dealing with a pH-sensitive enzymatic reaction, or simply an acid effect.

This observation also raises some question as to the biochemically active form of the gibberellins. The fact that barley responds to treatment with extraneous gibberellic acid would indicate that this compound, or a derivative, constitutes part of the growth regulatory mechanism during this stage of plant development. On the other hand, the absence of free endogenous gibberellic acid, as observed under mild extraction conditions, favors a derivative, or precursor, as the biochemically active component. This view is supported by the appearance of the marked radiopeak at R_{ga} 0.65 in Sample III-b which disappears upon exposure to an acidic pH (Sample III-a) for 24 hours. Additional data will be needed to resolve this question.

In another study (3) various plants were treated with tritium-labeled gibberellic acid, and were analyzed for residual gibberellic acid after the end of the growth period. The results obtained there indicated a higher than expected stability of the tissue-bound gibberellic acid, suggesting the possibility of stabilization by complex formation. On the other hand, in most samples relatively large amounts of residual tritium activity were associated with materials other than gibberellic acid, which at that time were considered to be decomposition products. This would have to be re-examined in the light of the existence of possible conjugated forms of gibberellic acid.

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Literature Cited

(1) Baumgartner, W. E., Lazer, L. S., Dalziel, A. M., Cardinal, E. V., Varner, E. L., J. Agr. Food Chem. 7, 422–5 (1959).
(2) Bowden, R. F., Dahlstrom, R. V., Sfat, M. R., Am. Soc. Brewing Chemists Proc. 1959, 137–41.
(3) Lazer, L. S., Dalziel, A. M., Baumgartner, W. E., Dahlstrom, R. V., Morton, B. J., Advances in Chem. Ser., in press.
(4) Phinney, B. O., Proc. Natl. Acad. Sci. 42, 185–9 (1956).
(5) Phinney, B. O., West, C. B., Ritzel, M., Neely, P. N., Ibid., 43, 398–404 (1957).
(6) Theriault, R. J., Friedland, W. C., Peterson, M. H., Sylvester, J. C., J. Agr. Food Chem. 9, 21 (1961).
(7) West, C. A., Phinney, B. O., J. Am. Chem. Soc. 81, 2424–7 (1959).

FERTILIZER-PESTICIDE MIXTURES

Homogeneity of Fertilizer-Pesticide Mixtures

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The use of fertilizer-pesticide mixtures has grown rapidly. Because mixtures prepared in the laboratory were relatively nonuniform, factors influencing their uniformity were evaluated. The mixtures were more uniform if insecticide were added as a solution than if added on a solid carrier. Mixing during addition of solution and use of closely sized fertilizer increased uniformity. The insecticide solution was preferentially adsorbed by the fine particles and by the phosphatic portions of a mixed fertilizer. The variation in insecticide content of random samples was large enough to cause poor analytical precision. Concentration of the toxicant on the fine portions of the fertilizer contributes to nonuniformity and forms toxic dusts. Preferential adsorption of toxicant by certain portions of a mixed fertilizer may accelerate decomposition of the toxicant.

FERTILIZER-PESTICIDE MIXTURES, introduced about 1950, have rapidly attained importance in agricultural practice. Their use was made possible by the development of toxic, chlorinated hydrocarbon insecticides that are stable in the soil and reasonably stable in mixtures with fertilizers. The latest data available indicate that 109,956 tons, equivalent to 0.74% of all mixed fertilizers, were used in the United States in the year ending June 30, 1956 (6).

Two general methods are used to formulate fertilizer-pesticide mixtures. Either solid carriers containing the insecticide or solutions of insecticide are incorporated into well cured fertilizers.

Carriers provide a simple method of producing fertilizer-pesticide mixtures, because the mixtures can be formulated in conventional fertilizer-mixing equipment. Solution addition of toxicant can cause less dilution of the plant nutrient content of the fertilizer, and is generally recommended for introduction of toxicant into granular fertilizers.

Most suggested methods of preparation of the mixtures (3, 7) are based primarily on plant-scale experience.

This paper presents data on the uniformity of mixing of toxicant with fertilizers by the above two methods, and the relative distribution of pesticides among the ingredients of mixed fertilizers.

Materials and Methods of Analysis

The chemical and screen analyses of the fertilizer materials used in this study are listed in Table I. With the exception of the 5–20–20 fertilizer, all were commercial products. The 5–10–5 mixture was a well cured, nongranular material. The granular 5–20–20 was an experimental product formulated from ordinary and triple superphosphates, potassium chloride, and an ammonia–ammonium nitrate solution.

