

test was obtained with seeds of *T. candida*, but with no other plant part of this species. The roots, stems, leaves, and seeds of *T. vogelii* all gave a positive response with both histochemical and extraction methods. The pods of *T. vogelii* (and all other species examined) failed to show the presence of rotenoids when assayed by the extraction method, but when tested by the Durham method they gave an ephemeral, but definitely positive, reaction in the few idioblasts which were present.

Discussion

The quantitative results presented are based on production of red color in the presence of rotenone and the necessary reagents. Other rotenoids, such as elliptone, deguelin, and dihydrodeguelin, give a red color under the conditions of the test. Mixtures of rotenone and other rotenoids are known to occur in several genera (6, 8), and the ratio of the mixtures may vary. Because the results

presented are based on a standard curve of pure rotenone, and the toxic principles may vary in proportions in different species, these results should be taken as an approximation of actual rotenoid content.

Eight of the 16 species studied have been reported to contain rotenone or rotenoids in some plant part (3). The remaining eight species have not been previously reported to contain rotenoids, although *T. grandiflora* has been reported to be of insecticidal value (6). Of the five species found to contain rotenoids in the leaves, only *T. vogelii* had been previously reported (7).

The amount of rotenoids and the range of variation in the rotenoid content of leaves of *T. vogelii* indicate that this species is the most promising as a new source of rotenone. Preliminary trials have shown that this species can be grown in the continental United States and is readily adaptable to mechanized cultivation.

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FERTILIZER-INSECTICIDE MIXTURES

Stability of Certain Insecticides in Mixtures with Fertilizers

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Relatively few data are available on the stability of insecticides in mixtures with fertilizers. Therefore the stability of a number of fertilizer-insecticide mixtures was studied at 30° and 100° C. using a chromatographic procedure to detect the appearance of degradation products and organic chlorine analyses to determine decreases in organic chlorine contents. Most mixtures had good stability for at least 1 month at 30° C. with losses of organic chlorine varying from negligible to more than 50% on aging for 8 months. At 100° C. nearly all mixtures were unstable, and lost approximately 20% of their organic chlorine in the first 24 hours. Instability of insecticides in fertilizer mixtures was related to minor characteristics of the fertilizer, such as iron content and surface acidity.

COMMERCIAL PRODUCTION and use of fertilizer-pesticide mixtures in the United States have increased rapidly since 1950. Consumption amounted to nearly 109,000 tons in the year ended June 30, 1956 (14). Such mixtures contain almost exclusively the recently developed chlorinated hydrocarbon insecticides and are used mainly for the control of soil insects and pests. Berry (2) showed that such mixtures were used in 34 of 43 states and were approved by state agricultural authorities in 20 states. Because the rate of insecticide application is usually not more than a few pounds per acre, utilization of fertilizer as a carrier has the advantage of convenience, uniformity of distribution, and potential economy in the over-all

cost of insecticide and fertilizer application.

The literature contains little experimental evidence relative to the compatibility of insecticides with fertilizers and their stability in fertilizer mixtures (7). Certain data, however, are available on DDT (4) and aldrin (5). The present work was initiated to expand the data on compatibility and stability. An effort also was made to evaluate some of the causes of the instability of insecticides in the presence of fertilizer salts.

Materials and Methods

Technical grades of the insecticides listed in Table I were used in this study. The listed materials include those re-

ported to have been the most frequently used in the formulation of commercial fertilizer-pesticide mixtures in 1956 (2). The test fertilizers are described in Table II. The 5-20-20, 8-16-16, and 10-20-0 grades were experimental products formulated from ordinary and triple superphosphate, potassium chloride, ammonium nitrate, and aqua ammonia. The other materials and mixtures were commercial products of unknown formulation.

