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Post-Application Volatilization of Pesticides under Field Conditions

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The results of several experiments on volatilization of pesticide residues in the field are summarized and evaluated. Measurements were all made using micro-climate techniques calculating fluxes from measured pesticide vapor profiles and supporting meteorological data.

Volatilization rates from plant or moist soil surfaces can be very large, with losses approaching 90% within 3 days for more volatile compounds. Losses from dry soil are much less. Strong adsorption of pesticides by the dry soil greatly lowers the vapor pressure to a level so that volatilization from exposed dry surfaces is almost entirely inhibited. Over longer periods the volatilization of preemergence herbicides applied to exposed soil surfaces is erratic, depending upon soil drying by evaporation and rewetting by rainfall. Volatilization of materials mixed into the soil are much less, seldom approaching 20% over the growing season. The amount lost depends greatly on the depth of mixing within the soil.

Because of the complexity of the weather, management systems, variations in the properties of the compounds and the different soil and crop surfaces involved, detailed calculation of pesticide volatilization on a general scale is not possible. In specific situations, where enough information on how much pesticide has been applied, and where suitable weather data are available, approximate estimates of the amount of a particular compound entering the atmosphere can be made.

Pesticide chemicals comprise several groups of compounds—insecticides, herbicides, fungicides, rodenticides, and fumigants, including several hundred individual chemicals of different kinds with a wide range of properties. The resulting variety, coupled with the wide differences in the manner in which various compounds are used makes any generalization about the impact of pesticide chemicals on the

atmosphere impossible when they are considered as a general group. The problem of assessment is also further compounded by the lack of any general data on the concentrations actually to be found in the air, even for those chemicals in widespread agricultural use. The lack of data does not, however, reflect any lack of concern for the possible environmental problem, but rather the technical difficulties of measurement of the amounts present and the expense and difficulty of sampling the atmosphere on the scale necessary to obtain meaningful data.

In recent years several research studies of actual volatilization rates of pesticide residues under field conditions have provided base data that permit some estimate of the rate of input to the air under typical conditions of use. In particular these results allow an assessment of the relative importance of post-application volatilization in comparison with the more generally recognized problem of evaporative losses during spray applications. This latter question is not considered in this paper.

The existence of phytotoxic effects of revaporized residues of the herbicide 2,4-D was recognized as long ago as 1945 by Staten¹ who found this to be the only possible explanation for damage to cotton growing at some distance from an area treated with this herbicide. In 1961 Harris and Lichtenstein² demonstrated the existence of vapor concentrations toxic to confined insects over soils treated in the laboratory with several insecticides. Lichtenstein and Schultz³ also noted the significance of volatilization as a pathway by which organochlorine insecticides disappeared from soils in the field.

The first direct measurements of concentrations in air were obtained in 1968, when Willis, *et al.*,^{4,5} measured concentrations of DDT and dieldrin in the air over plots treated with these insecticides. In the DDT study concentrations up to about 2 $\mu\text{g}/\text{m}^3$ were found within 10 cm of the surface during the first day after application. Concentrations fell rapidly with time after the first day and the amount of DDT recovered from the air was a very small fraction of that applied to soil; it may be noted that in these experiments the DDT was applied to the soil at more than ten times the normal rate of application. In the dieldrin studies⁵ average concentrations and fluxes were measured over 24 hr periods. Daily volatilization rates of up to 200 g/ha were observed from surface applications on moist soil during the first 30 days after application. These fell to less than 20 g/ha/day after the 40

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Measurements of F

In recent years several measurements have been reported. (Taylor *et al.*,⁶ and Parmelee *et al.*,⁷) through a horizontal crop canopy is given

where dc/dz is the vertical concentration gradient and K_z is the vertical eddy diffusivity. Since the value of K_z in the atmosphere is a function of the physical or chemical conditions, this behavior may then be assumed to be defined by

where $E\uparrow$ is the water vapor concentration where water flux is calculated directly. Without lysimeter Bowen Ratio method and humidity are measured.