The insecticides were undiluted technical grade products. Laboratory reagent quality benzene and acetone were used as solvents.

Carrier-insecticide concentrates (25%

Table I. Analysis of Fertilizers

Fertilizer	Nitrogen, % Total	NH₃N	P₂O₅, % Total	Citrate-insoluble	Available	K₂O %	MgO %	+14 mesh	−14, +35 mesh	−35, +100 mesh	−100 mesh
Ammoniated superphosphate	4.8	...	...	...	20.5	...	...	14.6	29.1	42.3	14.0
Ammonium nitrate	33.5	...	...	...	...	...	...	79.7	20.3	...	...
Ammonium phosphate (11–48–0)	11.20	10.95	51.26	2.71	48.55	...	...	48.9	28.9	15.1	7.1
Ammonium sulfate	20.5	...	...	...	...	...	...	0.1	52.4	42.2	5.3
Potassium chloride	...	...	...	...	...	60.5	...	0	34.3	54.9	10.8
Potassium magnesium sulfate	...	...	...	...	...	19.70	17.26	42.7	41.5	12.8	3.0
Superphosphate	...	...	20.51	0.49	20.02	...	...	14.3	34.3	42.0	9.4
Triple superphosphate, 1	...	...	48.04	1.25	46.79	...	...	43.5	25.9	20.0	10.6
Triple superphosphate, 2	...	...	48.70	2.14	46.56	...	...	23.2	37.4	35.8	3.6
Urea, coated	44.98	...	...	...	...	...	...	74.2	25.8	...	...
Urea, uncoated	46.04	...	...	...	...	...	...	52.9	47.1	...	...
5–10–5	4.99	3.78	11.32	0.70	10.62	5.12	...	14.6	29.1	42.3	14.0
5–20–20, granular	5.44	...	21.19	0.89	20.30	16.85	...	73.5	26.5	...	...

by weight) were prepared by adding insecticide solutions (20% insecticide by weight) from a pipet to 10 grams of a carrier such as attapulgite in a 15 × 8 cm. round, wide-mouthed bottle (16-ounce) contained in a rotating laboratory mixer. The mixer consisted of an open-ended drum 20 cm. in diameter, inclined about 20° from the horizontal, which was rotated at 46 r.p.m. After addition of the insecticide solution, mixing was continued for 10 minutes. The container was then warmed to 40° to 50° C., the pressure reduced to 150 mm. of mercury for 1 hour to evaporate residual solvent, and the mixture again stirred for 10 minutes before use. This method was employed to prepare all mixtures made from solids and insecticide solutions.

Acetone was used to extract the toxicant from carrier-pesticide and fertilizer-pesticide mixtures. Although heptachlor was easily removed from potassium chloride with cold acetone washes, the 5–20–20 mixtures required 4-hour Soxhlet extractions to remove the toxicant quantitatively. Acetone was removed by evaporation of the extract to near dryness on a hot plate. A small quantity of benzene then was added and the extract again evaporated to near dryness to remove any residual acetone. As all insecticides were highly chlorinated, organic chlorine analyses (2, 5) were used to determine the quantity of toxicant in the extracts. Untreated fertilizers used in this study contained no appreciable organic chlorine. Better than 99% recovery of the insecticide was indicated by this method.

The uniformity of distribution of toxicant in fertilizer-pesticide mixtures was studied by preparing a small sample, dividing it into several subsamples, extracting the toxicant from each subsample, and determining the organic chlorine content.

If insecticide distribution were perfect, variations in analyses of the subsamples

Table II. Uniformity of 5–10–5 1% Heptachlor Mixtures Made with Carriers and Insecticide Solutions

Solid Carrier or Solvent	No. of Mixtures Tested	Coefficient of Variation, %	Ratio of Maximum Deviation/ Mean
Carrier			
30/40 LVM attapulgite	2	7.2	15
Run-of-pile superphosphate[a]	2	7.5	16
Screened vermiculites[b]	3	16.7	34
Run-of-pile triple superphosphates[a]	2	18.0	37
Screened superphosphates[c]	3	26.0	65
Av. or total	12	15.2	..
Solvent			
Acetone	17	6.8	22
Benzene	4	6.0	14
Av. or total	21	6.4	..