Fertilizer-pesticide mixtures containing 0.5 to 1% pesticide were prepared by adding 10% solutions of pesticide in a volatile solvent such as acetone to 900-gram samples of fertilizer in a continuously rotating laboratory mixer. Any residual solvent was removed by sub-

Table I. Composition of Insecticides Tested

Insecticide	Formula ^a	Chlorine Content, %	
		Theoretical	Found
Heptachlor	C ₁₀ H ₆ Cl ₇	66.48	66.4
Chlordan	C ₁₀ H ₆ Cl ₈	69.22	63.4 ^b
Aldrin	C ₁₂ H ₈ Cl ₆	58.30	58.2
Dieldrin	C ₁₂ H ₈ Cl ₆ O	55.85	55.7
Endrin	C ₁₂ H ₈ Cl ₆ O	55.85	55.5
DDT	C ₁₄ H ₉ Cl ₅	50.01	49.9
Methoxychlor	C ₁₆ H ₁₅ Cl ₃ O ₂	30.77	30.6

^a Chemical structure (77).

^b Technical chlordan, a mixture of several related compounds, contains less chlorine than indicated theoretical value.

jecting each batch to reduced pressure (100 to 150 mm. of mercury) for 30 minutes.

For tests at 30° C., 80-gram portions of the mixtures were charged into narrow-necked 35-mm. borosilicate tubes of approximately 140-ml. volume. After loading, a short section of 0.5-mm. bore capillary tubing was sealed to the tube as a vent. The vent was protected with a loose-fitting glass tubing cover. Samples were aged for 1, 2, 4, and 8 months at 30° ± 0.5° C. At the end of these storage periods the tubes were cut open to recover the sample.

Samples were aged at 100° ± 0.5° C. in 35-mm. borosilicate glass tubes, sealed to prevent loss of insecticide, for 24, 48, and 96 hours. At the end of the aging periods and after cooling, the capillary tips of the tubes were broken to release any internal pressure and then larger openings were made for sample recovery.

Because the fertilizer-pesticide mixtures were formulated to contain only a single insecticide, paper chromatography (72) in conjunction with organic chlorine analysis was used to evaluate changes in insecticide content during the several aging periods. More complex and time-consuming methods, some of which may

be questioned as to their specificity, would have been required for direct determination of the insecticide or for biological evaluation of the residual insecticidal activity.

The chromatographic procedure used is believed to be capable of detecting as little as 5% of a contaminant differing from the major component by 0.02 or more of an R_f unit (ratio of travel of the component to that of the mobile solvent). Major changes in an insecticide could be detected, therefore, unless the mobility of the degradation products either coincided substantially with the parent

material or was high enough for the products to be obscured in the curtain above R_f = 0.85. The presence of decomposition products was noted in only a few instances.

The organic chlorine equivalent of the insecticide (3, 73) in the mixtures was determined as follows: Three 20-gram samples of mixture were shaken at intervals with 50 ml. of *n*-hexane or benzene in a 250-ml. stoppered Erlenmeyer flask. Solids were removed by pressure filtration and a 25-ml. aliquot was taken for analysis. Most of the solvent was removed on a hot plate and the residue was refluxed for 2 hours with excess sodium (about 1 gram) in 10 ml. of isobutyl alcohol. The resulting chloride ion was determined by the Volhard method. On test samples this shaking procedure was found to yield results comparable to Soxhlet extractions and it was more rapid.

Acid-soluble ferric iron was determined by stirring 1 part of fertilizer with 5 parts of 2*N* hydrochloric acid for 1 hour at room temperature, filtering, and evaluating ferric iron colorimetrically with potassium thiocyanate on an aliquot.

