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Deposition of Esfenvalerate on Brassica Vegetables

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Esfenvalerate, [(s)-cyano(3-phenoxyphenyl) methyl-(s)-4-chloro-alpha-(1-methylethyl) benzeneacetate] is the alpha isomer of the synthetic pyrethroid, fenvalerate. It has the highest insecticidal activity of the four fenvalerate isomers (Oouchi 1985) and its use (as Asana®) is currently replacing those for fenvalerate (Pydrin®) for food uses.

In contrast to fenvalerate, there is little information published on the disposition of esfenvalerate. Fenvalerate showed broad spectrum of activity against various pests on a wide range of food and non-food commodities. The mammalian toxicity of fenvalerate is relatively low (Bradbury and Coats, 1989). It is not a systemic insecticide (Lee et al. 1988) and is metabolized in plants to a small extent (Lee et al. 1988; Mikami et al. 1985). Fenvalerate residues on treated foliage declined with time after applicaion with the half-life of 2 days to 3 weeks depending on the crop and experimental conditions (Smith et al. 1989, Lee et al. 1988, Mikami et al. 1985, Hill et al. 1982, and Holmstead et al. 1978).

For this study, we examined the deposition and persistence of esfenvalerate on selected Brassica vegetables under field conditions. In addition, we examined the distribution of residues by determining the residue levels in the mat (solid) and water fractions of the foliage.

MATERIALS AND METHODS

Esfenvalerate (CAS 66230-04-4, purity 99%) was obtained from EPA Pesticides And Industrial Chemicals Repository (Research Triangle Park, NC). Stock solutions were made in hexane for the standard curve in quantitation, and in acetone for fortification. Asana® 1.9 EC or 0.66 EC containing 24% esfenvalerate was obtained from E.I. du Pont de Nemours & Co., Inc. (Wilmington, DE). All other reagents were HPLC grade or analytical grade obtained from Fisher Scientific Co. (Springfield, NJ).

Esfenvalerate, formulated as Asana 1.9 EC or 0.66 EC was mixed in

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water and applied to growing plants every week at a rate of 0.045 lbs active ingredient per acre. Rapidly maturing mustard greens, received four applications while Chinese cabbage var. bok choy and kale received eight applications. Trials (2 locations per crop) were conducted in Texas and Ohio for mustard greens, in Texas and Georgia for kale, and in Florida and Ohio for bok choy. Samples were harvested from four replicated plots at 1 to 14 days after the last application and stored at -30°C until analysis.

Esfenvalerate in the chopped crop (25.0 g) was extracted (Pesticide Analytical Manual, 1982) in 200 mL of hexane/isopropanol (3:1). The extract was filtered and partitioned with 100 mL of water three times. The organic layer was dried with anhydrous sodium sulfate and the volume was reduced by rotary evaporation. The final residue was dissolved in hexane for gas chromatographic analysis.

Residue levels were calculated from linear regression analysis. Reported values were mean ± standard deviations of 3-4 samples (only one sample was available in the Florida trial for bok choy harvested 14 days after application) and were not corrected for recovery. Average recovery of esfenvalerate from crop matrices was in the range of 83-118%. Storage stability studies showed that esfenvalerate was recoverable from crop matrices after storage at -30°C.

For the plant compartment study, water was removed from chopped samples by vacuum filtration through a Buchner funnel. An aliquot (25.0 g) of the mat and the filtrate (water) portions was extracted following the hexane/isopropanol protocol described in the previous section. Percent water was calculated as (weight of the water compartment/total wet weight) x 100 %. Concentration factor was calculated as the ratio of ppm in the mat fraction/ ppm in the chopped foliage before filtration.

Sample extracts were analysed by gas-liquid chromatography using a Hewett-Packard gas chromatograph equipped with a ^{63}Ni electron capture detector. The column used was a 15m x 0.53mm Bonded FSOT packed with polydimethylsiloxane 1.2 μm (RSL-150, Supelco Inc. Bellefonte, PA) and the carrier gas was ultrapure nitrogen with an average flow rate of 34 mL/min. The gas chromatograph temperatures were: oven at 225°C, injector at 235°C, and detector at 300°C.

RESULTS AND DISCUSSION

Foliar applications of Asana® under field conditions resulted in the deposition of esfenvalerate on the foliage of three Brassica vegetables, bok choy, mustard greens, and kale (Table 1). From 1 to 5 days after application, there was a rapid decline in the residue levels with the half-life less than 1 week. After 7 days, the residue levels were less than 1.50 ppm for all the samples. By 14 days, there was essentially no further decline in residues as shown by the residue trials with bok choy.

