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Cycling of Indoor Air Concentrations of *d-Trans*-Allethrin Following Repeated Pesticide Applications

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Pesticides are often applied in homes and buildings on a regularly scheduled basis. Thus, it might be expected that residues of pesticidal chemicals would be found in indoor air. Studies of pesticides in indoor air have either been surveys of homes that showed background pesticide concentrations for many compounds (Hsu et al. 1988), or examinations of the post-application concentration for a particular pesticide (Wright and Leidy 1978; Wright et al. 1981; Jackson and Lewis 1981; Wright and Leidy 1982; Leidy et al. 1982; Williams et al. 1987; Louis and Kisselbach 1987; Lewis et al. 1988; Wright et al. 1988). Despite these studies, many pesticides have yet to be studied post-application in indoor air. Also, those studies were made under ideal conditions i.e. the rooms were not in use.

Sampling of pesticidal chemicals in indoor air is generally performed by passing the air through an adsorbent which removes the chemicals from the air. The sorbant is subsequently extracted to remove the pesticidal chemicals. One screening study used high volume air sampling with polyurethane foam as an adsorbent (Hsu et al. 1988). Smaller volume samples are used for post application studies. One sorbant commercially available which has been shown to be effective for pesticidal chemicals is Chromosorb 102 (Thomas and Seiber, 1974; Thomas and Nishioka, 1985).

This paper reports on the cycling of indoor air concentrations of d-trans-allethrin and pyrethrin following bi-monthly applications of Whitmire PT565+ in a public community college cafeteria. The project was

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designed to examine a real rather than idealized situation. Thus, sampling was worked around the normal operations of the commercial applicator and the school.

MATERIALS AND METHODS

Samples were taken in the cafeteria of a local community college. The cafeteria is 28 yards long by 15 yards wide with 15 foot high ceilings. There was a group of 5 vending machines located along the wall in one corner of the room. Whitmire PT 565+ (Whitmire Research Labs., Inc. St. Louis) a formulation containing 0.25% pyrethrins and 0.25% d-trans allethrin was applied to this room bi-monthly on Friday afternoons. The pesticides were applied by a commercial applicator in accordance with their normal operating procedures (ACME Pest Control Co. Inc., New Haven). The total application time for the cafeteria took approximately five minutes with the largest proportion of the time spent at the back of the vending machines.

Air samples were taken simultaneously using two samplers. The first five series of samples were from two different sites in the room, one by the vending machines and the other in the opposite corner. The last two series were of duplicate samples from the vending machine area. Samples were taken both before and after application of pesticide and at different dates ranging from one to thirteen days after application.

Air was sampled using a MSA portable pump model S (MSA, Pitt., PA) to draw air through SKC Chromosorb 102 air sampling tube (SKC Inc., Eighty-four, PA) at a flow rate of approximately 100 liters per hour. The tubes had been previously opened and cleaned using a 16 hr Soxhlet extraction with hexane. The tubes were sealed with push-on caps. Air was sampled over time periods varying from one to six hours. After sampling the tubes were resealed until analyzed. The pump flow rate was calibrated using a Gilian Gilabrator primary standard airflow calibrator (Gilian Inst. Corp., Wayne, NJ).

For analysis the Chromosorb 102 resin was transfered from the tube to a brown glass vial. Standard solutions of d-trans allethrin, pyrethrins (EPA, Research Triangle Park) and 4,4-dichlorobenzophenone (Eastman Kodak, Rochester) were made. A 25 ul aliquot of the 4,4-dichlorobenzophenone solution was added as an internal standard. Then one ml of hexane was added and the vial was sonicated for 30 minutes in a water bath. Two ul of the hexane extract was analyzed on a

Hewlett-Packard 5890 gas chromatograph (GC) with electron capture detection (GC/ECD). The GC column was a 30 m SPB-5 (Supelco, Inc.) and the GC was temperature programmed as follows: 160° C for 1 min.; 5° C/min to 280° C; final hold for 5 min. Quantitation was performed using response factors for d-trans allethrin and pyrethrin as compared to 4,4'-dichlorobenzophenone developed with the standard solutions of these compounds.

