sorption on cellulose by means of physical bonds is to occur.

Conclusions

The results of this investigation indicate that studies of the mechanism of adsorption on well defined adsorbents can be useful in explaining the relationships between pesticide activity and chemical structure. The systematic variations in the molecular structure of the organic chemicals investigated show clearly which sites in the molecule can be involved in adsorptive processes, how various substituents may influence the extent of adsorption, and that the mechanisms operate preferentially. These observations were made possible only by first accounting for the relationship between solubility and adsorption. The results may be projected to an explanation of other studies in which a specific adsorption site is presumed to be operative, such as in the investigation of the inhibition by herbicides of the functioning of certain plant tissues or in the study of the adsorption of herbicides by certain soil fractions.

Only two of the chemicals investigated [isopropyl - *N* - (3 - chlorophenyl)carbamate and isopropyl-*N*-phenylcarbamate] have been used as commercial herbicides. The phytotoxicity of compounds cannot be evaluated therefore by their relative quantitative adsorption on a few adsorbents. Adsorption data, such as those presented here, may at present best be used to study the adsorptive relationships between herbicides and the soil environment and to evaluate this relationship in terms of the availability of the herbicide to the plant.

In the final analysis, complex structure-activity relationships, the sum of which mediate a herbicide's phytotoxic activity, may be presumed to involve a number of types of adsorptive sites, each of which imposes its own limiting features on the final expression of the relationship. Such complex systems can be understood only as the successive types of adsorptive sites involved in a given process are identified and the adsorption mechanisms clarified.

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Literature Cited

(1) Barker, M., Hunter, L., Reynolds, N. G., *J. Chem. Soc.* **1948,** 874.
(2) Burnside, O. E., Behrens, R., *Weeds* **9,** 145 (1961).
(3) Campbell, D. S. E., Cathcart, D., Giles, C. H., *J. Soc. Dyers Colourists* **73,** 546 (1957).
(4) Cassidy, H. G., "Adsorption and Chromatography," p. 81, Interscience, New York, 1951.
(5) Cluett, M. L., *Anal. Chem.* **34,** 1491 (1962).
(6) Frissel, M. J., *Verslag. Landbourok. Onderzoek.*, No. **67.3** (1961).
(7) Geissbühler, H., Haselback, C., Aebi, H., *Weed Res.* **3,** 140 (1963).
(8) Giles, C. H., Jain, S. K., Hassan, A. S. A., *Chem. Ind. (London)* **1955,** 629.
(9) Good, N. E., *Plant Physiol.* **36,** 788 (1961).
(10) Gould, E. S., "Mechanisms and Structure in Organic Chemistry," p. 376, Holt, Rinehart and Winston, New York, 1959.
(11) Harris, C. I., Warren, G. F., *Weeds* **12,** 120 (1964).
(12) Huffman, C. W., Allen, S. E., J. AGR. FOOD CHEM. **8,** 298 (1960).
(13) Huggins, M. L., *Am. Scientist* **50,** 485 (1962).
(14) Hunter, J., *J. Chem. Soc.* **1945,** 806.
(15) Klingman, G. C., "Weed Control: As a Science," p. 136, Wiley, New York, 1961.
(16) Moreland, D. E., Hill, K. L., J. AGR. FOOD CHEM. **7,** 832 (1959).
(17) Sherburne, H. R., Freed, V. H., *Ibid.*, **2,** 937 (1954).
(18) Steel, R. G. D., Torrie, J. H., "Principles and Procedures of Statistics," p. 161, McGraw-Hill, New York, 1960.
(19) Upchurch, R. P., Mason, D. D., *Weeds* **10,** 9 (1962).
(20) Vickerstaff, T., "Physical Chemistry of Dyeing," 2nd ed., p. 183, Oliver and Boyd, London, 1954.

