

be dependent upon the formation of *X* since all carbamates studied, active or inactive, give a similar compound. The formation of *X* may be taken as evidence that these compounds penetrated the plant, at least to the site of their conversion to *X*. Thus, the lack of herbicidal activity of carbamates analogous to barban cannot be blamed on penetration failure.

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SOIL EFFECTS ON HERBICIDES

Influence of Soil Properties on the Phytotoxicities of the *s*-Triazine Herbicides

THOMAS J. SHEETS¹

U. S. Department of Agriculture, Davis, Calif.

ALDEN S. CRAFTS and HAROLD R. DREVER

Department of Botany, University of California, Davis, Calif.

The initial and residual toxicities of nine *s*-triazines were compared in five soils, and the relationship of simazine phytotoxicity to organic matter, clay content, cation exchange capacity, and pH of soils was investigated. The chloro derivatives with a single methyl, ethyl, or isopropyl substituent on each amino group were more toxic than those with a single substituent on an amino group and two substituents on the other. The chloro derivative with two substituents on each amino group was least phytotoxic. In simple correlation analyses, the simazine *ED*₅₀ value was positively correlated with soil organic matter and cation exchange capacity, and negatively correlated with pH. Multiple regression analyses suggested that the negative correlation between the simazine *ED*₅₀ and pH was a consequence of the correlation between organic matter and pH. The relative values of the four soil properties for dosage predictions are discussed. Organic matter was best for predictions; and the use of other properties with organic matter did not improve predictability greatly. Under experimental conditions which prevented leaching, simetone was the most persistent of the nine herbicides. Atrazine, propazine, and norazine were only slightly less persistent than simazine in most soils.

SEVERAL *s*-TRIAZINES are currently used as selective pre-emergence herbicides in crops. The rates required for weed control vary with the chemical and weed species, but 2 to 6 pounds per acre are adequate for most weeds.

At rates used for selective weed control, the *s*-triazines may remain active in the soil for several months after application. At rates of 20 to 30 pounds per acre, simazine and several analogs are effective semipermanent soil sterilants. All of the *s*-triazines included in these experiments are rather persistent; however, in Europe and the U. S., simazine has been the most satisfactory *s*-triazine for soil sterilization.

A major problem in the efficient use of

these chemicals as selective herbicides on crop plants is their persistence in soils. Knowledge of the relationship of phytotoxicity to soil properties should aid in establishing safe, effective rates of these herbicides.

Limited data are available on the effect of soil properties on the phytotoxicity and persistence of simazine. Investigators reported that to produce the same degree of injury, less simazine was required in sand than in clay soils and soils high in organic matter (7, 2, 4, 12). Soil temperature appeared to influence the toxicity of simazine to corn (2); but whether the differences were caused by variations in availability of the chemical in the soil solution or absorption of the chemical by plant roots was not determined. In experiments by Aelbers and Homburg (7), simazine was inactivated more rapidly in clay and peat

than in sand soil. Dewey's (4) results showed that simazine was inactivated under conditions favoring growth of microorganisms, but little or no loss occurred under conditions unfavorable to microbial growth. Guillemat (5) reported that several species of fungi would inactivate simazine, particularly in the presence of other carbon and nitrogen sources. Therefore, simazine activity in the soil appears to follow patterns similar to those of other relatively persistent, organic herbicides with respect to soil properties and soil environment.

The objectives of the experiments reported here were to compare the initial and residual toxicities of nine *s*-triazines in five soils and to relate the phytotoxicity of simazine to organic matter, clay content, cation exchange capacity, and pH of soils.

¹ Present address: Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md.

Experimental Procedure

Approximately 400 pounds of each of 16 soils from California and Arizona were screened and thoroughly mixed. The mixed soils were sampled for analyses (Table I). Per cent organic matter was determined in duplicate by the Wakley-Black rapid titration method for organic carbon (10). Per cent clay was obtained from triplicate determinations by the hydrometer method (8). Duplicate cation exchange capacities were measured with slight modifications of the method described by Piper (10). Duplicate pH readings were made with a glass-calomel electrode system. Moisture equivalent values obtained by the standard centrifuge method (10) were used as a measure of field capacity.

