

INACTIVATION OF DDT DEPOSITS ON MUD SURFACES * †

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SYNOPSIS

The problem of the inactivation of DDT deposits on dry mud surfaces is presented and its causes outlined. The phenomenon is found to be due to adsorption of the DDT crystals present on the surface; this adsorption appears to be the initial step in the catalytic decomposition of DDT by the iron oxides present in soils, since there is a direct relation between the amount of oxides present and their capacity to inactivate DDT deposits.

The DDT-inactivating capacity of soils can be determined by testing them for catalytic activity in the thermal decomposition of DDT.

The adsorption of DDT by soil is influenced by environmental relative humidity. Inactivated deposits may be reactivated by increase of the atmospheric humidity.

Several substances proposed for the protection of the DDT deposit from inactivation were tested without success. Reference is made, however, to the encouraging findings of some other workers. Limewashing is recommended for the protection of DDT deposits.

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† The title of this paper requires an explanation. DDT has been successfully applied for more than six years in large-scale programmes against communicable diseases, and especially against malaria. At various times, contradictory results have been reported, implying that some factor has altered the normal residual activity of the insecticide. Among well-known factors may be mentioned the habits of the local population, climatic conditions, and the bionomics of the insects concerned. More recently Hadaway & Barlow have drawn attention to the importance of the particle size of the insecticide and of its sorption by some types of wall, such as mud walls (see *Bull. ent. Res.* 1951, 41, 603; 1952, 42, 769; 43, 91, 281). The present paper points out a new and hitherto unknown factor—chemical degradation. It has been demonstrated that when applied on porous materials, even in the form of water-dispersible powder, DDT may be inactivated either by simple sorption or by sorption and chemical degradation. Sorption is the prevalent factor and the one which is apt to occur more frequently under field conditions. By defining the mechanism and conditions of chemical degradation, the authors establish its value in relation to other factors.—Ed.

The residual effect of DDT deposits on various materials has been the subject of extensive experimentation, and the literature thereon is voluminous. The most suitable quantity of DDT to be applied per square metre has been an important question since the beginning of residual-spraying work. In some programmes the trend has been towards the repeated spraying of small doses. Most programmes have been based upon a dosage of 2 g per m² (approximately 200 mg per square foot) and experience has shown that this dosage on most surfaces will maintain a residual toxicity for several months or even for up to a year or more.

There have been, however, several contradictory reports on the effectiveness of residual DDT in the control of *Anopheles* which have led to some confusion.

The observations of Muirhead-Thomson¹⁵ with *A. gambiae*, for example, do not parallel the observations of Wharton & Reid¹⁷ with *A. maculatus*, of Swellengrebel & Lodens¹⁶ with *A. aconitus*, of Bertram² with *A. minimus*, or of Downs & Bordas⁶ with *A. pseudopunctipennis*.

The factors influencing such differences can be grouped in two sets: those which include patterns of behaviour peculiar to the mosquitos, and those which are intrinsic to the insecticide—including differences in products and preparations, in techniques of application, in repellent activity, and in inactivation of the insecticidal effect by substratum.

During a survey of the possibilities of malaria control in Mexico, we studied the residual activity of DDT on different building materials commonly used by the rural populations of Mexico. It soon became evident that, whereas on most of the common materials tested, DDT maintained its residual activity for a year or more, on adobe and other mud surfaces the duration of activity varied greatly from soil to soil. We then undertook to study this problem, with the aim of determining the causes of inactivation, and of thus being able to predict and forestall it.

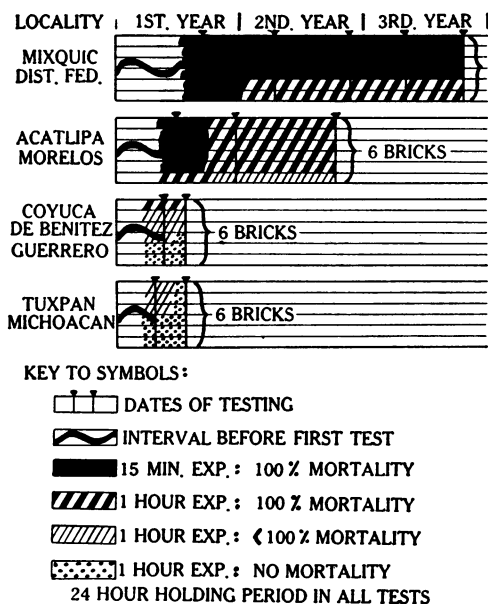
A preliminary note was published⁷ and a report prepared for distribution by the WHO Expert Committee on Malaria.⁴ A complete review of investigations to date is presented here.

Four types of soil from different sections of the country were selected: D.F.1 from Mixquic, Distrito Federal, near Mexico City (derived from lake-bottom loam with a high organic-matter content); Mor.1 from Acatlipa, Morelos (sandy clay from poorly-weathered volcanic ash); Gro.1 from the delta of the Rio Coyuca, Guerrero (deltaic deposit); Mich.1 from Tuxpan, Michoacán (a red lateritic clay).

Sun-dried bricks from these soils were sprayed with DDT and bioassayed (see Annex 1, page 52, for techniques, and criteria of evaluation). The results showed that, on the mud surfaces of D.F.1, the residual effect of DDT lasted three years (and was still active well into the fourth), whereas, in other soils, it had a shorter period of duration—i.e., one year

for Mor.1, six to eight months for Gro.1, and only a few weeks for Mich.1 (see fig. 1).

