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Insecticide Residues in the Ambient Air of Commercial Pest Control Buildings, 1993

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Data on the presence of certain organophosphates in the ambient air of commercial pest control buildings were first reported by WRIGHT and LEIDY (1980). Since then there has been little information published on the subject. Due to a major change in insecticides used and stored by commercial pest control firms since 1977 (eg. chlorinated and organophosphates) (WRIGHT and LEIDY 1980), a study was initiated to survey insecticides stored by firms and determine levels present in the ambient air of insecticide storage and office rooms.

MATERIALS AND METHODS

Insecticides in the storage rooms of 10 North Carolina commercial pest control firms were inventoried during February 1993. Five insecticide storage rooms were in buildings with the offices and 5 were in buildings separate from the offices. Bryon Model 90 air samplers (General Monitors, Inc., El Toro, CA) with Orbo 42 tubes (SUPLECO, Inc., Bellefonce, PA) were used to sample the ambient air during summer (Auqust) and winter (February). Two samplers,, calibrated to give a constant flow rate of 2L/min, were operated for 2 h (240L air) simultaneously in the office and insecticide storage room. of a company. Temperature and relative humidity were recorded.

Air samples were taken to the laboratory and analyzed for acephate, bendiocarb, chlorpyrifos, cypermethrin, diazinon, dichlorvos, malathion, permethrin, propoxur and resmethrin. The ORBO 42 tubes were scored with a cutter and front and rear portions of adsorbent were placed in separate 12 mL tubes. All samples were extracted with 10 mL of toluene:hexane:acetone (1.0:0.5:0.5) by vortexing the contents for 60 sec at 15-min intervals for 2.0 h, capping and allowing to sit overnight. Solvent was removed and filtered through a 0.45 µm pore-size Acrodisc (Gelman Sciences, Ann Arbor, MI). An additional 2.0 mL of extracting solvent were used to rinse the filter, and the combined extract was concentrated to 0.5 mL under a stream of dry N_2. Organophosphate insecticides were analyzed by GLC using a

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Hewlett Packard Model 5880A Gas Chromatograph equipped with an N/P detector, Model 7671A Autosampler and Level 4 Data Terminal. The column was a DB-5 fuzed silica wide-bore capillary (J&W Scientific, Folsom, CA), 30 m by 0.53 mm i. d. with a 1.5 µm film thickness. Helium was the carrier gas at flow rates of 4.1 mL/min (column) and 17.3 mL/min (detector). Gases to the detector were H_2 and air at flow rates of 4.5 and 60.9 mL/min, respectively. Samples were injected in the split mode from 2.0 mL vials containing a 250 µL glass insert. The split ratio was 34:1. A temperature program was run as follows: initial temperature, 140°C at 2.0 min then programmed to 250°C at 5°/min and held for 5.0 min. Data were quantitated by measuring the area of known concentrations of analytical standards and comparing them to samples.

Confirmations were performed on a Tracor Model 222 Gas Chromatograph equipped with an FPD operated in the phosphorous mode. The column was U-shaped glass (183 by 0.2 cm) packed with 1.5% SP-2250 + 1.95% SP-2401 on Supelcoport (100/120). Nitrogen was the carrier gas at a flow rate of 30 mL/min. Gases to the detector were H_2 and air at flow rates of 50 and 80 mL/min, respectively. Temperatures were as follows: oven, 175°C; detector, 190°C; inlet, 225°C. Data were quantitated by the peak-height method against standards of known concentration.

Pyrethroid insecticides were analyzed by HPLC using a Waters Model 590 Pump, Model 712 WISP Autosampler and Model 481 variable UV Detector operated at 214 nm and 0.1 AUFS. The column was a Waters C_{18} Radial Pak Cartridge (10 by 0.8 cm i. d.) (5 to 10 µm particle size) contained in a Waters Model 8x10 Module. The solvent system was CH_3CN:2-propanol:H_2O(l:l:O.5) at a flow rate of 1.2 mL/min. Samples were placed in 5.0-mL WISP vials containing a 250 µL insert. Injection parameters were as follows: standard injection volumes, 25 and 50 µL; standards injected after 5 samples; sample injection volume, 25 µL; run time, 15 min. Data were quantitated by the peak-height method against standards of known concentration.