[a] Screen analysis as in Table I.
[b] Data obtained from −8, +20-; −20, +48-; and −48, +150-mesh carriers.
[c] Data obtained from −8, +10-; −35, +48-; and −100, +150-mesh carriers.

should not exceed the variations attributable to errors in extraction and estimation of the toxicant. Because the variations observed for fertilizer-insecticide mixtures were considerably in excess of these errors, the coefficient of variation, C_v, was used as a measure of the uniformity of the mixtures (4, 8).

$$C_v = \frac{100\sigma}{M} = 100\sqrt{\frac{\frac{\Sigma(Y-M)^2}{N-1}}{M}}$$

where σ = standard deviation
Y = individual analysis
M = mean analysis
N = number of analyses

This index adjusts the standard deviations of the averages of several series of observations to a uniform basis for comparison. According to the distribution of the normal curve, 68% of the analyses of individual mixture should exhibit variations ≤ ± C_v, 95% ≤ ± 2 C_v, and 99% ≤ ± 3 C_v from the average. The magnitude of the analytical C_v was found to be ±0.4% by pipetting insecticide solution con-

taining 50 mg. of insecticide on each of four 5-gram samples of 5–10–5 fertilizer in a Soxhlet extractor. After evaporation of the solvent and extraction and analysis of the insecticide, the C_v for these samples was determined.

Uniformity of Carrier-Based Mixtures

Mixtures formulated with carrier-based toxicants were made by stirring the fertilizer-carrier mixtures for 10 minutes in the mixer previously described. The mean coefficients of variations of mixtures made with each solid carrier are shown in Table II. Run-of-pile superphosphate and 30/40 LVM attapulgite made the most uniform mixtures. The distribution cf toxicant was less uniform when vermiculite, triple superphosphates, and screened superphosphates were used as carriers.

In other related experiments, mixtures formulated with 30- to 60-mesh carriers and 5–10–5 fertilizer were more uniform than those prepared with other particle sizes of the same carriers. Mixtures made with longer mixing

times than 10 minutes did not improve in uniformity. In the case of soft materials such as superphosphate, particle size reduction occurred during mixing, creating dusts of high toxicity and fines that decreased the uniformity of the mixture.

Uniformity of Solution Formulated Mixtures

Mixtures made to determine the uniformity of formulations made with toxicant solutions were prepared by the method described for preparation of carrier-insecticide mixtures. The rates of addition were slow compared to those of commercial practice (Table III).

Data comparing variables investigated in solution formulations are shown in Table III. The use of fertilizers of narrow particle size range produced more uniform mixtures than those made with fertilizers of less uniform particle size. Stirring the fertilizer during insecticide addition also increased the uniformity of the product.

The type of solvent, rate of addition, and volume of the solution used to apply 1% of toxicant had little effect on the uniformity of the mixtures produced.

Solutions containing 31 to 500 mg. of toxicants per ml. were used in some cases to add insecticide to both 5-10-5 and 5-20-20 fertilizer. Application of the linear least squares procedure to

the data for each set of fertilizer-pesticide mixtures, however, indicated only negligible changes in uniformity with change in the solution volume used to add the 1% of toxicant to the fertilizers.

During mixing, only the solutions containing 31 and 63 mg. of toxicants per ml. visibly wet the fertilizer, and little redistribution of the toxicant was obtained on further mixing.

Comparison of Mixtures Made by Carrier and Solvent Additions

A comparison of mixtures formulated with solid carriers and solutions is shown in the averages of Table II. Mixtures formulated with solutions generally made more uniform mixtures than those made with carriers. When compounded under laboratory conditions, certain fertilizer-pesticide mixtures made with carriers, however, exhibited degrees of uniformity approximating those made with solutions.

Relative Sorptivity of Materials Used in Mixed Fertilizers

The relative adsorption of toxicants by fertilizers as it relates to composition and particle size of the adsorbing material was determined by impregnating mixtures of two fertilizers of different particle sizes with an insecticide solution, separating the materials, and determining their pesticide content.

Two 19.8-gram portions of materials of different particle size (either −8, +10 and −20, +28 mesh or −35, +48 and −100, +150 mesh) were mixed for 5 minutes in the laboratory mixer previously described. Then 4 ml. of a 10% solution of heptachlor in practical n-hexane was streamed onto the mixture from a pipet (delivery time about 20 seconds) and mixing continued for an additional 10 minutes. The residual solvent was evaporated as described and the two individual materials were recovered by screening on a sieve intermediate between the original particle size limits of the materials (14 mesh for coarse mixtures and 80 mesh for fine mixtures). Each fraction was weighed and its insecticide content determined.

Fertilizers of the desired narrow particle size range were obtained by screening the commercial materials. In some cases it was necessary to grind the fertilizers in order to obtain sufficient amounts of fines. The characteristics of fines obtained by grinding closely resembled those separated from the unground fertilizer.

