accelerated storage test as an indication of the probable long-term storage life of a given powder. These data also indicate that the present package volume is critical, and additional compaction would seriously affect the suspensibility after accelerated-storage treatment as well as after long-term storage. In fact, in the interest of good storage stability it would probably be prudent to increase the volume of the present container.

Aging of the DDT powder up to 1 week after air milling but before compaction does not affect its storage characteristics.

Acknowledgments

The authors wish to thank Carl Hughes for his valuable assistance in designing and constructing the laboratory compactor used in the experiments on compaction. These studies were accomplished as part of a contractural agreement between the National Communicable Disease Center and the Agency for International Development. The use of trade names is for identification only and does not constitute endorsement by the Public Health Service.

Literature Cited

(1) Miles, James W., Goette, Mary B., Grimm, Louis, Pearce, George W., *Bull. World Health Organ* **20**, 937 (1959).

(2) Miles, James W., Allen, Kenton, Woehst, James E., Grimm, Louis, *Bull. World Health Organ.* 27, 270 (1962).

RECEIVED May 3, 1967.

AP-42 Section 9.2.2
Reference 12
Report Sect.
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Evaporation of Pesticides

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Pesticides are subject to considerable loss by evaporation when they are thinly spread over large areas of crop exposed to moving air. In this situation they are subject also to biochemical, photochemical, and solution losses which make it difficult to assess directly evaporation under field conditions. The rate of evaporation of water is easily determined and has been the subject of much experiment. The relationship of loss of pesticide to loss of water from the same surface can be verified by laboratory experiments. Crystallization and solution in leaf substances exert some effect also. When the pesticide is distributed in the soil, evaporation of water can accelerate that of the water-soluble pesticide; the mechanism lies in capillary flow of solution and not in the evaporation process itself.

The saturation vapor concentration (SVC) of any pure substance is related to its vapor pressure at any one temperature. It is closely analogous to solubility—*i.e.*, saturation concentration in a liquid—and might be called the solubility in a vacuum or in air. For our purpose the composition of the rest of the gas phase can be ignored because it is only at pressures much higher than atmospheric that this has any influence on the SVC. Solubility in liquids, however, depends strongly on the nature of the liquid because the molecules in a gas spend nearly all their time apart, suffering only brief mechanical collisions, whereas molecules in a liquid are always under the strong influence of the force fields of their neighbors.

In high vacuum processes, which are related to our subject only by electron microscope technique, the rate at which a substance evaporates has an ultimate limit depending on the number of molecules having momentarily enough energy to break away. Thereafter, they follow a straight line until they collide with an object. When a substance evaporates into air (unless it is in the form of an isolated particle less than about 1μ diameter), its rate of evaporation is determined solely by the SVC and the rate of diffusion through the air closely surrounding the substance.

In air at 20°C. the mean distance traveled by water molecules between successive collisions is about 5×10^{-6} cm. Even if the stagnant air layer around the object were only 0.1 mm. thick, each escaping water molecule would experience 2000 collisions if these did not alter its direction. In fact, as a result of these collisions the molecule would be just as often going backards as forwards, and the number of collisions would be much greater (and proportional to the square of the thickness). If the water could be maintained at 20°C. and the outer air were dry, the rate of escape by diffusion would be about 3×10^{-4} gram/sq. cm. sec., whereas the ultimate rate in a high vacuum has been calculated to be about 0.25 gram/sq. cm. sec., some 600 times greater (*1*).

Rate of Solution or Evaporation

The rate of solution of a substance in a liquid depends even more strongly on diffusion in the surrounding liquid because in this denser population of molecules, diffusion is much slower. However, there are cases where the rate of solution is determined by other factors—*e.g.*, the anomalously slow rate of solution of anhydrous lithium carbonate. Such cases are exceptional, involving a special mechanism, and I know of no evidence that any organic substances enter this class.

The less soluble a substance is in a liquid or in air, the slower its absolute rate of diffusion into previously pure liquid or air. The final content of a limited volume at saturation is proportionately less, so that the rate at which any chosen proportion of the saturation capacity is reached does not depend on solubility or SVC. It depends only on the diffusion coefficient, which does not depend strongly on the size of the diffusing molecule. An empty flask or one full of clean water can be 99% saturated with parathion just as quickly as it can with benzene or sodium chloride—in fact more quickly, for two reasons. First, benzene diffusing into air or sodium chloride diffusing into water builds up a large density gradient which stabilizes the fluid against convection owing to slight temperature variations, while a substance of low solubility or SVC leaves the fluid subject to chance stirring. Secondly, considerable heat exchange occurs during solution or evaporation, so that the vessel containing the volatile or soluble substance must be allowed time to settle to ambient temperature. These differences are, of course, reduced by rapid stirring, which is therefore more necessary with higher solubility or SVC.

This point is important because many experimenters intuitively believe the opposite. They assume that the less soluble or volatile a substance is, the more difficult it is to saturate a given volume of liquid or air. Consequently, they resort to excessively violent agitation, and, in the case of liquids, may build up stable fine dispersions of significant concentration, thus introducing more errors than they avoid. The idea is latent in that description cherished by 19th century German chemists—"schwer löslich" —slavishly translated as "difficultly" soluble, the only context in which this adverb is used. The phrase may mean that the substance has the rare property shown by lithium carbonate—*i.e.*, that the rate of solution is not determined by liquid-phase diffusion, but it more often simply disguises the presence of complicating impurities, or the author just cannot be bothered to find out the facts. The phrase should be eliminated by editors of reputable journals.