In the more complex eddy diffusivity method the wind profile, temperature lapse rate and the thermal stability is then considered.

where c_1 and c_2 are windspeeds at the Von Karman's correction term. Pesticide concentrations over periods of at least 10 min averages are advantages of the method.

All these methods intensity of the source or sink intensity can be crop canopy or pesticide with evaporating from the canopy. The results are confined to the atmosphere.

Pesticide concentrations over surfaces are measured flow rate through absorbing media containing ethylene glycol used.^{4,5,8} More detailed molecular fluxes successfully to well below 1 m concentration profile and other such samplings over the surface.

Measurements of Field Volatilization

In recent years several measurements of volatilization rates have been reported. Techniques have been described by Caro, *et al.*,⁶ and Parmele, *et al.*⁷ The vertical flux of pesticide vapor ($F\uparrow$) through a horizontal plane at height z above the soil or crop canopy is given by the equation

$$F\uparrow = K_z (dc/dz) \quad (1)$$

where dc/dz is the gradient of vapor concentration with height and K_z is the vertical eddy diffusivity coefficient at the height z . Since the value of K_z depends upon the turbulent flow of the atmosphere into which the pesticide vapor is dissipated, it is a function of the meteorological conditions and not of any physical or chemical property of the pesticide provided that this behaves as a molecular vapor. The value of the coefficient may then be assumed to be the same as that for water vapor defined by

$$E\uparrow = K_z (dg_w/dz) \quad (2)$$

where $E\uparrow$ is the water vapor flux density and dg_w/dz is the water vapor concentration gradient. On the rare occasions where water flux data are available, the value of K_z may be calculated directly from this as reported by Taylor, *et al.*⁸ Without lysimeter data the equation may be solved by the Bowen Ratio method⁷ if data on net radiation, soil heat flux, and humidity and temperature gradients in the air are measured.

In the more commonly used "aerodynamic method" the eddy diffusivity coefficient is measured from the gradient of the wind profile over the surface. Measurements of temperature lapse rate are necessary to apply a correction factor for the thermal stability of the atmosphere. The vertical flux intensity is then calculated directly from the equation

$$P\uparrow = k^2 \frac{(c_1 - c_2)(u_2 - u_1)}{(\ln Z_2/Z_1)^2 \phi^2} \quad (3)$$

where c_1 and c_2 are pesticide concentrations and u_1 and u_2 are windspeeds at the heights Z_1 and Z_2 above the surface; k is Von Karman's constant ($= 0.4$) and ϕ is the thermal stability correction term. Measurements of the wind speed profiles and pesticide concentration gradients are taken during sampling periods of at least 1 hr to ensure that statistically acceptable time averages are obtained. A discussion of the limitations and advantages of each method has been published by Parmele, *et al.*⁷

All these methods give a measurement of the vertical flux intensity of the pesticide through a plane at some chosen height above the crop or soil surface. In the absence of any source or sink between this plane and the surface, the flux intensity can be equated with the volatilization rate from the crop canopy or soil surface. Measurement of the flux rates of pesticide within the crop, where it may be condensing or evaporating from leaf surfaces, presents considerable difficulties. The results discussed in this paper will however be confined to movements of pesticides in the free atmosphere.

Pesticide concentrations in the air above crop and soil surfaces are measured by drawing air at a known controlled flow rate through sampling devices containing a liquid or solid absorbing medium. In earlier work glass bubblers or scrubbers containing ethylene or hexylene glycol were commonly used.^{4,5,8} More recently absorbers such as polyurethane foam, Linde molecular sieves, and other solid media have been used successfully to measure pesticide concentrations in air at levels well below 1 ng/m^3 .⁹ For the measurement of pesticide concentration profiles needed to obtain volatilization rates, several such samplers are mounted at different chosen heights over the surface. Equipment used in a special study where a

large number of sampling points were used for precise determinations of profiles up to 2 m height over bare soil is shown in Figure 1. The concentrations found vary very widely. Although levels of up to $100 \text{ } \mu\text{g/m}^3$ have been observed at 1 meter heights over vegetation for short periods immediately after application,¹⁰ these were associated with very high and transient volatilization rates. Concentrations of 0.1 to $1.0 \text{ } \mu\text{g/m}^3$ appeared to be more typical at the 1 m height over freely evaporating surfaces for 1 to 2 weeks after application. Where pesticides are incorporated by soil cultivation, concentrations are much lower and rarely exceed the 100 ng/m^3 level (at 1 m height).