The initial and residual toxicities of nine *s*-triazines in five soils were investigated in two experiments. The methods were identical, and simazine was included in both for comparative purposes. The herbicides in the first experiment were chlorazine, trietazine, ipazine, simetone, 30451, propazine, and simazine. In the second experiment, simazine, atrazine, and norazine were compared. The structural names of the herbicides are listed in Table II.

A series of eight to 11 concentrations of each herbicide was used for each soil. Portions of soil, each 500 grams on an oven-dry basis, were weighed. Stock suspensions or emulsions were prepared from formulated, wettable powders or emulsifiable concentrates. The herbicide for individual cultures was removed from the stock and suspended in sufficient water to wet the soil to field capacity. The herbicides were combined with the soils by alternately adding one third of the soil and one third of the herbicide-water suspensions or emulsions to No. 2 metal cans. All concentration series were run in triplicate.

After the herbicides were added to the soils, 13 oat seeds (*Avena sativa* L., Kanota) were planted per can by pressing the basipetal end of each into the soil so that only about one fourth remained above the soil surface. The cultures were watered daily as required to maintain adequate soil moisture for growth of oats. Approximately 1 month after seeding, fresh weights of oat plants above the soil level were determined. After drying in place on the greenhouse bench for approximately 1 month, the soil in each culture was pulverized and thoroughly mixed, and the plant residue from the previous harvest was returned to the container. Water was added to wet the cultures to field capacity, and oats were seeded again. This scheme of alternate monthly crops of oats was continued for eight crops.

For comparisons among soil types and chemicals, a single numerical measure

Table I. Per Cent Organic Matter, Per Cent Clay, Cation Exchange Capacity, and pH of Soils

| Soil Type | Organic Matter, % | Total Clay, % | Cation Exchange Capacity, Meq./100 Grams | pH |
|------------------------|-------------------|---------------|--|-----|
| Sacramento clay | 4.83 | 63.6 | 48.6 | 5.6 |
| Stockton adobe clay | 3.84 | 45.5 | 31.9 | 6.1 |
| Sacramento silty clay | 1.66 | 55.0 | 27.0 | 7.8 |
| Madera silty clay | 3.03 | 40.9 | 27.4 | 6.8 |
| Yolo silty clay loam | 2.44 | 37.7 | 28.7 | 8.0 |
| Yolo silt loam | 2.43 | 26.6 | 22.2 | 7.2 |
| Yolo sandy clay loam | 1.42 | 20.8 | 14.0 | 6.8 |
| Aiken clay loam | 9.81 | 29.1 | 23.7 | 5.5 |
| Fresno silty clay loam | 3.41 | 38.5 | 23.9 | 6.8 |
| McClellan clay loam | 1.39 | 29.5 | 17.8 | 8.4 |
| Merced clay loam | 2.22 | 31.0 | 20.3 | 7.4 |
| McClellan loam | 1.13 | 21.5 | 12.0 | 8.1 |
| San Joaquin loam | 2.16 | 19.2 | 10.5 | 5.8 |
| Hanford loam | 1.58 | 15.0 | 8.7 | 6.8 |
| Hesperia sandy loam | 0.29 | 15.6 | 6.9 | 7.5 |
| Mohave sandy loam | 0.64 | 16.0 | 7.6 | 8.4 |

Table II. Common Names of Herbicides

| Herbicide | Common Name |
|--|-------------|
| 2-Chloro-4,6-bis(diethylamino)- <i>s</i> -triazine | Chlorazine |
| 2-Chloro-4-diethylamino-6-ethylamino- <i>s</i> -triazine | Trietazine |
| 2-Chloro-4-diethylamino-6-isopropylamino- <i>s</i> -triazine | Ipazine |
| 2-Methoxy-4,6-bis(ethylamino)- <i>s</i> -triazine | Simetone |
| 2-Chloro-4-isopropylamino-6- <i>n</i> -propylamino- <i>s</i> -triazine | 30451 |
| 2-Chloro-4,6-bis(isopropylamino)- <i>s</i> -triazine | Propazine |
| 2-Chloro-4,6-bis(ethylamino)- <i>s</i> -triazine | Simazine |
| 2-Chloro-4-ethylamino-6-isopropylamino- <i>s</i> -triazine | Atrazine |
| 2-Chloro-4-isopropylamino-6-methylamino- <i>s</i> -triazine | Norazine |
| 3-(<i>p</i> -Chlorophenyl)-1,1-dimethylurea | Diuron |