FIG. 1. DURATION OF ACTION OF RESIDUAL DDT ON ADOBE SURFACES *



Reproduced from Downs, Bordas & Navarro, 7 by kind permission of the editors of *Science*

* The duration of action of the DDT was measured by mosquito mortality. In each test six bricks were used; the mosquitos were held for 24 hours after exposure.

Three working hypotheses as to the cause of this inactivation were postulated :

- (a) decomposition of DDT by alkali ;
- (b) adsorption by soil ;
- (c) catalytic breakdown of DDT.

A simple chemical analysis of the soils was made, following the techniques described in the annex, and the results are summarized in table I.

The relatively insignificant differences in pH eliminated the possibility of alkali breakdown, and data on the base-exchange capacity led us to discard the possibility of adsorption by clay or humus. D.F.1 had the highest base-exchange capacity, which would lead one to expect the highest adsorption capacity, and yet it retained the DDT activity for by far the longest period.

The chemical analyses showed a correlation between the amount of iron present and the capacity of the soil to inactivate DDT. This correlation

TABLE I. RESULTS OF CHEMICAL ANALYSIS OF SOILS FROM DIFFERENT REGIONS OF MEXICO*

Soil	Humidity (%)	Loss on calcination (%)	pH	Base-exchange capacity (mEq/100 g)	Soluble chlorides (% chloride)	Silica (% silicon dioxide)	Total calcium (%)	Total aluminium (%)	Iron		
									total (%)	hot hydrochloric acid extract (% iron)	extractable oxides (% iron)
D.F.1	9.67	17.2	8.33	48.0	0.06	42.9	3.67	9.9	7.13	1.8	0.74
Mor.1	4.66	4.5	7.45	16.4	0	54.6	1.75	6.67	17.0	2.54	1.29
Gro.1	1.11	5.02	8.30	16.7	0	39.2	0.71	12.7	19.2	5.7	1.65
Mich.1	6.21	11.3	6.75	17.2	0.004	41.5	2.57	7.2	25.7	11.5	9.29

* All percentages are referred to dry weight of soil.

was found to be closer with the iron-oxide content than with the total iron content.

Catalytic Action of Soils on Thermal Decomposition of DDT

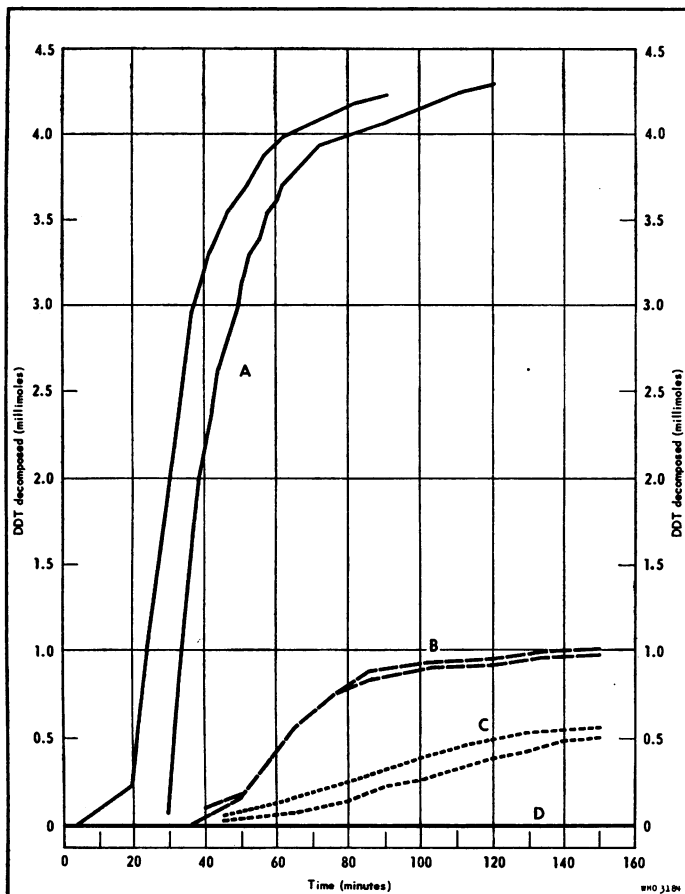
Earlier investigations by Fleck & Haller⁸ showed that ferric iron catalysed the thermal decomposition of DDT. Ferric chloride at 120°C will decompose DDT, yielding one molecule of hydrochloric acid per molecule of DDT decomposed. The hydrochloric acid evolved can be titrated, and thus the amount of DDT can be accurately estimated.

Applying the same technique to soils (see Annex 1), we found that a small amount of certain soils will decompose DDT in much the same way as ferric chloride does. The amount of DDT decomposed is in proportion to the amount of iron oxides present in the soils (see fig. 2 and 3).

Nature of the reaction

Curves obtained from the plotting of the hydrochloric acid evolved against time are S-shaped (fig. 2). The initial slow-reaction phase is followed by a more-rapid steady flow and then a final lag. The shape of these curves suggests the possibility of the formation of a substance capable of poisoning the catalyst. The precursors of this substance are present in technical-grade DDT. Pure *o,p*-isomer or *p,p'*-isomer DDT will decompose indefinitely and, in some cases, almost explosively. When residues from technical-grade DDT crystallizations were added to pure *p,p'*-isomer DDT, the reaction of decomposition was greatly inhibited. To date we have been unable to discover the nature of this inhibitory substance. The reaction will begin immediately with ferric chloride, provided the DDT is dry.