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HERBICIDES IN LEGUMES

Absorption, Translocation, and Residue Content of *n*-Propyl-1-C^{14}-*N*,*N*-di-*n*-propylthiolcarbamate in Legumes

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THE absorption, translocation, and residue content of ethyl-*N*,*N*-di-*n*-propylthiolcarbamate (EPTC) and *n*-propyl-*N*-ethyl-*N*-*n*-butylthiolcarbamate (PEBC) in several plant species have been reported (*2–4, 7*). This paper describes a similar study for *n*-propyl-1-C^{14}-*N*,*N*-di-*n*-propylthiolcarbamate (R-1607) in peanut and soybean plants.

Methods and Materials

Nineteen peanut seeds, variety North Carolina 4X, and 28 soybean seeds, variety Lee, were planted in each 25-pound freezer tin containing Newberg silty loam soil, and grown under greenhouse conditions. Twelve pots were used for each crop, divided into three groups of four pots each. The first group was used as a control and the second and third groups were treated with R-1607-C^{14} at the rate of 1 and 4 pounds per acre, respectively. Uniform application was achieved by dissolving 33.2 μc. of R-1607-C^{14} (2.21 mg.) for the 1-pound rate and 2.21 mg. R-1607-C^{14} plus 6.64 mg. of carrier R-1607 for the 4-pound rate in 100 ml. of distilled water and applying as a small stream from a plastic squirt bottle to the soil surface of each pot. The temperature of the greenhouse was maintained at 80° C. during the day and 70° C. at night. The daylight was supplemented with Sylvania VHF Gro-Lux fluorescent lights for 14 hours a day.

During the early stages, plants were harvested by digging up the entire plant, but during the latter part of the experiment, when the root system became too large to dig, the plants were cut off at the ground. Five peanut plants or ten soybean plants were harvested at each interval. The harvested plants were dissected into foilage, stem, roots, cotyledons, seeds, and seed pods. The plant parts were then weighed, dried in a vacuum oven at 60° C., and ground in a Wiley Micromill.

Unchanged R-1607 residue was extracted from a portion of the ground

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Studies on the absorption, translocation, and residue content of C^{14}-labeled *n*-propyl-*N,N*-di-*n*-propylthiolcarbamate (R-1607-C^{14}) in soybean and peanut plants were undertaken. The uptake of herbicide from soil was continuous as long as herbicide was available and was dependent on the application rate. Both radioautographic and radiochemical analyses demonstrated the distribution and translocation of herbicide in the plants. In both plant species, the radioactivity was distributed throughout the whole plant, but the translocation into the leaf was somewhat restricted; content was higher in the stem tissue than in the leaves. While the uptake of herbicide from soil is rapid, the ability of the plants to detoxify it is also rapid. The residue content at harvest would be undetectable by most chemical methods, but radioactive measurements showed several parts per billion.

tissue by the steam distillation and continuous extraction technique of Fang (*3*). It was necessary to increase the distillation time to 3 hours for complete removal of R-1607. The presence of R-1607-C^{14} residue in the iso-octane extract was confirmed by gas chromatography and radioactivity measurement of the peak fractions. Although several other peaks were evident from the chromatograms, no activity was found other than the peak corresponding to the R-1607.

The radioactivity in the iso-octane extracts was determined by a liquid scintillation technique. One-half milliliter of the sample to be counted was added to the counting solution consisting of 2 ml. of toluene and 2.5 ml. of a toluene solution containing 0.4% 2,5-diphenyloxazole (PPO) and 0.005% 2,2′-*p* - phenylenebis(5 - phenyloxazole) (POPOP). This system gave a counting efficiency of 53.8%.

The total radioactivity of the dried tissue was determined by counting directly a duplicate aliquot of samples with a gas-flow Geiger counter. This was calculated to total microgram equivalents of R-1607 per gram of dry tissue, using the known efficiency of the counting system.

Radioautograms were made of the intact sample plants harvested at different stages of growth. Harvested plants were washed thoroughly with water to remove any soil particles, blotted dry, pressed between two sheets of filter paper, and dried with a warm air stream. The pressed plants were then placed on sheets of no-screen medical x-ray film and stored for 2 to 3 months. At the end of the exposure period, the radioautograms were developed, washed, and dried.