Table III. Initial Toxicities of Nine *s*-Triazines in Five Soils as Shown by ED₅₀ Values for Oats (Crop 1)

| Experiment and Herbicide | Sacramento Clay | Madera Silty Clay | Yolo Silt Loam | Yolo Sandy Clay Loam | Hesperia Sandy Loam |
|-----------------------------|-----------------|-------------------|----------------|----------------------|---------------------|
| Experiment I | | | | | |
| Parts per Million by Weight | | | | | |
| Chlorazine | 130 | 26 | 45 | 28 | 6.5 |
| Trietazine | 4.9 | 0.95 | 2.3 | 0.91 | 0.25 |
| Ipazine | 4.5 | 1.0 | 2.6 | 1.1 | 0.34 |
| Simetone | 7.6 | 0.38 | 1.3 | 0.49 | 0.082 |
| 30451 | 2.3 | 0.38 | 1.2 | 0.42 | 0.10 |
| Propazine | 0.67 | 0.16 | 0.32 | 0.15 | 0.044 |
| Simazine | 0.65 | 0.13 | 0.35 | 0.095 | 0.028 |
| Experiment II | | | | | |
| Simazine | 1.3 | 0.19 | 0.47 | 0.22 | 0.042 |
| Atrazine | 1.2 | 0.22 | 0.54 | 0.23 | 0.053 |
| Norazine | 1.3 | 0.24 | 0.63 | 0.28 | 0.069 |

Table IV. Observed and Predicted ED₅₀ Values of Simazine in 16 Soils with Oats as Test Plant

| Soil Type | Observed ED ₅₀ Values, P.P.M. by Wt. | Organic matter | Predicted ED ₅₀ Values (P.P.M. by Wt.) | |
|------------------------|---|----------------|--|--|
| | | | Using Organic matter, clay, and cation exchange capacity | Using Organic matter, clay, cation exchange capacity, and pH |
| Sacramento clay | 0.65 | 0.44 | 0.59 | 0.61 |
| Stockton adobe clay | 0.49 | 0.35 | 0.39 | 0.41 |
| Sacramento silty clay | 0.14 | 0.15 | 0.04 | 0.03 |
| Madera silty clay | 0.12 | 0.28 | 0.30 | 0.30 |
| Yolo silty clay loam | 0.26 | 0.22 | 0.32 | 0.29 |
| Yolo silt loam | 0.43 | 0.22 | 0.32 | 0.31 |
| Yolo sandy clay loam | 0.14 | 0.13 | 0.15 | 0.17 |
| Aiken clay loam | 0.83 | 0.90 | 0.82 | 0.80 |
| Fresno silty clay loam | 0.12 | 0.31 | 0.28 | 0.29 |
| McClellan clay loam | 0.09 | 0.13 | 0.13 | 0.09 |
| Merced clay loam | 0.14 | 0.20 | 0.22 | 0.21 |
| McClellan loam | 0.06 | 0.10 | 0.09 | 0.07 |
| San Joaquin loam | 0.20 | 0.20 | 0.15 | 0.21 |
| Hanford loam | 0.20 | 0.14 | 0.12 | 0.15 |
| Hesperia sandy loam | 0.03 | 0.03 | -0.005 | 0.007 |
| Mohave sandy loam | 0.04 | 0.06 | 0.03 | 0.003 |

Table V. Simple Correlation Coefficients among Four Soil Properties and ED_{50} Values for Simazine on Seedling Oats

| Soil Property | Simazine ED_{50} | Organic Matter | Total Clay | Cation Exchange Capacity |
|--------------------------|---------------------|---------------------|--------------------|--------------------------|
| Organic matter | 0.880 ^a | ... | ... | ... |
| Total clay | 0.415 | 0.367 | ... | ... |
| Cation exchange capacity | 0.618 ^b | 0.524 ^b | 0.938 ^a | ... |
| pH | -0.722 ^a | -0.702 ^a | -0.274 | -0.413 |

^a Significance at the 1% level. ^b Significance at the 5% level.

