Factors Affecting the Volatility of DDT, Dieldrin, and Dimethylamine Salt of (2,4-dichlorophenoxy) acetic Acid (2,4-D) from Leaf and Glass Surfaces

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The volatilization of the so-called "non-volatile" pesticides such as p,p'-DDT and dieldrin has been the subject of several recent reviews (SPENCER et al, 1973, HAMAKER, 1972, EDWARDS, 1966 and HARTLEY, 1969). Most of the work in this area has dealt with volatilization of pesticides from soils, aqueous solutions or glass surfaces. Very few workers (e.g. STARR and JOHNSEN, 1968, GUNTHER, 1969), have studied volatilization of pesticides from plant surfaces using the volatilized material as the basis of analysis rather than residues. The factors controlling the release of pesticides from plants and soils are quite different. It would be expected that differential retention on plant surfaces will affect the degree of pesticide distribution to non-target sites in the environment. This would be analagous to work showing the importance of adsorptive forces in the volatility of pesticides from soils. In addition, if the pesticide does not penetrate markedly into leaf surfaces, then a big proportion of the originally applied pesticide is available for environmental dissipation by such agencies as wind, rain and sunlight.

EXPERIMENTAL

Reagents. Labelled 2,4-D [2,4-dichlorophenoxy)acetic acid] (ring UL-^{14}C, specific activity 1.10 m Ci/mM), p,p'-DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane] (ring UL-^{14}C, sp. act. 23.9 m Ci/mM), and dieldrin [1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene] (^{14}C sp. act. 72 m Ci/mM) were obtained from Mallinckrodt Nuclear. These chemicals were found to be more than 99% pure by gas-liquid and thin layer chromatography. All solvents used were dry, redistilled reagent grade chemicals.

The 1:1 dimethylamine salt of 2,4-D was prepared by adding a slight excess of reagent grade dimethylamine at room temperature to a benzene solution of labelled 2,4-D. The solution was shaken vigorously and the solvent and excess amine evaporated at room temperature under high vacuum. The resultant salt was dissolved in 25 ml of reagent grade methanol.

Apparatus. The pesticides were all volatilized in the apparatus described elsewhere by QUE HEE and SUTHERLAND (1974), similar to the one employed by STARR and JOHNSEN (1968).

Procedure. All volatilization experiments were carried out for 48 hr. in cabinets held at 35 ± 2.0% relative humidity (RH), at a temperature of 33.5 ± 1.5°C, in the presence of light emitted from a 100 watt incandescent bulb. The flow rate at the inlet tube was 940 ± 10 ml/min. The sprayed targets were whole sunflower

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seedlings or pyrex petri dishes (20 cm^2). At the end of the 48 hr. period, aliquots were taken from each midget impinger and the radioactivity estimated by the internal standard method on the same scintillation counter, and using the same counting solution, as reported earlier by QUE HEE and SUTHERLAND (1973).

For all experiments involving DDT and dieldrin, the interior of the glassware (except the target) was washed five times with hexane, the washings concentrated and the radioactivity of the washings then measured. Similarly, methanol was used in experiments with the amine salt of 2,4-D.

The original applied dose on each target was estimated in triplicate by spraying three similar targets and washing off the sprayed deposit with hexane or methanol.

The amount of pesticide volatilized was calculated by comparing the radioactivity content of the material collected in the two impingers plus that in the washings with the original applied dose on the target. The total reccovery of radioactive material was found by comparing the radioactivity volatilized plus that remaining on the target with the original applied dose.

All experiments were replicated four times.

Volatilization from pure films of pesticides on petri dishes. The concentrations of pure 2,4-D salt in methanol and of pure labelled dieldrin and DDT in hexane, were adjusted by dilution to produce approximately 200,000 dpm/ml (about 0.5 μgm/ml).

Thin films of the pesticides were formed by pipetting 1 ml of solution into a 5 cm petri dish (20 cm^2) and then evaporating the solvent under a gentle stream of air. The dish was then placed into the bell jar, and the volatility found as above.

If the applied deposit was liquid, the available surface area for evaporation/applied dose (Q) was ca 4×10^7 cm^2 gm^{-1}. This is likely because of supercooling of the deposit by the air stream (HARTLEY, 1969).

Volatilization of Droplets on Petri Dishes. Sufficient labelled pesticide was added to its corresponding commerical emulsion concentrate so that on dilution with distilled water to give 22 mg/ml of active ingredient, one microliter of the labelled aqueous solution produced a count rate of 2500 dpm. One microliter of this solution was sprayed onto a petri dish (20 cm^2), and the volatility found as above.

