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Comparative Volatility of Liquid and Granular Formulations of Chlordane and Heptachlor from Soil

Y. H. Atallah, D. M. Whitacre, and B. L. Hoo

Research Department, Environmental Sciences Section, Velsicol Chemical Corporation, 341 E. Ohio St., Chicago, Ill., 60611

The transfer processes which operate to move pesticides from application sites are well known. Soil transfer is both lateral and vertical. The rate of transfer depends on the characteristics both of the chemical and the soil. Drift and volatility are common routes of transfer to all pesticides. Volatility varies directly with vapor pressure and inversely with soil adsorption. Soil and crop persistence and volatility of several organochlorine insecticides have been studied by CARO (1971), PARMELE et al. (1972), TURNER et al. (1972), FREEMAN et al. (1975) and TAYLOR et al. (1976). Pesticide volatilization has been reviewed by SPENCER et al. (1973) who emphasized the importance of volatility in determining the dissipation and environmental fate of pesticides. Volatility can be the major route of transfer of pesticides from application sites. HINDIN et al. (1966) reported that much less than half of the DDT and other pesticides applied by aircraft reached application sites. The implication was that volatility-drift accounted for the greatest majority of applied materials.

The purpose of this experiment was to compare volatility rates each for a granular and liquid formulation of chlordane and heptachlor. Data derived from this study may be useful in identifying alternative agricultural practices to reduce volatilization from application sites.

MATERIALS AND METHODS

Chemicals and Reagents.- The commercial formulations of technical chlordane and heptachlor used were Belt 72 Emulsifiable Concentrate (EC; 8 lb/gallon), Belt 33.3 Granular (G; 33.3% active ingredient), Heptachlor 3 EC (3 lb/gallon) and Heptachlor 20 G (20% active ingredient).

Air samples were trapped in ethylene glycol which had been prewashed three times with n-hexane.

Address correspondence to: Y.H. Atallah, Ph.D., Velsicol Chemical Corp., 341 E. Ohio Street, Chicago, Illinois 60611

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Experimental Procedure.- "Ringwood Silt Loam" soil from Madison, Wisconsin, was used in this experiment. An amount of each formulation was added to 2 kg of soil and thoroughly mixed to equal a field application rate of 10 lb active ingredient (a.i.) per acre for chlordane or 2 lb a.i./acre for heptachlor. These rates are equivalent to about 6 ppm chlordane and about 1.2 ppm heptachlor if the insecticides were evenly distributed in the top 6 inches of soil. Each mixed soil sample was placed in a 7-L wide-mouth glass jar and soil moisture was maintained at 70% of 0.33 bar. Each treatment was duplicated.

Air Sampling.- A line drawing of the air sampling apparatus used in these studies is shown in Figure 1.

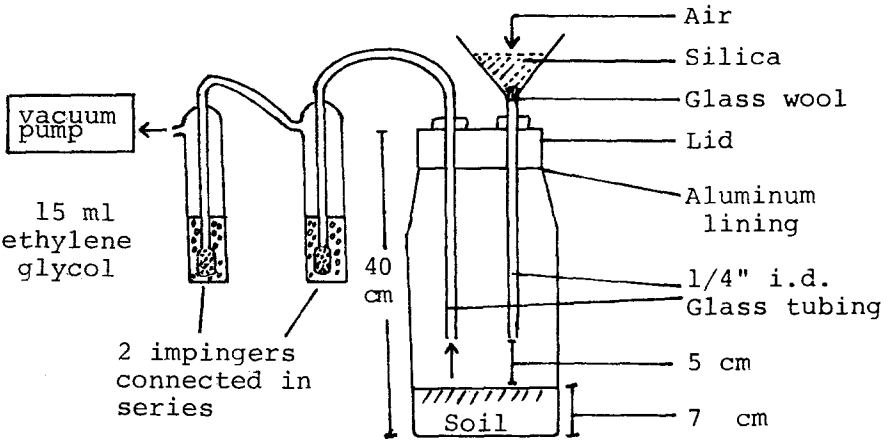

Figure 1. Air Sampling Apparatus.

Duplicate EC and G treatments were sampled simultaneously at each sampling interval. Fifteen mL of ethylene glycol was placed in each impinger (30 mL capacity, No. D 41848, LaPine, Chicago, Ill.). The air inlet to the wide-mouth jars was equipped with a silica gel trap to clean ambient air contaminants. Insecticide vapors were trapped by passing sampled air through two impingers, joined in series at the rate of 4.2 L/min for 4 h (1,008 L of air). Air samples were collected from each apparatus at 0, 1, 4, 7 and 13 (chlordane) or 0, 1, 4, 7 and 15 (heptachlor) days after treatment.