RESULTS AND DISCUSSION

The sampling efficiency was tested by spiking a pair of sampling tubes with 25 ng d-trans-allethrin then drawing air through one of the tubes for four hours. Both tubes were then analyzed using the experimental protocol. This experiment was repeated twice, with both tests showing equal amounts of d-trans-allethrin remaining on the resin. This indicated that breakthrough would not be a problem at the sample volumes (breakthrough would have been indicated by less compound on the sampled resin). However, both showed a recovery of 130% as compared to two samples of one ml hexane spiked with the standards to which no Chromosorb resin was added. The reported results were not corrected for the apparent excess recovery.

Table 1. Concentrations (ng/m^3) determined in duplicate samples.

Time (days)	Series A #1	Series A #2	Series B #1	Series B #2
-0.1	n.d.	n.d.	n.d.	n.d.
0.1	71	49	104	95
1	*	*	22	19
3	7.9	6.7	6.7	8.4
6	3.1	4.1	*	*
10	2.9	n.d.	3.4	n.d.

*- sample not taken
n.d.- not detected

Each of the six test samples reported above were injected into the GC five times to determine the precision of the instrumental method. The results showed an average relative standard deviation of ±15%. All field samples were analyzed twice by GC with the average results reported. The precision of the entire analytical method was tested with side by side samplers set up at the vending machine site for two application cycles. These results are reported in Table 1. The good agreement between these paired samples is apparent.

The average concentration of allethrin at each sampling site at a given time interval from the application is shown in Table 2. Several points should be noted. First, even the highest detected concentration is well below the OSHA (1989) permissible exposure limit (PEL) which is 5 mg/m^3 for pryrethrum (a mixture of the natural pyrethrins). Although no value is listed for allethrin, LD_{50}'s for pyrethrin and d-trans-allethrin are quite similar (Merck Index 10th ed.), and therefore would likely have a similar PEL (the material data safety sheets supplied with the formulation lists an ACGIH TLV/TWA of $5mg/m^3$).

Table 2. Average d-trans-allethrin concentration at selected times after application of pesticide.

Time (days)	Site A[1] (ng/m^3)	Site B[2] (ng/m^3)
before	0.6	n.d.
0.1	48	15
1	11	n.d.
3	5.5	n.d.
6	0.9	n.d
10	1.0	n.d.
13	0.2	n.d.

n.d- not detected
1. Average of seven different application dates with sampler located by the back of the vending machines. All times were not sampled for each application.
2. Average of five different application dates with sampler in opposite corner of vending machines. All times not sampled for each application.

Air samples were taken following seven different pesticide applications. Although the applied chemical formulation contained pyrethrin as well as d-trans allethrin, no pyrethrin was detected in any air sample. Chromosorb 102 had previously been shown to be an effective sampling resin for pyrethrin (Thomas and Nishioka, 1985). The non-detection may be due to pyrethrins instability in the presence of light and air (Elliot and Janes, 1973; Holmstead et al. 1977).

Figure 1 shows how the indoor air concentration varied over time for a series of four pesticide applications at the vending machine site. Note how each application shows the same profile, a rapid rise in the indoor air concentration immediately after application followed by a gradual fall. Figure 1 also shows that Friday afternoon applications minimizes population exposure since, by the time classes are in session Monday morning, indoor air concentrations have almost returned

