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A New Method for Spray Deposit Assessment[1]

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ABSTRACT: Solid fluorescent particles suspended in a spray liquid are distributed in direct proportion to the size of the spray droplets. Use of solid fluorescent particles is the basis of a new method for visual recognition of the size and number of droplets impinging on target and non-target portions of sprayed areas.

The forest is a three-dimensional environment in which the vegetation characteristics from top of the tree to ground level are critical factors in determining how spray drops are deposited. Until now the important third dimension in the forest--the vertical component of the environment--has for all practical purposes remained beyond standard analytical methods. And no method was available for determining directly the size and number of spray drops impinging on target and non-target insects and foliage.

The study reported in this note has shown that solid, insoluble fluorescent particles can be identified in spray deposits in the same relative ratio as a soluble insecticide and a soluble fluorescent dye. Subsequent field trials of helicopter spraying, to be reported separately, demonstrated the practicability of using this method for three-dimensional assessment of aerial spray deposits in the forest.

THE PROBLEM

Potts (1958) gives an excellent review of the status of the methods and problems of the application of agricultural sprays. Chamberlain et al. (1955) and Boyer and Brown (1964) have published extensive studies on the low level, two-dimensional deposition of aerial sprays from airplanes. The sampling of liquid sprays to evaluate the spray-drop-size spectrum has been studied by many research groups (Frazer 1957) using methods which include glass slides coated with magnesium oxide or other materials, coated paper, and oil sensitive cards (Davis and Elliott 1953; Isler 1963).

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In many cases, soluble fluorescent dyes have been added to oil and water sprays (Yates and Akesson 1963) to aid in the measurement of spray deposits. Analytical methods using soluble fluorescent dyes are more sensitive than those using soluble non-fluorescent dyes. However, most soluble dyes tend to fade rapidly in intense sunlight. And they are absorbed in an irregular, nonpredictable manner by foliage and insects.

We believed that these problems could be overcome by using micron-size solid fluorescent particles (FP's) suspended in the spray. Such use of these particles would require that they be distributed randomly, on a mass or volume basis, in the spray drops. The physics of formation of spray droplets in a typical spray spectrum allowed no a priori indication as to how these particles are distributed in the droplets formed in a spray nozzle or in droplets formed in the gas medium by subsequent breakup by air shearing processes. To investigate these possibilities, cooperative studies were conducted with Metronics Associates.

MATERIALS AND METHODS

Zinc-cadmium sulfide particles, 3.5 microns mass mean diameter, were used in this research. These particles emit an intense yellow fluorescence under ultraviolet light and are readily observed and counted. They are stable to sunlight and other elements for long periods of time.

An oil spray liquid (Chevron C-10 oil-base stock) containing 1.004×10^{-2} grams of dieldrin, 3.64×10^{-3} grams of soluble fluorescent dye, and 24.6×10^{7} FP's per milliliter were sprayed through a Devillbis type (oil-air) sprayer using air at 30 p.s.i. The soluble fluorescent dye used as an ancillary analytical method in these studies was Oil Soluble C-131 super concentrate.[2] It was furnished by G. K. Turner Associates, Palo Alto, Calif., who also carried out the analyses for the soluble fluorescent dye in the stock spray liquid and in the spray deposits. The dieldrin was recrystalized before use and was determined by the method of Pennel et al. (1964).

Three replicated spray tests were made. The spray was collected on foliage of two conifers and a hardwood tree, on Kromekote cards, on magnesium oxide-coated slides, and on clean 1- by 3-inch microscope slides.

The foliage, MgO-coated slides, and the Kromekote cards were examined under a microscope with ultraviolet illumination to determine the characteristics of the spray deposit and the distribution pattern of the solid FP's.

