Bull. Environ. Contam. Toxicol. (1996) 57:938-945

Bulletin of Environmental Contamination and Toxicology

Comparison of the Pesticide Capture Efficiency of Potential Passive Dosimeter Materials

L. M. Kirchner, R. A. J. Taylor, R. A. Downer, F. R. Hall

Laboratory for Pest Control Application Technology (LPCAT), Ohio Agricultural Research and Development Center, Wooster, Ohio 44691, USA

Received: 3 January 1996/Accepted: 3 May 1996

The linkage between capture data by passive dosimeters and definitive biological results, such as urinary metabolites, is obscure and poorly correlated. Consequently, the reliability of patch techniques used to measure dermal exposure has been questioned (Day *et al*. 1987). One reason for these difficulties is that the capture efficiencies of the dosimeters vary because natural surfaces differ widely in their ability to capture and retain particles impinging upon them. In general, capture efficiency of particles by the surface of an object is related to the object's shape, size, orientation to the wind, air flow through and/or around, and surface features, as well as to particle characteristics and meteorological conditions (Carlton *et al*. 1990). These parameters are of interest when considering the behavior of dosimeters because even though the majority of materials used as passive dosimeters are man-made or highly processed, their surfaces may differ widely in their architecture and hence their ability to capture drops and/or particles.

A definitive study of capture efficiencies of passive dosimeters in current use could bring clarity and understanding to some obvious differences in passive versus biological monitoring studies. One factor hampering such a study has been the lack of a reliable and robust estimation procedure of either absolute or relative capture efficiency. Traditional devices and methods used for determining capture efficiency all require a precise knowledge of the amount of test substance introduced to the device as well as the amount collected by the test surface (May & Clifford 1967). While the second requirement may be relatively easy to measure, the amount introduced is much more difficult to assess, and is usually estimated from the atomizer throughput or by summation of the amounts collected on the test surface and that collected by the device as the spray cloud exits. Both of these approaches can introduce major errors into the estimation procedure.

Correspondence to: F. R. Hall

Previous studies documenting worker exposure with passive dosimeters usually involved running calibration recovery curves under laboratory conditions and using these curves to interpret field data (Slocum & Shern 1991). This could result in misleading results if, for example, the recovery curve is constructed using a µl syringe, while the trial was performed using an ultra low volume greenhouse mister or orchard air blast sprayer which produce a large proportion of small droplets.

Recently, however, a new approach has been developed that removes the requirement to know the atomizer throughput. The method of Kirchner *et al*. (1996) increases the accuracy and practicality of capture efficiency estimation by direct measurement of the amount of spray incident on and retained by the dosimeter. The capture efficiency is then expressed as the ratio of the mass (or number) of drops collecting on a surface, M_d, to the mass (or number) of drops incident on the area projected by the surface M_i, expressed as a percentage (Carlton *et al*. 1990):

$$E' = 100 \cdot \frac{M_d}{M_i} \% \qquad 1.$$

which Kirchner *et al*. (1996) prefer to express as the difference of the logarithms:

$$E = \log[M_d] - \log[M_i] = \log[E'] - 2 \qquad 2.$$

The mass incident to the dosimeter surface M_i they determine using a Capture Efficiency Test Device (CETD) which measures the amount not captured by the dosimeter, $M_b = M_i - M_d$. The absolute capture efficiency is then obtained from

$$E = \log[M_d] - \log[M_d + M_b] - \log[A] \qquad 3.$$

where A is a constant determined by the geometry of the CETD and independent of the experimental materials.

MATERIALS AND METHODS

Seven potential dosimeter materials were tested in the CETD (Table 1). They were 100% natural bleached cotton (Fruit of the Loom), unbleached muslin, 65:35% cotton-polyester mix (Wrangler "Big Ben" coveralls), surgical gauze (Johnson & Johnson "Topper" dressing), alpha cellulose - acetanier P (ITT Rayoner), 50:50% cotton-polyester mix (J. E. Morgan Long Johns), and a disposable spray suit of spunbonded olefin (DuPont "Tyvek"). Five 22 mm^2 samples of each material were tested in a randomized complete block design; i.e. the order of testing of the different materials was randomized comprising five different blocks.

