Table 1. Variable coefficients for parathion, paraoxon, carbophenothion, and ethion decay on 'Valencia' orange leaves.

Compound	Ln initial concn	HDD	CR	CLW	T	Time	% variation explained: Weather + time
Parathion	3.4511	0.0069	−1.2311	−0.0916	−0.0159	35	90**
Paraoxon	3.2822	0.0825	−1.0610	−0.0424	−0.2975	79*	98**
Carbophenothion	4.2014	0.0201	−0.9280	−0.0205	−0.1336	47	93***
Ethion	5.3302	0.0110	−0.8153	−0.0021	−0.1201	57	94***

$\frac{dy}{dt} = (a_0 + a_1x_1 + a_2x_z + \ldots + a_nx_n)y$) y = pesticide residue, $x_1, .. x_n$ = environmental variables.

HDD = Cumulative heating degree days; CR = Cumulative rainfall (inches); CLW = Cumulative leaf wetness (hr); T = time (days).
*Significant at 5% level.
**Significant at 1% level.
***Significant at <1% level.

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WORKER REENTRY IN FLORIDA CITRUS: COMPARISON OF TWO PESTICIDE RESIDUE TECHNIQUES FOR CITRUS FOLIAGE[1,2]

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Abstract. **The official dislodgeable pesticide residue technique was compared with a vacuum method in Florida citrus. Trends in the data for both techniques correlated above 0.9 in 2 expts. The dislodgeable technique recovers 11 times or more pesticide residue compared to the vacuum method and consistently and conveniently provides a better assessment of pesticide residues on the surface of citrus foliage as related to field worker safety.**

Worker reentry acute intoxications in the western United States have been linked to relatively long-lived residues of organophosphate insecticides on foliage and soil surface as well as toxic metabolites produced in the environment (3). Carman et al. (1) first noted pesticide contaminated particulate matter could represent a hazard to agricultural field workers exposed during tillage, picking, pruning, and similar operations. This was supported by subsequent California studies which showed dust and debris was the actual vehicle for pesticide transfer to agricultural field workers (6, 9).

Because exposure of agricultural field workers to pesticides is primarily dermal, the U. S. Environmental Protection Agency recommends a dislodgeable surface particulate technique for reentry pesticide residue data in order to register pesticides. However, in a California study foliage particulate matter collected by vacuuming correlated better with dislodged airborne particulate matter (r = .985) than the recommended EPA technique (r = .687) (7).

The purpose of the study presented here was to assess the vacuuming method in a pesticide residue experiment and determine if vacuuming provides a better measure of foliage surface pesticide residues than the dislodgeable particulate residue technique under Florida conditions.

Materials and Methods

Application methodology was *previously described* (5).

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Each plot contained 4 'Valencia' trees and each treatment was replicated 4 times. Treatments were: (1) parathion (0,0 diethyl p-nitrophenylphosphorothionate) wettable powder (WP), 5 lb. 15 WP/100 gal; (2) parathion emulsifiable concentrate (EC), 32 oz 4E/100 gal; and (3) no spray (NS). Leaves were vacuumed with a vacuum head designed for citrus foliage according to the method described by Popendorf et al. (7). A Millipore 50 μ and a Whatman GF/A 1.6 μ glass fiber filter were used for vacuuming each 60 leaf sample.

An unvacuumed 40-leaf punch sample was taken from each plot for total dislodgeable surface residues according to Gunther et al. (2, 4).

Particulate size analyses were determined with a Millipore Model II MC particle measurement computer (Millipore Corp., Bedford, MA 01730) and with a reticle under 400X with phase contrast for sizes <5.0 μ. Particulate analyses were carried out directly on the 5.0 μ Millipore vacuumed filter and on dislodgeable residue samples after filtration with a Millipore 0.22 μ filter.

Leaf areas were obtained with Turrell's formula (8) and other analytical details have been described (5).

Results and Discussion

The data in Table 1 show that the use of the 5.0 μ and glass fiber filters resulted in significant differences in the vacuum removal of pesticide-laden particulate material. This difference appears to be related to the flow rate of the 5.0 μ filter (2250 fpm) and glass fiber filter (5000 fpm). The trend of the paraoxon and parathion data of these filters was highly correlated ($r = .99$). In addition, the paraoxon and parathion data of each filter was highly correlated with the parathion and paraoxon dislodgeable data (5.0 μ: $r = .99$; glass: $r = .99$). The amount of pesticide residue obtained by vacuuming was of a magnitude of 5.3 to 27 times less than obtained with the dislodgeable technique.