Microscope slides covered with spray deposit were placed in a funnel and washed with hexane to remove soluble dieldrin, soluble

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[2] Mention of trade names and commercial enterprises or products in this note is solely for information. No endorsement by the U.S. Department of agriculture is implied.

fluorescent dye (C-131), and the solid FP's. The wash liquid was filtered through a millipore filter with a 0.45μ pore size. The filtrate was transferred quantitatively to a volumetric flask, made up to volume, and analyzed for dieldrin and for soluble fluorescent dye. The millipore filter and the washed slide were counted to determine the number of FP's present.

RESULTS

DISTRIBUTION OF PARTICLES

Table 1 shows the micrograms of dieldrin, micrograms of C-131 fluorescent dye, and number of FP's on each of six slides. The amount of recovered dieldrin was used as a standard to calculate the ratios of dieldrin/C-131/FP's recovered in each experiment (table 2). Table 3 gives the ratio of the average of the above six deposit analyses in comparison with the ratio of dieldrin, fluorescent dye, and FP's in the stock spray liquid.

Table 1.--*Spray deposits of dieldrin, C-131 dye, and fluorescent particles on glass plates, 1x3-inches*

Slide	Dieldrin	C-131	FP's
	Micrograms		*Number*
1	26.0	10.8	661,000
2	18.4	7.6	525,000
3	71.6	25.6	1,776,000
4	69.4	22.0	1,943,000
5	44.0	16.7	1,117,000
6	41.0	15.2	1,159,000

Table 2.--*Ratios of dieldrin, C-131, and fluorescent particle deposits*

Slide	Deposit ratio
1	1 / 0.415 / 2.5 X 10^4
2	1 / 0.41 / 2.85 X 10^4
3	1 / 0.36 / 2.5 X 10^4
4	1 / 0.32 / 2.8 X 10^4
5	1 / 0.38 / 2.5 X 10^4
6	1 / 0.37 / 2.8 X 10^4
Average	1 / 0.37 / 2.66 X 10^4

Table 3.--*Ratio of spray deposit to spray liquid*

Item	Dieldrin/C-131/FP's
Original spray liquid	1 / 0.36 / 2.45 X 10^4
Average deposit	1 / 0.37 / 2.66 X 10^4

The experimental accuracy of the analytical methods used was estimated to be ±10 percent. Within the accuracy of the methods, the data indicate that the solid FP's distribute themselves in the spray liquid as a function of volume and that the count of FP's on a sprayed object is directly proportional to the amount (volume) of the spray deposited.

RELATION OF FLUORESCENT PARTICLES TO DROP SIZE

Measurements from the magnesium oxide-coated slides gave an indication of the drop size spectrum. But the FP's could not be counted in each drop crater because of interference and blocking by the MgO.

Inspection of the sprayed conifer needles showed that the FP's on the foliage were deposited in a fashion which made it possible to estimate the drop sizes impinging on each needle. The hardwood foliage gave a clear pattern of the number and size of drops deposited.

Inspection of the Kromekote cards showed a typical distribution pattern of drops, with the characteristic spread of the oil carrier clearly defined by the intense fluorescence of the soluble fluorescent dye. The insoluble FP's were observed to have remained in the center of the drop and to be readily counted.

A count of FP's and measurement of stain diameters on Kromekote cards was made. The larger drops showed a sharply defined deposition pattern about one-half the diameter of the drop stain.

The count of FP's was plotted on log-log paper as a function of stain diameter. A line fitted to this data showed the number of FP's per drop varied approximately as the square of the stain diameter. Later an FP suspension in Phillips Cycle Oil was sprayed on red-dyed Kromekote cards. The FP's were counted and the drop stains sized for two different spray tests (fig. 1). A fitted regression line of log N vs. log D (N is number of FP's and D is stain diameter), yielded the relationship

$$N = 2.3 \times 10^{-4} D^{2.19} \qquad (1)$$

Stain diameters D ranged from 90μ to 1,200μ, and N ranged from 3 to 1,000.

