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Sweat-patch Test for Monitoring Pesticide Absorption by Airblast Applicators

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Health researchers have relied on three major sources of information to determine potential and/or actual toxic levels of pesticides in field workers. They include clinical evidence when field workers seek treatment from physicians or clinics; analysis of the environment (air, dust, soil, foliage, agricultural products) in which they work (Iwata 1977,Gunther 1980, Berck et al. 1981, Wojeck and Nigg 1981); and direct measurement of urine (Elliot et al. 1960, Davis et al. 1966, 1976, Davis 1980); blood (Burse et al. 1980, Maiorino et al. 1980) and saliva (Skalsky et al. 1979, Ben-Aryeh and Gutman 1979) from exposed workers. All of these methods have drawbacks for large scale screening programs. Clinical studies eliminate those workers who do not present acute pathologic changes. Environmental exposure levels may not reflect the amount actually ingested or absorbed by the individual worker. Urine and blood samples may show only specific time levels. It is impractical with humans to use in-dwelling catheters for blood collection or to collect total 24-48 hour urine samples from workers in the field. Monitoring of saliva for pesticides is in a very preliminary state. Studies by Phillips et al. (1977, 1980a, 1980b) and Pawan and Grice (1968) have monitored total blood levels of alcohol and other drugs (Thaysen and Schwartz 1953, Stowe and Plaa 1968, Johnson and Maibach 1971, Nasik 1980) by analysis of sweat. Our laboratory designed a preliminary study to determine if sweat could be used for monitoring pesticide levels in exposed field workers.

MATERIALS AND METHODS

The study group consisted of a three-man spray crew from a citrus grove in central Florida. The volunteers were instructed to perform their normal work activities. Protocol was approved by the University of Florida Committee for Protection of Human Subjects and by the Florida Atlantic University Committee on Human Experimentation. The experimental period was for 3 days, 26-28 April 1983, with a follow-up of 3 days one week later. The study group was applying chlorobenzilate (ethyl 4,4'dichlorobenzilate CAS No.510-15-6) to citrus groves with air blast equipment at a rate of 2 lb AI/acre. The metabolite of the chlorobenzilate is 4,4'dichlorobenzilic acid. In the laboratory the 4,4'dichlorobenzilic acid was oxidized to 4,4'dichlorobenzophenone for analysis. These methods have been described by Nigg et al. (1984).

Following the technique described by Phillips et al.(1977) and Phillips (1980b) four patches (3M Manufacturing Co.), each with a sweat collection area of 1.33 cm^2 (total area = 5.32 cm^2), were applied to the back of each volunteer after alcohol lavage of the area and remained in place for 3 days. They were then removed, wrapped in aluminum foil, and stored at -20°C.

Daily 24 hour urine samples were collected from each volunteer for the 3 days of each experimental period. Samples were pooled for each subject and a 50 ml aliquot stored at -20°C.

The 4,4'dicholorbenzilic acid was extracted by placing the 3-day sweat pads from each worker into a screw top culture tube, adding 10 ml of acetone, and shaking for 30 min in a Gyrotory Shaker, Model #6-Z, at 350 RPM. The acetone mixture was poured into a 250 ml separatory funnel, and the tube rinsed once with a small volume of acetone which was added to the separatory funnel. A 10 ml aliquot of the urine was analyzed for 4,4'dichlorobenzophenone as follows: 25 ml of glacial acetic acid and 1 g of chromium trioxide (CrO_3) were added to the urine in a separatory funnel, mixed for 10 sec and allowed to stand for 20 min; 100 ml of water was then added and the mixture extracted 2X with hexane. Hexane and residual water were removed from the hexane fraction by evaporation on a Buchi rotary evaporator at 40° C using a small amount of methanol to facilitate removal of the water. The residue was transferred three times into 10 ml of isooctane. For analysis of the sweat pads the acetone extraction was substituted for the 10 ml of urine. GLC analysis of all samples was done on a Hewlett-Packard 5730A with a Ni63 Electron Capture Detector and 1.8 m x 2 mm i.d. column. Operating conditions were: injector 250°C, detector 300°C, N_2 = 20 ml/min.

Mean $\pm$ S.E.M. recoveries from sweat pads were 66 $\pm$ 5% and 72 $\pm$ 6%, and from urine were 83 $\pm$ 17% and 49 $\pm$ 7%, for fortifications of 10 µg and 1 µg, respectively.

RESULTS AND DISCUSSION

Extractions from sweat patches worn for one week by twelve unexposed volunteers (students) were all negative.

Table 1. Dichlorobenzophenone from sweat pads and urine.

Worker	Sweat Pads* ng/cm^2	Urine* ng/ml
1st Period(3 days)		
CB	22.2	136.9
GC	9.6	38.8
JS	36.8	120.5
2nd Period(3 days)		
CB	22.2	194.1
GC	15.8	33.1
JS	8.1	59.9

* 3 day average

The data for each exposed subject are shown in Table 1. Comparing sweat pads to urine gave a correlation of +0.599, significant at the 77% confidence level.

Table 2 shows the same data assuming for each subject a body area of 18000 cm^2 and a total urine excretion of 4500 ml for each three-day period (Nigg et al. 1984).

Table 2. Estimated total dichlorobenzophenone (DCB) from sweat vs estimated total dichlorobenzophenone from urine (3 days).

Worker	Sweat µg/subject	Urine µg/subject
1st Period(3 days)		
CB	400	616
GC	173	175
JS	662	542
2nd Period(3 days)		
CB	400	873
GC	284	149
JS	146	270

Regression line:
Urine DCB (µg) = (.908 $\pm$ .607) Sweat DCB (µg) +125
-OR-
Sweat DCB (µg) = (.395 $\pm$ .264) Urine DCB (µg) +171
with standard errors of the estimate of 210 µg and 139 µg respectively, and linear correlation coefficients of 0.599.

Although a linear relationship can be established, these results were based on a small sample (N = 6) and the standard errors in regression line slopes were quite large. Furthermore, the 95% confidence interval for the correlation coefficient (0.599) ranged from -0.416 to +0.949. In order to increase accuracy it will be necessary to increase the number of data points in a very tightly controlled experiment. Other than statistical, i.e. data volume considerations, this methodology has several other weaknesses. Neither the volume of sweat in each pad nor the total volume from each worker over the same period can be measured accurately yet. Not all pesticides are excreted in sweat. These same weaknesses apply to urine and, in some cases, to blood testing. This methodology, however, could apply to other pesticides, drugs, warfare agents, and other chemicals. It is non-invasive, may cover a period of days rather than the customary period of generally less than 24 hours, and is not as subject to "fraud" through substitution of bodily fluid from another person. We invite the development of this technology.

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