Bull. Environ. Contam. Toxicol. (1984) 33:476–483

Bulletin of Environmental Contamination and Toxicology

Sampling Efficiency of Five Solid Sorbents for Trapping Airborne Pesticides

E. M. Roper[1] and C. G. Wright[2]

[1]Pesticide Residue Research Laboratory and [2]Entomology Department, North Carolina State University, Raleigh, NC 27650

Air is an important mode of human exposure to organic pesticides. This is especially true when pesticides are used to control insect infestations or prevent damage to private dwellings and other structures frequented by man. As interest in the pollution of air by pesticides from both agricultural and structural pest control applications has increased, several different methods have been developed to trap and measure the amounts of pesticides in air (Vandyk and Visweswariah 1975, Lewis 1976, Seiber et al. 1975).

A number of different column packing materials for gas-liquid chromatography (GLC) have been utilized to collect pesticide vapors in the air. Melcher et al. (1978) found that GC-Durapak and Carbowax 400/Porasil F were about 95% efficient for collecting chlorpyrifos in the air. Russell (1975) tested Tenax GC resin and C_{18} (Porpak R and Porpak N) by direct thermal desorption to a GLC to measure airborne levels of chlorpyrifos and ronnel. C_{18} packing was also used by Hinkle et al. (1979) and Jackson & Lewis (1979) to measure levels of propoxur and methyl parathion in the air. Thomas and Jackson (1980) used chromosorb 102 to collect chlordane vapors and compared its sampling efficiency with ethylene glycol in an impinger. Chromosorb 102 has also been used to collect chlordane in military housing treated for termites (Lillie 1981).

Another solid sorbent, polyurethane foam, has been utilized in testing for a wide range of organic vapors, including pesticides (Lewis et al. 1977). It has been used to measure levels of a number of insecticides in the air of buildings and vehicles (Leidy et al. 1982, Wright et al. 1982). Wright & Leidy (1982) have utilized polyurethane foam to trap chlordane and heptachlor vapors in houses treated for termites.

Yobs (1971) recommends that for any air sampling study to be meaningful the efficiency of the sampling system must be verified. This had not been done with the methods of Leidy et al. (1982), Wright & Leidy (1982) and Wright et al. (1982). The purpose of

*Correspondence and reprint requests.

this study was, therefore, to determine and compare using these systems, the trapping efficiencies of 5 solid sorbents with 5 pesticides commonly applied in structural pest control.

MATERIALS AND METHODS

Trapping materials (sorbents) were as follows: Polyurethane foam diSPo plugs (16-22 mm OD X 32-35 mm height, American Scientific Products, McGaw Park, IL 60085), Chromosorb 102 (80/100 mesh, Johns Manville, Celite Division, Denver, CO 80217), Porpak C_{18} (5-10 um diameter, Waters Associates, Milford, MA 01757), Carbowax 20M on Gas Chrom Q (80/100 mesh), and Tenax GC (20/35 mesh, Applied Science Laboratories Inc., State College, PA 16801). Before use, batches of 10 polyurethane foam plugs were washed by soxhlet extraction in 250 mL acetone:hexane (1:1) and allowed to air dry. Chromosorb 102 was prewashed by placing 20 g of the sorbent in 100 mL of hexane and stirring for 1 min. The hexane was filtered through glass wool and the sorbent was placed in a 500 mL boiling flask and dried at 40°C under vacuum. All other sorbent materials were used as received from the manufacturer.

Diazinon, chlorpyrifos, chlordane, propoxur and resmethrin were analytical standards obtained from the EPA repository, Research Triangle Park, NC 27711. Standard concentrations for each pesticide were diluted as follows: diazinon 1.122 mg/mL (ethyl acetate), chlorpyrifos 1.000 mg/mL (ethyl acetate), chlordane 0.984 mg/mL (ethyl acetate), propoxur 1.123 mg/mL (acetonitrile) and resmethrin 1.108 mg/mL (ethyl acetate). For all analyses, diazinon, chlorpyrifos and chlordane were extracted and stored in ethyl acetate, while hexane was used with resmethrin and propoxur. Both solvents were glass distilled and the hexane was HPLC grade.