The test device is described in detail by Kirchner *et al*. (1996). In summary, the system is comprised of three components: a wind tunnel, a tracer atomizer, and the CETD. The CETD consists of a series of cylinders separated by nylon screens to intercept and

Table 1. Comparison of the efficiencies of seven potential dosimeter materials

Material	Fabric Description	Weight (g/m^2)	Thread (#/cm)
Bleached cotton	100% cotton jersey knit	134	NA
Unbleached muslin	100% cotton plain weave	118	31x25
Coveralls	65-35% cotton-poly twill weave	292	33x20
Gauze	Two layer non-woven dressing	51	NA
Cellulose	Alpha cellulose	726	NA
Cotton-Polyester*	50-50% cotton-poly double knit	161	NA
Tyvek	Nonwoven olefin	74	NA

* two separate yarns; one of cotton and one of polyester

capture the spray containing a tracer. The decline in tracer at the screens is used to determine the tracer incident on the first screen. This in turn is used to estimate the tracer incident on a test dosimeter. The capture efficiency of the dosimeter is then calculated from equation 2 with $A = 4L^2 / \pi D^2 = 0.0483$.

In this study, as in the previous one, the CETD and the atomizer were situated in the wind tunnel's observation chamber about 200cm apart. The atomizer was located 30cm above the floor and the test material, inside the CETD, was 24.5cm above the floor. The atomizer used was a Micron ulva spinning disc sprayer producing the spray size spectrum shown in Fig. la. The dosimeter, attached to a solid 22x22 mm mount, was situated at the opening of the first cylinder section of the CETD. A baffle system placed around the atomizer provides adjustment and control of the amount of spray material that is allowed to pass into the entrance of the CETD. The baffle opening was 1cm x 3cm.

Once the wind tunnel had reached the desired velocity, the atomizer was started, allowed to come to speed, and the flow valve was opened. Run time of the atomizer may be varied as needed. At the end of the run, the flow valve was closed and the atomizer turned off. Finally, the wind tunnel was turned off and the CETD removed. The test dosimeter and backup screens were removed to snap-cap jars for fluorimetric analysis. All fluorimetric analyses were done following a previously described method (Hall *et al*. 1993). The quantity of tracer extracted from the backup screens were then used to calculate the sample incident on the dosimeter by the method of Kirchner *et al*. (1996). The absolute capture efficiency was calculated from from equation 3 using the estimates of spray incident on, and captured by, the dosimeter.

RESULTS AND DISCUSSION

Table 1 presents the results from the capture efficiency trials of the seven materials. The 100% cotton sample had by far the highest efficiency, capturing 66% of droplets incident upon it. The other materials had a range of over 15%, with muslin the second best at 47%, substantially below 100% cotton. The two cotton-polyester