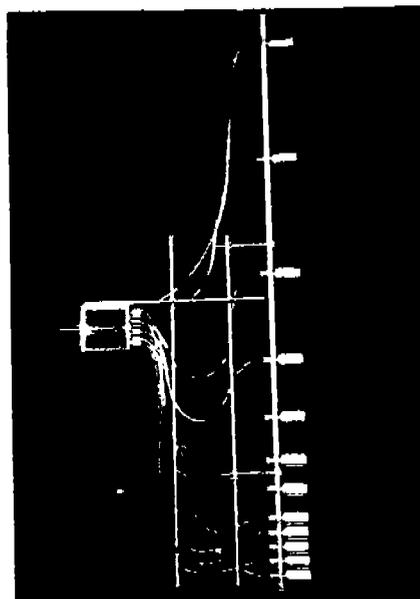


Figure 1. Air sampler system for measurement of pesticide concentration profiles up to 2 meters above treated soils or crops.

Results of Field Volatilization Studies

The details of the published experiments in which field measurements of pesticide volatility have been made are summarized in Table I.^{5,8,10-14} The description of each experiment includes the compound used, the nature of the surface from which volatilization was measured, the way the pesticide was used, the place and time, and a summary of the results. More detail on these points may be found in the original publication.

The table shows that the fastest losses are from exposed surfaces on plants or moist soils. Surface losses of heptachlor can exceed 30%/day, but losses of surface residues of dieldrin and chlorpropham are less than heptachlor or trifluralin, corresponding to their lower equilibrium vapor pressures. Rates are much less where the pesticides are incorporated even to shallow depths in soils. Incorporation of heptachlor, dieldrin, or trifluralin to the 7.5 cm depth reduced losses to less than 7% in 90 to 100 days, rates three orders of magnitude less than those for exposed residues of the same pesticides. Less efficient incorporation of trifluralin to the 2.5 cm depth gave a less marked reduction but the loss was still much less than unincorporated residues.

These observations suggest that a number of different factors may control pesticide volatilization depending upon the way the compounds are used and that incorporation of even the most volatile materials into the soil brings into play

Table I. Summary of management practices, experimental conditions, location and time in field experiments on pesticide volatilization, with general summary of results.

Compound	Equilibrium vapor press. (mm Hg at 25°C)	Experimental surface	Pesticide management	Season	Place	Fraction (%) volatilized in stated period	Reference
Heptachlor	3×10^{-4}	Bare soil moist	Surface application	August	Beltsville, Maryland	90% in 2-3 days	11
		Vegetation	Surface application	July	Beltsville, Maryland	90% in 7 days	11
		Soil under maize	Incorporated to 7.5 cm depth	May - October	Coshocton, Ohio	7% in 167 days	11
Trifluralin	2.4×10^{-4}	Bare soil moist	Surface application	August	Beltsville, Maryland	90% in 2-3 days	11
		Soil under soybeans	90% incorp. to 2.5 cm	June - October	Athens, Georgia	22% in 120 days	11
		Soil under soybeans	Incorporated fully to 7.5 cm	May - Sept.	Harford, New York	3.4% in 90 days	11
Chlorpropham	10^{-5} (est)	Soil under soybeans	Surface application (spray emulsion)	May - July	Frederick, Maryland	49% in 50 days	12
Dieldrin	2.8×10^{-6}	Bare soil	Surface application moist, irrigated soil	Sept. - Jan.	Baton Rouge, Louisiana	20% in 50 days	5
		Vegetation	Surface application	August	Beltsville, Maryland	90% in 30 days	10
		Soil under maize	Incorporated to 7.5 cm depth	May - October	Coshocton, Ohio	3.6% in 167 days	11

a rate-limiting mechanism that is inoperative for surface deposits. The nature of this mechanism will be discussed below.