In one important respect it is true that the less soluble or volatile a substance is, the longer it takes to saturate its environment—*i.e.*, when adsorbing surfaces are present. At extremely low solubility or SVC even the glass walls of a simple vessel may be significant, but the porous walls of a room, the greater area of the foliage in a crop, or the even greater area of particles in the soil are much more important. The amount adsorbed is limited by area and is generally a much greater fraction of the content of the total volume the less the solubility or SVC. For soil, much more substance may be adsorbed on particles than is dissolved in soil water or present as vapor in the air space. This adsorption does not reduce the rate at which a particle dissolves or evaporates. In fact, it increases it, but since more must dissolve or evaporate down a limited concentration gradient, the rate of saturation of the environment is decreased.

Influence of Air Currents

Since the rate of evaporation is determined by diffusion of vapor in the surrounding air, it depends strongly on air movement and the geometry of the exposed surface. Close to this surface there will be relatively no movement of air. The substance will be transported from the surface only by molecular diffusion. Further away from the surface there is movement of air which can carry away the vapor more rapidly than molecular diffusion. This air movement operates in two ways. It continuously replaces the air around the evaporating surface, which is the only important factor for a small object like an isolated drop of water. This mere replacement, however, would be of little help to evaporation from a large area such as a lake because the replacement air has already been saturated upwind.

Here the second factor enters, arising from the fact that wind is never smoothly laminar in flow, except a very gentle wind under inversion conditions (when evaporation of water is not occurring). Normally a "drying" wind is turbulent, having a complicated structure of eddies of various sizes. This leads to a mixing of air composition which, over long enough time and distance, follows the mathematical laws of diffusion but with a diffusion coefficient hundreds of times greater than that of molecular diffusion. The process, of enormous importance for the entire atmospheric behavior, is called "eddy diffusion" (*20*).

At the simplest, therefore, the evaporation of water from a large area can be represented as diffusion into a horizontally shearing volume of air, the coefficient of vertical diffusion increasing from the molecular value of 0.24 sq. cm./sec. to several hundred times this value with increasing height. Most of the increase from slow molecular diffusion to rapid eddy diffusion occurs in the first few millimeters above the surface. From a few meters upward the atmosphere becomes more stable except for major wind changes which, if we are considering a large evaporating area like Lake Superior, are largely determined by the evaporation itself.

Obviously the theory of evaporation from large areas is quite complex, requiring computer evaluation even if all relevant data were available. There is, however, a vast amount of accumulated experimental data about water evaporation, and if we can establish the relationship between water and pesticide evaporation, we can use this material for prediction. The evaporation of water over a large area can always be viewed either as a small- or large-scale process. Thus, we can measure total evaporation from a lake in relation to wind conditions and the humidity and temperature of the air as it reaches the lake, or from small identical open vessels floated at various locations on the lake surface. The first would show an average rate roughly proportional to the 3/2 power of the lake diameter (if circular), to the 1/2 power of the wind velocity, and to the humidity deficit of the incoming air. The second would show a rate approximately proportional to the local humidity deficit but more nearly proportional to vessel area.

The local measurement would at first seem the best comparison for the evaporation of a pesticide deposit, allowing for the humidity of the local air into which the water is evaporating and assuming that the pesticide is evaporating into "clean" air—*i.e.*, there is no counterpart to the partial previous loading of the air with vapor. However, this assumption cannot be made without careful consideration. Is there a significant general loading of the whole air above a large field with evaporated pesticide, or is the rate of loss from any local deposit the same as if the rest of the crop had not been sprayed?

Heat Effects in Evaporation

Before attempting an answer, we must closely examine the factors governing a small-scale evaporation process. The simplest case is that of a small drop in free fall or suspended on a thin thread. If the drop is in the range of 10–200μ diameter, the peculiar mathematics of spherically divergent diffusion dictate that the rate of evaporation is proportional to radius, not area, and almost independent of any air flow of realistic magnitude.

The rate of evaporation of water from such an isolated drop, although governed entirely by diffusion, is not governed entirely by diffusion of water vapor. Latent heat must be supplied during evaporation. The drop cools until this heat is conducted in from the air at a rate equalling the outward diffusion of water vapor. There is no other significant heat source since even if the drop were black, the direct radiation contribution of full sunlight would not be important for drops of this size.

The balance between conduction and diffusion still operates for a much larger isolated wet object, provided radiation is excluded. This is the basis of the wet bulb thermometer method for measuring humidity. The actual rate of evaporation now is not as simply determined and is influenced by wind. The wet bulb temperature is almost independent of wind condition, owing to a convenient accident. Heat conduction is a diffusion process, and the diffusion coefficient for water vapor in air (0.24 sq. cm./sec.) is numerically close to the diffusion coefficient of temperature in air (thermal conductivity/specific heat = 0.20 sq. cm./sec.). Hence, the exact way in which each molecular diffusion process merges into the more rapid eddy diffusion process is not important because no matter how complex the transition is, it must be quantitatively similar for the two processes.

Calculation of the balance of inward heat diffusion and outward vapor diffusion leads to Equation 1:

$$\Delta T = (1 - H)\,\frac{\lambda D C_o}{K + \alpha\lambda D C_o} \qquad (1)$$

where ΔT is the difference in temperature between dry and wet bulbs, H is the relative humidity of the outer air, C_o is the SVC of the evaporating substance at the temperature of the outer air, D is the diffusion coefficient of the vapor in air, K is the thermal conductivity of air, and λ is the latent heat of evaporation referred to the unit used in concentration (*i.e.*, if C_o is in grams/cc., λ must be in cal./gram); α is the relative variation of C_o with temperature, $\alpha = \frac{\lambda M}{RT^2} - \frac{1}{T}$, where M is the molecular weight if the gas constant R is expressed (as usual) in cal./mole. [Relative humidity is introduced only for evaporation of water since this is the only case when the air is already partly loaded to a significant extent with vapor. The correction for prior partial saturation of other substances is not usually important. If it were, it could not be treated as simply because the diffusion coefficient of other vapors is considerably less than that of temperature.]