The collection efficiency of the air traps was checked by passing a chlordane air sample into 3 impingers connected in series each containing 15 mL of ethylene glycol followed by a silica gel trap (8 g in a 16 mm i.d. glass tube). In addition, impingers containing 15 mL of ethylene glycol were fortified with chlordane and heptachlor. Air was passed through the fortified impingers for 4 h at the rate of 4.2 L/min and the retention of these insecticides in the impingers was determined.

Analysis.- The ethylene glycol from each impinger was quantitatively transferred into a 250 mL separatory funnel containing 150 mL distilled water and 15 mL of NaCl saturated water. This solution was extracted with 60 mL of pentane. The pentane layer was passed through a plug of Na_2SO_4 and collected in a 125 mL K-D concentrator. Five drops of heptane were added and the pentane evaporated on a 50 - 60°C water bath to ½ mL. The sample was diluted to 2 mL with heptane and ½ mL of 1:1/conc:fuming sulfuric acid was added. The heptane layer was immediately transferred to a clean centrifuge tube with a pipet and a small amount of Na_2SO_4 was added prior to electron capture gas chromatographic analysis (GLC-EC).

Chlordane residues were determined from a calibration curve by summing the 6 fingerprint GLC-EC peaks (Compound C, heptachlor, Compound E, alpha and gamma chlordane and t-nonachlor) characteristic of technical chlordane (McMAHON and SAWYER 1977).

Heptachlor residues were determined from calibration curves constructed with analytical reference standard heptachlor (99.8% pure). All analyses were c conducted on a U-shape glass column ¼" o.d., 4 mm i.d. x 1.8 m packed with 10% OV-101 on 80/100 mesh Gas Chrom Q. The electron capture detector utilized a ^{63}Ni source and was maintained at 275°C. Injector block and column temperatures were 225 and 200°C, respectively. N_2 was utilized as a carrier gas with a 60 mL/min flow rate.

RESULTS AND DISCUSSION

The collection efficiency averaged 87%, 8%, 1% and 5% for the 1st, 2nd, 3rd and 4th traps, respectively. Two ethylene glycol traps were used in air sampling which yielded a trapping efficiency of > 90%.

As an additional check on recovery the retention of chlordane and heptachlor in fortified ethylene glycol impingers was investigated. About 82% chlordane and 101% heptachlor was retained by the ethylene glycol

trap after 4 h of continuous aspiration at the rate of 4.2 L/min.

Data presented in Table 1 clearly demonstrate that chlordane EC was more volatile than the corresponding G formulation. At 0 day, residues from the EC treatment were nearly 20 fold greater than the G formulation. By day 13, residues of EC formulation were 9 fold greater than the G formulation.

Since application rates of heptachlor were one fifth those of chlordane (2.0 vs. 10 lb/acre) normalization of this rate difference indicates that heptachlor is probably more volatile from soil than chlordane when comparing the respective formulations. The heptachlor EC residues were always higher than those of the G formulation by a factor of 5 to 10.

TABLE 1

Comparative Volatility of Two Formulations of Chlordane and Heptachlor Incorporation Into Ringwood Silt Loam

Interval (Days)	ug/m^3 Average EC	G	Ratio EC/G
Chlordane[1/]			
0	1.743	0.089	19.6
1	0.955	0.059	16.2
4	0.813	0.046	17.7
7	0.646	0.049	13.2
13	0.640	0.071	9.0
Heptachlor[2/]			
0	0.544	0.057	9.5
1	0.390	0.039	10.0
4	0.121	0.026	4.7
7	0.118	0.015	7.9
15	0.189	0.027	7.0

[1/] BELT 72EC (8 lb/gal) 10 lb a.i./acre=5.2 µl/kg soil;

BELT 33.3 G (33.3%) 10 lb a.i./acre=2 mg/kg soil;

[2/] Heptachlor 3EC (3 lb/gal) 2 lb a.i./acre=2.8 µl/kg soil;

Heptachlor 20 G (20%) 2 lb a.i./acre=2 mg/kg soil

The limit of detectability for heptachlor and chlordane was 2 and 10 ng/m^3, respectively.

This study clearly demonstrates the propensity for minimizing volatility losses of chlordane-heptachlor from soils when G rather than EC formulations are used. The use of G formulations could reduce air residues and probably increase the efficacy of the product since losses are mitigated.

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