Results and Discussion

Distribution of Radioactivity in Plants. The radioautograms made from 2-, 3-, and 5-week-old peanut seedlings show a distribution of activity throughout the entire seedling (Figure 1). As would be expected, the roots closest to the source show the highest density and the density gradually decreases along the stem. At the earlier stages of growth the cotyledons have the greatest concentration, probably because of the passive absorption of R-1607 into the imbibing seeds. The concentration of C^{14} in the roots is next. The rapid movement of R-1607 from the roots is evident from the amount found in the stem and foliage (Table I). The entire stem contains more total radioactivity than the roots, although the specific activity (micrograms of R-1607 equivalent per gram) is lower (Table II). Translocation upward is continued to the foliage, and distribution through the leaf is uniform, except at the edge of the leaves, where considerable radioactivity is concentrated. Generally, younger leaves contain less C^{14} than older ones.

At a 1-pound rate during the first 3 weeks, the continued uptake of herbicide from soil by the roots is made evident by the increase of total radioactivity in the stem and foliage without loss from the roots. Treatment with 4 pounds per acre, however, may affect the further absorption of herbicide from the soil, since the increase of activity in the leaf is the result of a decrease in the stem and root, with no significant increase of total activity in the plant.

The percentage of activity present as residue is lower in the foliage than in the stem and root. Whether this is due to a decrease in ability to translocate the residue or to an increase of metabolism in the foliage is not known. Translocation of residue from root to stem appears to be active.

In general, the radioautograms demonstrate the ability of the peanut plant to translocate the C^{14} either as residue or as metabolites through the plant. This translocation process is comparable at both concentrations studied.

Radioautograms made from the 2- and 3-week-old soybean plants also show a distribution of radiocarbon throughout the seedling (Figure 2). Treatment at 1 pound per acre results in the greatest concentration of radioactive material in the roots and cotyledons. Translocation, however, is rapid toward the stem and foliage for the first 3 weeks; the total amount is almost evenly divided among the four parts (Table I). The residue remains fairly constant during this period, indicating a similar rate of uptake and

Table I. Total Micrograms of Equivalents of R-1607 and Residue Found in an Average Peanut and Soybean Seedling

Found, μg., as	Age, Weeks	1 Lb. per Acre				4 Lb. per Acre			
		Foliage	Stem	Cotyledon	Root	Foliage	Stem	Cotyledon	Root
					Peanut				
Equivalents	2	0.083	0.350	...	0.288	0.496	3.02	...	2.49
	3	0.146	0.460	...	0.342	0.948	3.60	...	2.00
	5	0.314	0.476	...	0.238	1.30	1.04	...	1.62
Residue	2	0.003	0.056	...	0.091	0.024	0.807	...	0.364
	3	0.005	0.105	...	0.098	0.040	0.636	...	0.468
	5	0.010	0.049	...	0.051	0.037	0.233	...	0.177
					Soybean				
Equivalents	2	0.015	0.017	0.296	0.270	1.00	1.16	1.16	1.65
	3	0.187	0.208	0.195	0.247	1.17	1.35	1.12	1.42
Residue	2	0.0006	0.004	0.003	0.007	0.011	0.046	0.013	0.077
	3	0.0007	0.005	0.003	0.007	0.007	0.027	0.018	0.083

Table II. R-1607-C^{14} Residue and Total Radioactivity in Peanut Plants Harvested at Various Times Following Pre-emergence Treatment

Time after Treatment, Weeks	μg. per Gram Dry Tissue					
	Foliage		Stem		Root	
	R-1607	Total C^{14}	R-1607	Total C^{14}	R-1607	Total C^{14}
	1 Lb./Acre					
2	0.07	0.50	0.19	1.18	0.72	2.28
3	0.02	0.52	0.30	1.31	0.61	2.11
5	0.02	0.59	0.09	0.84	0.29	1.37
6	0.01	0.32	0.01	1.06	0.09	0.74
10	0.04	0.40	0.01	0.28	0.03	0.44
14	0.02	0.30	0.01	0.16	0.09	0.10
	4 Lb./Acre					
2	0.15	3.18	2.28	8.48	2.17	14.87
3	0.17	3.73	1.94	10.96	2.76	11.76
5	0.08	2.69	0.45	2.00	1.09	10.00
6	0.03	1.43	0.07	1.55	0.41	5.12
10	0.15	1.48	0.39	1.30	0.29	2.20
14	0.09	0.47	0.04	0.67	0.01	0.34

metabolism in the plant. The radioautogram of the fourth week seedling which was treated at 1 pound per acre shows more radioactive material in the older than in the new foliage. This would suggest that translocation of C^{14} from the mature tissue is negligible and once incorporated in the leaf is only slightly remobilized.