The $\frac{1}{T}$ term in α allows $\frac{\lambda}{RT^2}$ to determine $\frac{d \log p}{dT}$ (p = vapor pressure), whereas we expect diffusion rate to be determined by concentration and therefore $\frac{d \log C}{dT}$ to be required. This is arguable since complications arise in any diffusion process in a temperature gradient. For more accurate discussion, a treatise such as that by Fuchs (*15*) should be consulted. We are concerned only with approximate values, note that $\frac{1}{T}$ is much smaller than $\frac{\lambda M}{RT^2}$, and ignore it.

We can then show that for rate of evaporation through a stagnant layer of thickness l,

$$\text{Rate} = \frac{C_o\,(1-H)}{l} \Big/ \left[\frac{1}{D} + \frac{\lambda^2 C_o M}{KRT^2}\right] \qquad (2)$$

For water and an ambient temperature of 20°C. Equation 1 gives $\Delta T = (1 - H)/0.084$, consistent with the Smithsonian tables, and Equation 2 gives:

C_o = SVC
H = rel. hum.
l = thickness

$$\text{Rate} = \frac{C_o\,(1-H)}{l} \Big/ (4.17 + 10.84) \qquad (3)$$

Equation 3 shows that if water must evaporate from a surface which can receive heat only from air through the same surface, it will evaporate at only about 0.27 of the rate which obtains under isothermal conditions (where there is no second term in the denominator). The thermal component of the total resistance is thus about four times the mass-diffusion component.

The thermal term, being proportional to C_o, becomes relatively less important at lower temperatures and with less volatile substances. It is greater for ether than for water, and for ether the temperature drop is so great that another factor enters—namely, condensation of water from the air on the evaporating surface. For xylene at 20°C. the thermal term reduces the evaporation rate from an isolated surface to about 0.6 of the isothermal value (*cf.*, to 0.27 for water), and for most pesticides (except the fumigants) the reduction is negligible.

In applying Equation 2 to pesticides, therefore, we can set the second term in the denominator equal to zero; however, since we want to use this equation mainly for comparison with other substances (since l can only be measured by this equation), we have a complication—*i.e.*, the best known comparison substance, water, may have any value for this second term between 0 and 4 times the first (at 20°: at 10°C., *ca.* 0 to 2.3). The first condition could apply to a smear of water on a copper plate provided with vanes below to conduct heat as quickly as possible from the air, the second to an isolated drop or a wet cloth or paper. Practical surfaces, leaves, soil, etc. will be somewhere in between. Insofar as significant heat is received on such surfaces by radiation or supplied by conduction from the soil, its effect will be nearly the same on water and pesticide and does not therefore disturb the comparison.

Laboratory Comparison of Evaporation Rates

Some indirect method of measuring evaporative loss is needed because of the difficulty of direct measurements. Total amounts in random crop samples at various times after spraying can be measured by residue analytical methods (radioactive tracer or otherwise). The rate of loss so determined is subject to large statistical errors and includes losses by chemical and biochemical reaction and perhaps translocation in the crop as well. Exposure of typical test surfaces treated with some model substance, preferably less volatile than water but sufficiently volatile for simple gravimetric procedure, would seem the most suitable. We will see, however, how successful water is as a model for providing rough estimates.

Crude experiments were performed in the laboratory with substances unlikely to show significant weight change by adsorption of water or oxygen and sufficiently volatile for loss to be recorded conveniently on an ordinary balance. Petri dishes (41 sq. cm. area) were used to contain the substances, mostly liquids and used in the pure state. Two solids were included: p-dichlorobenzene and naphthalene. These were layered in coarse powder form, and the surface was sprayed with a solution of low molecular weight polyisobutene in petroleum ether until it was sticky enough to prevent blowing of the powder in the wind it was intended to use.

Not all measurements could be conducted together because the loss of weight rates covered a range of over 1000-fold. Moreover, it was desirable to use three replicates of each substance and arrange the dishes on a grid through which the draught from an ordinary room fan could blow, occupying a sufficiently small area for the wind to be reasonably uniform. Dishes were removed for weighing at intervals and replaced in different positions to randomize ventilation. The experiments were conducted in three groups over different time intervals according to volatility, with anisole and n-octanol forming the common compounds linking the groups.

Mean room temperature was 20°C., and no thermostatic measures were taken, but the rates were recorded relative to that of one of the standards. Water and xylene received closer study (described below) to illustrate particular points. For the most volatile group three ventilating conditions were used: (1) no deliberate ventilation, (2) gentle fanning, (3) more violent fanning with the wind directed about 45° downward onto the grid of dishes. The third condition visibly disturbed the liquid surfaces. The wind velocity at dish level was about 10 m.p.h. (used only for the less volatile groups).