Table VII. Lowest Concentration of Nine s-Triazines Which Reduced Yield of Oats for Crop 8 (Approximately 15 Months after Treatment)

| Experiment and Herbicide | Sacramento Clay | Madera Silty Clay | Yolo Silt Loam | Yolo Sandy Clay Loam | Hesperia Sandy Loam |
|-----------------------------|-----------------|-------------------|-----------------|----------------------|---------------------|
| Parts per Million by Weight | | | | | |
| Experiment I | | | | | |
| Chlorazine | 64 ^a | 8 ^a | 16 ^a | 8 ^a | 8 |
| Trietazine | 16 | 8 | 8 | 4 | 4 |
| Ipazine | 32 | 8 | 8 | 4 | 4 |
| Simetone | 8 ^a | 2 | 2 | 2 | 1 |
| 30451 | 32 | 8 | 8 | 8 | 8 |
| Propazine | 16 | 8 | 4 | 2 | 4 |
| Simazine | 8 | 4 | 2 | 2 | 2 |
| Experiment II | | | | | |
| Simazine | 8 | 4 | 4 | 2 | 2 |
| Atrazine | 16 | 8 | 4 | 4 | 4 |
| Norazine | 16 | 8 | 4 | 4 | 4 |

^a Lowest concentration maintained during crop 8, and this concentration reduced fresh weights.

of toxicity of each herbicide was needed for each soil. The fresh weight data were used for establishing ED_{50} values (17). The ED_{50} was similar to the GR_{50} of Upchurch (16). For each concentration series within a replication, the fresh weight as per cent of the control was plotted against the logarithm of the herbicide concentration. A free-hand curve was constructed to fit the points. The antilogarithm of the point on the concentration axis which corresponded with the point of intersection of the curve and the 50% yield level was an estimate of the ED_{50} in parts per million by weight.

The relationships among simazine phytotoxicity and four soil properties were studied in detail. A concentration series for simazine in each of 16 soils was prepared. Culture of the plants was identical with that in the previous experiments. These cultures were cropped only once. ED_{50} values for simazine in each of the soils were used in relating simazine phytotoxicity to the four soil properties. Mean values of the various measurements were subjected to simple correlation and multiple regression analyses (15).

Results and Discussion

The initial toxicities of nine s-triazines in five soils are shown by ED_{50} values for the first oat crop (Table III). The chemicals were most toxic to oats in Hesperia sandy loam and least toxic in

Sacramento clay. The phytotoxicities of the chemicals in the other three soils were intermediate between these two extremes. That more simazine is required in clay and organic soils than in sandy soils to produce the same degree of injury has been demonstrated (7, 2, 4, 12). Lower dosages of the herbicides were required in Madera silty clay than in Yolo silt loam to reduce the fresh weight by 50%, although the organic matter per cent, clay per cent, and cation exchange capacity were greater in the Madera than in the Yolo soil. ED_{50} values in the Madera soil were very close to those in Yolo sandy clay loam, a soil which contained about half as much organic matter and clay as Madera silty clay. Also, the cation exchange capacity in Yolo sandy clay loam was approximately half that of the Madera soil. Such variations in herbicide phytotoxicity among soils are observed often.

In these two experiments, the chloro derivatives with a single methyl, ethyl, or isopropyl substituent on each amino group—simazine, propazine, atrazine, and norazine—were more toxic to oats growing in treated soil than chloro derivatives with a single substituent on one amino group and two substituents on the other—ipazine and trietazine. Chlorazine, with two substituents on each amino group, was least phytotoxic. Simetone, a methoxy derivative, was less phytotoxic than the corresponding chloro derivative, simazine. Generally, ipazine

Table VI. Per Cent (r^2 or R^2) of Variation in Simazine ED_{50} Values Which Was Predicted from Soil Properties Singly and in Combination

| Soil Properties | r^2 or R^2 |
|--|----------------|
| Organic matter | 77 |
| Total clay | 17 |
| Cation exchange capacity | 38 |
| pH | 52 |
| Organic matter plus total clay | 78 |
| Organic matter plus cation exchange capacity | 81 |
| Organic matter plus pH | 80 |
| Organic matter plus cation exchange capacity plus total clay | 86 |
| Organic matter plus cation exchange capacity plus pH | 83 |
| Organic matter plus cation exchange capacity plus pH plus total clay | 87 |

and trietazine are more selective as pre-emergence herbicides than simazine and propazine (6). This selectivity might be attributed partially to greater adsorption of ipazine and trietazine compared to that of simazine and propazine, a condition which would promote retention in the soil-surface layers and restrict downward movement of the herbicide. In addition, however, inherent differences in toxicity also exist among these compounds (9).