The air sampling system (trap) consisted of an 11 mL polypropylene disposable column (Biorad Econo-Column, Bio-Rad Laboratories, Rockville Centre, NY 11571) packed with 2 cc of one of the packing materials or with a polyurethane diSPo plug. The trap was attached to a personnel-type air pump (Monitaire Sampler, Model S, Mine Safety Appliances Co., Petersburg, PA 15208) with Tygon tubing.

Recovery (extraction) efficiencies for the 5 pesticides from each of the 5 sorbents were determined by applying 9.0 uL of a pesticide standard to a trap of each sorbent type. The trap was allowed to stand for 30 minutes in order for the carrier solvent to evaporate. Each pesticide-sorbent combination was replicated 3 times.

Polyurethane foam plugs were extracted by soaking 3 times for 10 min in 50 mL of the appropriate solvent in a 200 mL beaker, squeezing 3 times with a glass rod. The solvent was placed in a 500 mL boiling flask, and the beaker was rinsed with three 5 mL portions of the solvent. The washings were added to the extract,

and the pesticide residues were concentrated under reduced pressure at 40°C. The pesticide residues were rinsed from the flask with 10 mL of the appropriate solvent and stored for chromatographic analysis. The GC column packings were extracted by placing 10 mL of the appropriate solvent in the column (trap) and filtering it through the packing. The filtrate was collected and stored for analysis. Propoxur and resmethrin extracts were reduced to a volume of 2 mL under a stream of nitrogen. Analysis of the other pesticides was done from the 10 mL volumes as collected. Residues recovered were compared with solvent samples of known concentration.

Retention efficiencies for the 5 sorbents with the 5 pesticides were determined by placing 9.0 uL of each pesticide standard on the sorbent in a trap and then pumping air through the trap for 1 h at the rate of 2.8 L/min (0.168 M^3). Each pesticide-sorbent combination was replicated 3 times. The pesticides were extracted as described above and the amount of pesticide remaining in a trap was compared with samples of known concentration.

Sampling efficiencies for the 5 sorbents with each pesticide were determined by means of a closed system in which pesticide vapors were generated in the air stream in front of the sorbent. Pesticide vapors were generated in a 7 cm piece of glass tubing inserted into a rubber stopper fitted into the mouth of the trapping column. A small glass wool plug was inserted in the glass tubing and the pesticide standard was placed on the glass wool. The system was allowed to stand for 30 minutes before pumping to allow the carrier solvent to evaporate. Air was pumped through the system for 1 h at 2.8 L/min. Because of its high vapor pressure, resemethrin vapors were generated by wrapping the glass vapor generating tube with heat tape and heating the tube to 130°C. The 5 sorbents were assigned to 5 pumps in a latin square design. A different pesticide was tested each day of the week with all 5 sorbents, with 5 weeks as replications.

Extraction efficiency for the glass wool and vapor generating tube was determined by placing 9.0 ul of the pesticide standards on the wool, allowing the carrier solvent to evaporate and then extracting the pesticide by pouring 10 mL of solvent through the tube and glass wool. The solvent was collected and the amount of pesticide recovered was compared with fortified samples. The extraction procedure was repeated 3 times for each insecticide.

The amount of pesticide which evaporated from the glass wool was determined by extracting the glass wool and glass tube and comparing the amount of pesticide recovered with the amount originally applied to the glass wool. Comparison was made using fortified solvent samples.

To determine the sampling efficiencies the pesticides were extracted from the traps as described for the extraction study. The sampling efficiency of each sorbent for the 5 pesticides was

calculated by dividing the amount of pesticide recovered from the trap by the amount of pesticide which had evaporated from the glass wool in the vapor generating tube.

Analysis of diazinon and chlorpyrifos was by gas-liquid chromatography (GLC) using a Tracor Model 222 GLC equipped with a flame photometric detector operated in the phosphorus mode. The column was U-shaped glass (1 M X 0.2 cm ID) packed with 4% SE-30 + 6% OV-210 on Gas Chrom Q (60-80 mesh). The carrier gas was nitrogen with a flow rate of 55 mL/min. Hydrogen and air flow to the detector were 45 and 100 mL/min respectively. Temperature conditions were as follows; oven:175°C, detector:180°C, inlet:200°C. Pesticide levels were quantitated using the peak height method compared with standards of known concentration.