Table I. Laboratory Determination of Evaporation Rates

Ventilation	*Substance*	*Vapor Pressure (p), mm. at 20°C.*	*Molecular Weight (M)*	*Rate of Loss (W) grams/min. × 10^4*	$W/p\sqrt{M}$
Still	Water	17.5	18	59	1.12[a]
	2,2,4-Trimethylpentane	37	114	540	1.37
	m-Xylene	6.2	106	76	1.19
	Anisole	2.8	108	30	1.03
Slow wind	Water	17.5	18	93	1.79[a]
	2,2,4-Trimethylpentane	37	114	717	1.82
	m-Xylene	6.2	106	174	2.72
	Anisole	2.8	108	102	3.50
Stronger wind	Water	17.5	18	108	2.07[a] [7.45]
	2,2,4-Trimethylpentane	37	114	1186	3.01
	m-Xylene	6.2	106	267	4.18 [6.7]
	Anisole	2.8	108	158	5.04
Stronger wind	Anisole	2.8	108	158	5.04
	p-Dichlorobenzene	0.80	147	54	5.6
	N,N-Dimethylaniline	0.66	121	41	5.6
	n-Octanol	0.073	130	4.1	4.9
Stronger wind	*n*-Octanol	0.073	130	4.1	4.9
	Naphthalene	0.049	128	3.3	6.0
	Exp. compound	0.022	162	1.5	5.4

[a] Corrected for 30% relative humidity of ambient air. Figures in brackets allow for full wet bulb depression.

The data available on the molecular diffusion coefficient of organic vapors in air are meager, but they indicate (in accordance with approximate theory) an inverse proportionality to the square root of molecular weight. The rate of mass transfer by molecular diffusion will be proportional to the diffusion coefficient and to the SVC, itself proportional to vapor pressure times molecular weight (M). We should expect, therefore, under standard conditions of ventilation, that the rate of loss will be proportional to vapor pressure × $\sqrt{M}$. The ratio of observed rate to this product is listed in the last column of Table I. For anisole and compounds less volatile in the strong wind, the ratio is as constant as the crudity of the measurements and assumptions would allow us to expect.

The mechanism of deviation of the ratio from a constant value for the more volatile substances has already been indicated. For these substances the heat demand slows evaporation. This effect is greater when the high wind blows on the evaporating surface because the heat exchange through the base of the dish is relatively less important. The water evaporation rate has been corrected, in forming the product in the last column, for the ambient air being at 30% relative humidity (RH).

We wish only to show that we can reasonably predict evaporation rate on the basis of vapor pressure if the data for a model substance which is not too volatile are known.

Results reported by Phillips (*19*) for evaporation of aldrin (labeled with ^{36}Cl) from a 20-sq. cm. area on a flat plate are six times greater than predicted from Table I, taking the vapor pressure as 4×10^{-6} mm. Hg, from Martin (*18*).

The rates calculated for xylene and water (into 30% RH) diffusing through a 1 cm. depth of stagnant air over an area of 40 sq. cm. are (in units of 10^{-4} gram/min.) 84 and 70 under isothermal conditions and 52 and 19 when heat can diffuse only by the same route by which vapor diffuses out.

Comparison with experimental results shows that the higher the ventilation rate, the more closely the ratio approaches that expected for the isolated condition, but it does not fully reach it. The values in brackets in the last column of Table I are corrected on the assumption that full temperature difference was built up. Clearly an intermediate condition still prevailed, and in fact the water temperature in this condition was found to be 5.1° below ambient compared with 8.3° below for a wet bulb.

Under field conditions water evaporation normally occurs from the same surfaces as evaporation of pesticide. Any temperature effect caused by the former will therefore affect the latter, and in this repect the state of affairs is simpler. On the other hand, leaves can restrict water evaporation, and the soil surface is very complex; hence, other complications appear under field conditions. All these factors, however, will make the pesticide evaporation rate (if the pesticide is fully exposed on an outer surface) faster than that calculated from the water rate.

Comparison with Table I shows also that the effective depth of the stagnant air layer above the liquid is of the order of 10 mm. in still air and 3 mm. in strong wind. van den Honert (*16*) quotes figures for outside conditions ranging from 10 to 0.4 mm. in a much stronger wind.

An important factor in laboratory "still air" evaporation of volatile liquids is self-stirring caused by the difference in density between saturated and "clean" air. Dry air at 20°C. becomes 1.05×10^{-5} gram/cc. (about 0.85%) lighter when it is saturated with water vapor at the same temperature. When, however, it is saturated at the temperature of the wet bulb—*i.e.*, in contact with a surface of isolated water, it becomes about 3% heavier. Self-stirring above water therefore depends on the heat transfer conditions. Air saturated with xylene vapor is 2.4% heavier than clean air when both are at 20°C., and in this case any temperature drop increases the difference. From a flat vessel, therefore, the xylene vapor tends to spill over the edge and thus to limit the stagnant layer depth. In a deep vessel, the density gradient stabilizes the air layer for xylene but ceases to do so for water if heat conduction through the vessel walls is important.

Vessels of the same diameter as those used for the experiments reported in Table I but of greater height were filled to various depths with water and xylene, and measurements in still air were repeated (Table II). Where the evaporation rate of xylene is reduced in approximate proportion to the height, that of water is much less influenced.

Table II. Evaporation of Water and Xylene through Different Heights

Substance	*Loss (grams/min. × 10⁴) when Vertical Distance between Liquid Level and Vessel Rim is:*			
	1 cm.	*5 cm.*	*10 cm.*	*20 cm.*
Xylene	56	14	7.5	4.3
Water	48	39	28	22

In field conditions this complication would not occur. We are not likely to be concerned with a pesticide with as heavy a vapor as xylene (except in fumigation work), and convection from wind and local heating will always be more important than that produced by the vapor itself. This experiment is quoted as an example of a complication to avoid in laboratory work.