The droplet spectrum delivered by the spray nozzle to a horizontal magnesium oxide surface shown in Figure 1, was calculated using the method of MAY (1950). The volatility was found as above.

The Q value for these experiments was calculated using the mean droplet radious (r) obtained from Figure 1, the equation

$$A = (4/3)^{\frac{2}{3}} \pi r^2 [1 - \cos \theta + 1/3 (\cos^3 \theta - 1)]^{-\frac{2}{3}} \qquad (1)$$

where A = surface area
r = mean droplet radius
θ = contact angle

derived from the results of HARTLEY and BRUNSKILL (1958) and assuming the area wetted by the drop was the same as that exposed to the air with θ = 60° in the presence of surfactant (BECHER and BECHER 1969). The area covered by, as well as the exposed

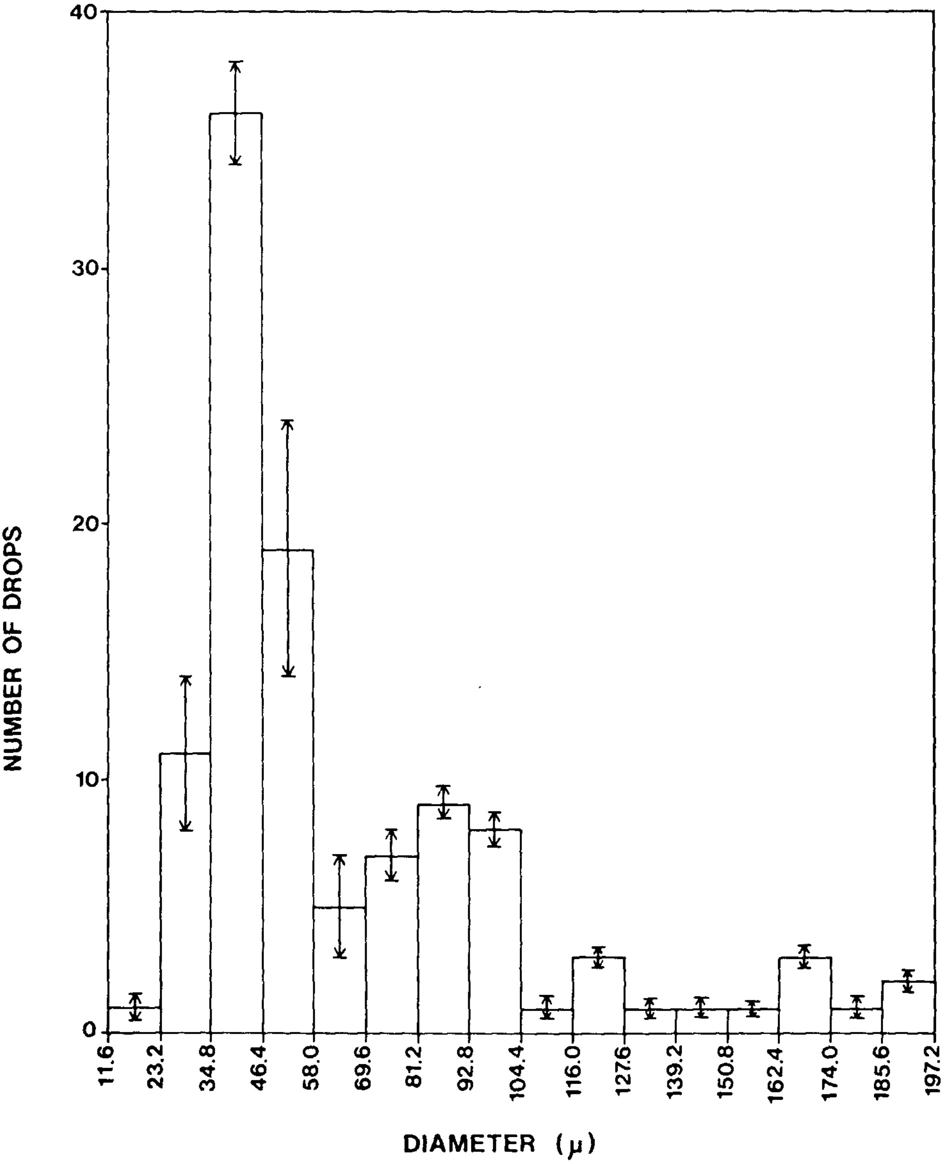

Figure 1. Droplet spectrum delivered by spray nozzle to a horizontal magnesium oxide surface.

surface area of, one droplet would be 4350×10^{-8} cm^2. For the sake of argument, if the drop before impaction is assumed spherical its volume is 34×10^{-9} cm^3. If all the drops are this volume, the total number of drops per dish expected from one microliter is approximately 3×10^4. Thus, the total area on one dish covered by droplets, and hence droplet area exposed to the air stream, would be approximately 1.3 cm^2, leading to an original Q value of approximately 6×10^4 cm^2 gm^{-1}.