FIG. 2. DECOMPOSITION OF DDT BY DIFFERENT TYPES OF ADOBE SOIL AT 120°C*



* DDT : 5.0 millimoles ; adobe : 50 mg

A = Mich.1
 B = Gro.1
 C = Mor.1
 D = D.F.1

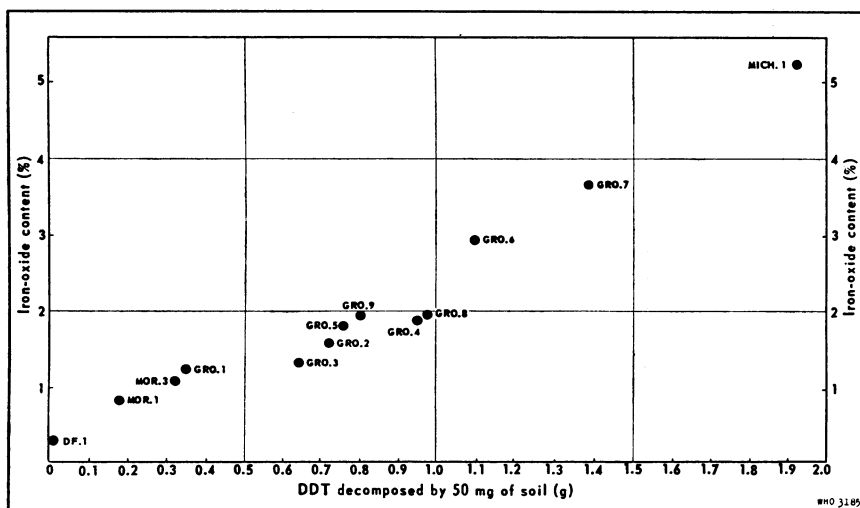
Precipitated ferric hydroxide, as well as soils, has an initial lag period that may last for as much as an hour.

Inhibitors

Water is the principal inhibitor of the reaction and we can safely state that the reaction will not take place in its presence. If the soil to be tested is introduced wet or in the form of pellets, the reaction will start slowly, if at all. This is important in testing for inhibitors. For such tests a soil

was mixed with a solution of the suspected inhibitor ; after drying, the mixture was ground, strained, and tested.

FIG. 3. RELATION BETWEEN IRON-OXIDE CONTENT OF DRY SOIL AND DECOMPOSITION OF TECHNICAL-GRADE DDT



The following substances were tried as inhibitors : sodium chloride, sodium bisulfite, boric acid, potassium thiocyanate, potassium cyanide, sodium sulfide, *o,o'*-dihydroxy DDT, tannic acid, and "Versene Fe₃ specific" (a sequestrant). Of these, only tannic acid and *o,o'*-dihydroxy DDT inhibited the reaction to a considerable degree.

It is interesting to note that Maes,¹³ in a recent publication, reports good inhibiting effect by phosphate.

Other catalysts

Aluminium chloride and manganese dioxide showed some catalytic activity, but in a much lesser degree than ferric chloride. However, it is not improbable that the decomposition observed might have been due to small amounts of iron present, as impurities, in the reagent.

Nickel oxide, titanium oxide, magnesium chloride, chromium chloride, sodium chloride, ferrous sulfate, potassium ferricyanide, and ferric ammonium sulfate did not show any activity ; it would thus appear that ferric complex ions are inactive.

Grade of DDT

Batches of technical-grade DDT from different sources showed differing reactivity under the same amount of catalyst (see table II). Here it should

TABLE II. SUSCEPTIBILITY TO CATALYTIC THERMAL DECOMPOSITION OF DIFFERENT TECHNICAL-GRADE DDT SAMPLES FROM DIFFERENT MANUFACTURERS *

Manufacturer	Sample	DDT decomposed (mEq)
A	1	37.6
	2	23.3
	3	40.4
	4	39.1
	5	42.1
	6	39.1
B	1	28.7
	2	25.1
	3	22.1
	4	22.0
	5	25.1
	6	32.8
	7	22.3
	8	20.3
	9	29.5
	10	31.5
C	1	7.0
	2	14.5
	3	17.3
	4	12.9
	5	13.6
	6	6.1
D	1	40.2
	2	35.4
E	1	0.4

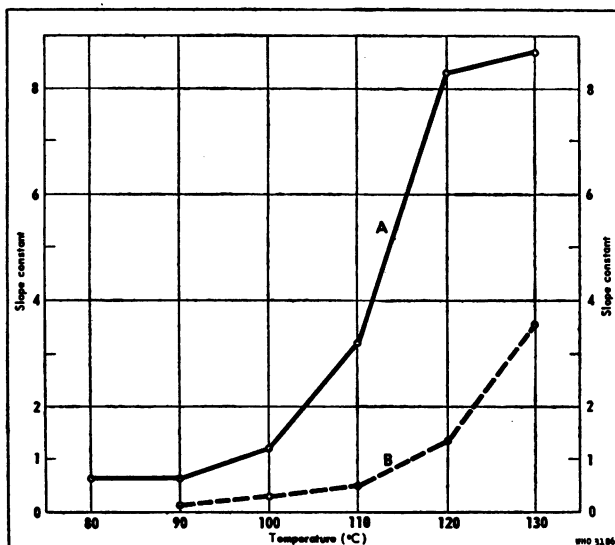
* Catalyst : soil Mor.1 (50 mg) ; temperature : 130°C ;
DDT (1.77 g) : 5.0 mEq (theoretical)

be pointed out that the evidence is supported by repeated testing of each sample and that all samples contained from 70% to 75% *p,p'*-isomer DDT. It became necessary, therefore, to standardize the technical DDT before using it as reagent for the test.