Factors Controlling Volatilization Rates from Plants

The simplest relation between volatilization rate and time is shown by losses from leaf surfaces. Decreases in heptachlor and dieldrin residues on orchard grass measured by Taylor, *et al.*¹⁰ are presented in Figure 2. These losses could be accounted for by volatilization, chemical degradation being negligible. These curves, which are typical of those characterizing losses from vegetation,¹⁵ show an initial rapid loss for about one week, during which the rate decreases in proportion to the residue remaining. After this the remaining residue is lost much more slowly.

These curves may be interpreted in terms of the decreasing coverage of the leaf surfaces by the layer of pesticide residue. Initially, during the time the coverage is complete, the loss rate is governed by evaporation through the boundary layer of still air very close to the leaf surface. The concept of this boundary layer has been discussed by Rose,¹⁶ who pointed out that, even when the flow of air over the plants is fast enough to be turbulent, a thin layer exists very close to the leaf surfaces where the flow is essentially laminar. The movement of vapor from the surface through this layer to the region of turbulent mixing is governed by molecular diffusion. Provided the vapor pressure of the pesticide residue on the leaf surface is not reduced by chemical adsorption reactions and the leaf surface remains completely covered, the volatilization per unit area of leaf will not be affected by the amount of pesticide present, since the depth of the solid (or liquid) film of residue will not affect the rate of diffusion to the boundary layer. If this film is not of uniform thickness, rapid volatilization will lead to the formation of shrinking "islands" of residue, and the volatilization rate per unit of leaf area will decrease as the remaining islands decrease in size, as illustrated in Figure 3. In practice where pesticides are applied as water-based sprays or wettable powders which are deposited as droplets, complete coverage of leaf surfaces will not be attained. No initial period of constant volatilization per unit area will then exist and the rate

will decrease as shown in the first sections of the curves of Figure 2.

Where two pesticides are present in the same deposit and where the boundary layer remains saturated, the relative rates of volatilization (F_1 and F_2) from the pesticide covered surface should follow the equation proposed by Hartley¹⁷

$$F_1/F_2 = (P_1/P_2) (M_1/M_2)^{1/2} \quad (4)$$

where P_1 , M_1 and P_2 , M_2 are the equilibrium vapor pressures and molecular weights of the two compounds. This equation

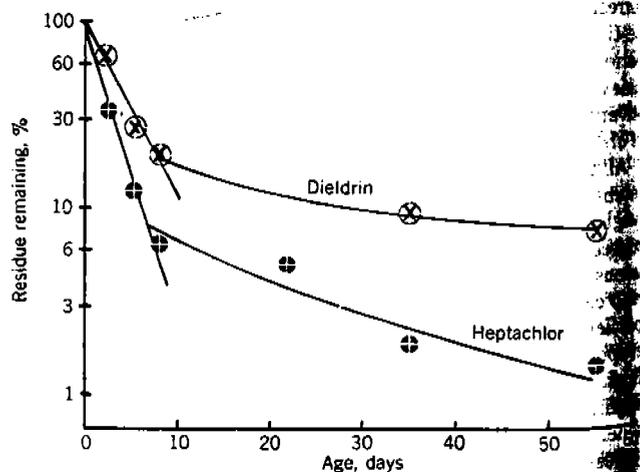


Figure 2. Loss of dieldrin and heptachlor residues by volatilization from vegetation for 55 days after application.

however represents a limiting case which is not met under field conditions except perhaps for compounds of low volatility whose residues may persist for extended periods. Table I shows the rates of volatilization of heptachlor and dieldrin observed by Taylor, *et al.*¹⁰ during the first 13 hours after application of a mixture of equal amounts of these insecticides

to orchard grass loss should be the experime difference sug much higher differences in di (4) inapplic The slower week (Figure This first sug larities on the will be the las residues may "islands": the amount of res that the last f which has pe adsorbed in ir of such a frac tifications of residues in p will lower th reduce the vo are likely to b to be drawn.