Volatilization of droplets on leaves. Each leaf of plotted sunflower (Helianthus annuus, L. "Peredovik") seedlings in the fourleaf stage was sprayed with the same droplet spectrum as above using one microliter of the same labelled aqueous commercial emulsion concentrate as above. The pots containing the treated plants were placed in petri dishes containing water to prevent wilting during the experiment.

The bell jar described by QUE HEE and SUTHERLAND (1974) was placed over the plant and rested on slotted aluminum plates supported by the top of the plant pot. Air entered only through the small hole (approximately the same cross-section as the inlet tube used for the petri dish experiments) through which the plant stem passed. The leaves were as uniform in size as possible, and did not touch the sides of the bell jar. The plant was always put in approximately the same geometrical position relative to the air inlet and outlet. After the volatilization period, the portion of the plant within the bell jar was washed five times with 10 ml of hexane to determine the radioactive residue. The midget impingers were sampled, and the insides of the glassware washed, as described above.

The air flow pattern inside the bell jar is completely different from that in the above two experiments. In effect, the air is being changed continuously and is the nearest approach to field conditions.

The original Q value would be approximately the same as for the droplets impacted on glass, i.e. 6×10^4 cm^2 gm^{-1}.

Volatilization of aqueous emulsions on petri dishes. One milliliter of the same labelled commercial aqueous emulsion as above was pipetted into a 5 cm petri dish, the dish placed in the bell jar, and the volatility then found. The original Q value was ca 10^3 cm^2 gm^{-1}.

Characterization of the volatilized insecticides. DDT or dieldrin trapped in the ethylene glycol contained in the impingers, were extracted three times with hexane after dilution with water and the resultant hexane solutions concentrated under reduced pressure. Before electron capture (tritium) glc analysis, the radioactive components were separated by TLC on silica gel using 95:5 hexane/acetone. The radioactive spots were eluted from the gel by hexane, and were examined by glc on a 5 ft long 1/8" aluminum capillary column filled with 5% SE-30 on 80/100 mesh Chromosorb W (DCMS-AW), using nitrogen carrier gas at a constant flow of 42 ml/min at an injector temperature of 200°C and a column temperature of 180°C. The retention times of the peaks from the samples were compared with those of reference compounds. The identities of suspected compounds were confirmed by comparing the mass-spectra of the compounds present in the sample with those of reference compounds.

RESULTS AND DISCUSSION

Table 1 shows the percentage volatility, and total recovery of the various substrates on particular targets. The approximate corresponding volatilization rates (±20%) in μg cm^{-2} 2 $days^{-1}$ are also given. The reason for the use of the latter units is that the absolute volatilization rates can only be deduced knowing the form of the kinetic plots characterizing the volatilization. It cannot be assumed that volatilization is linear with respect to time or surface area. In fact, previous work (QUE HEE and SUTHERLAND, 1974) has shown that the volatilization process for pure films of 2,4-D esters is usually first order, and thus large errors may occur if the kinetic plot is unknown.

The pure film on glass produces the greatest percentage volatility for each of the three substrates (Table I). However, the absolute volatilization rates are the lowest. Table 1 shows that as the applied dose increases, so too does the absolute volatilization rate, but the percentage volatility after 2 days decreases. This suggests that at the light doses, the air stream sampled was not saturated with pesticide, and as no kinetic curves were done, the absolute rates of volatilization in this case may be misleading.