Surface acidity (8, 75) was measured by immersing vacuum-dried fertilizer

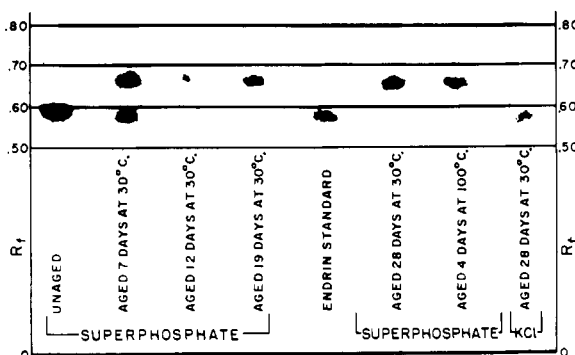


Figure 1. Endrin chromatograms

Table II. Analyses of Fertilizers Used

Material	Reaction ^a pH	Nitrogen, %		P ₂ O ₅ , %			K ₂ O, %	Acid-Soluble Iron, ^b P.P.M.	Surface Acidity, µeq./G.	
		Total	NH ₃ N	Total	Citrate-insol.	Water-sol.				Available
Ammoniated superphosphate	3.7	...	4.41	19.31	3.06	7.13	16.25	...	2900	19
Ammonium nitrate ^c	4.6	33.0	400	18
Ammonium phosphate, 11-48 ^c	3.8	11.01	10.96	50.46	1.10	44.74	49.36	...	2000	222
Ammonium sulfate	3.0	20.0	400	43
Potassium chloride, 60% K ₂ O	4.9	59.14	1250	11
Potassium-magnesium sulfate	6.0	20.28	2600	5
Superphosphate, 20% P ₂ O ₅	2.2	21.24	0.11	17.69	21.13	...	2500	116
Urea	7.9	46.17	40	2
5-10-5	3.4	4.99	3.78	11.32	0.70	6.87	10.62	5.12	5000	204
5-20-20 ^c	3.1	5.35	3.87	21.38	0.26	14.55	21.12	17.30	1500	116
8-16-16 ^c	3.1	7.77	5.22	17.12	0.42	9.21	16.70	15.50	1560	110
10-6-4	5.5	9.11	7.28	7.15	0.28	3.00	6.87	6.08	2300	103
10-20-0 ^c	3.9	10.4	7.5	20.9	0.4	8.82	20.5	...	2400	117
12-12-12	4.0	12.0	7.5	12.4	0.0	4.10	12.4	12.9	2100	147

^a 1 part water per part fertilizer.

^b Ferric iron soluble in 1 hour at room temperature in 5 parts 2*N* hydrochloric acid per part sample.

^c Granulated materials.

samples in dry benzene containing an excess of benzylamine for 2 days. Excess benzylamine was determined on a pressure-filtered aliquot of the benzylamine-benzene mixture by titration in 60% ethyl alcohol-40% water solution with 0.025*N* hydrochloric acid, using methyl red as indicator.

Experimental Results

The initial organic chlorine content and the change on aging at 30° and 100° C. are shown in Tables III and IV, respectively. Only in the cases of endrin-superphosphate mixtures aged at 30° and 100° C. and aldrin mixtures aged at 100° C. were chromatograms obtained which definitely indicated the presence of halogenated materials not initially present. Little correlation was found between aging data at 30° and 100° C.; hence fewer mixtures were aged at the higher temperature. Satisfactory correlation, however, has been reported between room and elevated temperature aging for heptachlor (9).

As shown in Figure 1, endrin in endrin-superphosphate mixtures was rapidly converted at both 30° and 100° C. to a halogenated material with an *R_f* value of 0.67 compared to 0.57 for the original endrin.

Aldrin mixtures heated at 100° C. gave chromatograms indicating 10% or more halogenated decomposition products. These were formed when aldrin mixtures, except those made with the 5-10-5 fertilizer, were heated in air at 100° C., but were not formed when the mixtures were aged at 30° C. or heated at 100° C. in a vacuum. Presumably oxidation was involved at 100° C. because the product formed on heating aldrin mixtures in air had the same *R_f* value as dieldrin, an epoxide of aldrin.

As expected, the loss of insecticide at 30° C., as measured by the decrease in organic chlorine content, increases with increased aging time, although the average decrease at 2 and 4 months does not differ significantly at the 1% probability level.