Resmethrin and propoxur were analyzed by high performance liquid chromatography (HPLC) using a Waters Associates M-45 pump and a Waters Associates WISP 710B autosampler. The column, 25 cm X 0.8 cm ID Radial-Pak B (C_{18}, 5-10 um diameter), was connected to a Schoeffel Model 770 UV/VIS detector with an 8 uL capacity flow cell set at 223 nm, 0.04 AUFS. The liquid phase was acetonitrile:water:isopropanol (2:1:1) at a flow rate of 2 mL/min for resmethrin and 1.2 mL/min for propoxur. There was no resolution of cis and trans isomers for resmethrin. Quantitation was by the peak height method compared to standards of known concentration.

A randomized analysis of variance was used to determine differences between the trapping efficiencies of the 5 sorbents for the 5 pesticides. Comparison of the sampling efficiency of individual sorbents with selected pesticides was made using the students t-test.

RESULTS AND DISCUSSION

Pesticide recovery from the glass wool and glass tube was 100% for diazinon, chlordane, propoxur and resmethrin and 92% for chlorpyrifos. The mean percent evaporation of the 5 pesticides with their respective standard errors and the equivalent ug of pesticide per M^3 of air generated in the closed system are shown in Table 1.

Table 1. Evaporation of the 5 pesticides from the vapor generating tube

Pesticide	Percent Evaporation	ug Evaporation	Equivalent ug/m^3
Chlorpyrifos	80.6 ± 12.6[a]	14.1 - 18.2[b]	96.0
Chlordane	84.7 ± 8.7	15.2 - 18.1	99.2
Diazinon	93.7 ± 4.8	20.0 - 22.0	125.1
Propoxur	45.1 ± 19.0	8.2 - 12.1	60.3
Resmethrin	57.7 ± 14.8	10.9 - 14.7	76.1

[a] ± SE of 25 values
[b] Range of 25 values

Table 2. Percent extraction, retention and sampling efficiencies of 5 solid sorbent materials with 5 insecticides.[a]

		C_{18}	Carbowax GC	Chromosorb 102	Polyurethane Foam	Tenax GC	Mean for Insecticides
	E	88	89	112	99	89	95 ± 10[b]
Chlorpyrifos	R	94	99	95	88	113	98 ± 12[b]
	S	101	86	95	92	75	90 ± 14[c]
	E	99	101	100	101	98	100 ± 2
Chlordane	R	102	69	98	100	100	94 ± 13
	S	100	58	104	89	81	86 ± 18
	E	91	97	100	81	99	94 ± 13
Diazinon	R	104	28	111	94	112	90 ± 33
	S	92	44	92	86	73	77 ± 20
	E	93	99	105	130	97	105 ± 18
Propoxur	R	87	141	97	107	130	112 ± 23
	S	33	85	100	85	83	77 ± 20
	E	126	117	88	115	103	110 ± 17
Resmethrin	R	103	96	90	95	90	95 ± 9
	S	94	56	83	79	53	73 ± 24
Mean for	E	100 ± 17[b]	101 ± 11	101 ± 13	105 ± 19	97 ± 9	
Sorbents	R	98 ± 12[b]	87 ± 39	99 ± 8	97 ± 10	109 ± 15	
	S	84 ± 29[c]	66 ± 20	95 ± 12	86 ± 15	73 ± 18	

[a]E = Extraction efficiency, R = Retention efficiency, S = Sampling efficiency
[b]SE of 15 values
[c]SE of 25 values

The mean recovery (extraction), retention and sampling efficiencies for the 5 sorbents with the 5 pesticides are shown in Table 2. The significance level for all comparisons was 5%. There was no significant difference between the mean recoveries for the sorbents with all the pesticides. Recovery of resmethrin from the sorbents was significantly higher than for chlorpyrifos and diazinon.

There was no significant difference between the retention efficiency of the 5 sorbents. For the pesticides, propoxur was retained at a significantly higher percentage than resmethrin. There was no significant difference between the retention of the other pesticides on the five sorbents.

Chromosorb 102 was a significantly better sampling agent than Tenax GC and Carbowax GC for the 5 pesticides studied. Polyurethane foam was a significantly better trapping agent than Carbowax GC for all 5 pesticides. Chlorpyrifos was trapped at a significantly higher percentage than resmethrin by all the sorbents. The other pesticides were trapped with similar efficiencies by all 5 sorbents.

Carbowax GC and Tenax GC had significantly lower sampling efficiencies for sampling the 3 most volatile pesticides, diazinon, chlorpyrifos and chlordane, than the remaining sorbents and therefore they will not be considered further.