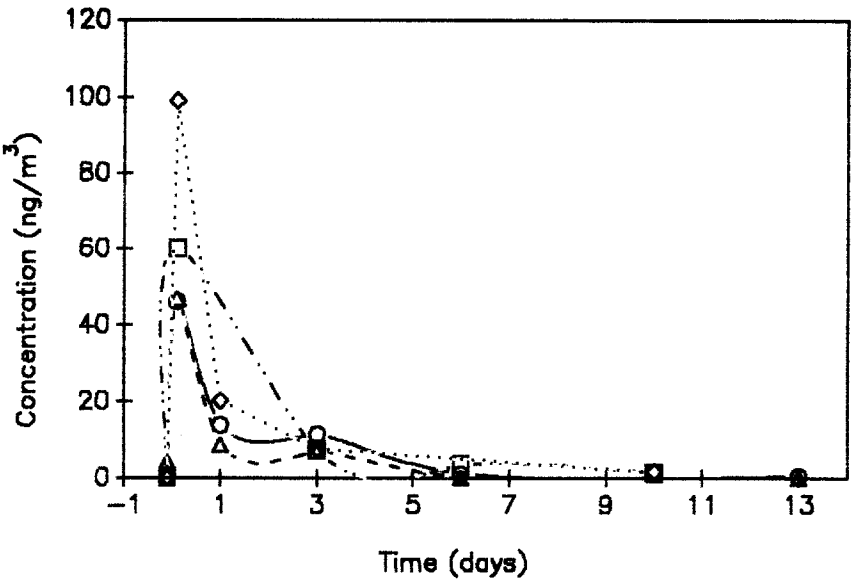

Figure 1. Concentration of d-trans-allethrin plotted as a function of time after the application of pesticide.

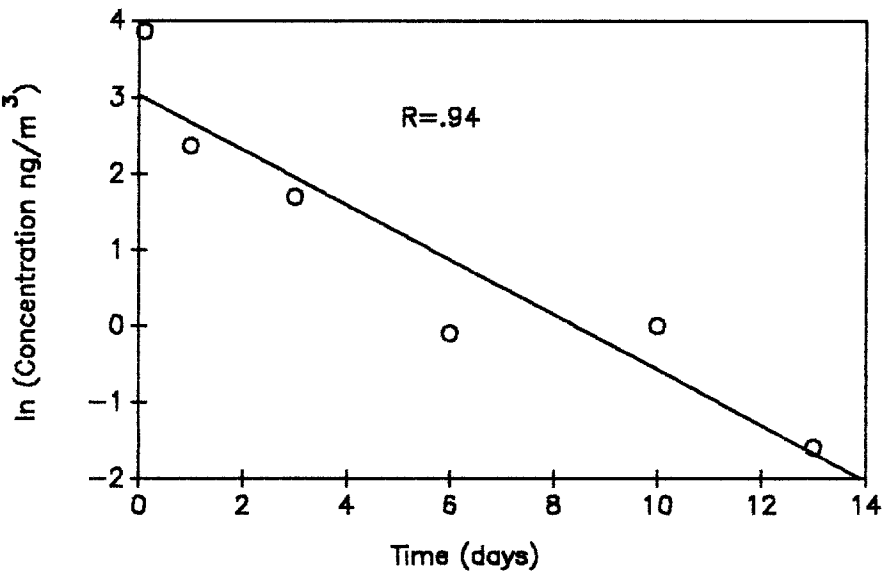

Figure 2. Linear regression of natural log of d-trans-allethrin concentration with time after application of pesticide.

to pre-application conditions. Some of the variability is likely the result of differences in the amount of pesticide applied, since this was a commercial application.

Second, there is an obvious difference between the two sites. Site A is by the vending machines, a likely pest problem area and has a greater amount of pesticide applied. The fact that the two sites within a single room show different concentration levels over a long period of time indicates that the measured air concentrations are a direct indication of the volatility of allethrin at the applied site. The decay of the airborne allethrin must be at a rate greater than that for the mixing of the indoor air.

One method of gauging the decay rate is to plot the natural log of the concentration over time. This is illustrated in Figure 2 (correlation coefficient R=0.94). The slope of the regression line was then used to determine that the d-trans-allethrin had a half-life of 1.9 days. Although it was not measured, it is likely that the air changeover in the room is more rapid. The differences between the two sites suggests that there are two different decay rates; a slow rate before the d-trans-allethrin volatilizes and a more rapid rate after it is airborne.

This report shows the concentration of d-trans-allethrin in indoor air following its application. The concentrations measured, and rapid decay of the airborne material, however, suggests that in these tests human exposure through a respiratory pathway would be a low.

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