The decrease in organic chlorine from fertilizer-pesticide mixtures was dependent on the characteristics of both the fertilizer and the insecticide. Of the insecticides studied methoxychlor formed the most stable mixtures, followed by aldrin or dieldrin which were about equivalent, then by DDT, heptachlor, endrin, and chlordan. Variations in chlorine loss were rather large and varied from negligible amounts for methoxychlor to about 24% for chlordan at the end of 8 months. Among the fertilizers tested urea, ammonium nitrate, ammonium sulfate, and ammonium phosphate mixtures gave the smallest decreases in organic chlorine and were not significantly different statisti-

Table III. Initial Organic Chlorine Contents of Fertilizer-Pesticide Mixtures and Decrease in Organic Chlorine with Aging at 30° C.

Fertilizer	Initial ^a Organic Chlorine, %	Aging Period, Months			
		1	2	4	8
Decrease in Organic Chlorine, % ^b					
Heptachlor Mixtures					
Ammoniated superphosphate	0.721	8.8 ^c	12.3 ^c	9.9 ^c	17.6 ^c
Ammonium nitrate	0.687	0 ^d	0 ^d	0.0	4.9
Ammonium phosphate, 11-48	0.695	1.7	0 ^d	0 ^d	3.4
Ammonium sulfate	0.705	0.9	1.3	0.4	4.1
Potassium chloride, 60% K ₂ O	0.745	10.8 ^c	4.4	4.1	3.9
Potassium-magnesium sulfate	0.704	9.5 ^c	1.7	5.4 ^e	4.4
Superphosphate, 20% P ₂ O ₅	0.610	6.7 ^c	2.3	2.6	9.2 ^c
Urea	0.721	2.9 ^c	3.3	1.4	8.3
5-10-5	0.668	8.0 ^c	9.3 ^c	4.2	18.3 ^c
5-20-20	0.545	7.9 ^e	0 ^d	3.3	13.6 ^c
8-16-16	0.624	7.8 ^e	7.3 ^c	7.4 ^c	13.4 ^c
10-6-4	0.690	8.2 ^e	3.5	7.6 ^c	13.8 ^c
10-20-0	0.596	14.5 ^e	15.4 ^c	14.8 ^c	13.9 ^c
12-12-12	0.705	18.6 ^e	9.7 ^c	5.5 ^e	25.7 ^c
Chlordan Mixtures					
Ammoniated superphosphate	0.645	4.6	4.9	4.9	28.5 ^c
Ammonium nitrate	0.645	0.6	1.7	5.8 ^e	4.7
Ammonium phosphate, 11-48	0.657	0 ^d	1.3	8.0 ^c	9.2 ^c
Ammonium sulfate	0.657	0.7	1.8	1.6	3.3
Potassium chloride, 60% K ₂ O	0.404	6.9 ^c	13.2 ^c	8.1 ^c	36.4 ^c
Potassium-magnesium sulfate	0.679	7.7 ^c	6.7 ^c	4.7	24.3 ^c
Superphosphate, 20% P ₂ O ₅	0.461	15.9 ^c	27.0 ^c	17.7 ^c	41.4 ^c
Urea	0.659	0 ^d	2.4	1.5	3.8
5-10-5	0.460	19.4 ^c	27.1 ^c	20.9 ^c	51.4 ^c
5-20-20	0.516	4.2	5.0	11.7 ^c	6.2 ^e
8-16-16	0.541	4.8	6.5 ^e	18.1 ^c	7.6 ^c
