Collecting Foliar Pesticide Residues Related to Potential Airborne Exposure of Workers

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■A technique is presented for collecting foliar dust samples for pesticide residue analysis. The proposed procedure is intended to collect that fraction of the foliar residue that can become airborne due to the activity of workers engaged in harvesting or thinning crops. The foliar dust levels measured by this procedure were experimentally shown to be highly correlated with airborne dust concentrations. The variability of replicated measurements of foliar dust levels using this technique was experimentally estimated. Dust level data collected over a five-month period using the new procedure in the Central Valley of California show increasing levels on citrus foliage over the spring and summer months.

Both the route and the extent of exposure of agricultural workers to organophosphate pesticide residues apparently vary with certain environmental and physical conditions. Although vapors (*1, 2*) and direct contact with moisture (*3*) may be important exposure vehicles in some circumstances, pesticide contaminated foliar dust appears to be more widely implicated as central to the residue intoxication hazard (*4–7*). As a result, a means of collecting foliar residue samples was sought which would be highly correlated with the potential airborne exposure of workers to these pesticide-laden dusts. A vacuuming procedure has been developed and is described in this paper together with results of experimental comparisons with the "dislodgeable" residue technique of Gunther et al. (*8*)

Design Considerations

The basic requirements imposed on the sample collection method are that: (a) the particulate removal principle be sensitive to the comparative "availability" of the surface residue to be dislodged and aerosolized during picking operations; (b) the method be applicable to any crop with foliage; (c) the method result in readily interpretable and reproducible quantities—i.e., μg of pesticide residue per cm^2 of leaf area; and (d) the sampling unit be portable and preferably operable by one person.

Initial investigations indicated that a vacuuming technique might meet these requirements. The current version of the vacuum assembly, Figure 1, employs a modified commercial crevice tool fitted with spacing skids, joined to a bell mouth which, in turn, is coupled to modified hi-vol air sampling accessories. Suction is provided by a Lamb two-stage direct air-flow vacuum motor operating at a vacuum of 73 ± 3 in. of water (*9*). The dust available to the moving air stream is collected on a preweighed 90-mm membrane filter positioned at the open end of the bell mouth.

The flow characteristics at the nozzle gap were selected largely from judgment and limited prototype experience. Average velocities in the 2.3 mm (0.090 in.) gap are 7.5 ± 1 m/sec (1500 ft/min). The constrained flow through the gap produces boundary layer conditions quite dissimilar to natural wind over the leaf surface. With the gap height as the characteristic dimension, the calculated Reynolds number equals 1100. An equal velocity free flow across a flat 50-mm leaf would have an average Reynolds number of 12,500. These assumptions indicate that boundary layer conditions in the gap are equivalent to natural winds of 10 times the speed in the gap, i.e., ~170 mph.

The air flow as it approaches the gap over a rough leaf surface is not "ideal," but Blasius' boundary layer equations predict a boundary layer thickness of 300 μ, the velocity decreasing smoothly below free stream conditions in this region. Fluctuations in surface contours, particle position, size, and shape make a detailed investigation of particle adhesion and removal very complex. The depth of the dust deposit and accumulations of the pesticide in natural leaf cusps at the time of application are two important factors affecting not only the available fraction of the surface deposit but also the residue chemical composition. That these aerodynamic removal forces would ideally match those during picking would be fortuitous, at best. However, it was suspected that the airborne particulate residue availability would be more closely assayed by this method than by washing procedures.