To calibrate the Kromekote cards, an electrostatic drop generator was set up to give uniform drops at a known rate of delivery. The range of drop sizes used in the calibration was from 80μ to 660μ. Stain diameters ranged from 300μ to 4,500μ. Both yellow fluorescent dye and Du Pont Oil Red Dye were mixed with Phillips light cycle oil, and drops were produced on both undyed and red-dyed cards at the same time. These drop stains were then sized under white light and ultraviolet light.

It was not possible to see the outline of the fluorescent dye on the red-dyed cards, but the outline was very sharp on the undyed cards since the apparent spread of the fluorescent dye was slightly greater than that of the oil red dye. The stain diameters of oil red dye on undyed cards also were slightly larger than those on the red-dyed cards because of the greater contrast on the undyed cards. This difference amounted to only a few percent, however, so that a single regression line was fitted to the data (fig. 2). The fitted regression line yielded the relation

$$d = 0.947\ D^{0.773} \tag{2}$$

or

$$d^3 = 0.85\ D^{2.32} \tag{3}$$

in which d and D are the drop and stain diameters respectively. From equations 1 and 3 the relation between number of FP's and drop diameter is

$$N = 2.68 \times 10^{-4}\ d^{2.83}. \tag{4}$$

Equation 4 is represented by the solid line in figure 3. Using the actual concentration of FP's in the Phillips cycle oil--2×10^8 particles per cc--and equation 3, the dashed line in figure 1 was derived showing the number of FP's per drop as a function of stain diameter. The line falls slightly below that of the fitted regression line for small drops, but is in excellent agreement for the larger drop sizes. It is evident that the difference in slope of the dashed and solid lines is well within the limits of experimental error, and that the number of FP's is in fact proportional to the drop volume or to the cube of the drop diameter. If the concentration of FP's in terms of the number per unit volume is known, the drop size collected on foliage may be determined merely by counting the number of FP's.

ASSESSMENT OF DEPOSITS

A maximum liklihood estimate may be made of drop size as a function of the observed number of particles in a drop, if the number of particles in the bulk liquid is known.

The Poisson probability is:

$$P_k = \frac{e^{-x}\, x^k}{k!}$$

in which:

P_k = probability of seeing exactly k particles in a particular drop.

x = the average number of particles per drop.

These probabilities are shown in figure 4 for several values of k. It can be shown that P_{k-1} is greater than P_k for any value of x less

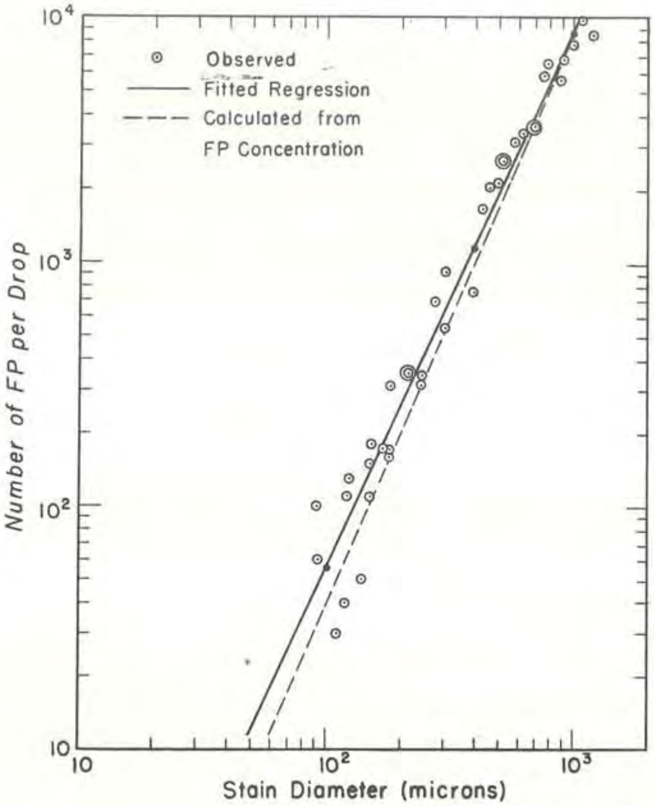


Figure 1.--Number of FP's per drop as a function of stain diameter on Kromekote cards dyed with Du Pont Oil Red Dye.