Effect of temperature

Increase of temperature will speed up the reaction but will not have any effect on the total amount of DDT decomposed. The effect of temperature on the reaction is shown in fig. 4. For speed and accuracy, the reaction should be conducted at between 120°C and 130°C.

FIG. 4. EFFECT OF TEMPERATURE ON RATE OF DECOMPOSITION OF DDT



A = iron hydroxide
B = ferric chloride

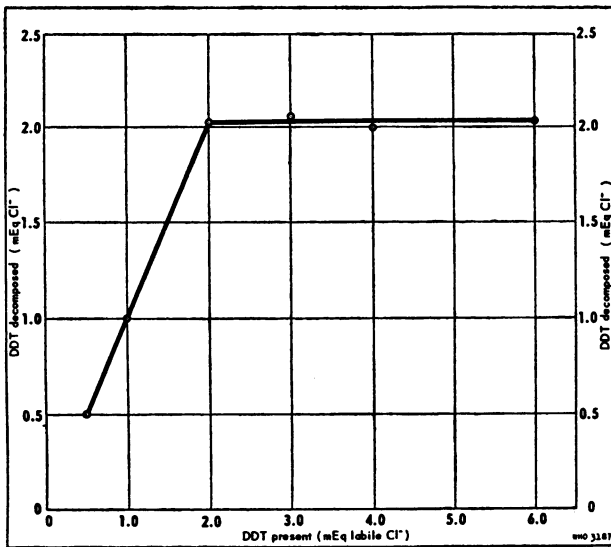
The slope constant of the velocity curves has been calculated from the slope of a straight-line tangent to the curve at the point of maximum velocity. The data obtained give the velocity of reaction disregarding the time of start.

Concentration of reagents

For a given grade of technical DDT, the amount decomposed is dependent on the amount of catalyst present. DDT in excess will not be decomposed, nor will an excess of DDT influence the final result of the reaction. This is illustrated in fig. 5.

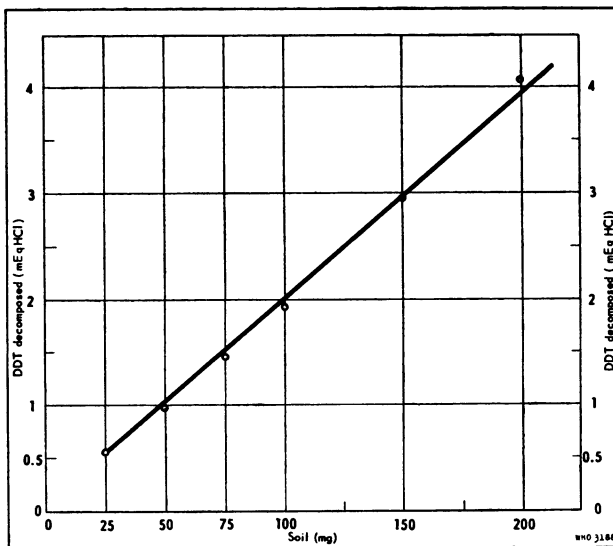
On the other hand, an increase in the amount of catalyst present will result in an increase in the amount of DDT decomposed. When the catalyst is a soil of low or medium activity, the amount of DDT decomposed will be in direct arithmetical proportion to the amount of soil present (see fig. 6). This direct arithmetical proportionality does not hold with soils of high reactivity; in such cases, added increments of soil decompose somewhat less than the expected amount of DDT.

FIG. 5. EFFECT OF AMOUNT OF DDT PRESENT ON AMOUNT OF DDT DECOMPOSED



Soil used as catalyst : 100 mg of Gro.1
 Temperature : 120°C

FIG. 6. RELATION BETWEEN AMOUNT OF SOIL PRESENT AND AMOUNT OF DDT DECOMPOSED



Soil used as catalyst : Mor.1

Adsorption of DDT in Dry Mud

The first results obtained from the studies of the catalytic action of soils on DDT suggested that the inactivation of DDT deposits on dry mud surfaces was due to catalytic breakdown of the insecticide. However, complete extractions of DDT from entire sprayed mud panels showed that, where there was a loss of insecticidal activity within a year after spraying, the amounts of DDT recovered varied from 60% to 90% of the original amount sprayed. The presence of unchanged DDT in the mass of dry mud suggested that the primary cause of the inactivation of the DDT deposit was adsorption. Microscopic examination of surfaces where water-wettable DDT had become inactive showed the mud surface to have an oily appearance; the DDT particles were no longer visible. The inert powder mixed with the DDT appeared glued to the soil particles, and the original whitish colour of the sprayed surface had disappeared, in some cases, after one month.

Hadaway & Barlow^{9, 10} present detailed data on this phenomenon of sorption and also on the effect of particle size. They show that large crystals are not adsorbed as readily as small ones.

We believe that adsorption represents the initial step of the catalytic breakdown of DDT. Depending on external conditions, the final breakdown may proceed at different speeds.