Comparison of data obtained with both techniques with EC and WP parathion (Table 2) shows significantly less pesticide residue was obtained with the vacuum method compared to the dislodgeable method. The data trends for vacuum and dislodgeable residues were highly correlated for EC ($r = .91$) and WP ($r = .99$) formulations. The vacuum method removed significantly less pesticide material with the EC formulation whereas the day 1 residue samples with the dislodgeable technique were equal (application rates were also equal) (Table 2). This observation supports the supposition that, where natural conditions are not dusty, an EC formulation is safer than a WP formulation as regards field worker exposure.

These residue data are supported by particulate analyses (Fig. 1 and 2). The vacuum method removes about 1/5 the particulate matter compared to the dislodgeable technique (WP formulation). The vacuum method also removes about 1/4 the particulate matter comparing the EC to the WP formulation. A California study obtained about 1/5 the particulate matter by weight with the vacuum technique as compared to the dislodgeable technique (7).

On a concn basis, however, the comparison of the 2 techniques is different. Excluding the residue data for day 1, the dislodgeable technique averages 11 times more pesticide residue when compared to the vacuum technique, regardless of formulation. The area of the vacuum sample however is about 6 times that of the dislodgeable technique, but the number of particulates is about 1/5. Thus, the vacuumed particulates on the average contain about half the pesticide compared to dislodgeable particulates. This observation is inconsistent with a transfer of pesticide to leaf wax in tightly adhering particles reducing the pesticide level in particles obtained with the more stringent dislodgeable technique and it also appears that the loosely adhering dislodeable material can be about twice as dangerous to agricultural field workers as compared to the vacumable particulate load on the leaf surface.

These observations might not be significant if other special qualities of the vacuumed sample were evident. However, this is not the case. Vacuumed samples do not contain special amounts of any particulate size which would determine whether exposure of humans would be dermal, oral, or respiratory. Nor did vacuumed samples contain extraordinary levels of the oxon metabolite.

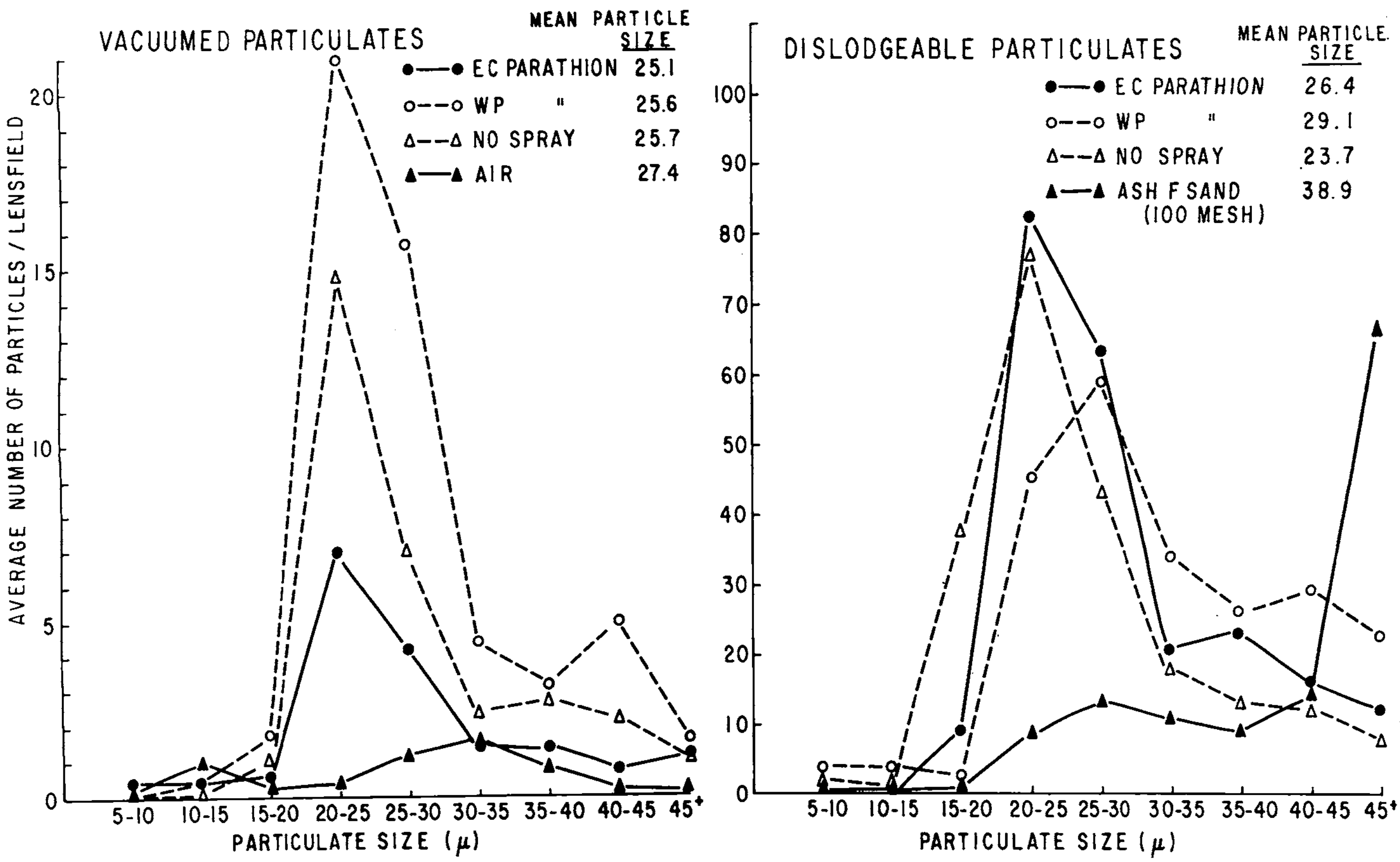
The primary difference between these 2 techniques is in