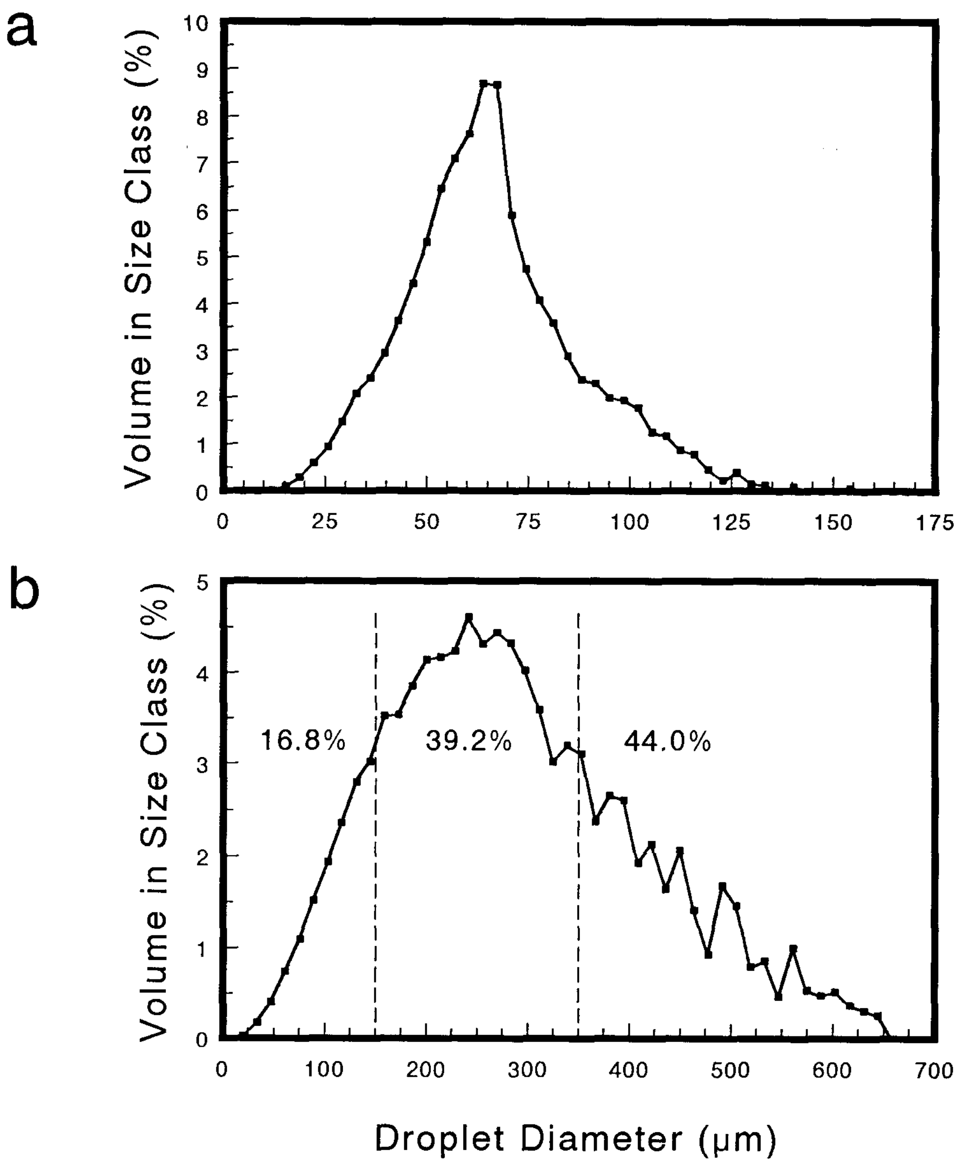

Figure 1. Droplet spectra obtained using an Aerometrics PDPA 100-1D. a) Monodispersed spectrum of tracer with 0.25% Ortho X-77 atomized using a Micron Ulva spinning disc sprayer at 12 volts. b) A typical droplet spectrum produced by an agricultural nozzle, showing the driftable component (diameter <150μm) which contributes most of the pesticide movement and exposure for which effective dosimeters are needed.

materials were ranked in order of the proportion of cotton: the coveralls with 65% cotton lying between 50:50% cotton-polyester and 100% cotton. The least efficient material was Tyvek which captured only 32% of incident droplets. No doubt the slick surface characteristics of polyester and Tyvek contributed significantly to their lower efficiencies. Surprisingly, the complex surfaces of gauze and muslin had lower efficiencies than cotton. We suppose this is due to their much coarser weave allowing droplets to pass clear through to the support.

The capture efficiency of dosimeters depends critically on several factors: surface characteristics, porosity, shape, and size. Surface features, as used here, refers to the fibers located in the peripheral layers of the surface and includes such factors as the number of fibers per unit area, total surface area of the fibers, fiber diameters, and the pattern and orientation of the weave. Previous research on the capture efficiency of natural surfaces has shown that very large differences in capture occur between objects of similar shape depending on whether hairs or fibers are present or absent. Thus, objects with hairs and/or increased surface roughness are much more efficient collectors than are smooth objects (Spillman 1984). Surfaces can thus vary widely in their ability to capture drops and particles when exposed to identical external conditions i.e. drop size distribution, wind velocity, etc.