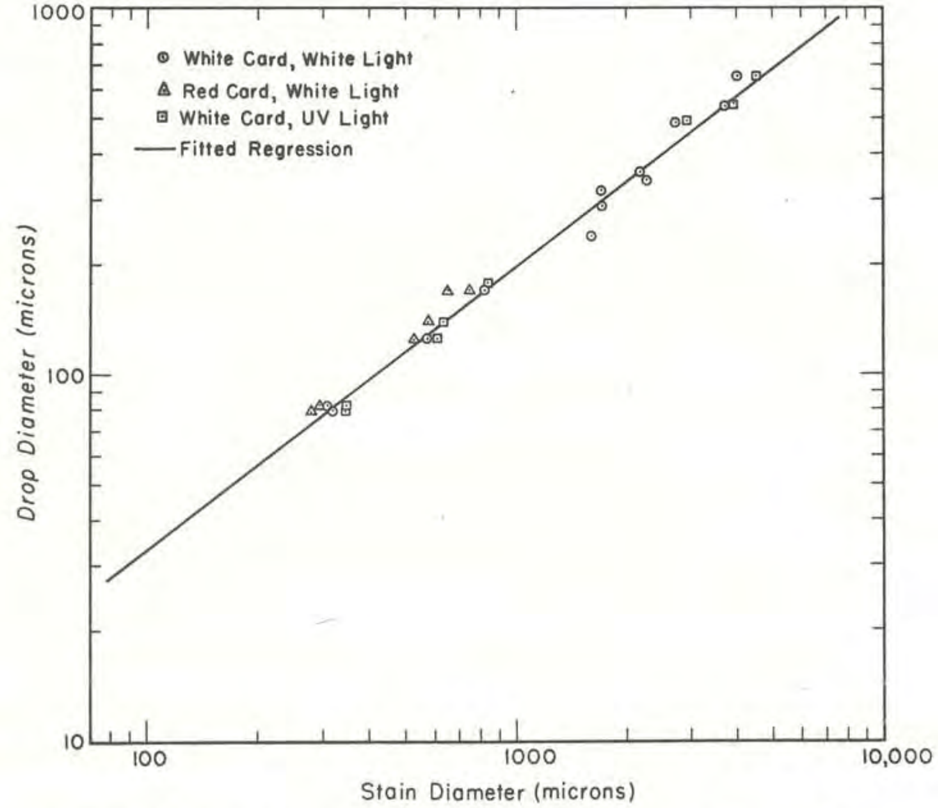
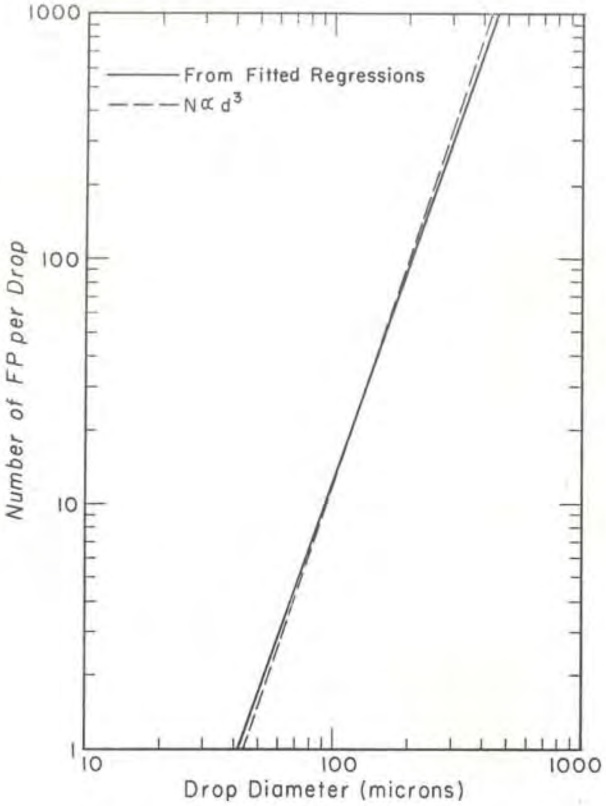