Decrease of Evaporation Rate with Time

The rate of loss of substance from a complete surface of constant area is independent of the depth of the layer below the surface. Under constant conditions of ventilation, therefore, the rate will be constant until so little substance remains that it can no longer cover the surface. The way this rate then falls off will be complex. There is no reason whatever, from theory or experiment, to suppose that the loss will be exponential. There is a tendency to assume that the natural form of any rate of decay is exponential, but this is only true of a uniformly distributed noninteracting population. For evaporation, exponential loss can be expected only for a volatile dilute component of an otherwise involatile and stirred solution, where the vapor pressure will be proportional to concentration. This could correspond to some field conditions of residues but not without other complications.

Evaporation from glass plates must always be quoted in absolute terms, and the conditions must be specified. Statements, which could be quoted from the literature, such as "23% of the deposit is lost in 24 hours" (density of deposit not stated) are meaningless.

The factors which decrease evaporation rate with time are (1) retreat of an initially continuous deposit into discrete small areas as it gets too thin to be coherent, (2) influence of adsorption or solution in the porous, oily, or wet surface, (3) retreat of a deposit, initially lying on the outer surface, into deeper capillary spaces.

The third factor introduces some important additional ones, especially for loss from the soil, and is discussed separately below. The second factor, for water-soluble substances, is associated with the third. Solution in superficial leaf oils and applied solvents is also considered separately.

There is already a well-known parallel to the influence of the first factor in the control of evaporation from leaves by the stomata. Much work has been done since the classic researches of Brown and Escombe (8). It is not possible here to summarize it adequately, but it is generally agreed that the stomata, which are present (if at all) at a high population density of many per square millimeter, have little effect under normal wind conditions until they become nearly closed. For the resistance of a pattern of holes to be important compared with that of the gross stagnant layer, the width of the holes must be very small compared with their distance apart, or their distance apart must be large compared with the effective thickness of the stagnant air layer. The latter condition is not met by stomata. The first condition is not likely to be important for pesticide deposits because small particles are usually grouped together within the coarser pattern of the spray droplets or the drainage pattern determined by the leaf structure.

It is therefore reasonable to assume that the evaporation rate of residue is proportional to the gross area of spray deposit for a pesticide remaining exposed on a leaf surface. The pesticide will be lost at a constant rate, under constant conditions of ventilation, until the contaminated area decreases significantly.

Evaporation from Solution

At the surface of a solution, equilibrium exists between the uppermost layer of liquid and the vapor in the lowest layer of air. The evaporation rate is determined by the stirring condition in both air and liquid and diffusion in the stagnant layers. Since diffusion coefficients in air are of the order of 10^4 times those in liquids, one might at first expect the more important resistance to be located in the liquid, but this is more than compensated by two other factors. First, the concentrations (and therefore gradients) are usually many times greater in the liquid. Secondly, the viscosity of water is about 60 times that of air, while the density is some 850 times. A given velocity is therefore more slowly arrested in water than in air; it is in fact easier to agitate water than air close to a fixed surface. Self-stirring of liquids by composition changes is greater than the corresponding effect in air, and the same would apply to temperature changes were it not for the great difference in specific heat. A 1°C. difference at 20°C. makes a 2×10^{-4} gram/cc. difference in the density of water but only 6×10^{-7} gram/cc. in the density of air, but the same amount of heat absorbed in the same volume makes 12 times as much difference in air density as in water density.

Benzene and carbon tetrachloride are about equally volatile. From solutions of equal concentration in methylnaphthalene they are lost, at first, at about the same speed, but while the rate of loss of benzene from an unstirred vessel remains constant, that of carbon tetrachloride falls rapidly. Loss of benzene leaves the surface solution heavier, and self-stirring occurs; loss of carbon tetrachloride leaves it lighter, and a concentration gradient is stabilized.

During evaporation from soil or field crops, the stirring of liquid layers is not important, but it should not be neglected in laboratory comparisons. Pesticide solutions subject to evaporation in the field occur in three main situations:

(1) Where the pesticide is dissolved in the superficial oils or cutin of the leaf.

(2) Where it is dissolved in plant sap (*e.g.*, systemic insecticides).

(3) Where it is dissolved in soil water.

In the first case, the layer of solution is so thin that diffusion within it is probably unimportant. In the case of the mesophytes, to which group nearly all crops belong, surface oils and waxes rarely amount to as much as 100 μgrams/sq. cm. of leaf surface (*i.e.*, mean thickness less than 0.5μ on each side) (*3, 13*). Internal oils, much less accessible, may be present in about the same amount (*9*). Some fruits may have more superficial oils or soft waxes—*e.g.*, on apple skin there is about 400 μgrams/sq. cm. (*3*). The polymeric cutin itself, highly lipophilic but not too swollen by fatty solvents, is generally 1—3μ thick (200–600 μgrams/sq. cm. taking both sides) (*4*). One pound of a pesticide uniformly distributed over a flat acre leaves a deposit of 11 μgrams/sq. cm. Pesticides are rarely applied as uniformly. There is more likely to be about one-tenth of a flat acre actually covered, in which the deposit density will be correspondingly higher. It is therefore unlikely that much of an oil-soluble pesticide will be dissolved in superficial oils except on fruits. Such solution may delay the later stages of evaporative loss (approximately exponentially) because the rate of equilibration within the thin oil layer will be rapid (about 1 sec. for 1-μ thickness at $D = 10^{-8}$ sq. cm./sec.—*i.e.*, 1/100 of rate in normal liquids). Within the crosslinked cutin, D could be much lower, and a long delay in the release of a small "tail" fraction of pesticide could be expected.

In the third case, we are concerned with a considerable depth of water distributed in fine channels and small pockets where there is negligible stirring. Since the result is important and its explanation is often misunderstood, it is discussed separately under wick-evaporation.

Steam Distillation

Where a solution of a moderately volatile organic substance in water is distilled, the distillate is often richer in organic substance than the residue and may form two separate phases. The evaporation of pesticide along with water from wet soil is often referred to as steam distillation or codistillation. The implication that the pesticide evaporates more rapidly because of the presence of the water is entirely correct, but to imply that steam distillation is the explanation directs attention to the wrong part or the total process.

The word distillation in the chemical laboratory is usually confined to a process in which the liquid or mixture in the boiler actually reaches the pressure allowed within the apparatus so that rapid bulk flow of vapor takes place from boiler to condenser. The speed of transfer rises enormously when this pressure is reached. If water were not present in a steam distillation, the other components would not reach the necessary pressure at the same temperature, and only slow diffusive transfer in the gas phase would occur. The presence of water does not assist diffusive transfer but only lowers the temperature at which diffusion gives place to bulk flow. The use of steam as a carrier gas allows easy collection.

During evaporation from moist soil, there is no distillation in this sense. Evaporation of both water and pesticide occurs purely by diffusion. The mechanism in a laboratory apparatus by which water accelerates diffusion into a bulk flow distillation is not operative here.

Loss of DDT during evaporation of water from very dilute solutions or suspension has been investigated by Bowman *et al.* (*2, 7*), who refer to co-distillation to explain the loss of DDT accompanying the loss of water, without any real evidence that the water has any influence. No parallel experiments on vessels without water are reported, and only in one comparison trial was distillation involving gas flow carried out. In all other cases water and DDT were diffusing together, probably with no mutual influence, through air. In fact, in the earlier paper the ratio of rates of evaporation was found to be close to those predicted from the known vapor pressures. Unfortunately, the rates were assumed to be proportional to the product of vapor pressure and molecular weight, true for flow distillation only, whereas for diffusive distillation the square root of molecular weights (*see above*) is more likely to be relevant. This correction reduces the predicted DDT/water ratio to about 0.23 of the authors' calculation. In the later paper the experimental ratio is revised upward so that we have DDT evaporating about 10 times faster than expected.

In these experiments the DDT would almost certainly be in the supercooled liquid state, which persists for a surprisingly long time in much more concentrated suspensions than those used. The vapor pressures quoted from Balson (*5*) and the later, higher figures of Dickinson (*10*) refer to crystalline DDT. The supercooled liquid would be expected (since the solubility of the solid in best solvents corresponds to about one-ninth on a mole fraction basis) to have about nine times the vapor pressure at room temperature of the crystals. There is little discrepancy left. In view of the facts that all measurements had to be made at less than 1 p.p.m. concentration, that DDT loss had to be obtained by difference, and that adsorption on vessel walls is difficult to allow for, this work leaves me with no anxiety for the validity of classical physicochemical theory. Distillation from supercooled droplets on a glass plate to growing crystals has been demonstrated by Feichtmeir (*12*).

Wick Evaporation

There is abundant evidence that water can accelerate the evaporation of pesticides from the soil. Two mechanisms operate: one which depends on the evaporation of water, the other requiring only its presence. The first is best called wick evaporation and is the phenomenon which should be referred to by the agronomist when he speaks of steam distillation.

When evaporation occurs from the exposed surface of a wick dipping into the liquid in an otherwise closed vessel, liquid moves up the capillaries of the wick to replenish that lost at the top by evaporation. The diffusive escape in the vapor phase causes an actual mass flow in the wick. It is easy to show that at practical rates in the field diffusion in the liquid phase competes poorly with this mass flow. If the liquid contains a low concentration of a less volatile solute, the latter will increase in concentration near the evaporating surface and cannot diffuse back down the wick as quickly as it accumulates.

One of three results follows:

(1) The solute increases to such a high concentration at the surface that water evaporation is greatly reduced. This happens in a glycerol–water solution.

(2) The solute increases to a concentration at which its rate of evaporation balances its rate of arrival.

(3) The solute increases to a concentration limited by its solubility, leading for example to the "efflorescence" of salt crystals seen on the surface of crumbs on a fertile soil after drying.

These results are not mutually exclusive, and actual results may be a combination of these effects.

The second effect can greatly increase evaporation of a moderately volatile, moderately water-soluble pesticide. The pesticide will tend to be lost along with the water in the ratio present in the undisturbed soil water, not because of any peculiarity in the evaporation process but because the bulk flow of the solution up the capillaries is too fast for diffusion in the soil water to compete. Surface concentrations are automatically adjusted until evaporation occurs in the ratio supplied. A mixture of water, alcohols, ketones, etc., allowed to evaporate only from the top of a wick 30 mm. or more long, does so without any change of bulk composition. The phenomenon is exploited in the odor-masking devices sold. If excessively involatile constituents are avoided, any mixture can be evaporated automatically at constant composition if allowed to do so only through a wick.

If the rate of evaporative loss per unit gross area of surface—"negative" rainfall—is v (cm./day) and the effective total cross-sectional area of water in continuous soil capillaries is s, the mean linear rate of upflow in the soil water is v/s. If diffusion coefficient of the solute is D (sq. cm./sec.), it can be shown that the concentration at the steady state falls off with distance x (cm.) from the surface according to

$$C = C_o \exp\left[-\frac{vx}{sD \times 8.6 \times 10^4}\right] \qquad (4)$$

Inserting reasonable (*see below*) values ($v = 0.15$, $s = 0.2$, $D = 3 \times 10^{-6}$), the value of the exponent is about $3x$. This enforces about a 20-fold increase of concentration at the surface compared with original concentration for 1-cm. depth or 400-fold for 2-cm. depth.