Table 1. Expt. 1. Comparison of dislodgeable and vacuumed residues of WP parathion ($\mu g/cm^2$) on Valencia orange leaves.

	Day post treatment					
	1		5		9	
	Paraoxon	Parathion	Paraoxon	Parathion	Paraoxon	Parathion
5.0 μ filter	.005 ± .001	.067 ± .030	.003 ± .001	.006 ± .002	.001 ± .0004	.001 ± .0003
Glass filter	.007 ± .0002	.198 ± .044	.005 ± .001	.011 ± .002	.002 ± .0003	.002 ± .001
Dislodgeable	.037 ± .014	1.812 ± .487	.050 ± .017	.083 ± .039	.015 ± .006	.008 ± .006
Dislodge/5.0 μ	7.4	27.0	16.7	13.8	15.0	8.0
Dislodge/glass	5.3	9.2	10.0	7.5	7.5	4.0

Table 2. Expt. 2. Comparison of dislodgeable and vacuumed residues of WP and EC formulations of parathion ($\mu g/cm^2$) on Valencia orange leaves.

	Day post treatment					
	1		6		8	
	Paraoxon	Parathion	Paraoxon	Parathion	Paraoxon	Parathion
EC vacuum (glass filter)	.0001 ± .0005	.002 ± .0003	.0003 ± .0004	.0004 ± .0001	.00004 ± .00001	.0003 ± .00005
EC dislodgeable	.026 ± .002	1.122 ± .222	.002 ± .0005	.006 ± .002	.0006 ± .0001	.0003 ± .0004
EC dislodge/vac.	260.0	561.0	6.7	15.0	15.0	1.0
WP vacuum (glass filter)	.001 ± .0002	.016 ± .004	.0005 ± .0006	.002 ± .0005	.0002 ± .00008	.0008 ± .0001
WP dislodgeable	.031 ± .008	1.647 ± .600	.005 ± .0005	.025 ± .010	.004 ± .0007	.018 ± .008
WP dislodge/vac.	31.0	102.9	10.0	12.5	20.0	22.5



Figs. 1, 2. Particulate size analyses. Fig. 1. Dislodgeable particulates from 10 whole leaves. Fig. 2. Vacuumed particulates, 5.0 μ filter.

the amount of actual pesticide residue recovered. However, it has not been determined what level of pesticide-laden particulate material would represent a hazard to agricultural field workers. The dislodgeable residue particulate technique is more representative of the total potential hazard to agricultural field workers in Florida.

Additional advantages of the dislodgeable technique are evident.

(1) The area of the leaf sample is automatically determined by the size of the punch and the number of punches.

(2) Sampling time of 3 min for the typical 40-punch sample is considered rapid.

(3) An analytical chemist can easily determine extraction efficiency by fortifying a no-spray wash solution.

The data presented here, reenforced by the obvious technical advantages, justify the conclusion that the recommended leaf punch dislodgeable residue particulate technique is the technique to use for protecting agricultural field workers when registering pesticides for use on Florida citrus.

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