Treatment at the 4-pound rate results in an increased uptake and more even distribution of total activity throughout the entire plant. The younger leaves always showed less concentration of radioactive material. The roots and cotyledons contain the greatest concentration per unit area; however, the total amount of material does not differ greatly from that found in the stem.

The total amount of residue found in the various tissues remains small in comparison to the total radioactivity, and the residue in the various parts remains fairly constant over the time period studied.

The distribution of radioactivity in soybean and peanut seedlings treated with R-1607-C^{14} generally resembles those obtained with EPTC-S^{35} (*4*, *7*). As was the case with EPTC-S^{35}, absorption and translocation of R-1607-C^{14} are rapid; more radioactivity is found in the aerial portions of the plants, both residue and total activity. Increasing the rate of R-1607 increases the amount of uptake from the soil, as was the case with EPTC-S^{35}; however, this uptake is not proportional to the rate of application.

Evaluation of R-1607 Breakdown and Residues in Peanuts. Analysis for the total activity of both unchanged residue and metabolized R-1607 shows (Table II), as would be expected, the highest concentration in the roots. A maximum is reached between 2 and 3 weeks after treatment and rapidly decreases thereafter.

Table II also shows the amount of unchanged residue found at the various harvest periods. The concentration of R-1607 residue drops rapidly after reaching the maximum. The concentration in the stem also reaches a maximum at between 2 and 3 weeks, then rapidly decreases to about 1.01 μg. per gram of dry tissue for both rates after 26 weeks. The maximum concentration of R-1607 in the foliage never exceeds 0.07 μg. per gram for the 1-pound rate and 0.168 μg. per gram for the 4-pound rate. At 26 weeks, the concentrations are decreased to 0.01 and 0.04 μg. per gram, respectively.

The seed pod and pedicels are analyzed individually only at the final harvest (26 weeks); otherwise they are included with the nut for analytical purposes. These show a residue level generally five times that of the nut itself, and somewhat comparable to the level in the foliage (0.01 and 0.04 μg. per gram of dry tissue for 1- and 4-pound rates, respectively). The nut contains only a trace of residue at harvest and the uncertainty of this figure is largely due to the extremely low counting rate.

Generally, while the uptake of herbicide from the soil is rapid, the ability of the peanut plant to metabolize and degrade R-1607 to CO_2 is also rapid.

Evaluation of R-1607 Breakdown and Residues in Soybean Plants. The general pattern of degradation and accumulation of R-1607 residues in soybean plants is similar to that in peanuts. The roots possess the highest concentration of both residue and total equivalents of herbicide (Table III). The samples harvested at 2 weeks have the highest activity, which falls off rapidly. The concentration for residue and equivalents of R-1607 might be even higher if the samples were harvested before the date.

Again, the same pattern is found in the stem and the foliage, with much lower values. At maturity (26 weeks), the