Insecticides were selectively adsorbed by the finer portions of an individual fertilizer. A net grinding or aggregation effect was observed during mixing and separation of the different particle sizes. In consequence it was necessary to correct the observed insecticide concentrations for these effects.

In the case of over-all net grinding, the simplifying assumption was made

Table III. Effect of Mixing Conditions on Uniformity of 5-10-5 1% Heptachlor Mixtures Formulated with Solutions

Variable	Coefficient of Variation, %
Solvent	
Acetone	6.0
Benzene	6.0
Volume of solution, ml./g. fertilizer	
1.6	10.1
0.1	8.5
Rate of solution addition, ml./g. fertilizer/min.	
40	6.2
10	5.9
Agitation	
Solution added with stirring	4.4
Solution added without stirring	7.2
Particle size range	
Unscreened[a]	7.2
Screened[b]	4.2

[a] Screen analysis of 5-10-5 fertilizer as in Table I.
[b] Data from −48, +65- and −14, +20-mesh fertilizer samples.

Table IV. Relative Distribution of Heptachlor Added as Solution between Particle Size Fractions and Fertilizer Components of Fertilizer-1% Heptachlor Mixtures

Fertilizer Component		Ratio of Heptachlor Contents		
		Coarse to fine particle sizes of component A, obsd.	A to B Components of Mixtures	
A	B		Obsd.	Calcd.[a]
Potassium Chloride Reference Mixtures				
Attapulgite	Potassium chloride	0.77	14.7	...
Superphosphate	Potassium chloride	0.63	13.3	...
Ammoniated superphosphate	Potassium chloride	0.58	9.7	...
Triple superphosphate, 1	Potassium chloride	0.77	7.8	...
Ammonium phosphate (11-48-0)	Potassium chloride	0.76	7.5	...
Triple superphosphate, 2	Potassium chloride	0.65	6.4	...
Ammonium nitrate	Potassium chloride	0.52	3.0	...
Potassium magnesium sulfate	Potassium chloride	0.54	2.3	...
Urea, coated	Potassium chloride	0.41	1.8	...
Ammonium sulfate	Potassium chloride	0.27	1.4	...
Urea, uncoated	Potassium chloride	0.48	1.3	...
Potassium chloride	Potassium chloride	0.50	1.0	...
Nonreference Mixtures				
Urea, uncoated	Urea, coated	...	0.70	0.72
Triple superphosphate, 1	Superphosphate	...	0.62	0.59
Triple superphosphate, 2	Triple superphosphate, 1	...	0.64	0.82
Ammoniated superphosphate	Triple superphosphate, 1	...	2.0	1.24
Ammonium phosphate	Triple superphosphate, 1	...	1.10	0.96
5-20-20	Potassium chloride	...	7.6	6.2

[a] Calculated from observed potassium chloride distribution ratios of materials in mixtures.

that the distribution of the insecticide solution was complete before any appreciable subdivision occurred. Thus the fine fraction was a mixture of the original fines plus fines produced from the coarse particles, and the insecticide concentration was intermediate between the true values for the original fine and coarse material. It was assumed that the analysis of the coarse fraction remained unchanged.

A similar method of reasoning was used in correcting for samples showing net aggregation on processing. In general, the transfer of material from one size fraction to the other ranged from 0 to 6%.

The corrected data were used to calculate the distribution ratios of the insecticide concentrations in the coarse to fine particles shown in column 3 of Table IV.

These data indicated selective toxicant deposition on the fines. In mixtures made with a single fertilizer (Table IV, column 3), ammonium sulfate had the greatest concentration of toxicant in its fines, followed by the other nonphosphatic fertilizers. The phosphatic fertilizers gave the lowest concentration of toxicants in their fines.

The unusually high concentration of the insecticide in the fines of ammonium sulfate in comparison to other materials of similar crystal structure was attributed to the adsorption of toxicant by a contaminant concentrated in the fines. This impurity was soluble in organic solvents and the ratio of contaminants in the coarse and fine particles as estimated from the absorbances of acetone extracts at 350 mμ was equal to the insecticide distribution ratio for the same two particle sizes. Presumably the contaminant was associated with the by-product ammonia used in the manufacture of the sulfate.

The lower pesticide concentrations in the fines of the phosphates as compared with other materials resulted from the porous nature of phosphate particles. As a result, the area available for insecticide deposition increased more slowly with size reductions than materials composed of less porous particles.