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to orchard grass. According to Eq. (4) the rate of heptachlor loss should be 108 times that of dieldrin. Even at the start of the experiment the rate was less than 5 times greater. This difference suggests that even very soon after application the much higher volatilization rate of the heptachlor caused differences in distribution of the two insecticides, making Eq. (4) inapplicable.

The slower rate of volatilization loss observed after the first week (Figure 2) may be explained by two different hypotheses. This first suggests that residues entrapped in surface irregularities on the leaves, in leaf whorls, or at leafstem junctions will be the last to volatilize. As illustrated in Figure 3, these residues may be deeper than those of the quickly evaporating "islands": the loss will then be no longer proportional to the amount of residue remaining. The second hypothesis suggests that the last fraction of the residues to evaporate will be that which has penetrated the leaf tissue and become chemically adsorbed in intercellular material or leaf waxes. The existence of such a fraction has been demonstrated by Caro¹⁸ in investigations of methods for the analytical determination of residues in plants. The internal adsorption of such residues will lower the equilibrium vapor concentration and hence reduce the volatilization rate. In practice both mechanisms are likely to be present and the data do not permit distinctions to be drawn.

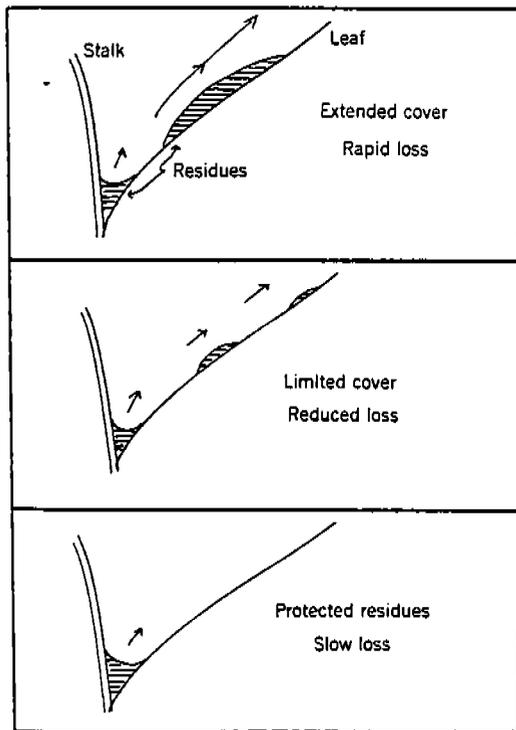


Figure 3. Effect of exposed area of pesticide residues on rate of volatilization from vegetation.

Volatilization of Residues on Soil Surfaces

Volatilization losses from soil surfaces are of particular importance in the management of pre-emergence herbicides, many of which are applied to and left exposed on bare soils to control weeds before the emergence of the planted crop. A recent review of the subject by Plimmer¹⁹ reveals that, while much information is available on the vapor pressures and other factors controlling herbicide volatility, most has been obtained in the laboratory. Except in the experiments listed in Table I most field information is concerned with measurements of herbicide persistence. Estimates of volatilization

Table II. Volatilization rates of heptachlor and dieldrin residues, during consecutive 2-hr periods over the first 14 hr following application to orchard grass pasture. (Application rate 5.6 kg/hr)

Sampling period (hours after application)	Volatilization rate (g/hectare/hr)		Ratio (H/D)
	Heptachlor	Dieldrin	
1-3	822	169	4.86
3-5	296	80	3.7
5-7	128	61	2.1
7-9	29	16	1.8
9-11	1.4	0.6	2.3
11-13	0.6	0.2	3

losses based upon measurements of decreasing residue concentrations are confounded by concurrent losses due to chemical or biochemical degradation.

In comparing the factors governing volatilization from soil with that from plant surfaces, the dominant effect of adsorption forces that reduce the vapor pressures of pesticides adsorbed on dry soils becomes apparent. Studies by Spencer, *et al.*^{15,20} and Parochetti and Warren²¹ have shown that the adsorption of many pesticides, including dieldrin, trifluralin, and chlorpropham, is very strongly influenced by soil moisture. Under very dry conditions strong adsorption reduces the vapor pressure of the residues to negligible values, but when sufficient moisture is present to cover the surface of the soil colloids to a depth of a few molecular layers, the vapor pressures rise to values close to those of the pure compounds. The moisture content at which this transition takes place varies from soil to soil depending upon the texture (i.e., the clay content) and organic matter content, but it is in the range of less than 3 to 8%. This is much less than the water content to which surface soil is wetted by rainfall or irrigation.

