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Analysis of Airborne Pesticides in a Commercial Pesticide Storage Building

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A large number of pesticides, formulated into a variety of mixtures, are usually stored in commercial storage buildings prior to their sale and use. Regardless of the formulation, it has been shown that some pesticides do enter and contaminate the air in the storage facilities (Elgar and Steer 1972; Winnett and Siewierski 1975; Wright and Jackson 1976; Ware and Cahill 1978; Wright and Leidy 1978; 1980; Wehner 1982). Since pesticides vary in toxicity, the presence of a complex mixture of airborne pesticides could constitute a serious health hazard to workers in those buildings.

Studies to detect and quantify airborne pesticides in storage buildings often tend to be limited to a few selected chemicals (Wright and Leidy 1980). This may be partly due to the lack of an appropriate analytical tool to conduct a blanket analysis of a complex mixture of pesticides likely to be airborne in those buildings. There is also the added problem that low volume air samplers may not be efficient enough to trap measurable amounts of pesticides. On the other hand, high volume air samplers provide relatively large samples, with short sampling times and concentrate extremely small quantities of airborne pesticides (Seiber and Woodrow 1975).

In this paper we report results of studies on the monitoring of airborne pesticides in a storage building using high volume air samplers. Our aim was to determine only chemicals that are absorbed on XAD-4 and/or XE-340 resins.

MATERIALS AND METHODS

Reagents and materials were analytical grade (Baker Resi-grade) and were used as received. XAD-4 resin was cleaned prior to use by the method of Hermann and Seiber (1981), while XE-340 resin was cleaned as follows. Dry XE-340 resin (500 mL) was soaked in 1 L methanol for 10 min. The supernate was decanted and the washing in methanol was repeated. The resin was then Soxhlet extracted with 6% ethyl ether in hexane for 24 hr (or 48 cycles). After the extraction, the resin was dried at room temperature for 30 min and stored in brown jars sealed with aluminum foil-lined caps.

Two high volume air samplers (Staplex model TF 1A) were set up inside an agricultural services building located in the Sacramento Delta area. The building serves the farming community in the area and had various quantities of over 40 different pesticides in stock.

XAD-4 (or XE-340, 100 mL in each case) was used in each air sampler, which was operated at a rate of 60 m^3 of air/hr for 3 hr. The samplers were placed on a table about 24" above the concrete floor inside the building. A resin blank (100 mL XAD-4 or XE-340) was brought to the building but was not removed from the bottle prior to analysis. A control sampler, with 100 mL of corresponding resin was collected at a farm about one mile from the storage facilities. The samples were collected in early spring when most farms were not under cultivation.

After the sampling period, the resin was transferred to amber bottles, which were capped with aluminum foil-lined caps. The samples were returned to the laboratory and stored at room temperature until extraction, about 2 1/2 hrs later.

The resin was extracted by gyrotory shaking for 90 min with 200 mL ethyl acetate. The extraction process was repeated with two 100 mL volumes of ethyl acetate, each time shaking for 60 min. After the last extraction, the resin from each sample was transferred to a filter and was rinsed with several aliquots of ethyl acetate totaling 150 mL. The combined filtered extracts from each sample were concentrated to 5 to 10 mL in a 1 L round bottom flask using a rotary evaporator at 40°C. The concentrated extract was quantitatively transferred to 15 mL screw (Teflon lined) centrifuge tubes. The extract was then concentrated to 0.5 mL under a stream of nitrogen (at 35°C) and analyzed by a gas chromatograph equipped with a nitrogen phosphorus detector (GC-NPD), and/or a gas chromatograph-mass spectrometer (GC-MS).

A Hewlett-Packard model 5710A GC-NPD equipped with a 30 m DB-1 capillary column (J & W Scientific) was used for most of the study. The carrier gas, He, had a flow rate of 1.5 mL/min, and a split ratio of 111:1. Flows to the detector were: H_2 at 3, air at 40 and makeup He at 35 mL/min. Operating temperatures were: injector and detector, 200°C each; column, isothermal at 190°C. The attenuation was set on the HP 3390A recording integrator at 2°, while chart speed was 0.5 cm/min. Each injection had a volume of 2 µL.

All GC-MS analyses were performed on a Finnigan (Sunnyvale, CA) 3200 GC-mass spectrometer equipped with a Model 6000 data system. Chromatographic separations were accomplished by using a 25 m DB-5 capillary column operated isothermally at 190°C. Injector temperature was 230°C. Injections (3 µL) were made on a split mode of 35:1. Mass spectrometer operating parameters were the following: scan time, 2.16 sec; multiplier voltage, 1600 v; electron energy, 70 v. Total ion chromatograms were collected and individual compound spectra were manually compared with computerized library

mass spectra to provide and/or confirm qualitative identifications. All quantitative measurements were made relative to respective authentic standards.

RESULTS AND DISCUSSION

The estimated levels of compounds identified in the ambient air of the commercial pesticide storage building are summarized in Table 1. The building was of wooden frame construction, and the space which served as the storage room for pesticides had the dimensions of 12.2 × 12.2 × 3.7 m (40 × 40 × 12 ft). The temperature inside the building was 22°C but increased gradually to 24°C during the 3-hr sampling period. The pesticides were either scattered on 30% of the floorspace in the storage room or on shelves on the walls of the building.