Experimental Procedures

To estimate the variability of the proposed vacuum procedure, to evaluate its potential as a predictor of airborne dust levels during picking, and to contrast the measurements with Gunther's dislodgeable residue procedure, a set of field experiments was undertaken. In these experiments attention was focused on the physical availability of the dust, and no chemical analyses were performed. However, organophosphate vapor retention characteristics of the membrane filter are reported as very good (*10*). The possible loss of pesticide due to vaporization and the resulting significance of differences in measured residue concentra-

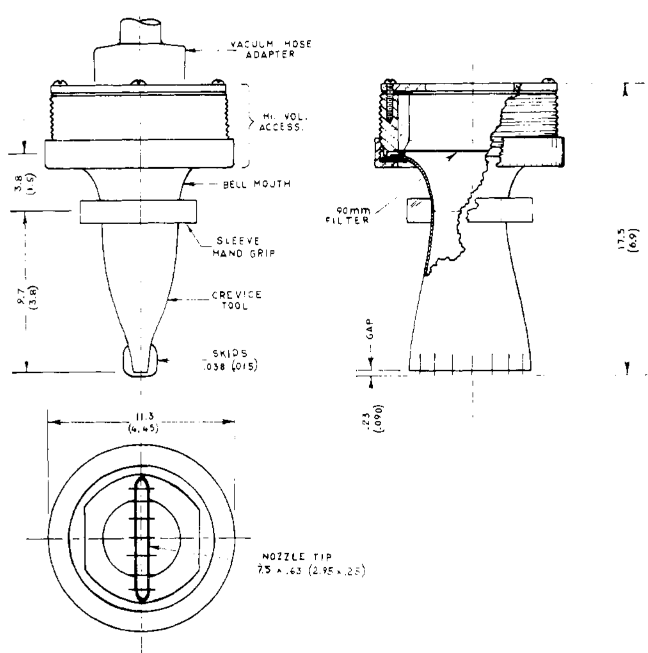

Figure 1. Vacuum nozzle and filter assembly
Dimenions are in cm (inches in parentheses). Materials are aluminum with plastic sleeve, steel skids, and neoprene seals

tions between the vacuuming technique and the dislodgeable residue technique of Gunther await future investigation.

Six representative orange groves were selected in three citrus-growing regions of California: three in the San Joaquin Valley, two in southern California, and one on the coast. None of the fields had been sprayed with pesticides for at least 30 days. Within each grove, a rectangular block of six trees was chosen at random. Eight sampling points on each tree were evenly spaced at 45° intervals and at a height of 5–6 ft, similar to the sampling procedure outlined by Gunther et al. (*8*). Each of the replicated samples consisted of 48 whole leaves, one from each sampling point on each tree. Five to 10 min were required to vacuum each sample.

The sampling procedure consists of collecting a number of whole leaves, each leaf being carefully clipped at the stem, placed on a covered board and vacuumed on both sides, top side first. After vacuuming, the leaves are mounted flat on a sheet of paper and spray painted to produce individual shadows subsequently sized to give leaf area. The filter is carefully removed from the holder assembly, desiccated, and postweighed to determine collected dust weight.

Table I. Tabulated Sample Values (Rank Ordered) and Their Basic Statistics in Each Grove

Grove number, i =	1	2	3	4	5	6
A. Vacuum Samples, μG Dust/Cm² Leaf						
$j^a = 1$	30.1[b]	32.0[c]	25.2[c]	55.4[c]	67.8[d]	51.6[c]
2	34.7[d]	33.6[b]	29.8[b]	57.2[c]	76.6[d]	56.9[c]
3	36.8[c]	34.4[c]	29.9[b]	61.2[b]	76.9[d]	59.3[c]
4	38.1[b]	38.8[b]	30.5[c]	63.0[c]	79.6[d]	65.6[b]
5	40.8[c]	41.1[b]	31.8[c]	78.5[b]	83.0[d]	72.0[b]
6	41.2[b]	46.2[c]	32.9[b]	91.2[b]		85.3[b]
7						105.6[b]
Mean, $\bar{x}_i$	36.9	37.7	30.0	67.7	76.8	70.9
Variance, s_i^2	17.2	29.0	7.0	198.9	31.8	357.3
B. Leaf Punch Samples, μG Dust/Cm² Leaf						
$j = 1$	278	289	206	420	352	282
2	285	289	213	422	357	289
3	290	297	232	473	422	293
4	304	313	240	480	438	327
Mean, $\bar{x}_i$	289	297	223	449	392	298
Variance, s_i^2	121	128	253	1036	1947	401
C. Personal Air Samples, Mg Dust/M³ Air						
$j = 1$	31.1	23.9	15.0	38.0	...	61.2
2	28.4	25.7	8.3	76.2	...	64.4
Mean, $\bar{y}_i$	29.7	24.8	11.7	57.1	...	62.8