To ensure that there were no unresolved components co-chromatographing with the C_{18} column, a C_8 Radial Pak column (10 by 0.8 cm) (5 to 10 µM particle size) using a solvent system of H_2O:CH_3CN:2-propanol (2:l:l)at a flow rate of 1.5 mL/min was used to quantitate and compare residue levels. All other chromatographic parameters remained the same. Although most values remained with 0.05 µg, large differences (ca. >0.2 µg) were resolved by subtracting the concentration differences from the two runs.

To determine the analytical efficiency of the methods used, the insecticides being studied were added in known amounts to opened ORBO tubes, the solvent was allowed to evaporate, and the tubes were extracted and analyzed with the sample sets. Two fortified ORBO tubes were analyzed with each sample set.

Data were analyzed by an analysis of variance (ANOVA). A Waller-Duncan k-ratio T test for variable: amount was performed to determine significant differences at the 5% levels.

RESULTS AND DISCUSSION

Forty-one insecticides were inventoried in the 10 insecticide storage rooms (TABLE 1). The minimum number of insecticides present in a company was 10, with an average of 21. The number of insecticides present varied from one container in one facility to their being present in all of the storage facilities inventoried. Frequently there were several different formulations of an insecticide present in a storage room. Some containers of insecticide were recently purchased, while others, by their appearance, appeared to have been in stock for a number of years. Quantities of an insecticide formulation in stock varied from < 236 mL to many liters.

Table 1. Insecticides inventoried in storage rooms of 10 North Carolina commercial pest control companies, 1993.

Insecticide	No. companies with insecticide in storage rooms
Chlorpyrifos, pyrethrins	10
Bendiocarb, Diazinon	9
Hydramethylnon	8
Boric acid, cyfluthrin, methroprene, resmethrin	7
Lambda-cyhalothrin	6
Acephate, cypermethrin, dichlorvos, malathion, propoxur, silica gel	5
Allethrin, carbaryl, fenoxycarb, lindane, sulfuramid	4
Abamectin, borates, hydroprene, methomyl	3
Demise, dimethoate, dicofol, Di-Syston, esfenvalerate, permethrin, propetamphos	2
Bifenthrin, chlorobenzilate[a], cycloprate[a], dioxathion, isofenphos, rotenone, sodium fluoride, sumithion trichlorfon	1

[a]Production and sale discontinued in the United States.

Recoveries from ORBO 42 tubes, fortified with the various insecticides, are shown in TABLE 2. Recovery ranges for varied individual insecticides, but all were in the 80 to 90 percent range.

The presence of minute quantities of insecticides were found in the ambient air of office and insecticide-storage rooms by company, season and insecticide. Even with the minute quantities there was range in levels detected for a number of the insecticides. Several factors may have influenced these levels, or vapor pressure of insecticide, spillage of concentrate or diluted formulation while transferring between containers and transfer to an office room via a person's body, clothing or shoes following their contamination in the insecticide storage room.

When all air sample data were combined higher (P=0.01) insecticide levels were detected in the summer than winter and in storage over office rooms. There was no difference in insecticide levels in the air of office rooms with the insecticide storage room in the same building or in a different building.

Table 2. Recoveries of insecticides from fortified sampling tubes.[a]

Insecticide	No. Samples	Amount added (µg)	Amount found (µg)	Recovery (%)
Acephate	8	0.5 - 5.0	0.35 - 4.8	92
Bendiocarb	6	0.5 - 5.0	0.38 - 4.7	88
Chlorpyrifos	8	0.5 - 5.0	0.45 - 4.9	94
Cypermethrin	8	0.5 - 5.0	0.49 - 4.9	86
Diazinon	8	0.5 - 5.0	0.49 - 4.9	95
Dichlorvos	6	0.5 - 5.0	0.39 - 4.7	84
Malathion	8	0.5 - 5.0	0.40 - 4.8	90
Permethrin	8	0.5 - 5.0	0.39 - 4.6	87
Propoxur	6	0.5 - 5.0	0.37 - 4.8	89
Resmethrin	8	0.5 - 5.0	0.41 - 4.8	91

[a]Analytical-grade standards added to Orbo 42-tube contents, contained in 12-mL tubes, solvent allowed to evaporate for 2 h and extracted with the sample sets. Two sets of recoveries analyzed with each set of samples from 5 pest control firm offices and storage areas.

The highest insecticide level detected was 14 µg/m^3 for resmethrin in an insecticide storage room during summer. The air sample taken concurrently in the office room of the firm contained the highest level, again resmethrin, at 5 µg/m^3. Pyrethroid insecticides are often persistent and remain for long periods of time, A study of the persistency of permethrin and fluvalinate residues on tobacco, flue-cured by conventional means showed losses averaging 65% during a process where leaves are heated gradually to temperatures of ca. 65°C (Leidy et al 1986). In addition, small quantities of cypermethrin were detected (ca. 0.2 µ/m^3) in a controlled study in a dormitory 84 days after application (Wright et al 1993). Organophosphate insecticides generally show losses of 99+% during the flue-curing process. Thus, it is possible that amounts of the pyrethroids, adsorbed to the outside of containers or on floors or walls could contribute to the levels seen in this study. It is interesting that no bendiocarb or propoxur were detected in the samples since they were present in the insecticide storage rooms of 9 and 7 companies, respectively. The failure to detect these 2 insecticides could have been due to infrequent use and/or small quantities in stock. Bendiocarb has been detected at 24 h, but not at 48 h following its application in rooms for pest control while all of the other insecticides have been detected in the air for longer periods of time (WRIGHT et al 1981). Insecticide level differences (P-0.05) in the air were detected for 3 of the

Table 3. Insecticides (µg/m^3) detected in the ambient air of insecticide storage and office rooms of commercial pest control buildings in a 2 h period during winter and summer.[a,b,c]

	Acephate				Bendiocarb				Chlorpyrifos				Cypermethrin			
	Summer		Winter		Summer		Winter		Summer		Winter		Summer		Winter	
Company	O	S	O	S	O	S	O	S	O	S	O	S	O	S	O	S
Office and insecticide storage rooms in one building																
A	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	.70	2.75	.64	1.52	NP	NP	NP	NP
B	.74	2.57	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	.07	.27	.27	.48	NP	NP	NP	NP
C	NP	NP	NP	NP	NP	NP	NP	NP	P	2.94	.36	.34	NP	NP	NP	NP
D	.05	1.88	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	2.94	.65	.60	.36	1.2	11.66	P	P
E	<0.01	<0.01	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01	.60	.07	2.4	4.15	P	.02
Office and insecticide storage rooms in one building																
F	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	.14	.07	<0.1	.05	.16	2.82	P	.47
G	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	.02	.48	.49	.52	NP	NP	NP	NP
H	.53	.16	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	.61	1.75	.85	.21	NP	NP	NP	NP
I	.17	3.03	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	.83	1.90	.87	.07	P	P	P	P
J	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	<0.01	.68	.20	.06	<0.01	<0.01	.01	.02

[a]When all samples were combined there was more (P=0.05) insecticide detected in storage than office rooms.- With additional replicates there should have been more in summer than winter (P=0.07). No difference in levels were detected in either type of room where insecticide rooms were in the same or different buildings.

[b]O=office room, S=Insecticide storage room.

[c]NP=insecticide not present in the insecticide storage room nor above the detectable level in air.

[d]Insecticide not inventoried in the insecticide storage room, but detected in the air of the insecticide storage or office room.

Table 3 (cont.). Insecticides (μg/m³) detected in the ambient air of insecticide storage and office rooms of commercial pest control buildings in a 2 h period during winter and summer.[a,b,c]