Simazine ED_{50} values obtained experimentally for 16 soils are shown in Table IV. The observed ED_{50} values ranged from 0.03 p.p.m. by weight for Hesperia sandy loam to 0.83 p.p.m. by weight for Aiken clay loam. Therefore, approximately 28 times as much simazine was required in the Aiken as in the Hesperia soil to reduce growth of oats by 50%. All other ED_{50} values were between these two.

The simazine ED_{50} was positively correlated with organic matter per cent and cation exchange capacity and negatively correlated with pH (Table V). The highest correlation involving simazine ED_{50} values was measured between soil organic matter and ED_{50} .

Highly significant correlations were found between clay per cent and cation exchange capacity and between organic matter per cent and pH; a significant correlation was found between organic matter per cent and cation exchange capacity (Table V). Such relationships among soil properties are frequently observed; therefore, caution must be used in interpreting the results as causative relations. In addition to interrelations of soil properties which were determined, other soil properties which were not considered could influence herbicidal activity. Types of clay minerals have been implicated for phenylurea herbicides (3, 7).

Multiple regression analyses indicated that the simazine ED_{50} value was more closely related to soil organic matter

than to the other three soil variables. The same conclusion was drawn from the simple correlation coefficients, but the results of the multiple regression were much more convincing. In the multiple regression, however, the simazine ED_{50} was not significantly related to pH, whereas in the simple correlations, this relation was highly significant. This apparent disagreement can probably be explained by the highly significant simple correlation between organic matter and pH (Table V).

The amino groups of the *s*-triazines may impart weak basic properties to the molecules. Simazine was removed from solution by a cationic exchange resin and not by an anionic resin, thus indicating that the molecule was electrically positive (14). Hence, simazine may take part in ion-exchange reactions. However, the correlation between the ED_{50} value and cation exchange capacity was considerably poorer than the correlation with organic matter. Hence, a sizable portion of simazine inactivated initially in soils may be bound by forces other than those involved in ion exchange. The high correlation of the ED_{50} with organic matter suggests some specific involvement of organic matter, perhaps through a mechanism that is inactive with clays. This problem needs further study.

The relative values of the four soil properties and several combinations of properties for prediction purposes were calculated (Table VI). Organic matter was the best single predictor of the four, with 77% of the variation in the simazine ED_{50} predictable by organic matter. By using three properties in addition to organic matter, the per cent of variation in the simazine ED_{50} value which was accounted for by variations in soil properties was increased only from 77 to 87%. Of several soil properties, organic matter was also the best for predicting response of plants to diuron in soils (16).

Prediction equations were calculated for per cent organic matter, for a combination of per cent organic matter, per cent clay, and cation exchange capacity, and for a combination of the four soil properties. ED_{50} values calculated with these equations are shown in the last three columns of Table IV. A comparison of the predicted values shows the poor precision with which the ED_{50} values were predicted with the three equations. In most soils, one or two of the predicted values were fairly good. All predicted values for Madera silty clay and Fresno silty clay loam were more than twice the value of the observed ED_{50} . One predicted value for Hesperia sandy loam was negative. More research must be performed before an adequate method can be perfected for predicting the amount of soil-applied chemical required to control weeds.