[a] Replicate number. [b] Vacuum samples taken by inexperienced sampler. [c] Vacuum samples taken by experienced sampler. [d] Vacuum samples taken jointly.

The magnitude of available dust is thus directly expressible as μg of dust per cm² of leaf surface. Subsequently, the filters can be extracted and chemically analyzed for the pesticide in question, the residue value given as ppm of dust or ng/cm² of leaf surface.

Four leaf punch samples were taken in the same pattern as vacuum samples, each comprising 48 3-cm disks. These samples were then washed as described by Westlake et al. (*6*) to remove surface detritus which was then collected on desiccated Whatman GF/C glass fiber filters (*11*).

To generate an aerosol, a simulated picking exercise was conducted for approximately 30 min on trees in each grove. No data were collected in grove No. 5 due to high wind conditions. For this experiment, two workers wearing membrane filter personal air samplers stood side-by-side about 1 ft from the tree's outer foliage and uniformly stroked the fruit-bearing branches in a manner designed to simulate the disturbance of foliage which would take place in an actual picking situation. The workers moved completely around each tree, remaining at each "picking" station for 10 sec to allow for aerosol dissipation before changing their positions. Uniformity between trees and groves was stressed more than the recreation of the exact motions of a picker. Filter flow rates (3.0 ± 0.25 l/min) and dust gravimetric analyses were determined in accordance with standard practice (*12*).

Results and Discussion

Table I contains the ordered replicated values of vacuum samples, leaf punch samples, and personal air samples from each grove. To assess the variability of the vacuum procedure, the data from Section A of Table I were subjected to an analysis of variance (unbalanced, twofold nested classification based on components of variance model). The components considered were variability between groves (σ_G^2), between individuals taking the samples (σ_S^2), and residual variability (σ_R^2).

Table II gives the results of this analysis which indicate that the variability between the six groves as well as between the experienced and inexperienced samplers was significant at the 1% level. That is, the vacuum procedure results indicate that the six groves in fact had different levels of vacuumable foliar residues. Further, there are independent detectable differences in the measurements that can be attributed to the fact that different persons conducted the sampling procedure (i.e., significant variability among samplers). In particular, 77.9% of the total variation in the data of Table I Section A can be attributed to the differences among groves, 10.6% to differences among samplers, and 11.4% to residual variation.

The residual variance was further partitioned into components attributable to the experienced sampler (A), the inexperienced sampler (B), and both working together (C).

Table II. Analysis of Variance for Vacuum Samples

Source of variation	Sum of squares	Degrees of freedom	Mean squares	Estimate of mean squares	F statistic
Total	16,029.4	35			
Groves, G	12,497.1	5	2499.4	$\sigma_R^2 + 3.32\sigma_S^2 + 5.99\sigma_G^2$	8.8[a]
Samplers + residual	3,532.0	30	117.7	$\sigma_R^2 + 0.536\sigma_S^2$	
Samplers, S	1,702.8	6	283.8	$\sigma_R^2 + 2.68\sigma_S^2$	3.72
Residual, R	1,829.5	24	76.2	σ_R^2	
Sampler A	210.6	9	23.4	σ_a^2	
Sampler B	1,491.6	11	135.6	σ_b^2	
Sampler C	127.3	4	31.8	σ_c^2	

[a] Approximate F value. $F_{5,24}$ (1%) = 3.90. $F_{6,24}$ (1%) = 3.67.