Figure 2.--Drop diameter vs. stain diameter on Kromekote cards.

Figure 3.--Number of FP's as a function of drop diameter.



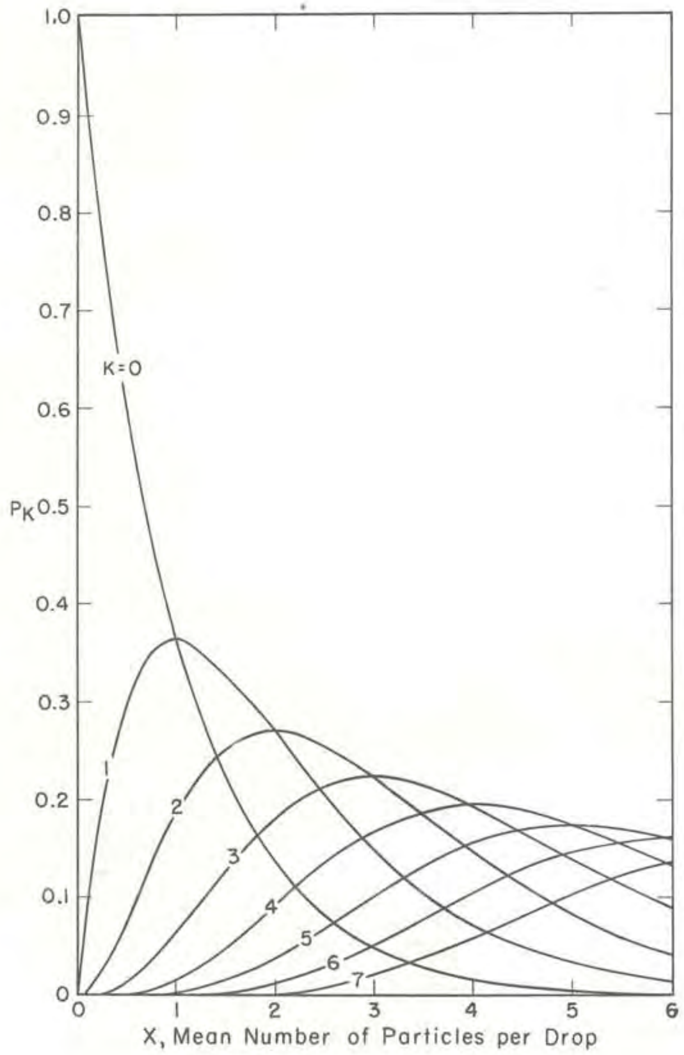


Figure 4.--Probability of observing exactly K particles in a drop as a function of the mean number of particles per drop.