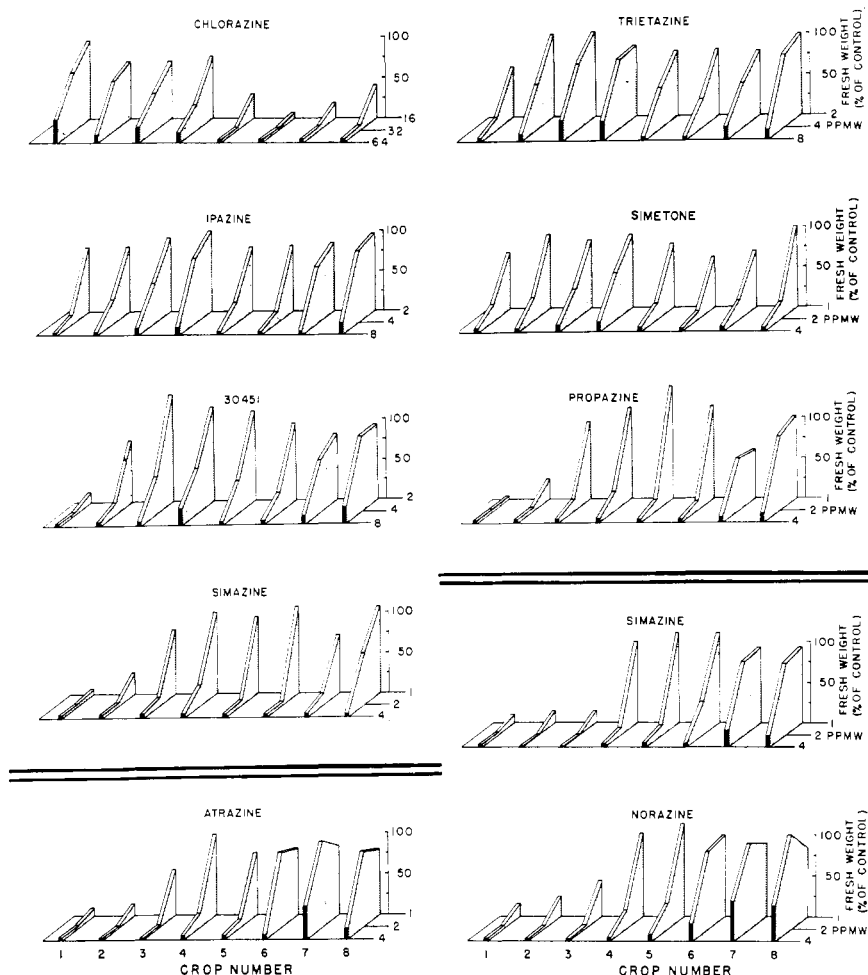


Figure 1. Comparative residual activities of nine *s*-triazines as shown by fresh weights (per cent of control) of eight successive crops of oats from cultures of Yolo silt loam at three concentrations of each herbicide

The seven graphs above the double line represent one experiment; the three graphs below represent another. Simazine was the standard in both experiments

After eight crops (approximately 15 months after treatment), herbicidal activity varied widely among chemicals and soils (Table VII). The data in Figure 1 provide a more detailed comparison of the residual activities of the herbicides in Yolo silt loam. Fresh weights fluctuated from crop to crop. This fluctuation is illustrated by the 1 p.p.m. by weight concentration of simetone. This response appeared to be related to environmental conditions in the greenhouse. During damp, cloudy weather which favored a slow rate of transpiration, oat plants growing in cultures containing low concentrations of herbicides produced more growth relative to the control than plants growing in the same cultures during dry, sunny weather. Accumulation of carbon¹⁴-labeled simazine or metabolites in leaves of oat and cotton seedlings growing in solutions containing the labeled herbicide was related to the rate of transpiration (13).

Differences in the fresh weights of oats among croppings of chlorazine cultures (Figure 1) probably reflect some response

to environmental changes during the test period. However, an alternative explanation can be offered for the marked toxicity increase. If one ethyl group was lost from one amino group, trietazine would be formed; whereas, if one ethyl group was lost from both amino substituents, simazine would be the product. Trietazine and simazine are much more phytotoxic in soil applications than chlorazine. Conversion of only a small amount of chlorazine to trietazine or simazine would explain the increased toxicity; however, this conversion has not been demonstrated experimentally.