An efficient wick is woven so that most of its fibers are parallel to its length; hence the capillaries are uninterrupted as far as possible. Soil is mostly particulate rather than fibrous, and the capillaries are easily and frequently interrupted; hence, soil is a poor wick. Soil scientists know that evaporation from soil surface is approximately constant and rapid as long as the surface remains wet—*i.e.*, as long as water is flowing up capillaries to compensate for evaporative loss. The capillary transport breaks down when it has to conduct more than a few centimeters upward, depending on soil type. The surface soil then dries, and the rate of evaporative loss falls sharply since the limiting vapor-phase diffusion must now operate over a much greater depth. It is during—and only during—the initial rapid water-loss phase that evaporation of water indirectly accelerates that of the pesticide. Many experiments have confirmed this acceleration (*11, 17*).

The growing plant itself may be likened crudely to a wick. Water is taken up by cellular flow, transported by channel flow in the continuous xylem vessels, and evaporated from the leaf surface. Unquestionably systemic insecticides supplied to the soil are concentrated in the leaves in this way. They are not, however, concentrated in the epidermal cells of the leaf as much as we might expect from the passive-wick model, for two reasons. Protoplasmic streaming in the leaf cells accelerates diffusion and so reduces the concentration gradient. Also the general direction of flow before final evaporation is perpendicular to the large leaf area, so that the final linear flow rate is much less than in the xylem vessels. The distance traversed in this final flow is small—about half the leaf thickness. This is about 100μ in most crop leaves. One is tempted to speculate that if it were much greater (*cf.* Equation 3), lethal concentrations of various substances would accumulate as long as transpiration were rapid. Is this why leaves of rapidly transpiring plants are thin, and fleshiness is only possible if transpiration is restricted?

Adsorption Displacement

The second effect of water on evaporation, requiring only the presence of water, arises from the fact that many clay surfaces (and some organic ones) are strongly hydrophilic but also capable of adsorbing other molecules. The pesticide may therefore be held sufficiently strongly on a dry soil for its evaporation to be greatly reduced. When the soil is wetted, however, the stronger affinity of the water displaces the pesticide.

EPTC (S-ethyl di-*N,N*-propylthiocarbamate) is about the most volatile of the common herbicides, and evaporation limits its persistence under normal conditions and makes incorporation rather than surface application desirable. Nevertheless, it can be reactivated by rain many weeks after application under arid conditions.

Other examples are known from the work of Barlow and Hadaway (*6*) on insecticides in porous wall materials, who note examples of reactivation by moisture for cellulosic materials. The direct observation is recovery of insecticidal activity, but undoubtedly when the insecticide becomes available to the insect, it also becomes available for diffusion in the vapor phase.

Evaporation from Crystalline Deposits

Table I lists two materials evaporating from the crystalline solid. There is nothing very inhibitory about the solid state. Ice evaporates much faster than lubricating oil and naphthalene much more rapidly than glycerol. However, when we have a substance which can exist for sufficient time in the supercooled liquid state (*e.g.*, impure DDT in thin films), it is significantly more volatile and more soluble in this form. As a rough rule, a crystalline substance becomes about one-third to one-fourth as volatile and as soluble as the supercooled liquid for each 50°C. below the melting point.

Deposits which start as liquids may crystallize after exposure, and their evaporation rate will fall. Supercooling is more likely to occur and lead to this complication when the deposit density is extremely low, as often happens with radiotracer methods.

The Quantitative Picture

In the mild summers of England, moist soil can easily lose as much as 6 tons of water per acre per day by evaporation. This is more than the average rainfall in the driest month in the driest part of the country and a little less than the year-round average, consistent with the fact that the soil, in the driest area, dries out in the summer and wets up again in winter.

Over most of the United States the potential evaporation is higher. That it may not in fact be higher only serves to emphasize the fact that the soil surface is wet only for a small part of the summer. Only by one mechanism (wick evaporation) does evaporation of water assist that of the pesticide. If the pesticide is on the surface and water is not, the surface is hotter than it would be if the water were there, and the evaporation rate of pesticide is therefore greater with respect to water.

A value of 6 tons/acre-day as the potential evaporation rate from wet soil is conservative (low). If the pesticide is fully exposed—not dissolved, or adsorbed—its rate of loss will be less than expected by multiplying the 6 tons by the vapor pressure of the pesticide and the square root of its molecular weight and dividing by half this product for water (the half allowing for average 50% humidity of the air initially).

This way we obtain the predicted rates of loss for some pesticides, taking the vapor pressure data recorded from Martin (*18*), Balson (*5*), Dickinson (*10*), or Friedrich and Stammbach (*14*) (for simazine).

Table III.

Substance	*Vapor Pressure, mm. 20°C.*	M	*Predicted Rate of Loss from Acre of Glass Plate*	
			Rate	*Units*
EPTC	0.15	189	768	lb./day
2,6-Dichlorobenzonitrile	5.5×10^{-4}	172	2.7	lb./day
Parathion	3.8×10^{-5}	291	0.24	lb./day
Lindane	9.4×10^{-6}	291	1.8	lb./month
DDT	1.7×10^{-7}	355	1.2	lb./year
Simazine	6.1×10^{-9}	202	0.04	lb./year
methyl parathion	0.97×10^{-5}	263	?	lb/yr

Although EPTC is quite volatile under field conditions, the predicted loss seems much too high, and one must doubt the quoted vapor pressure, which is about the same as that of a saturated paraffin of the same molecular weight (tridecane, *M*- 184, v.p. at 20°C., *ca.* 0.14 mm.).

Obviously evaporation is a potentially important factor in loss of deposit for any except the very involatile pesticides.