Effect of relative humidity

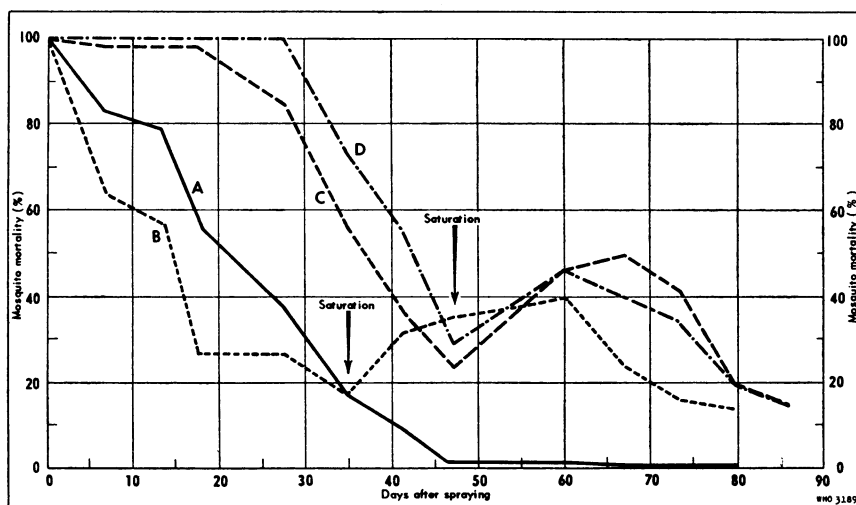
Since water will inhibit the catalytic activity of soil on the thermal decomposition of DDT, it seemed possible that environmental humidity might affect the adsorption of DDT on mud surfaces, and therefore the duration of the insecticidal action of the deposit.

Twenty panels of very active mud (Mich.2) were sprayed with 2 g of DDT per m² and separated in four lots. Three of them were held in tight boxes with humidity-regulating solutions of sulfuric acid at relative humidities of 90%, 75%, and 60%, respectively. The fourth lot was left, as a control, under the varying environmental conditions of the laboratory.

The panels were tested weekly for biological activity. The results obtained showed that the higher the relative humidity, the slower the inactivation of the insecticide. When the mortality of mosquitos was at about 20% for one-hour exposure, and the panels were restored to a box with a relative humidity near saturation, there was a short period of reactivation of toxicity, followed by a final drop. The control panels were not kept in an atmosphere of saturation, and showed no reactivation (fig. 7).

The reactivation of a deposit of DDT with the increase in relative humidity was shown under field conditions by the following experiment.

FIG. 7. EFFECT OF RELATIVE HUMIDITY ON DECOMPOSITION OF DDT, MEASURED BY MOSQUITO MORTALITY



A = control *

B = 60% relative humidity

C = 75% relative humidity

D = 90% relative humidity

* The control panels were not placed in a saturated atmosphere after loss of activity. Points were calculated by moving averages of three points.

An adobe house was built at Acatlipa, Morelos, and the inside was coated with a thin layer of very active mud (Mich.2) and, in July 1951, sprayed with DDT wettable-powder at a rate of 2 g per m². Observations with *A. pseudopunctipennis* were carried on as in other similar experiments.⁶ Good insecticidal activity was observed during the months of July and August 1951, but observations ended that year with the close of the mosquito season in mid-September. At the beginning of the mosquito season in April 1952, no toxic effect was noted; the observations were discontinued because of the drop in mosquito densities at the end of August. The relation between increase in relative humidity and activation of the DDT is illustrated in fig. 8. Whereas in April and May less than 5% of the total number of mosquitos captured in this house were killed (four separate captures totalling 222 mosquitos), later in the season, after relative humidities had risen, between 70% and 90% of the mosquitos were killed. The relative humidities correspond to readings at or about 19.00 hours, the time of evening mosquito activity and of the maximum daytime relative humidity.

Protection of DDT deposits

To prevent the adsorption of DDT deposits on mud surfaces, three possibilities are offered :

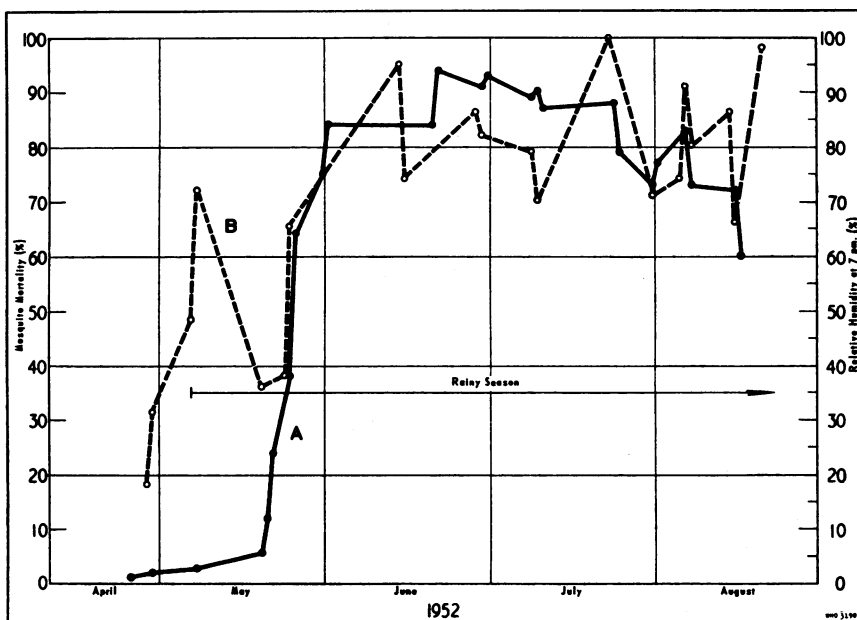
- (a) mechanical protection by limewashing;

(b) saline or water coating of the adsorbant with salts or hygroscopic substances;

(c) chemical inactivation of the iron oxides.