10-6-4	0.352	1.3	24.2 ^c	21.9 ^c	37.5 ^c
10-20-0	0.540	0 ^d	18.1 ^c	28.3 ^c	26.0 ^c
12-12-12	0.656	28.1 ^c	36.9 ^c	53.5 ^c	53.4 ^c
Aldrin Mixtures					
Ammoniated superphosphate	0.576	5.9 ^e	1.4	4.0	1.9
Ammonium nitrate	0.559	0 ^d	3.0	3.4	0 ^d
Ammonium phosphate, 11-48	0.565	0 ^d	4.3	2.7	0 ^d
Ammonium sulfate	0.565	0.6	0.3	1.4	1.9
Ammonium chloride, 60% K ₂ O	0.285	3.2	7.0 ^c	0 ^d	0 ^d
Potassium-magnesium sulfate	0.555	0 ^d	0 ^d	3.4	0.9
Superphosphate, 20% P ₂ O ₅	0.267	3.2	9.3 ^c	2.0	3.5
Urea	0.487	0 ^d	0 ^d	0 ^d	0 ^d
5-10-5	0.262	0.8	4.0	2.4	2.7
5-20-20	0.405	3.7	7.6 ^c	2.9	4.5
8-16-16	0.439	9.9 ^c	11.2 ^c	5.8 ^e	8.7 ^c
10-6-4	0.284	16.8 ^c	14.6 ^c	15.0 ^c	14.5 ^c
10-20-0	0.420	2.9	1.5	4.7	2.5
12-12-12	0.556	6.5 ^e	9.7 ^c	19.2 ^c	6.8 ^c
Dieldrin Mixtures					
Ammoniated superphosphate	0.555	0 ^d	3.6	6.3 ^e	19.2 ^c
Ammonium nitrate	0.560	0 ^d	2.3	10.4 ^c	0.7
Ammonium phosphate, 11-48	0.570	6.2 ^e	3.6	8.3 ^c	9.0 ^c
Ammonium sulfate	0.570	5.8 ^e	3.4	3.5	6.4 ^e
Potassium chloride, 60% K ₂ O	0.230	0.2	0 ^d	0 ^d	0 ^d
Potassium-magnesium sulfate	0.564	6.7 ^c	0 ^d	7.6 ^c	15.1 ^c
Superphosphate, 20% P ₂ O ₅	0.259	3.0	5.8 ^e	9.7 ^c	9.0 ^c
Urea	0.565	5.2	7.2 ^c	0.5	4.2
5-10-5	0.222	0 ^d	0 ^d	0.8	3.0
5-20-20	0.384	0 ^d	0 ^d	0 ^d	14.9 ^c
8-16-16	0.444	1.4	2.8	2.3	0.4
10-6-4	0.271	6.2 ^e	11.2 ^c	0 ^d	8.6 ^c
10-20-0	0.418	4.2	0.7	11.1 ^c	0 ^d
12-12-12	0.476	0 ^d	5.3 ^e	6.3 ^e	5.2 ^e
Endrin Mixtures					
Potassium chloride, 60% K ₂ O	0.291	19.5 ^c	12.0 ^c	6.9 ^e	9.7 ^c
Superphosphate, 20% P ₂ O ₅	0.276	51.4 ^c	52.8 ^c	51.4 ^c	52.6 ^c
5-10-5	0.248	4.1	0 ^d	12.4 ^c	4.0
10-6-4	0.270	2.9	2.4	7.5 ^c	5.4
DDT Mixtures					
Ammoniated superphosphate	0.491	0.1	0 ^d	0.9	3.1
Ammonium nitrate	0.491	0 ^d	3.0	1.7	0.2
Ammonium phosphate, 11-48	0.510	2.6	1.5	4.4	1.8
Ammonium sulfate	0.496	2.5	2.3	2.1	1.0
Potassium chloride, 60% K ₂ O	0.505	4.3	3.7	0.3	2.0

(Continued on page 110)

cally. Potassium chloride and the 5-20-20 mixture were next most stable, followed by potassium-magnesium sulfate, ammoniated superphosphate, and 8-16-16. Superphosphate or 5-10-5 was next in order, followed by 10-20-0, 10-6-4, and 12-12-12, which formed the most unstable mixtures.

