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EVALUATION OF POLYURETHANE FOAM AS A TRAPPING MEDIUM FOR HERBICIDE VAPOR IN AIR MONITORING AND WORKER INHALATION STUDIES

KEY WORDS: bromoxynil octanoate, 2,4-D-iso-octyl ester, 2,4-D-n-butyl ester, 2,4,5-T-n-butyl ester, triallate, trifluralin, herbicides, polyurethane foam, adsorbent, inhalation/respiratory exposure levels

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ABSTRACT

Polyurethane foam was an efficient adsorbent for trapping vapors of butyl esters of 2,4-D (2,4-dichlorophenoxyacetic acid) and triallate (S-(2,3,3-trichloroallyl)diisopropylthiocarbamate) in high volume air monitoring studies and of butyl esters of 2,4-D, iso-octyl ester of 2,4-D, n-butyl ester of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), bromoxynil octanoate (3,5-dibromo-4-hydroxybenzonitrile), triallate, and trifluralin (α,α,α-trifluoro-2,6-dinitro-N-N-dipropyl-p-toluidine) in short-term, low volume, worker inhalation exposure studies. The collected herbicide vapor was readily desorbed under soxhlet extraction with n-hexane and subsequently analyzed with electron-capture GLC. The overall efficiencies, for both trapping and extraction, were over 90%, using a single plug, for all herbicides, except triallate. In the case of triallate, two plugs in series were required for efficient trapping under the high volume air monitoring situation.

INTRODUCTION

The atmospheric compartment is now recognized to be the major route for the widespread transportation and a temporary deposition of herbicide residues.[1,2] The pesticides in the air may originate as droplets or vapor during spraying or after application.[3,4] The off-target drift from the large scale use of phenoxy herbicides in the Canadian prairies and elsewhere has been a major concern as a source of potential contamination of the atmospheric environment.[5,6] However, a critical evaluation of the current methods of collecting and measuring atmospheric pesticide residues and especially the herbicide residues, has been undertaken only recently.[7,8,9]

Earlier monitoring of 2,4-D ester residues in the air used liquid sampling trains to trap atmospheric residues.[5,10,11] However, solid adsorbent traps using silica gel and XAD-resins have been evaluated recently for trapping of 2,4-D esters and other volatile herbicides.[12,13] These solid adsorbents have been used successfully to monitor 2,4-D ester residues in the air.[5,6] More recently, solid organic polymer foams, such as polyurethane foam, have been shown to successfully trap atmospheric trace residues of several herbicides such as trifluralin, dacthal, chlorpropham and EPTC.[14,15,16]

These foams permit high air flow rates, thus allowing high air contact volumes and the adsorption is usually readily reversible.

This report evaluates the use of polyurethane foam as a trapping medium for atmospheric residues of butyl esters of 2,4-D and triallate, another relatively volatile herbicide now used extensively on the Canadian plains. In addition, small plugs of polyurethane foam were evaluated for trapping several commonly used herbicides to assess their potential as an adsorbent for worker inhalation studies, at flow rates commensurate with the standard, battery-operated, portable personal monitors.

MATERIALS AND METHODS

Herbicides

Analytical-grade iso-octyl ester of 2,4-D (Unilab Research Corp. Berkeley, CA), bromoxynil octanoate (Amchem Products Inc., Ambler, PA), triallate

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(Monsanto Co., St. Louis, MO), trifluralin (Eli Lily & Co., Greenfield, IN) and technical-grade n-butyl esters of 2,4-D (Dow Chemical, Midland, MI) and 2,4,5-T (K & K Laboratories Inc., Jamaica, NY) were used throughout these studies.

Adsorbent

The gray, ester variety of polyurethane foam, about 5 cm in thickness, was obtained from Read Plastics, Inc., Rockville, MD. Circular plugs, 20 or 15 mm in dia by 50 mm long, were cut from the sheet, using a sharp, stainless-steel, cork borer type cutter mounted on a lathe. The new plugs required more exhaustive clean-up than was reported earlier. [14] The plugs were soxhlet extracted for 40 h with a 1:1 mixture of acetone and n-hexane, using a large soxhlet extractor (Corning No. 3885) which accommodated up to 15 large size plugs. After the initial clean-up, each plug was soxhlet extracted for another 40 h individually, using 250 ml of 1:1 acetone and n-hexane. The plugs were then air-dried and stored in wide-mouth jars fitted with teflon-lined screw caps.

Vapor Sampling Procedure

An all-glass vapor sampling train, similar to one described earlier, was used. [13] It consisted of a U-tube and the adsorbent chambers were modified to accept small or large foam plugs in series. One ml of n-hexane solution, containing 1 to 100 ug of the appropriate herbicide was pipetted to the bottom of the U-tube and the apparatus assembled immediately, using the spring-loaded pinch clamps. The lower half of the U-tube was immersed in a water bath, maintained at 50 C to facilitate volatilization of the herbicides. Air was then drawn over the herbicide in the U-tube and through the foam plug chambers for varying durations and at different flow rates. At the end of each run the U-tube was rinsed with n-hexane and the rinse made up to volume for GLC analysis. All experiments were carried out in duplicate and repeated as required.

Extraction of Herbicides from Foam Plugs

Each foam plug was transferred to individual soxhlet extractors and the herbicide extracted with 250 ml of n-hexane for 2 h. After this, the volume was reduced to 10 ml using a rotary evaporator. An appropriate aliquot was then injected into a gas chromatograph for analysis.