The laboratory tests have been limited to economically feasible techniques involving the least extra labour. Limewashing has been recommended by Maier, Rendtorff & Suárez¹⁴ in Venezuela and by Clapp, Fay & Simmons.⁵

FIG. 8. REACTIVATION OF DDT DEPOSIT ON MUD BY RELATIVE HUMIDITY



A = mosquito mortality
 B = relative humidity
 DDT sprayed July 1951, observations April-August 1952

In the laboratory we obtained good residual activity of DDT on lime-wash 18 months after application. The same holds true for mortar. Laboratory tests with limewashed adobe surfaces are under way and the first results are encouraging, but more experience is needed before proof is established.

A field experiment is in progress to the same effect, and definite data are still lacking, although whitewashed mud surfaces have shown good activity for a period of 18 months. Panels of very active mud, in lots of five, were sprayed with 2 g of DDT per m², the wettable powder suspended in the following solutions: 5% sodium chloride, 5% calcium chloride, 5% ammonium sulfate, 5% glycerol, 5% molasses, 5% ethylene glycol.

The deposits lost their insecticidal effect after 20 days, as did the untreated panels.

Panels of the same mud were pre-treated with 2% tannic acid, 2.5% "Versene Fe_3 ", 2% animal glue, and 20% Na_2SiO_3 , and then sprayed with DDT wettable-powder. None of these treatments showed any inhibitory effects on the adsorption of the DDT deposit. No toxicity was noted after 20 days.

It may be mentioned here that Kruse & Konchady¹² in India reported some success with the use of coconut charcoal and cow-dung, and Maes¹³ in the Belgian Congo reports good protection with phosphates.

Discussion

In many regions of the world, a large proportion of the population of rural malarious zones lives in houses of mud construction of one type or another.

Hadaway & Barlow^{9,10} showed that inactivation of residual sprays on mud surfaces occurs not only with DDT but also with Gammexane, aldrin, and dieldrin, and suggest that the fumigant activity of Gammexane would compensate for the lack of contact toxicity in control of mosquitos. This fumigant activity should not be underestimated in cases where it can be useful, especially when several sprays a year are economically feasible. We found in the field that the fumigant activity of lindane, when sprayed on paper and covered with cloth, has little effect on the control of *A. pseudo-punctipennis* (Bordas & Navarro³). Repellent effect was pronounced for a period of one month, but mosquitos were not killed.

It is therefore necessary to find methods whereby insecticides may be protected from the adsorbing properties of mud.

The action of relative humidity is important and should be borne in mind when treating zones with high atmospheric humidities. The reactivation of DDT deposits with the return of high atmospheric humidity (sometimes concomitant with the mosquito season) is important in cases of mildly active muds where the DDT has not penetrated deeply and remains adsorbed on the surface. This reactivation may be responsible also for the long duration of DDT deposits on mud observed by Downs & Bordas⁶ on Mor.1 soil where for two to three years good residual activity has been noted in the field on a surface which, when tested under laboratory conditions, showed activity for only 15 months.

The persistence of non-crystalline DDT on mud surfaces subject to desorption and reactivation may depend not only on the intrinsic activity of the soil but also on its texture and compactness. This may vary individually for each construction.

Until more data become available, it seems today that the cheapest way to prevent the action of mud on DDT is to apply a good coat of

limewash, but this should be made up in a suitable formulation to avoid scaling-off.

The degree of activity of a particular soil may be determined by the catalytic decomposition test. As a general guide, however, it may be said that red clays and lateritic soils are very active against DDT deposits.

Annex 1

METHODS AND TECHNIQUES OF ANALYSIS

Mud surfaces

The early experiments were made with sun-dried bricks, but very soon it was found more convenient to work with mud panels made as follows: ground adobe bricks were strained through a 20-mesh sieve, moistened very slightly, and then pressed into wooden frames nailed to plywood panels; the size of the mud panel was 15 cm × 15 cm. The press bench was homemade and the press was an 8-ton hydraulic jack.

Spraying

DDT wettable-powder^a was used in all the experiments. The panels to be sprayed were surrounded with filter-paper. The DDT was weighed accurately into a flask, suspended in water, and sprayed over the filter-paper and the mud surface simultaneously. Then the filter-paper was analysed for DDT and the amount of DDT present in the mud surface calculated by difference. Blank sprayings and determinations showed that, with this method, it was possible to obtain a 2 g per m² deposit on the mud surface with a 3% maximum error. The sprayer used was a deVilbiss throat atomizer; the source of pressure was a rotary pump operating at 7 pounds per square inch (about 0.5 kg per cm²) pressure.

DDT analyses

All DDT determinations were made by petroleum-ether or alcohol extraction in a Soxhlet flask, and alkali dehydrochlorination and Volhard titration of chlorides, using titrating solutions N/10 or N/100 as required.

Biological testing

For the biological tests, colony-reared *A. aztecus* and *A. albimanus* were employed. Some 15 mosquitos, anaesthetized with carbon dioxide, were placed on the surface to be tested, under a Petri dish containing a wad moistened with sugar solution, and left for exposure periods of 15 minutes and one hour. After exposure the mosquitos were again anaesthetized and transferred to a clean sheet of paper under a Petri dish with a wad of sugar solution, and were held for 23 hours. Mortality was recorded at 15 and 30 minutes, and at 1, 2, and 24 hours after exposure. All tests were rigidly controlled, both with parallel runs on unsprayed bricks and with runs on cloth panels treated with accurately determined deposits — 10, 25, 50, and 100 mg per square foot (about 100, 250, 500, and 1,000 mg per m²) — of 75% *p,p'*-isomer DDT, deposited on the cloth panels from an acetone solution. Duplicate runs were made at each testing period.