Porosity of the dosimeter surfaces vary widely as indicated by fabric weight and thread count (Table 1). This is clearly evident from examination of the surfaces at different magnifications. For example, muslin and gauze have surfaces that are very open with numerous, large pores, while Tyvek has a relatively smooth surface with fewer, regularly spaced pores (Hall *et al*. 1992). The other materials are mostly intermediate in porosity.

The shape of the target can affect its ability to capture drops from a spray cloud. Dosimeter shape is dictated by the shape of the body surface upon which the dosimeter lays, thus a dosimeter placed on the wrist or lower leg roughly takes on the shape of a large cylinder. Other locations of the body may be considered to be other shapes; i.e. chest or back as a flat surface. Like shape, the size of the dosimeter may need to be considered in terms of the body surface to which it is attached, thus the cylinder diameter for a dosimeter attached to the wrist would be the diameter of the wrist itself.

Generally, researchers conducting dermal exposure studies employ passive dosimetry as a means to estimate potential exposure of a worker to a pesticide during an application situation. Numerous studies have been done using a variety of dosimeter types. Unfortunately, with the wide array of materials used, comparisons between studies employing different materials are more difficult to make, as are correlations between exposure estimates and biological monitoring of pesticide blood levels or urine metabolite measurements.

Table 2. Comparison of the efficiencies of seven potential dosimeter materials*

Material	*p*	se[*p*]	*N*	se[*N*]	*E*	*E'*%
Bleached cotton	0.295	0.273	1.569	1.924	-0.181	66.0%
Unbleached muslin	0.300	0.334	1.315	1.700	-0.330	46.8%
Coveralls	0.265	0.184	2.081	2.790	-0.334	46.3%
Gauze	0.272	0.228	1.753	2.350	-0.372	43.5%
Cellulose	0.282	0.198	2.144	2.474	-0.390	40.7%
Cotton-Polyester	0.270	0.195	2.000	2.619	-0.435	36.7%
Tyvek	0.282	0.295	1.322	1.952	-0.453	32.2%

* *p* and *N* are the estimates of the probability of capture and population of droplets from which the efficiency *E* and *E'* (equation 2) are calculated (details in Kirchner et al. 1996).

It seems reasonable to assume that dosimeters are intended to mimic skin as well as clothing. But, human skin is highly variable in terms of its capture efficiency, due to the varying degrees of hairiness of different individuals. Finding an exact mimic is not likely to be possible without the cooperation of human volunteer targets. Passive dosimeters should be designed to have collection efficiencies and recovery rates as close as possible to the real target, skin and clothing. The dosimeter materials used in this study were selected for use in the assessment because of their widespread use as dosimeters or clothing.

Since the major route of application exposure is through operation of boom and especially airblast sprayers, a standard method for quantifying the potential exposure from mists in the air as the operator traverses the field would be useful in aiding the assessment of risk of such operations. Patches, rather than entire clothing, are likely to be the standard assessment protocol because of the risk of contamination involved in the removal of the suits, etc. Clearly, less troublesome and more accurate methods could improve the exposure estimating process. Data on capture efficiency of an array of patch simulations would allow a more accurate assessment of potential hazards from particular delivery systems and conditions. This study of the capture efficiency of the various materials combined with tests of clothing and human skin should give us a much better understanding of why passive dosimeters tend to overestimate real exposure hazards; i.e. why pads overestimate exposure to the head (Fenske 1985, 1987).