Fate of Evaporated Residues

When 6 tons of water evaporates from an acre in a day and from many contiguous acres, where does it go? Let us assume that each cubic meter above the crop can hold, in addition to what was initially present, half the SVC of water at 20°C. This is about 8.6 grams, corresponding to about 35 kg. or 77 lb. per acre. A depth of nearly 200 meters is therefore necessary to accommodate the 6 tons. In fact a greater depth still is affected in the upper part of which condensation (cloud formation) may occur at a temperature reduced by adiabatic convection. Although molecular diffusion near the evaporating surface determines locally the rate of evaporation, a very deep layer of air is necessary to accommodate the total amount evaporated.

Because rate of loss is roughly proportional to $p\sqrt{M}$, but the capacity of a given volume of air is proportional to $p \times M$, a smaller depth of air is necessary to accommodate the predicted evaporation of pesticide, around 50 meters instead of 200 meters. This is still substantial, but two qualifications are necessary.

First, a pesticide evaporating from spot-wise deposits within a crop will largely be adsorbed on other parts of the crop. This does not happen with water since if one leaf is transpiring, so are the others. This must accelerate the predicted rate of loss from each local deposit but will delay the total loss at low application rates, by reducing the available vapor pressure.

Secondly, much of any pesticide vapor escaping to 50 meters or more above the crop will ascend even higher by eddy diffusion and eventually reach the highly photochemically active ionosphere. I suggest that except for the destructive reactions occurring in the upper atmosphere, all life would probably have succumbed to intoxication by its own waste products, let alone by-products of the chemical industry.

Literature Cited

(1) Adam, N. K., "Physical Chemistry," p. 110, Oxford, 1954.
(2) Acree Jr., F., Beroza, M., Bowman, M. C., *J. Agr. Food Chem.* 11, 278 (1963).
(3) Baker, E. A., Batt, R. F., Fernandes, A. M. Silva, Martin, J. T., *Ann. Rept. Agr. Hort. Res. Station, Bristol* 106 (1963).
(4) Baker, E. A., Batt, R. F., Martin, J. T., *Ann. Appl. Biol.* 53, 59 (1964).
(5) Balson, E. W., *Trans. Faraday Soc.* 43, 54 (1947).
(6) Barlow, F., Hadaway, A. B., *Soc. Chem. Ind. (London), Symp. Monograph* 29, 3 (1968).
(7) Bowman, M. C., Acree Jr., F., Schmidt, C. H., Beroza, M., *J. Econ. Entomol.* 52, 1038 (1959).
(8) Brown, H. T., Escombe, F., *Phil. Trans. Roy. Soc. London, Ser.* B 193, 223 (1900).
(9) Dewey, O. R., Hartley, G. S., McLauchlan, J. W. G., *Proc. Roy. Soc. (London), Ser. B.* 155, 532 (1962).
(10) Dickinson, W., *Trans. Faraday Soc.* 52, 31 (1956).
(11) Fang, S. C., Thiessen, Patricia, Freed, V. H., *Weeds* 9, 569 (1961).
(12) Feichtmeir, E. C., *Phytopathology* 42, 200 (1952).
(13) Fernandes, A. M. Silva, Baker, E. A., Martin, J. T., *Ann. Appl. Biol.* 53, 43 (1964).
(14) Friedrich, K., Stammbach, K., *Chromatography* 16, 22 (1964).
(15) Fuchs, N. A., "Evaporation and Droplet Growth in Gaseous Media," Pergamon Press, London, 1959.
(16) van den Honert, T. H., *Discussions Faraday Soc.* 3, 146 (1948).

(17) Lichtenstein, E. P., Schulz, K. R., *J. Econ. Entomol.* 54, 517 (1961).

(18) Martin, H., "Guide to Chemicals Used in Crop Protection," 4th ed., Canada Dept. Agr., 1961.

(19) Phillips, F. T., "Radiation to Radioisotopes Applied to Insects of Agricultural Importance," p. 147, International Atomic Energy Agency, Vienna (1963).

(20) Sutton, O. G., "Micrometeorology," McGraw-Hill, New York, 1953.

RECEIVED July 31, 1967.

12

Evaluation of Spray Drift Potential

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A small, low speed wind tunnel was used to measure the proportion of a flat-fan spray occurring as small, drift-susceptible droplets. In-flight evaporation of the falling droplets was accounted for. Comparison of the volume percentage of a spray occurring in a selected droplet size range with similar data for sprays formed from various thickened liquids was taken as indicative of potential spray drift in the field. The method appeared to be sufficiently precise to allow selection of candidate spray liquids for field evaluation. Liquids imbibed in sized particles of lightly crosslinked polymers ("particulate" sprays) were found to form sprays having a very small volume percentage of droplets in the very small droplet size range.

Spray drift from agricultural sprays is determined by many factors, including nozzle design, spray pressure, air velocity past the nozzle, fluid properties, and meteorological factors (*1, 2, 5*). It is apparent that the proportion of the spray occurring as small droplets is of paramount importance, and methods for studying spray drift have been based largely on the size of droplets produced in the spray (*2, 3, 4, 20*).

Several investigators have measured the number of droplets occurring in each of several size ranges, either by collecting the droplets on prepared flat surfaces or by photographic methods (*8, 9, 11, 18*). In this approach, the droplet size distribution curve is obtained. It is then easy to calculate the fraction of droplets in the smaller size ranges and any of the several mean droplet diameter values. Fraser and Eisenklam (*8*) proposed a dispersion value as a measure of droplet size uniformity. Their approach is simple but suffers from the considerable difficulty of adequately observing the very small droplet component (*5*). All direct observation methods require measuring and counting large numbers of droplets.