^a Santobane 50, Monsanto Chemical Co New York, N.Y.

Analyses of soil

Soil analyses were made as follows : pH, determined with a Beckman potentiometer on a fresh 50% water suspension of soil; soluble chlorides, by washing a 10-g sample of soil with hot water several times in a Buchner funnel and determining the chlorides by the Volhard method; base-exchange capacity, using the technique of the Association of Official Agricultural Chemists.¹ Total calcium and total aluminium were determined after alkaline fusion. Iron was determined by three different procedures : first, after alkaline fusion, to determine total iron; second, after hot concentrated hydrochloric acid extraction, to determine total extractable iron present in the form of oxides and hydrated silicates; and third, a method using nascent-hydrogen reduction in a concentrated oxalate medium, as described by Jeffries.¹¹

Jeffries' ¹¹ Technique for Determination of Iron Oxides in Soils*Material*

Place 2 g of dry soil in a 100-ml centrifuge tube.

Oxidation of organic matter

Add to the soil 5 ml of hydrogen peroxide, 20 vol. Allow to stand for 2 hours at room temperature, then place in a steam-bath and evaporate to dryness. Repeat until free of organic matter. Twice is ample.

Decomposition and reduction

(1) To soil in tube, add 4.5 g of potassium oxalate and 40 ml of water. Stir to homogenize. Heat at about 80°C.

(2) Add 0.95 g of oxalic acid in 10 ml of water and heat to 90°C.

(3) Place a strip of magnesium ribbon about 8 inches (20 cm) long in the hot suspension, stir, maintain temperature at 90°-95°C for 3-5 minutes, and remove ribbon.

(4) Add 0.48 g of oxalic acid to 10 ml of water. Heat until clays and sands are grey or white (3-20 minutes).

Soils with a high amount of oxides will require more magnesium ribbon at stage (3) and longer reduction at stage (4).

Avoid complete decomposition of the magnesium ribbon or mixing of its residue with the soil.

Washing

Centrifuge at once and wash free of iron with 50-ml fractions of 5% sodium chloride. Four or five washings are sufficient.

Iron determination

(1) Place magnesium ribbon and washings in a 500-ml Kjeldahl flask. Add carefully 20 ml of concentrated sulfuric acid, chemically pure.

(2) Place flask under draught hood and heat slowly to evaporate water and hydrochloric acid, and finally to decompose the oxalate. When sulfur dioxide vapours are evolving, withdraw from heat.

(3) Cool and add 250 ml of water and potassium permanganate solution until pink colour persists for over 2 minutes.

(4) Pass solution through a Jones reducer.

(5) Determine iron by permanganometry.

Recommendations

For most soils, the amount of soil and reagents can be reduced to one-half.

This technique requires skill and judgement and we recommend repeating the analysis of one sample until constant results are obtained.

Interpretation of data

Results obtained by the method of Jeffries can be interpreted as follows :

<i>Percentage of iron oxides in dry soil</i>	<i>Duration of activity of 200-mg deposit of DDT wettable-powder</i>
Up to 1	One year or more
1-2	12-6 months
2-3	Less than 6 months
3-4	Less than 3 months
Over 4	A few days

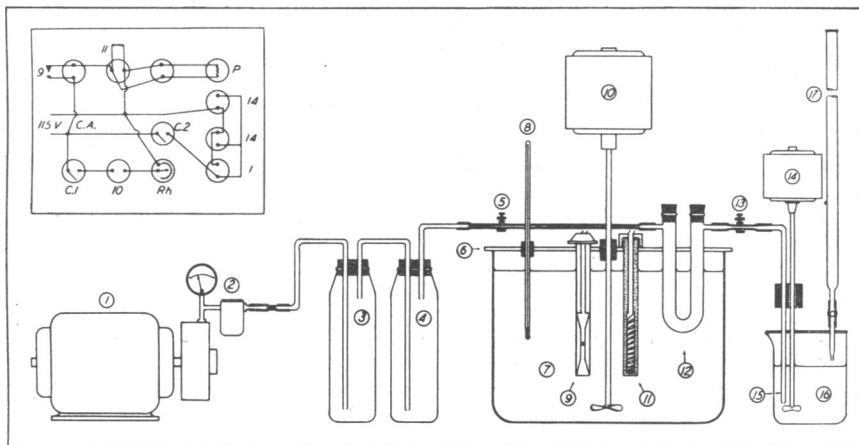
Determination of Catalytic Activity of Soils in Decomposition of DDT

Apparatus

Description. Essentially the apparatus consists of :

(a) a thermostatically controlled oil-bath to heat a mixture of DDT and soil;

FIG. 9. APPARATUS * FOR DETERMINATION OF CATALYTIC ACTIVITY OF SOILS IN DECOMPOSITION OF DDT



1. Vacuum and air-pressure rotary pump
2. Oil-trap of pump
3. Flask with soda lime
4. Flask with calcium chloride pellets
5. Screw-clamp on rubber tubing
6. Lid of oil-bath (1/4-inch (6-mm) bakelite)
7. Oil-bath (No. 20 automobile oil)
8. Thermometer to 200°C
9. Fenwal thermostat (range : 10°C to 148°C)
10. Bath stirrer
11. 250-watt heating unit, sealed
12. U-tube (internal diameter 20 mm)
13. Screw-clamp
14. Dispersing stirrer for HCl-air mixture
15. Bubbler for HCl-air mixture
16. Water with phenolphthalein
17. Burette with N/10 potassium hydroxide

* Inset: wiring diagram

- (b) an air-current system to produce a flow of dry and carbon-dioxide-free air to draw the hydrochloric acid produced in the reaction;
- (c) a collecting device to dissolve and titrate the hydrochloric acid evolved (for detailed description see fig. 9).