Leonas (1991) compared pesticide transmission through apparel fabrics using a drop method and a spray method of exposure. The results showed significantly higher amounts of pesticide transmission with the drop method of exposure. Thus, the type of exposure being tested in the field should be simulated when preparing recovery curves; e.g. using µl amounts for experiments at the mixer-loader stage of exposure, and using small droplets when working with spray drift in the field or greenhouse. Discrepancies can still occur, even if the same atomizer is used in the laboratory as in the field. A typical agricultural nozzle produces a wide range of drop sizes (Fig. 1b). The spray spectrum in the field at distances away from the atomizer, (which is where many contamination trials are carried out) is likely to be quite different from that measured close to the nozzle in the laboratory. A higher proportion of smaller droplets are detected as downwind distance increases (Franz *et al.* 1987, Maybank 1988, Miller 1988) due to the earlier sedimentation of the larger droplets. The higher recovery rate from small droplets could bias the recovery data considerably, resulting in the over-estimation of exposure. The CETD results presented here suggest that degree of exposure, as indicated by different dosimeter surfaces and resulting capture efficiencies, are potentially very different. Standardization of dosimeter material could add clarity to the current disparity in exposure data. We should also point out that the CETD simulates the situation with spray drift very well, and could easily be modified to look at alternative scenarios, including capture by non-target organisms. LPCAT currently has a cooperative research oroject with the USDA-ARS Application Technology Research Unit (ATRU) on the elucidation of capture efficiencies of off-target vegetation as well as non-target arthropods.

Acknowledgements. The authors acknowledge the following who had significant impact on this project: USDA-ARS for the use of the wind tunnel facility, Andrew Dokolovic for constructing the capture efficiency test device, Tina Hoffstetter for her assistance in the wind tunnel studies and fluorimetric analysis, and Anugrah Shaw (University of Maryland, Eastern Shore) for assistance with fabric characterization. This research was supported by US-EPA grant R-817429-01 and State and Federal funds appropriated to the OARDC and The Ohio State University.

REFERENCES

Carlton JB, Bouse BF Stermer RA, Kirk IW (1990) Aerial spray deposit analysis. I: Cylindrical collector drop size effects. Trans ASAE 33:1795-1800.

Day E, Eberhart D, Knarr R, Mazzetta D, Nielsen A, Reinart J (1987) Development of a generic database for use in evaluating mixer-loader application exposures. Proc Int Congr Pest Chem 8D:14-20.

Fenske RA (1987) Assessment of dermal exposure to pesticides: a comparison of the patch technique and the video imaging fluorescent tracer technique. Proc Int Congr Pest Chem 8D:7-13.

Fenske RA, Leffingwell JT, Spear RC (1985) Evaluation of fluorescent tracer methodology for dermal exposure assessment in dermal exposure related to pesticide use. ACS Symp Ser 273:377-393.

Franz E, Reichard DL, Carpenter TG, Brazee RD (1987) Deposition and effectiveness of charged sprays for pest control. Trans ASAE 30:50-55.

Hall FR, Kirchner LM, Downer RA (1992a) Some practical limitations of fluorescent tracers to measure off-target pesticide deposition. In Pesticide Formulations and Application Systems: 12th Volume, ASTM STP 1146 (Eds Devisetty BN, Chasin DG, Berger PD) American Society for Testing and Materials, Philadelphia.

Hall FR, Cooper JA, Downer RA, Kirchner LM, Reichard DL (1992b) Pesticide capture efficiencies to validate passive dosimeter methodologies. ACS Symposium: Minimizing Human Exposure to Pesticides San Francisco.

Kirchner LM, Taylor RAJ, Downer RA, Hall FR (1996) Calibrating the pesticide capture efficiency of passive dosimeters Pestic Sci 46:61-69.

Kurtz DA, Bode WM (1985) Application exposure to the home gardener in dermal exposure related to pesticide use. ACS Symp Ser 273:139-161.

Leonas KK (1991) The mechanism of pesticide transmission through apparel fabrics: A comparison of drop and spray exposure methodologies. Arch Environ Contam Toxicol 20:427-431.

May KR, Clifford R (1967) The impaction of aerosol particles on cylinders, spheres, ribbons and discs. Ann Occup Hyg 10:83-95.

Maybank J (1988) Testing the effectiveness of reduced rate herbicide applicators. Aspects Appl Biol 17:331-338.

Miller PCH (1988) Engineering aspects of spray drift control. Asp Appl Biol 17:377-384.

Slocum AC, Shern LC (1991) Spray deposition patterns during simulated work activities by lawn care specialists. J Environ Sci Health B26:259-278.

Spillman JJ (1984) Spray impaction, retention and adhesion: an introduction to basic characteristics. Pestic Sci 15:97-106.