The distribution of insecticide between two different fertilizers was also determined by the same techniques. For this purpose two mixtures were made with each pair of fertilizers, the material in the fine portion of one being the coarse portion of the other. After correction of the observed toxicant concentrations of the two fractions of a mixture for aggregation or grinding, the ratios in column 3 of Table IV were used to adjust the toxicant concentration of one component to that of the other particle size of the mixture. The calculated concentration ratios then are independent of differences in the particle sizes of the components. The ratios

entered in column 4 of Table IV are the averages of ratios calculated in this manner.

The relative distribution of insecticide solutions on fertilizers ranged from unity for the potassium chloride reference material to 13 for the sample of ordinary superphosphate. All phosphates tested had many times the sorbency of potassium chloride.

The effective surface area of the fertilizer particles determined the relative distribution of toxicant. All phosphatic fertilizers were composed of granules that were aggregates of much smaller particles. The particles in superphosphate were estimated to be equal to or less than 0.06 mm. in diameter. Toxicant absorption by the phosphates paralleled their large surface area. In materials of nonporous structure, the ratio of toxicant in the coarse to that in the fine particles approximated the ratio of the areas calculated for their particle sizes.

The amount of insecticide retained by a fertilizer was increased by the use of coating agents. Coated urea retained more insecticide than the uncoated material; the ammonium nitrate containing a relatively large amount of coating agent (water-insoluble content greater than 4%) had the highest toxicant retention of the nonporous fertilizers. The increase in the relative distribution ratio attributable to coating agents was not as great as that observed for aggregated materials.

The distribution ratios in Table IV, column 4, observed for mixtures not containing reference fertilizers are in fair agreement with those calculated from potassium chloride reference data. The observed 5–20–20 potassium chloride distribution ratio approximated the ratio calculated on the assumption that relative distribution was proportional to the quantity and distribution ratio of the individual fertilizer components.

Although heptachlor was used in most of the work, solutions of DDT, aldrin, and dieldrin, as shown in Table V, exhibited similar distribution ratios with superphosphate and potassium chloride. It is reasonable to assume, therefore, that the data relative to fertilizer-heptachlor mixtures are characteristic of most fertilizer-insecticide mixtures.

Conclusions

Uniform distribution of the toxicant in laboratory trials was not accomplished by either of the two methods used to prepare fertilizer-pesticide mixtures. Mixtures made with the 30/40 LVM attapulgite and run-of-pile superphosphate carriers were the most uniform.

Most mixtures made with insecticide solutions were more uniform than those made with carriers. The uniformity of mixtures made with insecticide solu-

Table V. Distribution of 1% of Aldrin, Dieldrin, DDT, and Heptachlor in Solution on Potassium Chloride and Superphosphate

Insecticide	Ratio of Insecticide in Coarse Particles to Insecticide in Fine Particles	
	Potassium chloride	Superphosphate
Aldrin	0.44	0.41
Dieldrin	0.44	0.39
DDT	0.52	0.38
Heptachlor	0.39	0.44
Mean	0.45	0.41

tions was increased by using a fertilizer of a narrow particle size range and stirring the fertilizer during toxicant addition. The nature of the solvent, solvent volume, and rate of solution addition had little effect on the uniformity of the mixture.

The variations in insecticide distribution noted in this study are large enough to cause poor precision in the determination of toxicant content of fertilizer-pesticide mixtures, unless considerable care is exercised in sampling and in sample preparation.

Toxicants were preferentially adsorbed by the fines of individual fertilizer materials. The phosphatic portions of mixtures of two fertilizer materials accumulated nearly all of the insecticide. Selective distribution of a toxicant on the fines and phosphatic portions of a mixed fertilizer decreases the uniformity of insecticide distribution, increases the toxicity of any dust, and may concentrate insecticide on materials that accelerate decomposition of toxicant (7).

Literature Cited

(1) Creamer, R. M., Lamont, T. G., J. Agr. Food Chem. 7, 107 (1959).
(2) Donovan, C. G., Soap Sanit. Chemicals 22, No. 6, 165 (1946).
(3) Flockemer, F. B., Loeffler, E. S., "Aldrin-Fertilizer Manual," Shell Chemical Corp., Denver, Colo., 1954.
(4) Paterson, D. D., "Statistical Technique in Agricultural Research," p. 22, McGraw-Hill, New York, 1939.
(5) Phillips, W. F., De Benedictis, M. D., J. Agr. Food Chem. 2, 1228 (1954).
(6) Scholl, W., Wallace, H. M., Crammatte, F. B., Com. Fertilizer 98, No. 2, 24 (1959).
(7) Smith, V. C., Ibid., 92, No. 5, 30 (1956).
(8) Snedecor, G. W., "Statistical Methods," p. 40, Iowa State College Press, Ames, 1940.