This means that the occurrence of empty drops should be minimized, which requires that particle concentration is large enough (typically $>10^{12}\,\mathrm{l}^{-1}$, from Table 3 and Figure 2).
The presented theory relies mainly on Poisson statistics. This is only valid as long as particle size is much smaller than the droplets containing them. When such a condition does not apply, binomial statistics may be more appropriate. Yet the resulting differences turn out to be relatively small.

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