Pesticides are usually applied as droplets of aqueous emulsions in the field. The initial diameters of impacted droplets may range from 10 to 200 microns (μ), and as the more volatile materials volatilize off, more pesticide will be available for volatilization instead of being held preferentially in solution. The results of experiments with droplets on glass and leaves show that volatility from a given area and with a given geometry and temperature also depends on the type of surface, and molecule involved (Table 1). Thus, droplets of approximately the same diameter on both glass and leaves were equally volatile for DDT (40 to 46%), but for dieldrin, droplets on glass (70%) were significantly more volatile than on leaves (54%). The low recoveries for the leaf experiments may imply that some pesticide had penetrated into the leaves. The 2,4-D amine salt was much less volatile than DDT or dieldrin. (Table 1)

The percentage volatility for all substrates from thick films of formulations ($Q \sim 10^3$ cm^2 gm^{-1}) were much lower than for droplets of thin film experiments, although the absolute rates of volatilization were higher. The high absolute rates of volatilization may be ascribed to the air stream being closer to saturation because of the larger applied dose.

The above results show that if a small mass is applied over a large area (i.e. high Q values), then the overall percentage volatility may be high even though the absolute volatilization rate per unit area may be low. The air stream is not saturated by the low dose thus resulting in low apparent rates of volatilization per unit area. However, big surface areas are available to the moving air stream which disperses the evaporated molecules, resulting in high percentage volatilities. This situation is the one usually met in the field, where coverage may vary anywhere from 10^2 to 10^5 cm^2 gm^{-1}. Previous work has shown that such chlorinated pesticides as

TABLE I

Volatilization of p,p^1-DDT, dieldrin, and the dimethylamine salt of 2,4-D at 33°C, 35% R. H, and 2 mph wind

Substrate/ Target	DDT			Dieldrin			2,4-D Dimethylamine salt		
	% Volatility (48 hrs)	% Total Recovery	Vaporization Rate in 2 days ($\mu g\ cm^{-2}$)	% Volatility (48 hrs)	% Total Recovery	Vaporization Rate in 2 days ($\mu g\ cm^{-2}$)	% Volatility (48 hrs)	% Total Recovery	% Vaporization Rate in 2 days ($\mu g\ cm^{-2}$)
Pure film (glass) $Q \sim 4 \times 10^7\ cm^2 gm^{-1}$	97.1 ± 3.2 (87.5±2.4)[a]	101 ± 4.0 (88.0±2.5)[a]	> 0.024	78.6 ± 1.1 (83.5±7.2)[a]	90.0 ± 3.0 (85.1±7.6)[a]	~ 0.020	7.6 ± 0.3	98.0 (±4.0)	~ 0.002
Droplets (glass) $Q \sim 6 \times 10^4\ cm^2 gm^{-1}$	46.0 ± 5.0	85.0 ± 8.0	~ 6.7	70.3 ± 6.6	92.0 ± 11.0	~ 12	7.1 ± 1.0	103.0 ± 7.0	~ 1.2
Droplets (leaves) $Q \sim 6 \times 10^4\ cm^2 gm^{-1}$	40.6 ± 4.1	69.0 ± 10.0	~ 5.9	53.5 ± 4.8	81.0 ± 12.0	~ 9.1			
Formulation Film (glass) $Q \sim 10^3\ cm^2 gm^{-1}$	5.5 ± 0.1	85.0 ± 4.0	~ 55	12.5 ± 0.5	93.0 ± 3.0	~ 125	0.64±0.2	91.0 ± 3.0	~ 6.4

(a) at 0% relative humidity (RH).

p,p'-DDT and dieldrin are relatively persistent on soils though volatilization may be important under certain conditions (SPENCER et al, 1973; LICHTENSTEIN, et al,(1968); WILLIS, et al,(1971); CARO and TAYLOR, 1971). The results reported here show that insecticides deposited on leaves may be highly volatile, even if the absolute rates of evaporation per unit area are low. This would also be expected to be dependent on the surface roughness of, retention on, and penetration into, leaves as well as such physical factors as temperature, air flow profile and rate, type of molecule, and surface area exposed. This is analagous to the situation in soils, where soils of differing chemical composition show different volatilities of adsorbed pesticides (GUENZI and BEARD, 1970). Previous work by PHILLIPS (1971) using glass surfaces, and GUNTHER (1969) who estimated evaporation rates from a citrus grove, suggested that the surface area exposed to a turbulent or stagnant air stream may affect the volatility of applied pesticides, but neither has stressed this point, nor noted that a low volatilization rate per unit area does not imply that the total volatility is necessarily low.

Mass spectrometric and glc analysis confirmed that both dieldrin and p,p'-DDT volatilized into the air without degradation in the two-day volatilization period. Traces of o,p'-DDT and p,p'-DDT were found in all samples, but these were also in the original labelled compound and formulation. The importance of the analysis of the original formulation and labelled copound is thus highlighted, as degradative pathways may be hypothesized which could be misleading.

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