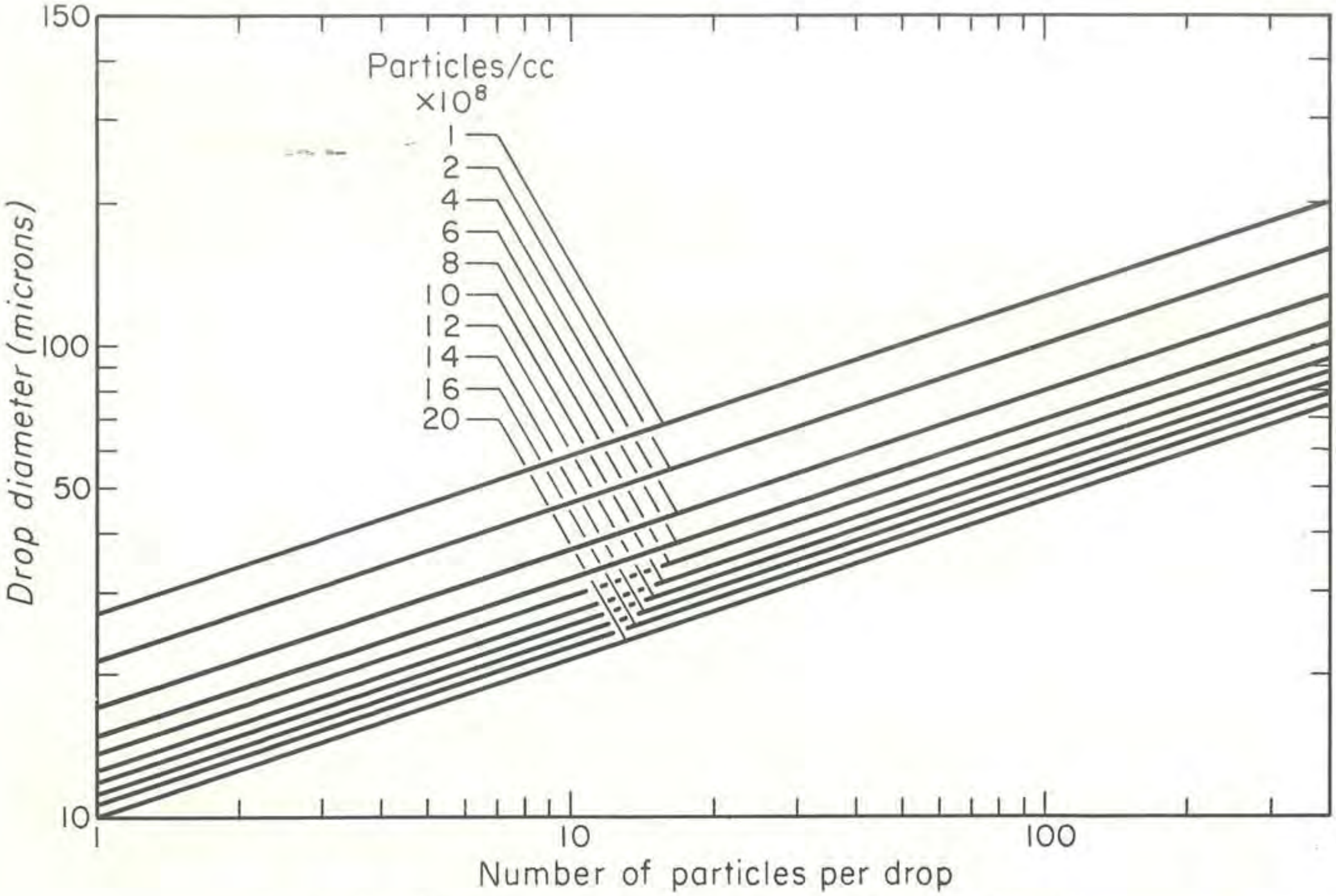


Figure 5.--Mean number of particles per drop (K) as a function of drop size and number of particles per cc of bulk liquid.