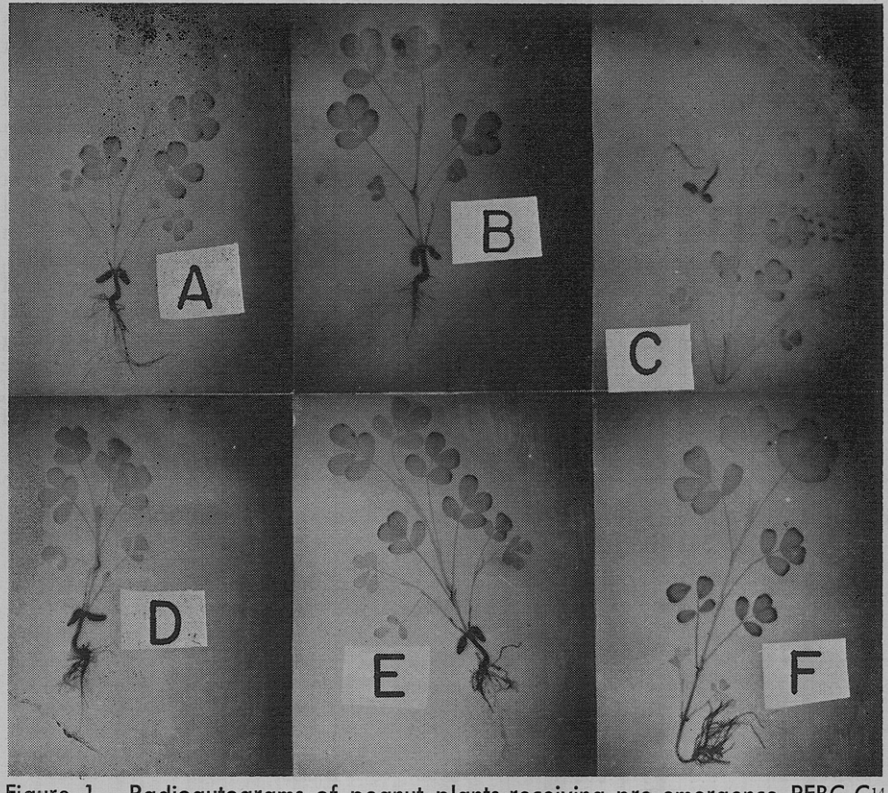

Figure 1. Radioautograms of peanut plants receiving pre-emergence PEBC-C^{14} treatment

Top. 1 lb./acre rate
A. 2 weeks
B. 3 weeks
C. 5 weeks after treatment

Bottom. 4 lb./acre rate
D. 2 weeks
E. 3 weeks
F. 5 weeks after treatment

Table III. R-1607-C^{14} Residue and Total Radioactivity in Soybean Plants Harvested at Various Times Following Pre-emergence Treatment

Time after Treatment, Weeks	Cotyledon		Foliage		Stem		Root	
	μg. per Gram Dry Tissue							
	R-1607	Total C^{14}	R-1607	Total C^{14}	R-1607	Total C^{14}	R-1607	Total C^{14}
	1 Lb./Acre							
2	0.10	10.35	0.01	3.37	0.09	3.67	0.52	21.00
3	0.13	9.35	0.01	1.84	0.05	2.12	0.36	13.60
4	...	...	0.02	1.21	0.03	1.01	0.06	9.05
5	...	...	0.02	1.25	0.02	1.25	0.07	6.86
8	...	...	0.00	0.39	0.00	0.36	...	...
12	...	...	0.01	0.35	0.01	0.35	...	...
	4 Lb./Acre							
2	0.44	40.40	0.34	22.24	1.00	25.52	5.28	112.00
3	0.98	60.00	0.06	10.54	0.25	12.36	4.82	82.48
4	...	...	0.13	7.96	0.09	6.16	0.10	61.60
5	...	...	0.03	3.64	0.07	2.57	0.25	45.20
8	...	...	0.01	2.50	0.02	1.84	...	...
12	...	...	0.04	0.82	0.05	1.05	...	...