At 100° C., most of the fertilizer-pesticide mixtures lost about 20% of their organic chlorine content during the initial 24 hours with only minor additional losses during the next 72 hours. Reasonable uniformity of loss was observed. On the average the greatest losses were from the endrin mixtures (35%) and the least from the DDT mixtures (18%). Potassium chloride formed the most stable and superphosphate formed the least stable mixtures with the insecticides tested.

After aging trials were completed, a Perkin-Elmer Model 21 double-beam infrared spectrophotometer became available for use and was used to determine the spectra of the insecticides extracted from fertilizer-pesticide mixtures which were still available. Carbon disulfide solutions of the insecticides were used in determining the absorption spectra between 2 and 15.5 microns. These spectra paralleled the spectra of insecticides aged out of contact with fertilizer for the same periods, were similar to the spectra of reference grade insecticides, and closely approximated published spectra (6). Therefore the data indicate that the chlorinated materials extracted from these aged mixtures were substantially the unaltered insecticides. Quantitative estimates made from the infrared spectra are in fair agreement with the organic chlorine analyses (Table V). Because DDE, the primary decomposition product of DDT, contains no hydrolyzable chlorine, the data in Table V also confirm the presence of DDT in its aged mixtures.

No aged samples of fertilizer-endrin mixtures were available for infrared examination. Chlorine losses from methoxychlor mixtures were so low as to render insignificant any insecticide loss by dehydrohalogenation.

Discussion

Loss of insecticidal activity or of organic chlorine from fertilizer-insecticide mixtures may occur as a result of at least three mechanisms. The most probable causes of such loss are volatilization, molecular rearrangement of the toxicant to an inactive form, and decomposition of the insecticide.

Volatilization of insecticide did not seem to be of consequence under the experimental conditions imposed, although under practical conditions it may be of consequence (5). Molecular rearrangement is most probable in the relatively complex insecticides aldrin,

Table III. (Continued)

Fertilizer	Initial ^a Organic Chlorine, %	Aging Period, Months			
		1	2	4	8
DDT Mixtures					
Potassium-magnesium sulfate	0.519	3.8	9.1 ^c	6.7 ^c	12.5 ^c
Superphosphate, 20% P ₂ O ₅	0.625	5.8 ^c	6.8 ^c	0 ^d	3.4
Urea	0.484	0 ^d	0 ^d	2.8	0 ^d
5-10-5	0.503	5.5 ^c	6.5 ^c	4.6	6.0 ^c
5-20-20	0.347	0.9	4.3	0 ^d	11.0 ^c
8-16-16	0.401	2.1	5.7 ^c	2.0	7.9 ^c
10-6-4	0.504	6.6 ^c	6.6 ^c	0.0	8.2 ^c
10-20-0	0.442	17.2 ^c	21.8 ^c	19.3 ^c	33.5 ^c
12-12-12	0.456	0 ^d	14.1 ^c	13.1 ^c	15.8 ^c
Methoxychlor Mixtures					
Potassium chloride, 60% K ₂ O	0.320	6.1 ^c	2.1	0 ^d	1.0
Superphosphate, 20% P ₂ O ₅	0.317	0.8	1.9	4.8	1.0
5-10-5	0.292	0.2	2.3	0.2	0.9
10-6-4	0.299	0.6	0 ^d	0 ^d	1.0

^a Standard deviations of triplicate analyses ranged from 0.17 to 6.65% of individual means.

^b Average of triplicate analyses.

^c Slight increase.

^d Significant decrease at 1% level by analysis of variance.

^e Significant decrease at 5% level by analysis of variance.

Table IV. Initial Organic Chlorine Contents of Fertilizer-Pesticide Mixtures and Decrease in Organic Chlorine with Aging at 100° C.

Fertilizer	Initial Organic Chlorine, % ^a	Aging Period, Hours		
		24	48	96
Heptachlor Mixtures				
Potassium chloride, 60% K ₂ O	0.745	14.9 ^c	14.3 ^c	17.0 ^c
Superphosphate, 20% P ₂ O ₅	0.610	28.9 ^c	27.5 ^c	32.0 ^c
5-10-5	0.669	31.8 ^c	42.5 ^c	39.8 ^c
10-6-4	0.690	32.7 ^c	31.0 ^c	35.6 ^c
Chlordan Mixtures				
Potassium chloride, 60% K ₂ O	0.454	8.1 ^c	6.6 ^c	7.4 ^c
Superphosphate, 20% P ₂ O ₅	0.461	20.0 ^c	25.0 ^c	27.1 ^c
5-10-5	0.461	25.6 ^c	34.1 ^c	41.3 ^c
10-6-4	0.352	25.8 ^c	39.0 ^c	10.0 ^c
Aldrin Mixtures				
Potassium chloride, 60% K ₂ O	0.228	15.6 ^c	12.0 ^c	24.1 ^c
Superphosphate, 20% P ₂ O ₅	0.207	23.7 ^c	18.7 ^c	18.6 ^c
5-10-5	0.235	27.7 ^c	29.5 ^c	37.0 ^c
10-6-4	0.228	14.8 ^c	20.9 ^c	15.8 ^c
Dieldrin Mixtures				
Potassium chloride, 60% K ₂ O	0.230	9.4 ^c	14.2 ^c	14.0 ^c
Superphosphate, 20% P ₂ O ₅	0.259	36.6 ^c	27.9 ^c	31.9 ^c
5-10-5	0.222	24.7 ^c	31.5 ^c	19.7 ^c
10-6-4	0.271	22.4 ^c	21.5 ^c	18.7 ^c
Endrin Mixtures				
Potassium chloride, 60% K ₂ O	0.298	26.2 ^c	39.7 ^c	42.3 ^c
Superphosphate, 20% P ₂ O ₅	0.275	56.6 ^c	57.2 ^c	56.0 ^c
5-10-5	0.247	11.8 ^c	40.2 ^c	22.6 ^c
10-6-4	0.270	18.0 ^c	30.6 ^c	22.8 ^c
DDT Mixtures				
Potassium chloride, 60% K ₂ O	0.505	2.2	1.6	4.5 ^b
Superphosphate, 20% P ₂ O ₅	0.625	22.0 ^c	22.2 ^c	21.6 ^c
5-10-5	0.530	27.3 ^c	23.1 ^c	15.2 ^c
10-6-4	0.535	21.4 ^c	21.3 ^c	28.0 ^c
Methoxychlor Mixtures				
Potassium chloride, 60% K ₂ O	0.314	9.4 ^c	13.4 ^c	5.5 ^b
Superphosphate, 20% P ₂ O ₅	0.318	10.6 ^c	16.4 ^c	15.3 ^c
5-10-5	0.292	10.8 ^c	16.6 ^c	14.1 ^c
10-6-4	0.299	39.0 ^c	42.2 ^c	61.1 ^c

^a Average of triplicate analyses.

^b Significant decrease at 5% level by analysis of variance.

^c Significant decrease at 1% level by analysis of variance.

Table V. Equivalent Insecticide Contents of Selected, Aged Fertilizer-Pesticide Mixtures by Different Analytical Procedures

Fertilizer Component	Insecticide Component and Method of Analysis									
	Heptachlor		Chlordan		Aldrin		Dieldrin		DDT	
	Organic chlorine ^a	Infrared absorption, ^b	Organic chlorine ^a	Infrared absorption, ^b	Organic chlorine ^a	Infrared absorption, ^b	Organic chlorine ^a	Infrared absorption, ^b	Total organic chlorine ^b	Hydrolyzable chlorine ^{b,d}
		12.70 microns ^c		11.12 microns ^c		8.56 microns ^c		12.40 microns ^c		
Potassium chloride Superphosphate, 20% P ₂ O ₅	1.00	0.74	0.69	0.56	0.47	0.39	0.46	0.47	0.99	1.00
5-10-5	0.89	0.93	0.61	0.53	0.44	0.35	0.33	0.34	1.06	1.04
10-6-4	0.88	0.82	0.38	0.25	0.41	0.35	0.45	0.38	1.07	1.06

^a Aged 12 months at 30° C.