The resulting effect of soil moisture on the volatilization is evident in the data on chlorpropham volatilization obtained by Turner, *et al.*¹² The herbicide was applied as a spray of water-based emulsion to a bare and very dry soil. The volatilization rates during the first 5 successive 1 hr sampling periods immediately after application are presented in Table III. Despite continuous sunshine and a steady wind the volatilization decreased steadily as the moisture applied in the spray was evaporated. Despite a 4° C decrease in air temperature a marked rise was observed after the soil was moistened by a rain shower at 1500 hours. On the third day, when the soil moisture content had been raised to 18% by an intervening period of rain, the volatilization exceeded that of the first day.

Over longer periods of time additional complications also arise because the soil surface becomes sheltered from radiation and wind by the growing crop. Residues may also be washed downward into the upper layers of the soil surface by rain, when their volatilization pattern will become similar to that of soil-incorporated residues. These are much less than those of exposed residues.

Volatilization of Soil-Incorporated Residues

If it is assumed that a spray of pesticide applied to a bare soil at a rate of 1 kg/hectare remains in the top 1 mm of soil, the local concentration may be expected to be about 75 to 100 ppm. At this soil concentration, except in extremely dry soil, the vapor pressure will be close to that of the parent compound, as shown by Spencer, *et al.*^{15,20} for dieldrin and trifluralin. On incorporation to a depth of 7.5 cm, as commonly done by cultivation with a disk implement, the concentration in this layer of soil will be reduced to 1 to 1.25 ppm. At this lower pesticide concentration adsorption becomes more important and less sensitive to water content. Consequently, except for the small fraction of exposed material that remains on the surface after cultivation and which is readily lost, the

Table III. Volatilization of surface residues of chlorpropham, applied to clay loam soil as a spray of water-based emulsifiable concentrate at 1.5 kg a.i./hectare, during the first and third days after application.

Day	Sampling period (EDT)	Volatilization (g/hect/hr)
1	11-1200	29.4
	12-1300	10.0
	13-1400	7.6
	14-1500	10.4
	15-1600	28.7
3	07-0900	2.0
	09-1100	17.6
	11-1300	21.9
	13-1500	21.8
	15-1700	8.9
	17-1800	4.0

volatilization of the remaining pesticide is greatly restricted, becoming dependent upon the rate of upward movement of pesticide through the soil to the surface. The factors controlling this have been discussed in detail by Spencer, *et al.*,¹⁵ who compared the volatilization patterns to be expected where movement is controlled by a simple diffusion gradient to that where bulk movement of pesticide to the surface is controlled by the upward movement of soil water. Owing to the strong adsorption forces that develop, diffusive movement in dry soil layers is very slow and volatilization almost ceases, as shown by the data of Harper, *et al.*,²² who found that trifluralin volatilization from a Cecil Sandy Loam soil became very small when the moisture content of the surface soil (0 to 0.5 cm) fell below about 2% (by volume).

Movement of pesticide to the surface by bulk flow in the soil water is the dominant mechanism controlling volatilization of incorporated pesticide from moist soils. The mechanism has been discussed in detail by Spencer, *et al.*¹⁵ When a pesticide is incorporated into a moist soil the concentration in solution is controlled by desorption from the surface of the soil solids into the soil water, as illustrated in Figure 4a. At soil pesticide concentrations of less than 1-5 ppm, the vapor pressure over the surface is much less than the equilibrium vapor pressure of the pure compound (relative vapor density less than 100%). In the absence of water movement, pesticide is lost from the surface until diffusion flow becomes limiting (Figure 4b). Where upward movement of water is induced by evaporation the resulting continuous upward flow of pesticide prevents the development of a rate limiting diffusion gradient, and there is a continuous supply of pesticide at the surface as long as the water evaporation continues (Figure 4c). This mechanism is described as the "wick effect" by analogy with water movement to the exposed ends of moist fibers.