GLC Analysis

A Tracor model 560 gas chromatograph, equipped with ^{63}Ni, linearized electron capture detector was used. The glass column, 4 mm i.d. by 1.75 m long, was packed with Ultrabond (a trade mark of RFR Corp., Hope, RI). The injector and detector temperatures were 220 C and 350 C, respectively. The column temperatures were 180 C for triallate and trifluralin, 200 C for 2,4-D and 2,4,5-T esters and 220 C for bromoxynil octanoate. The flow rates of the carrier and purge gas, 5% methane in argon, were 40 and 20 ml/min, respectively. The recoveries were determined by comparison with GLC analysis of the corresponding standard solutions of each herbicide, with each determination carried out in duplicate.

RESULTS AND DISCUSSION

Air Monitoring Studies

A single, 45 mm dia by 50 mm long polyurethane foam plug retained 99 to 100% of the evaporated n-butyl ester of 2,4-D at flow rates in the range of 1 to 50 l/min over the 24 h period (Table 1). The ester was readily desorbed from the foam plugs after soxhlet extraction with n-hexane for 2 h, with total recoveries at the 1 to 10 µg range from 92 to 115%. The use of the foam plugs should allow at least a 10-fold increase in the sample volume over the 24-h period as compared to the earlier studies using solid adsorbents such as XAD-resins or silica gel. [12,13]

POLYURETHANE FOAM

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Air flow rate (l/min)	Total air volume (m^3)
0.3	1.
10.0	14.
20.0	28.
25.0	36.
50.0	72.

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Worker Inhalation

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TABLE 1

Collection efficiency for 2,4-D butyl ester on 45 x 50 mm polyurethane plugs over 24 hours

Air flow rate	Total air volume	Amount in U-tube		Amount found in foam plug		Total Recovery
		added	left	1	2	
(l/min)	(m^3)	(µg)		(µg)		(%)
0.8	1.2	10	0.23	9.3	0.05	96
10.0	14.4	10	1.54	8.6	0.08	102
20.0	28.8	10	1.02	8.3	0.02	93
25.0	36.0	10	1.76	9.7	0.0	115
		1	0.39	0.53	0.0	92
30.0	72.0	10	0.17	9.8	0.02	100
		1	0.05	1.0	0.0	105

A single 45 mm dia foam plug also retained over 90% of triallate at flow rates of 10 to 15 l/min over the 24 h sampling period (Table 2). However, two plugs in series were required to retain triallate vapor at higher flow rates. Triallate was also readily desorbed from the foam plugs after soxhlet extraction with n-hexane for 2 h, with total recoveries at the 1 to 100 µg range from 97 to 112%.

Worker Inhalation Studies

A single, 20 mm dia by 50 mm long polyurethane plug retained 97 to 100% of the evaporated herbicides at a flow rate of 4 l/min over the 6 h period (Table 3). All the herbicides were readily desorbed from the foam plugs after soxhlet extraction with n-hexane for 2 h, with total recoveries at the 10 µg level from 99 to 113%.

TABLE 2

Collection efficiency for triallate on 45 x 50 mm polyurethane plugs over 24 hours

Air flow rate	Total air volume	Amount in U-tube added	Amount in U-tube left	Amount found in foam plug 1	Amount found in foam plug 2	Total Recovery
(l/min)	(m^3)	(µg)		(µg)		(%)
10	14.4	10	0.18	11.0	0.06	112
		100	3.85	95.0	0.19	99
15	21.6	100	0.24	90.0	7.48	98
20	28.8	100	1.58	67.5	27.63	97
25	36.0	1	0.00	0.6	0.40	101
		10	0.00	6.0	5.10	111
		100	0.64	88.0	16.93	106

TABLE 3

Collection efficiencies for herbicide vapor on 20 x 50 mm polyurethane plugs over six hours at air flow rate of 4 l/min

Herbicides	Amount in U-tube added	Amount in U-tube left	Amount found in foam plug 1	Amount found in foam plug 2	Recovery
	(µg)		(µg)		(%)
2,4-D (n-butyl)	10	0.0	9.7	0.7	104
2,4-D (iso-octyl)	10	0.6	9.3	0.0	99
2,4,5-T (n-butyl)	10	0.0	10.0	0.0	100
bromoxynil (octanoate)	10	4.9	5.8	0.6	113
triallate	10	0.0	9.8	0.3	101
trifluralin	10	0.0	10.4	0.0	104

ate on 45 x 50 mm

24 hours

Amount found in foam plug 1	Amount found in foam plug 2	Total Recovery
(ug)		(%)
11.0	0.06	112
95.0	0.19	99
90.0	7.48	98
67.5	27.63	97
0.6	0.40	101
6.0	5.10	111
88.0	16.93	106

cide vapor on 20 x 50 mm

t air flow rate of 4 l/min

Amount found in foam plug 1	Amount found in foam plug 2	Recovery
(ug)		(%)
9.7	0.7	104
9.3	0.0	99
10.0	0.0	100
5.8	0.6	113
9.8	0.3	101
10.4	0.0	104

In conclusion, polyurethane foam is an efficient and simple trapping medium for the accumulative collection of herbicide vapor from an air stream over time. The collected vapor can then be soxhlet extracted unchanged for analysis in the laboratory. For air monitoring studies, where high flow rates may be needed to detect trace amounts, it is essential that collection efficiencies be established for each compound to establish the necessity of using one or more plugs in series. However, for worker exposure level studies where low flow rates of about 2 l/min are standard on portable-battery operated pumps and the duration of sampling is at the most a 8-h work period, a single foam plug would be adequate under most situations.

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