^b Aged between 28 and 33 months at room temperature.

^c Indicated absorption maxima.

^d Original DDT contained 10.5% hydrolyzable chlorine.

^e Skellysolve B solvent, corrected for solvent absorption.

chlordan, dieldrin, endrin, and heptachlor derived from cyclopentadiene. Endrin is known to rearrange (7) and others may behave similarly. Although such rearrangements do not involve chlorine loss, they may inactivate the insecticide. The available chromatograms and the infrared spectra do not indicate that such rearrangements occurred to any appreciable extent in the aged fertilizer-pesticide mixtures.

The observed decreases in organic chlorine may have occurred in several ways. Being technical materials, all the insecticides used contained chlorinated by-products. Minor decreases in organic chlorine may have been due to the decomposition of these by-products, with but minor effect on the toxicity of the insecticide. Major losses of chlorine probably occurred as a result of decomposition of the major component of the insecticide. The method of decomposition largely determines the chlorine loss. DDT and methoxychlor dehydrohalogenate losing 1 mole of hydrochloric acid per mole of insecticide with subsequent larger chlorine losses under certain conditions (10). Endrin in superphosphate mixtures and heptachlor under alkali reflux conditions lose about three chlorine atoms per molecule.

It appears likely that extensive decomposition of the insecticide occurred where large chlorine losses were observed, inasmuch as the supplemental tests on the aged mixtures indicated that the residual organic chlorine was present predominantly as the unaltered insecticide. The failure to detect chlorinated decomposition products in the mixtures may have resulted from their high volatility, decreased solubility in the extracting medium (heptachlor resinifies in part under alkali reflux), or conversion to forms undetectable by the methods employed.

As can be seen from Table III, a wide range in the stability of mixtures made with different insecticides was observed. Although none were used in these tests,

the stability of certain insecticides can be increased by incorporation of a stabilizer (7, 9, 11). The low ratio of insecticide to fertilizer, however, probably would make rather large quantities of stabilizer necessary to achieve adequate stabilization.

The characteristics of the fertilizers were studied to determine the properties contributing either to stability or instability of the insecticide in fertilizer in fertilizer-pesticide mixtures. The acidity of the sample as measured by the pH of an aqueous suspension did not greatly affect stability, with the possible exception of the superphosphate-endrin mixtures. Feebly basic urea (pH 7.9), however, was the only alkaline fertilizer tested. More basic materials may cause appreciable decomposition of alkali-sensitive insecticides such as DDT.

Surface acidity and acid-soluble iron contents of fertilizer components were found to affect the stability of insecticides in mixtures, in agreement with observations of other investigators (7, 9). Experimental observations indicated that the decrease in organic chlorine of fertilizer-pesticide mixtures was proportional to the magnitude of both characteristics. Empirical equations developed for the relationship among surface acidity, iron content, and decrease in organic chlorine indicated that aldrin and heptachlor were sensitive to both surface acidity and iron concentration, whereas chlordan, DDT, and dieldrin were sensitive chiefly to iron concentration. The average loss on 8 months' aging at 30° C. increases about 0.003% per p.p.m. increase in ferric iron and about 0.03% per microequivalent per gram increase in surface acidity. Among the fertilizers tested, those giving the more stable mixtures contained less than 1000 p.p.m. iron and below 100 µeq. per gram surface acidity.

As expected, the mixed fertilizers contained appreciable amounts of acid-insoluble residue, mainly silica. Ammonium nitrate also contained finely

divided acid-insoluble material probably used as a coating agent. Because the stability of insecticides with siliceous material varies with the source of the material (4, 9), consideration should be given to this factor in formulating fertilizer-pesticide mixtures.

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