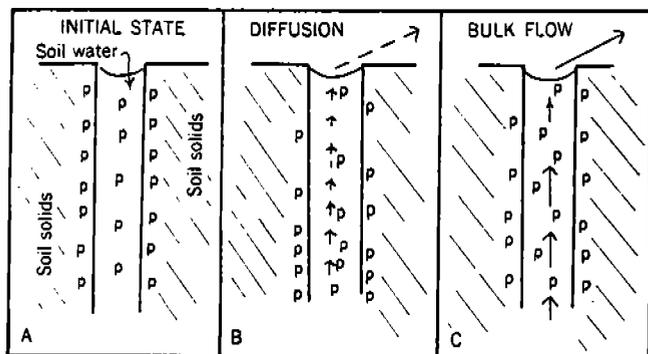


Figure 4. Diffusive and bulk flow (Wick Effect) mechanisms in controlling volatilization rate of pesticides incorporated into soil.

Analysis of the field data by Taylor, *et al.*⁸ showed that wick mechanism could explain both the diurnal and seasonal variations in the volatilization of incorporated dieldrin and heptachlor. The diurnal variations, with a marked maximum at solar noon, were shown to be closely correlated with the evaporation of soil water which was directly controlled by the intensity of solar radiation. The seasonal decline in volatilization was associated with the shading of the surface by growing corn and the decreased loss of moisture from the surface owing to the transpiration demand by the crop.

Comparison of the trifluralin data obtained by White, *et al.*¹³ in Georgia with that obtained by Taylor¹⁴ in New York revealed the wide variations there may be in the volatilization of an individual compound due to differences in soil conditions, climate, and management. The loss of 22% in the Georgia experiment resulted from incorporation to a limited depth in a soil of sandy texture (Cecil Sandy Loam) with low organic matter content (0.55% O.M.) In the New York experiment the trifluralin was mixed to the full 7.5 cm depth in a soil of heavier texture (Howard Loam) and much higher organic matter content (3 to 4% O.M.). This difference, coupled with the cooler and wetter weather in New York at the time of the experiments, can entirely account for the marked difference in the amounts of trifluralin lost to the atmosphere in the two experiments.

Shallow cultivation of soils containing incorporated residues leads to increased volatilization loss due to the fresh exposure of part of the buried residues on the open surface. Lichtens and Schultz³ showed that losses of incorporated DDT were increased by about 70% and aldrin by 33%, when the soil was cultivated daily for 3 months after application. The increase due to single cultivations is however, of short duration, being limited to the small fraction of the residue on the newly exposed surface. Field observations by Taylor, *et al.*¹⁰ revealed a sharp increase in dieldrin and heptachlor volatilization the day after fall disking (October 16th) of a treated field that had not been cultivated since the insecticides were applied on April 30th. Although the losses were high on the morning after disking, they declined rapidly during the day as the surface exposure was exhausted. Unlike disking or harrow cultivation which causes extensive stirring of the upper soil layer, plowing may drastically reduce volatilization because the turning results in deeper burial of the residues. Other observations reported by Taylor, *et al.*¹⁰ showed that volatilization losses of dieldrin in the second year after application, when the field had been plowed, were ten times lower than in the first year, although 90% of the dieldrin application still remained in the plow layer.

Rate of Dispersal in the Atmosphere

Examination of the measured volatilization rates in all the experiments summarized in Table I shows that the volatilization process is essentially always controlled by the volatilization process at the soil or plant surface. Comparison of the observed vapor concentrations in the air with the saturated vapor densities of the compounds shows that at height of more than 1 m above the soil or crop the air was always highly undersaturated with pesticide vapor. Except for a period immediately after application in one experiment,¹⁰ relative vapor densities at this height were always below 5 to 10%, and values of less than 1% were frequently observed. The exception to this was found during the volatilization of dieldrin from forest vegetation during the first 2 hr after application, when a saturated atmosphere of dieldrin vapor was maintained up to about 15 cm from the ground within the grass layer. In the case of heptachlor vapor formed from the same application, although higher in concentration, was undersaturated at all heights at all times.¹⁰