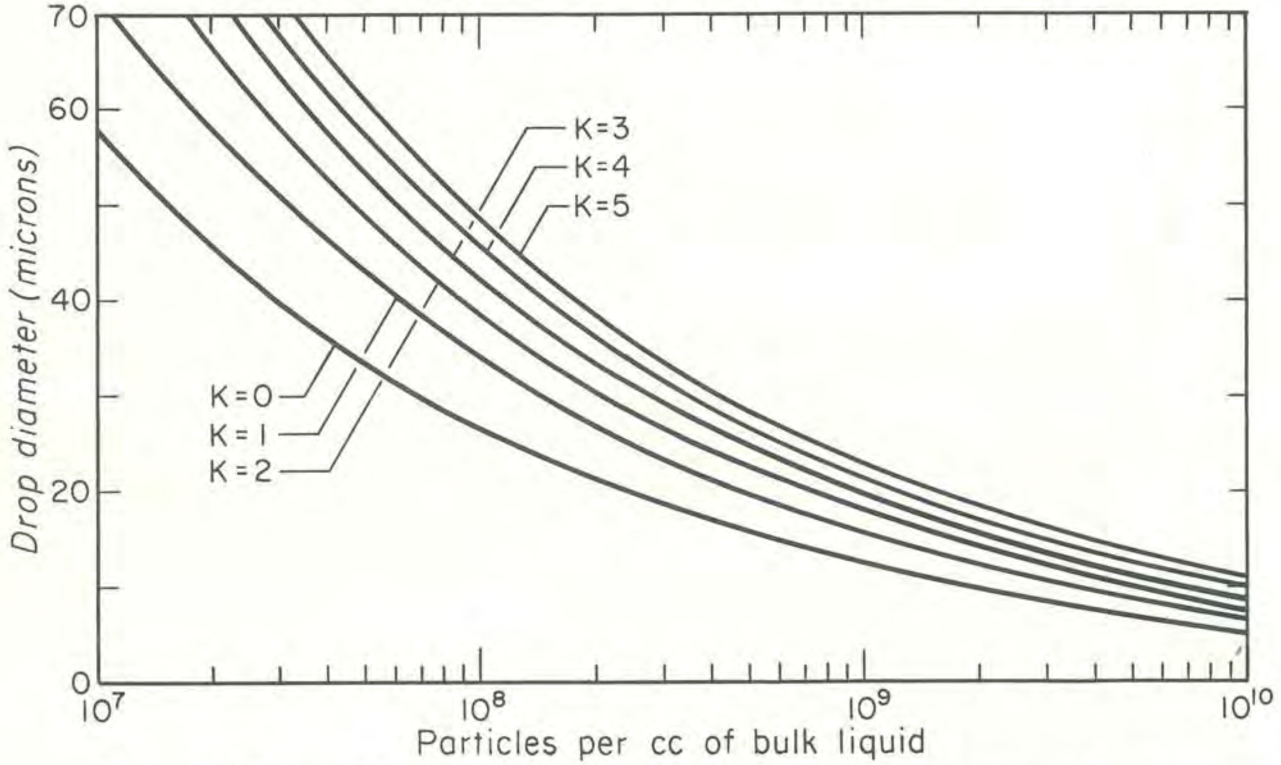


Figure 6.--Maximum liklihood estimate of drop size range as a function of K, the number of particles in the drop and the concentration of particles in the bulk liquid.

than k; hence, P_{k-1} is greater than any other P within the range $k-1<x<k$. Thus, $P_{k=1}$ is greater than any other P_k when x is less than 2 (ignoring $P_{k=0}$ since a drop without an FP is not distinguishable). Similarly, $P_{k=2}$ is greater than any other P_k when the value of x lies between 2 and 3.

Given the number of particles in a known amount of bulk liquid and specifying a value of x uniquely determines the size the drops must be if they are of uniform size. This relation is shown in figure 5 and is used to obtain the family of curves shown in figure 6. Entering the figure with the known concentration of particles in the bulk liquid, the ordinates of the two curves above and below a given value of k are the limits of the drop size range which has the maximum liklihood of containing k particles.

Since spray droplet size and number of FP's are directly related, the initial size of individual spray drops and the total deposit on different substrates can be determined for all types of liquid spray applications by merely counting the FP's present.

These findings are the basis of a new method of assessing spray deposits. The method was successfully used during the summer of 1965 to determine the number and size of spray drops reaching target and non-target insects and foliage, and to determine drift, in an experimental helicopter spray project in Montana. The results will be reported in a separate paper.

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