The storage room was well ventillated and isolated from the work area. The office was also separated from the storage room by an empty room whose doors both to the office and the storage room remained closed throughout the sampling period. No attempt was made, however, to sample the ambient air in the office for pesticide residues.

There was a characteristic odor of pesticides in the building throughout the sampling period. Only eight of the 43 pesticides inventoried (Table 2) were detected and quantified. All the compounds identified were stored in the building at the time air samples were taken. Airborne residues of pesticides previously stored in the building, such as DDT, chlordane, parathion, etc., but not on the current inventory were not detected. It therefore appears that residues of such pesticides do not remain airborne in detectable levels for extended periods under these conditions.

Table 1. Pesticides detected in the ambient air of a commercial pest control building in a 3-hr period.

Substance	Type of Formulation	Amount Detected (ng/m^3 air)
Methomyl	Liquid concentrate	13.7
Tillam	Liquid concentrate	10.7
Eptam	Wettable powder	20.0
Captan	Wettable powder	108.0
Sulfur	Dust	233.6
PCNB	Dust	1,560.0
Orthene	Soluble powder	15.0
N-Serve (nitrapyrin)	Liquid concentrate	18.0

Table 2. Inventory of chemical pesticides in a commerical pesticide storage building within the period March 1, 1983 to April 8, 1983.

Aflatox (Methoxychlor / Diazinon)	Isotox Seed Treater (BHC)
Atrazine	Karmex (Diuron)
Balan (Benfluralin)	Krenite (Fosamine / Ammonium)
Banvel (Dicamba)	Lasso (Alachlor)
Bayleton (Triademephon)	Malathion
Bladex (Cyanazine)	Meta-Systox
Butoxone	Monobor Chlorate
Captan	Notron (Ethofumesate)
Chem Hoe (Propham)	N-Serve (Nitrapyrin)
Desmedipham (Betanex)	Nudrin (Methomyl)
Dibrom	Nutrasol
Difolatan	Orthene
Diphenamid	PCNB
Disyston (Disulfoton)	Pyramine (Chloridazon)
Dithane (Maneb)	Ramik (Diphacinone)
Dowfume MC2 (methyl bromide)	Ro-Neet (Cycloate)
Enid (Dinoseb / Diphenamid)	Roundup (Glyphosate)
Eptam	Sevin (Carbaryl)
Furadan (Carbofuran)	Sulfur
Furloe (Chloro-1PC)	Sutan
Hyvar (Bromacil)	Tillam (Pebulate)
	Treflan (Trifluralin)

The detected pesticides were in different formulations as shown in Table 1. Generally, the levels of the pesticides identified in the air were appreciably low except for sulfur, captan and PCNB. The higher levels of these latter compounds suggest that the ambient air of the storage building under study had more pesticide residues bound to particulate matter than those vaporized from liquid formulations. Residues of pesticides which were detected at relatively lower ambient air concentrations were all liquid formulations and were stocked in very high quantities. However, the low airborne levels of the liquid formulated pesticides, and the fact that none of the remaining 35 pesticides was detected in the ambient air, could not be due to the inefficiency of the trapping media for pesticide vapors.

The sampling module used in this study has been shown to yield recoveries ranging from 67-110% for most of the pesticides on inventory in the pesticide storage facility (Seiber et al. 1980; Wehner 1982). Thus from a preliminary evaluation, it was apparent that airborne levels of most of the pesticides were too low to be detected.

The detection of high amounts of airborne captan was not unexpected since a bag containing the pesticide was open throughout the sampling period. Of the eight pesticides detected and quantified,

only methomyl was trapped by both XE-340 and XAD-4 resins. The others were all trapped in the XAD-4 media. There was, however, no significant difference in the methomyl concentrations in samples collected on the XE-340 and XAD-4 resins.

Table 3 shows the threshold limit values (TLV) of three pesticides compared to the amounts detected in this study. Levels of these three pesticides measured in the ambient air of the commercial pesticide storage building were far below the allowable limits. Corresponding values for the remaining five pesticides detected were not available for comparison.

Table 3. Threshold Limit Values (TLV) of three of the pesticides detected compared to the amount detected to be airborne in the pesticide warehouse.

Pesticide	TLV-TWA[a] ($\mu g/m^3$)	Detected in warehouse[b] ($\mu g/m^3$)
Methomyl	2,500	0.18
Captan	5,000	1.44
N-Serve	10,000	0.24

[a] Threshold Limit Values - Time Weighted Average: Time weighted average concentration for a normal 8-hr workday or 40-hr work week (American Conference of Governmental Industrial Hygienists 1982).

[b] Actual level detected in warehouse is converted from a 3-hr sampling period to a 40-hr work week.

Wehner (1982) found airborne concentrations ranging from 3.1-15.0 ng/m^3 for diazinon, methyl parathion, ethothrop and malathion in an institutional pesticide storage building. Wright and Leidy (1980) also reported ambient air concentrations ranging from 128-617 ng/m^3 air for diazinon, malathion, DDVP and Chlorpyrifos, in the storage room of a commercial pest control building. Airborne pesticide levels observed in this study were comparable.

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