Except where volatilization is inhibited by surface drying, marked diurnal variations in volatilization rates with noonday maxima are frequent. Comparison of the flux rate

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with the gradients of concentration in the air showed however that the reduction in flux at night is a consequence of the reduced vaporization and is not due to reduced dispersal by reduced turbulence. The high relative vapor densities that would be reached close to the surface if vaporization continued in the absence of turbulent dispersion are not evident in any of the available data.^{8,10,13}

This conclusion is confirmed by calculation of the "residence time" of the vapor below the 1 m height, calculated as the total amount present between the surface height divided by the flux rate through it. Typical figures obtained for residence time both by Harper, *et al.*²² and Taylor, *et al.*^{8,10} are of the order of 10 to 40 sec during periods of high flux rates around solar noon with increases of up to 2 to 10 min in the morning and evening. These data show that the rate of atmospheric dispersion is never the rate limiting step even under the stable conditions present in the atmosphere close to the ground during nocturnal radiation cooling, since pesticide vapor formation then ceases almost completely.

Conclusions

Experimental measurements of post-application volatilization of pesticides made under field conditions reveal a wide range of rates depending upon the chemical properties of the particular material, the way it is used, and the substrate to which it is applied. The most rapid losses occur when the more volatile chemicals such as trifluralin or heptachlor are applied to the surface of moist soil or vegetation. Under warm and humid conditions losses of up to 90% or more of the volatile compounds may occur within 2 or 3 days. The rates of volatilization during periods of rapid loss appear to be principally governed by the distribution of the residues over the plant or soil surfaces. Volatilization is however never complete since a small fraction of residue is retained by chemical adsorption or occlusion within sheltered areas or crevices on the surface. The volatilization of this last fraction of the residues may be very slow.

Losses from field soils where the surface moisture content falls below about 5% are much less owing to the strong adsorption of pesticides by dry soils. Volatilization from such soils may show erratic variations as the soil surface is wetted or dried by varying weather. Washing of residues into the soil by heavy rain will greatly reduce the rate of volatilization which will then be controlled by its rate of return to the surface either by upward diffusion or bulk flow in soil water.

The lowest volatilization rates are found for pesticides incorporated with the soil by cultivation immediately after application. These rates are controlled by the bulk flow of pesticide to the soil surface with the upward movement of evaporating soil water. Drying of the surface soil, causing a break in the continuity of the water columns and the exposure of dry soil layers of high adsorption capacity, may entirely inhibit volatilization by this route. The amount of the incorporated pesticide residues lost appears to be governed largely by the depth through which they are incorporated and how well they are mixed. Weather effects are also of prime importance, the highest rates being expected when the soil is subject to continuous water evaporation without ever becoming very dry on the surface.

No simple relationships between rates of volatilization and the amounts of residue remaining were found in any of the experiments. Distribution of the residues either over the soil or plant surfaces or within the soil profile appeared to be the dominant factor. This, together with the sensitivity of the volatilization rate to the microscale climate at the soil or plant surfaces, makes detailed predictions of losses a complex problem.

The experiments have however revealed the basic elements that control the volatilization process. An understanding of these, with laboratory measurements of vapor pressures and adsorption isotherms taken together with sufficient infor-

mation on weather variables such as temperature, evaporation, rainfall and solar radiation may permit meaningful estimates to be made for sufficiently well defined field situations.

Prediction of rates of volatilization of residues from the surface of field soils is likely to prove extremely complex, requiring a knowledge of the vapor pressure of the compound and the extent to which this is reduced by adsorption in both wet and dry soil, its water solubility and a detailed history of the change in water content of the upper layers of the soil over a period of about 3 weeks after the application. Control of the volatilization of compounds such as pre-emergence herbicides which are applied to soils in this way, is best achieved through incorporation to shallow depths or the use of slow release formulations. Such formulations have been shown to reduce volatilization to about 20% of that of conventional applications with a consequent increase in efficiency of weed control and reduced environmental impact.¹²

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