For diazinon and chlorpyrifos there was no significant difference between the sampling efficiencies of the three remaining sorbents. Herman et al. (1978) found a sampling efficiency of 50% when polyurethane foam was used to collect diazinon vapors at flow rates of 1 M^3/min. The increased sampling efficiency of diazinon by polyurethane foam, 90% in this study, was probably due to the lower volume of air (2.8 L/min) passing through the sorbent material.

The sampling efficiency of C18 was not significantly different from chromosorb 102 and polyurethane foam for chlordane. Chromosorb 102, which has been used extensively by the United States Air Force to measure chlordane levels in base housing (Lillie 1981, Livingston & Jones 1981), was significantly better at trapping chlordane than was the polyurethane foam. At high sampling volumes (200-250 L/min) Jackson and Lewis (1979) found no difference in the sampling efficiencies of chromosorb 102 and polyurethane foam. Though chromosorb 102 may be more efficient than polyurethane foam for sampling chlordane vapors at low sampling volumes it has the disadvantage of giving some interferences with GLC analysis even after it has been pre-cleaned. Chromosorb 102 can be spilled during transport and use and tends to become more densely packed during pumping, thus requiring more frequent adjustment of the pumping rate. This results in a poorer estimate of the total volume of air sampled. Polyurethane foam has the advantage of lower initial cost and it can easily be

reused. Because of these factors it is felt that polyurethane foam may be the sorbent of choice for sampling chlordane vapors in the field.

Acknowledgments. Paper No. 9100 of the Journal Series of the N.C. Agric. Res. Serv., Raleigh NC 27650. Use of trade names in this publication does not imply endorsement of the products named or criticism of similar ones not mentioned. Part of a dissertation submitted to the faculty of North Carolina State University by E. M. Roper in partial fulfillment of the requirements of a Ph.D. in entomology.

REFERENCES

Hinkle DK, Suggs JE, Jackson MD (1979) Environmental and biological effects of propoxur-impregnated strips within a laboratory animal room. Lab Anim Sci 29:466

Jackson MD, Lewis RC (1979) Volatilization of methyl parathion from fields treated with microencapsulated and emulsifiable concentrate formulations. Bull Environ Contam Toxicol 21:202

Leidy RB, Wright CG, Dupree HE (1982) Concentration and movement of diazinon in air. J Environ Sci Health B17:311

Lewis RG (1976) Sampling and analysis of airborne pesticides In: Lee RE (ed) Air Pollution from Pesticides and Agricultural Practices. CRC Press, Cleveland, OH, p 51

Lewis RG, Brown AR, Jackson MD (1977) Evaluation of polyurethane foam for sampling of pesticides, Polychlorinated biphenyls and polychlorinated napthalenes in ambient air. Anal Chem 49:1668

Lillie TH (198) Chlordane in air force family housing: A study of houses treated after construction. USAF OEHL report 81-45. USAF Occupational and Environmental Health Laboratory. Aerospace Medical Division (AFSC) Brooks AFB, TX 78235

Melcher RC, Garner WL, Severs LW, Vaccaro JR (1978) Collection of chlorpyrifos and other pesticides in air on chemically bonded sorbents. Anal Chem 50:251

Russell JW (1971) Analysis of air pollutants using sampling tubes and gas chromatography. Environ Sci Tech 9:1175

Seiber JN, Shafik TM, Enos HF (1975) Determination of pesticides and their transformation products in air. In: Hague F, Freed VH (eds) Environmental dynamics of pesticides Plenum Press, NY, p 17

Thomas TC, Jackson JW (1980) Chlordane sampling efficiency with chromosorb 102 and ethylene glycol. Amer Indust Hyg Assoc J 41:599

VanDyke LP, Visweswariah K (1975) Pesticides in air: Sampling methods. Residue Reviews 55:91

Wright CG, Leidy RB (1982) Chlordane and heptachlor in the ambient air of houses treated for termites. Bull Environ Contam Toxicol 28:616

Wright CG, Leidy RB, Dupree HE (1982) Diazinon and chlorpyrifos in the air of moving and stationary pest control vehicles. Bull Environ Contam Toxicol 28:19

Yobs AR (1971) National monitoring program for air. Pest Monit J 5:67

Received January 12, 1984; accepted February 6, 1984