Company	Diazinon				Dichlorvos				Malathion			
	Summer		Winter		Summer		Winter		Summer		Winter	
	O	S	O	S	O	S	O	S	O	S	O	S
Office and insecticide storage rooms in one building												
A	.36	.48	.05	.07	NP	NP	NP	NP	<0.01	.40	.02	.03
B	.13	.25	.04	.36	<0.01	.34	0.01	0.01	NP	NP	.04	1.33[d]
C	NP	NP	.02	.01	NP	NP	NP	NP	<0.01	7.75	<0.01	<0.01
D	<0.01	<0.01	.11	.11	4.18	2.35	.06	.04	3.57	1.56	<0.01	<0.01
E	<0.01	<0.01	.06	<0.01	NP	NP	NP	<0.01	<0.01	<0.01	<0.01	<0.01
Office and insecticide storage rooms in different buildings												
F	.05	<0.01	.02	.02	NP	NP	NP	NP	NP	NP	NP	NP
G	<0.01	.03	.13	.13	<0.01	<0.01	.01	.37	NP	NP	NP	NP
H	.04	.09	.05	.12	NP	NP	NP	NP	NP	NP	NP	NP
I	<0.01	<0.01	.11	.16	8.28	6.98	.01	<0.01	<0.01	<0.01	<0.01	<0.01
J	<0.01	<0.01	<0.01	<0.01	<0.01	2.51	NP	NP	<0.01	3.00	NP	NP

[a]When all samples were combined there was more (P=0.05) insecticide detected in storage than office rooms. With additional replicates there should have been more in summer than winter (P=0.07). No difference in levels were detected in either type of room where insecticide rooms were in the same or different buildings.

[b]O=office room, S=Insecticide storage room.

[c]NP=insecticide not present in the insecticide storage room nor above the detectable level in air.

[d]Insecticide not inventoried in the insecticide storage room, but detected in the air of the insecticide storage or office room.

Table 3 (cont.). Insecticides (µg/m³) detected in the ambient air of insecticide storage and office rooms of commercial pest control buildings in a 2 h period during winter and summer.[a,b,c]

Company	Permethrin				Propoxur				Resmethrin			
	Summer		Winter		Summer		Winter		Summer		Winter	
	S	O	S	O	S	O	S	O	S	O	S	O
Office and insecticide storage room in one building												
A	2.34	.20	<0.01	.05	NP	NP	NP	NP	NP	NP	NP	NP
B	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	<0.01	.59	<0.01	<0.01
C	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	NP	NP	NP	NP
D	<0.01	1.94	<0.01	<0.01	NP	NP	NP	NP	<0.01	<0.01	<0.01	<0.01
E	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP
Office and insecticide storage rooms in different buildings												
F	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	<0.01	.31	<0.01	<0.01
G	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	<0.01	.63	<0.01	<0.01
H	NP	NP	NP	.03[d]	<0.1	<0.1	<0.1	<0.1	<0.01	2.18	<0.01	<0.01
I	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	14.10	5.22	<0.01	<0.01
J	NP	NP	NP	NP	<0.1	<0.1	<0.1	<0.1	<0.01	1.09	<0.01	<0.01

[a]When all samples were combined there was more (P=0.05) insecticide detected in storage than office rooms. With additional replicates there should have been more in summer than winter (P=0.07). No difference in levels were detected in either type of room where insecticide rooms were in the same or different buildings.

[b]O=office room, S=Insecticide storage room.

[c]NP=insecticide not present in the insecticide storage room nor above the detectable level in air.

[d]Insecticide not inventoried in the insecticide storage room, but detected in the air of the insecticide storage or office room.

insecticides. Dichlorvos levels were higher in summer than winter and cypermethrin and diazinon levels were higher when the office and insecticide storage rooms were in the same building than when in different buildings. Large variances in detected levels dictated the absence of other differences.

Table 4 gives mean levels detected for all samples of individual insecticides. The total number of air samples available for analysis by insecticide ranged from 10 (permethrin) to 40 (chlorpyrifos). Detected levels ranged from highest for resmethrin to lowest for the carbamates. Large standard errors in detected levels for individual insecticides precluded additional significant differences.

Table 4. Mean insecticide quantity detected in the ambient air of company rooms, with all air samples for an insecticide combined[a].

Insecticide	No. samples	Air level (ug/m^3)
Dichlorvos	17	1.48[a]
Cypermethrin	20	1.15[a,b]
Resmethrin	28	0.86[a,b]
Malathion	23	0.77[a,b]
Chlorpyrifos	40	0.75[a,b]
Acephate	20	0.46[a,b]
Permethrin	10	0.45[a,b]
Diazinon	38	0.08[b]
Bendiccarb	36	0.00[b]
Propoxur	28	0.00[b]

[a]Analysis by Waller-Duncan k-Ratio T test for variable: amount. Values with different letters are significantly different (P=0.05).

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