Table 1. Loss of esfenvalerate residues (ppm) from Brassica vegetables, mustard greens, kale, and bok choy after foliar applications.

		Locations	
Commodity	Days	Florida	Ohio
Bok choy	7	0.35±0.09 ppm	0.38±0.21 ppm
	10	na[1]	0.42±0.02
	14	0.15±0	0.34±0.16
		Texas	Ohio
Mustard greens	1	2.48±0.27 ppm	na[1]
	3	1.34±0.16	0.45±0.21 ppm
	5	na[1]	0.31±0.07
	7	0.81±0.30	0.16±0.03
		Texas	Georgia
Kale	1	1.78±0.34 ppm	na[1]
	3	0.45±0.12	2.63±0.64 ppm
	5	na[1]	1.83±0.88
	7	0.21±0.10	1.20±0.33

[1]na=samples were not collected.

Most published studies conducted field trials at the same location thus limiting variability due to environmental conditions. By taking samples from different locations, residue levels may be more variable but will be more representative of actual residue levels to be expected under different growing conditions. In our study, the data showed that while the general trend was similar in all the trials, there was a difference in magnitude. For example 3 days after application, there was a greater than 5 fold difference in the residue levels in the kale samples between the two trials. Similarily, there was a 3 fold difference in the levels in the mustard greens samples harvested after 3 days.

While environmental factors are important in the determination of the foliar deposition of pesticide on the plant tissue (Bentson 1990), another consideration is the composition of the plant in terms of the water weight since residue levels are expressed as amount of pesticide in total plant weight of the sample. We have observed that some vegetables (such as bok choy) contained more water than others (such as kale). We analyzed for esfenvalerate in the mat and in the filtrate to derive a concentration factor that indicates the influence of water weight on the total residue level. Our data showed that essentially all of the residues were in the mat fraction resulting in the concentration factors directly proportional to % total weight as water (Figure 1). For bok choy where 78% of the total weight was water, the concentration factor was 4.5. That is, when the water or crop juice is removed from the foliage, the residue level will increase 4.5 fold. On the other hand for kale which contained 44% water, the factor was only 1.6. This direct relationship is expected since esfenvalerate is lipophilic and nonsystemic. Spittler et al. (1982 and 1984) have reported that fenvalerate was distributed only on the skin of apples and tomatoes, and not on the processed fractions such as the juice.

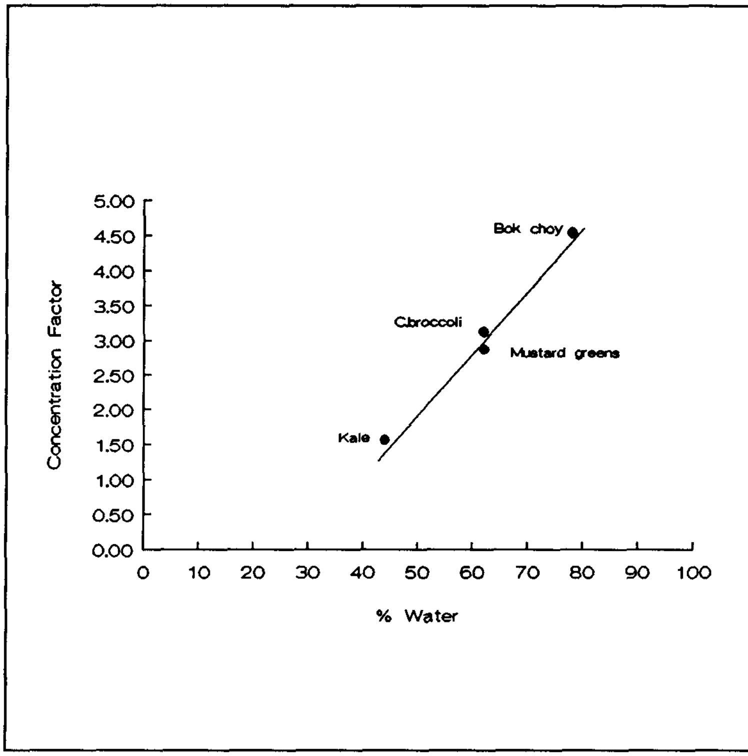

Figure 1. Relationship between % total weight as the water compartment and the ratio of ppm in the mat fraction/ppm in total crop expressed as the concentration factor for four Brassica vegetables, bok choy, Chinese broccoli, mustard greens, and kale.

The relationship between % total crop weight as water versus distribution of pesticide in the mat fraction may be useful in extrapolation of residue levels from fresh samples to processed or dried samples.

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