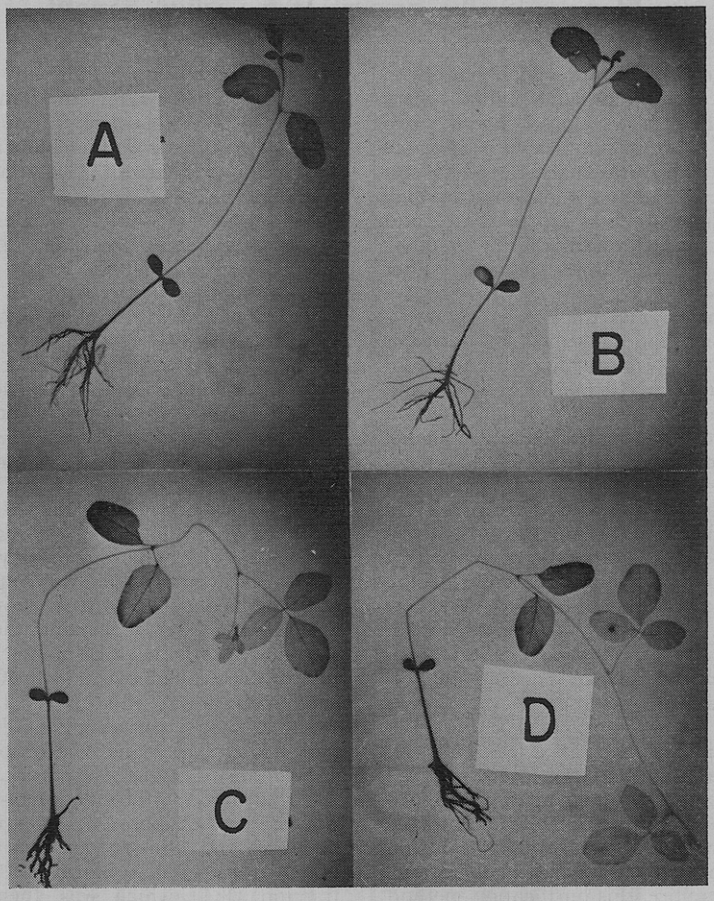

Figure 2. Radioautograms of soybean plants receiving pre-emergence PEBC-C^{14} treatment

A. 1-lb. rate, 2 weeks old
B. 4-lb. rate, 2 weeks old
C. 1-lb. rate, 3 weeks old
D. 4-lb. rate, 3 weeks old

residue level in the stem has dropped to 2 and 17 parts per billion for the 1- and 4-pound rates, respectively, and approximately to 5 p.p.b. in the foliage. The pod and seed contain no significant amount of residue.

The cotyledons continue to accumulate both residue and metabolites until they are abscinded, at which time they still contain considerable quantities of both form (Table III). During the first 2 weeks, while still affixed to the seedling, they contain both residue and total equivalents in a ratio proportional to the original rates of application—i.e., 1 to 4. At 3 weeks, however, the cotyledons receiving 4 pounds per acre doubled the concentration of both residue and total radioactivity equivalents while those treated at the lower rate remain unchanged.

Analysis of the seed and seed pod at both 20 and 26 weeks reveals no significant residue. At the 1-pound rate, the residue is less than 6 p.p.b. in either the seed or pod. At the 4-pound rate, the residue is less than 20 p.p.b.

The same general conclusions may be reached concerning the breakdown of R-1607 and residue concentrations in soybeans as for peanuts. Both soybeans and peanuts are tolerant to R-1607, thus making this herbicide useful for the control of grassy weeds. Since the residue in the seeds, after pre-emergent treatment, is below pharmacological limits, they may be used directly as food or as a source of oil. The stem, foliage, seed pods, and seed pulp all have negligible residues at harvest, and therefore their use as stock feed should not be cause for concern. Higher concentrations of residue can be expected if postemergent application is utilized but the final concentration at harvest would have to be determined.

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Literature Cited

(1) DeHertogh, A. A., Hooks, J. W., Klingman, G. C., *Weeds* **10,** 115–8 (1962).
(2) Fang, S. C., Fallin, Elizabeth, *Ibid.*, **13,** 152–5 (1965).
(3) Fang, S. C., Theisen, Patricia, J. Agr. Food Chem. **7,** 770–1 (1959).
(4) *Ibid.*, **8,** 295–8 (1960).
(5) Foy, C. L., Lyons, T., Carlson, S. P., *Calif. Agr.* **16,** 12–4 (1962).
(6) Klingman, G. C., Schramm, R. J., Cardenas, H., *Proc. Southern Weed Control Conf.* **14,** 63–8 (1961).
(7) Yamaguchi, S., *Weeds* **9,** 374–80 (1960).

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