Table III. Estimated Standard Errors of the Mean Assuming One Sampler and Several Samplers

No. of observations in the sample = n	Single sampler[a]	Several samplers[b]
$n = 1$	8.73	10.85
$n = 3$	5.04	6.27
$n = 5$	3.90	4.85
$n = 10$	2.76	3.43

[a] $S_{\bar{x}} = \sqrt{\frac{76.2}{n}}$. [b] $S_{\bar{x}} = \sqrt{\frac{117.7}{n}}$.

Table IV. Product Moment Correlation Coefficients Relating Sampling Methods

Methods	Correlation coefficient	p-Value	n
Vacuum vs. punch	0.750	<0.05	6
Punch vs. air sample	0.687	<0.10	5
Vacuum vs. air sample	0.985	<0.001	5

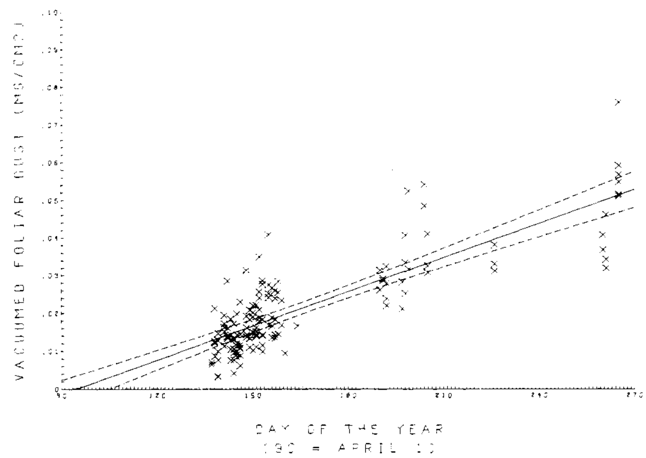

Figure 2. Summary of available foliar dust (mg/cm²) collected with vacuum device in central California orange groves during 1973

The results, also shown in Table II, indicate that the inexperienced sampler showed a variance over five times that of the experienced man. In addition, both working together produced a variance intermediate between their individual values.

Table III shows the standard error of the mean ($S_{\bar{x}}$) for various numbers of replicates from the same grove based on the data of Table II and assuming a single sampler, Column 2, and several samplers, Column 3. If, for example, five replicated vacuum measurements were made in a single grove by a single sampler and the mean value of the five measurements was 53.3, then the true mean value can be said to lie in the interval 53.3 ± 7.64 with 95% confidence (assuming the original measurements are samples from a normal distribution).

The relationship between the vacuum measurements, the leaf punch measurements and the air sampler values is demonstrated in Table IV, which shows the correlation between the mean values obtained in each grove (r), the probability of observing the listed value of the correlation coefficient by chance alone (p-value), and the number of groves compared (n). When the correlation coefficients are calculated using the observations rather than the respective mean values only minor differences occur. Based on these limited data the vacuum technique is a better predictor of the airborne levels as evidenced by a correlation coefficient of 0.985 versus a value of 0.687 for the leaf punch technique.

In addition to the calibration experiment described above, the vacuum procedure was extensively field tested during the spring and fall of 1973 in the orange groves of central California. All of these data are displayed on Figure 2 which shows the vacuumable residue in milligrams of dust per square centimeter of foliage versus time, with day 90 being April 1 and day 270 being September 27. The estimated linear regression line is bounded by the 95% confidence band (dashed) about that line.

These data show the increasing level of foliar dust with time. It is of interest that an extrapolation of the regression line to zero dust level occurs on April 4. The last significant rainfall (0.48–0.98 in.) occurred on March 26 with scattered showers (0.04–0.25 in.) on April 30. The lack of rainfall during the summer months is characteristic of this region. Furthermore, the magnitude of natural or "fugitive" dust in this region, believed to be generated largely from agricultural sources, is a recognized air pollution problem (*13*). If foliar dust is subsequently confirmed to be central to the exposure process, these data may give a clue to the reasons underlying the frequency of reported intoxication incidents in this region of California.

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