Operation. (a) Heat oil-bath with gas burner to 130°C; once this temperature has been reached, the coil and thermostat will maintain the temperature constant.

(b) Check the air-flow system, adjusting the flow by valve 13 to about 5 bubbles per second at the receiving beaker. Check adequate diffusion of bubbles by mechanical stirrer 14.

(c) Add phenolphthalein to water in beaker and bring water to a faint pink with 2 drops of N/10 solution of potassium hydroxide. Fill the 50-ml burette to zero-mark with N/10 solution of potassium hydroxide.

(d) Pour into U-tube 3 g of technical-grade DDT and the amount of soil or other substance to be tested for catalytic activity. Immerse tube in oil-bath and connect to air-system. Enter in notebook exact time as 0 minutes.

(e) Run air through system every five minutes, and add potassium hydroxide from burette to beaker each time, until faint pink colour persists. Enter in notebook time in minutes and burette reading.

Reaction is considered finished when the amount of hydrochloric acid evolved in 5 minutes can be neutralized with 2 drops of the potassium hydroxide solution. In most cases, the reaction is completed in 2-3 hours.

Valve 5 should always remain shut when air is not circulating, to avoid backflow of hydrochloric-acid gas to the air-cleaning flasks.

Standardization of DDT

Materials. Alcoholic solution of ferric chloride; barium sulfate powder.

Procedure. Weigh as accurately as possible 2.7032 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Baker's), dissolve in about 5 ml of distilled water in a 100-ml volumetric flask, and fill to the mark with pure 96% ethanol. This will make an M/10 solution.

Weigh about 1 g of barium sulfate powder (Baker's) containing no more than 0.0005% iron as impurities, and pour into a U-tube. With a pipette, measure 0.05 ml of the ferric chloride solution and add to the barium sulfate carefully, seeing that the liquid does not come into contact with the glass of the tube. Shake to mix the contents of the tube thoroughly, and add 3 g of the technical-grade DDT to be standardized. Place tube in oil-bath as directed above, and determine amount of hydrochloric acid liberated in 5 hours.

Repeat the test twice and average results. These should agree to within 5%.

Obtain the decomposition rate for 0.1 ml and 0.15 ml of the ferric chloride solution in the same manner.

Testing the soils

Procedure. Prepare soil sample, grinding finely, and strain through a 60-mesh sieve. Weigh on an analytical balance 3 g of the standardized technical-grade DDT powder and to it add exactly 50 mg of the soil to be tested. Pour all carefully into a U-tube. Place tube in oil-bath, connect air-flow system, and proceed as directed above.

Compare the hydrochloric acid evolved at the end of the reaction with the data obtained with ferric chloride.

Interpretation of data. Prepare a table of comparison—e.g.,

<i>Ferric chloride (M/10) equivalent of soil *</i>	<i>Approximate duration of residual activity of DDT **</i>
< 0.05 ml	12 months
0.05 ml	6 months
0.10 ml	3 months
0.15 ml	1 month

* 50 mg soil \equiv x ml M/10 ferric chloride solution

** 200 mg DDT per square foot (approximately 2 g/m²) of adobe deposit

Apply the following criterion :

When 50 mg of soil will decompose one-half the amount of DDT decomposed by 0.05 ml of the ferric chloride solution, a 200 mg per square foot (about 2 g per m²) deposit can be expected to retain its activity for about a year. If the amount decomposed is about the same as is decomposed by the 0.05 ml of ferric chloride solution, the duration of activity of a 200 mg per square foot deposit will be approximately six months.

When the amount is about the same as is decomposed by 0.1 ml of the ferric chloride solution, the effect of the residual spray under the same conditions will be approximately three months. Decomposition-rates higher than this will be given by soils that are so active that a deposit of 200 mg per square foot will retain its activity for only a few days.

RÉSUMÉ

L'adsorption des cristaux de DDT par les surfaces de boue séchée prélude à la décomposition thermique du DDT, catalysée par l'oxyde ferrique du sol; il existe un rapport direct entre la teneur des sols en oxyde ferrique et la quantité de DDT qu'ils décomposent. On peut déterminer expérimentalement la faculté inactivante des sols, en les utilisant comme catalyseurs dans la réaction de décomposition thermique. Cette inactivation peut être inhibée par certaines impuretés, présentes dans le DDT technique, et plus encore par l'eau. L'adsorption du DDT par les sols est influencée par l'humidité relative ambiante. Les dépôts de DDT inactivés peuvent être réactivés lorsque l'humidité atmosphérique augmente.

Plusieurs substances susceptibles d'exercer un effet protecteur sur le DDT pulvérisé ont été essayées, sans succès. Il semble pourtant qu'en blanchissant les parois à la chaux, on obtienne des résultats encourageants.

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