Simazine was more toxic initially in all of the soils than simetone (Table III). By crop 8, the two chemicals were about equal in toxicity in Yolo sandy clay loam and Yolo silt loam, and in the other three soils simetone was more toxic than simazine (Table VII). Hence, the rate of inactivation of simetone was probably slower than that of any of the other chemicals. The containers in these experiments did not drain. This experimental condition might influence

the rate of herbicide inactivation; it would tend to minimize differences among soil types caused by the effects of moisture and aeration on microbial activity. Loss of chemicals by leaching was eliminated by the experimental conditions. Since the solubilities of these herbicides in water vary from about 5 p.p.m. for simazine to about 3200 p.p.m. for simetone, the relative residual activities would probably be quite different for field applications where leaching by rainfall or irrigation water occurs. Differential volatilities would probably also influence the pattern of residual activity in the field.

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RADIOLABELED INSECTICIDES

Synthesis of *N*-Methylcarbamates via Methyl Isocyanate-C¹⁴ and Chromatographic Purification

JATAPROLU G. KRISHNA,
H. WYMAN DOROUGH, and
JOHN E. CASIDA

Department of Entomology,
University of Wisconsin,
Madison, Wis.

The increasing interest in *N*-methylcarbamates as insecticides prompted their radiolabeling. A convenient radiosynthesis procedure is reported for Sevin, Hercules 5727, Bayer 39007, Bayer 37344, and Zectran. Acetyl-C¹⁴ chloride and sodium azide were reacted to yield methyl isocyanate-C¹⁴ which was then reacted with the appropriate phenol. A two-compartment reaction tube with a break-seal was utilized. Yields on a 0.5-mmole scale were routinely 40 to 70%. Chromatographic procedures for isolating the *N*-methylcarbamates from their reaction mixtures are reported.

SEVERAL *N*-methylcarbamates possess desirable characteristics for use as insecticides. Sevin, 1-naphthyl-*N*-methylcarbamate, has been widely used. Others of particular current interest include the *N*-methylcarbamates of *m*-isopropylphenol (Hercules 5727, Union Carbide 10854), *o*-isopropoxyphenol (Bayer 39007), 4-methylthio-3,5-xyleneol (Bayer 37344), and 4-dimethylamino-3,5-xyleneol (Zectran). Intensive synthesis and screening programs now underway on this type of compound may yield others with desirable properties for development as insecticides.

Radiosynthesis of the carbamate insecticides has been restricted to Sevin-C¹⁴ prepared from 1-C¹⁴-naphthol (5, 73). Labeling of the methyl or carbonyl group appeared desirable based on the following considerations: The synthetic procedure might be applicable for radiolabeling a variety of *N*-methylcarbamates; the *N*-methylcarbamoyl group is the toxophoric group based on structure-activity studies (8, 75) and the finding

that cholinesterase may be carbamoylated by this type of compound (2, 76, 77); *N*-methylcarbamates may hydrolyze to yield methyl isocyanate (7, 4) as an intermediate before formation of methylamine and carbon dioxide and the biological fate of this intermediate has not been investigated; and the problem of cleanup for C¹⁴-counting is greatly facilitated with these labeling sites as methylamine-C¹⁴ and carbon dioxide-C¹⁴ can be readily released and trapped for counting.

A simple and efficient procedure for C¹⁴-labeling of *N*-methylcarbamate insecticides is reported. The chromogenic reagents for phenols and chromatographic systems used in developing this procedure are also considered.

Materials and Methods

Chemicals. The acetyl-C¹⁴ chloride (Volk Radiochemical Co., Skokie, Ill.) used was labeled in the 1-position and varied in specific activity from 1 to 5 mc.

per mmole. Use of the 2-C¹⁴ compound would yield the label in the methyl group of the *N*-methylcarbamate. The phenols (Table I) were obtained from manufacturers of the *N*-methylcarbamates, or by thermal decomposition or saponification of the *N*-methylcarbamates. The purified phenols were dried over phosphorus pentoxide before use. The benzene utilized was thiophene-free and dried over anhydrous sodium sulfate, and the triethylamine was the technical material (Distillation Products, Eastman Kodak Co.). Sodium azide was activated by triturating with hydrazine hydrate and then precipitating from an aqueous solution with cold acetone and drying the product according to a modified procedure described by Smith (74). It was held for up to 20 days before use, and thereafter activity was regenerated at any time by dissolving in hot water and precipitating with cold acetone and drying.

Samples of *N*-methylcarbamates were obtained from the following sources: