formed and a less severe effect is measured. On the other hand, when a series of compounds is compared, the less active members will not demonstrate any activity, because of this dilution. Thus, a concentration range of 5 and 8 pounds per acre was chosen which was felt to demonstrate optimally both the more and the less active members of the series.

The carbamates tested are more phytotoxic than the corresponding imidodicarboxylates. Thus, out of 10 comparisons, the carbamate was of equal or greater activity than the imidodicarboxylate in seven instances irrespective of the substituent on the benzene ring. A similar comparison between the two types with respect to activity due to para or meta substitution shows that seven out of eight compounds were more toxic with substitution in the latter position, the sole exception being the 4-iodophenyl imidodicarboxylate.

This evidence also leads to the broader conclusion that an imino group is not requisite for activity in compounds of these types because substitution of the hydrogen by the isopropyl carboxylate group or by similar groups does not destroy, but only alters, the toxicity.

Literature Cited

(1) Blouch, R., Fults, J., *Research Rept. 13th Western Weed Control Conf.* **1952,** 148.
(2) Ennis, W., *Botan. Gaz.* **109,** 473 (1948).
(3) Fuelleman, R. F., *Research Rept. 6th Annual North Central Weed Control Conf.* **1949,** 112.
(4) Moore, D. H., George, D. K., Martin, V. O., Garman, J. A., J. AGR. FOOD CHEM. **1,** 1155 (1953).
(5) Roland, M., *Vaxtodling* **4,** 49–58 (1949).
(6) Shaw, W. C., Swanson, C. R., *Weeds* **1,** 352 (1952).
(7) Stefanye, D., Howard, W. L., Beidler, W., *J. Am. Chem. Soc.* **77,** 3663 (1955).
(8) Templeman, W., Sexton, W., *Proc. Roy. Soc. (London)* **B133,** 480 (1946).

Received for review April 19, 1956. Resubmitted December 31, 1958. Accepted March 9, 1959.

HERBICIDE RESIDUES

Dalapon Residue in Bird's-foot Trefoil

MARVIN M. SCHREIBER

Crops Protection Research Branch, Crops Research Division, U. S. Department of Agriculture, and Department of Agronomy, Cornell University, Ithaca, N. Y.

A detectable amount of dalapon due to a residue in a forage crop may appear in a food product. The effects of rate and time of application of dalapon to bird's-foot trefoil were determined. Residues were found in all samples, the amount depending upon initial rate, weather conditions, growing season, and stage of growth at the time of application. Spring applications up to 5.0 pounds per acre effectively controlled grass and produced residue levels below 25 p.p.m. when the time interval between treatment and harvest exceeded 100 days. Applications resulting in extremely low dalapon residues closely correspond to the present and proposed use of dalapon in bird's-foot trefoil seed fields and seedling establishments. These residues may be undetectable in animal products.

DALAPON, 2,2-dichloropropionic acid, an effective grass herbicide (*5, 12–14*), is readily absorbed by the foliage of plants (*1, 2, 10*) as well as by the roots of forage grasses and other plant species (*2, 9, 11*).

The presence of grass in legume seed fields, particularly in bird's-foot trefoil seed fields, has a marked effect on the potential seed yield (*7*)—generally, the more grass, the lower the yield of seed.

Extensive tests show that grass in bird's-foot trefoil stands can be controlled by the proper use of dalapon. If there is any seasonal application advantage, it is spring, primarily on the basis of less broad-leaved weed encroachment.

Dairy animals fed forages containing dalapon residue may produce milk containing measurable quantities of dalapon. Bird's-foot trefoil, even though grown for seed, may be used as a feed crop once the seed has been harvested. Seed production may fail and the forage be directly cut for hay or left for pasture.

This paper summarizes 3 years' data, which are applicable to the use of dalapon in bird's-foot trefoil seed fields, in pasture renovation for grass suppression or elimination (*9, 13*), and in legume seedling establishment (*5, 6, 8*). All reference to dalapon is on the basis of acid equivalent.

Materials and Methods

Experiment 1, Location 1. A 12-year-old stand of Empire bird's-foot trefoil at Lodi, N. Y., a variety which constitutes a high percentage of the crop grown for seed and forage in New York, was treated with 5, 10, and 20 pounds of dalapon applied in 30 gallons of water per acre. Treatments were applied in replicated 6 × 50 foot plots using a tractor-mounted sprayer modified especially for plot spraying, calibrated to ensure uniform coverage. Applications were made April 23, 1955, when the bird's-foot trefoil plants were 1 to 2 inches tall. Forage samples for residue analyses were taken from the first cutting of hay on July 18, 1955. Random samples were taken from each treated plot and untreated strips, immediately oven-dried at 70° C. for 14 hours, packed in plastic bags, and sent to The Dow Chemical Co. for dalapon residue analyses. Because of the reduced forage in all experiments on the plots receiving the high rates of dalapon (15 and 20 pounds per acre), the forage from each replication for these rates was pooled for one analysis.

Experiment 1, Location 2. A 6-year-old stand of Empire bird's-foot trefoil located at Ithaca, N. Y., was treated with 10 pounds of dalapon applied in 30 gallons of water per acre. Replicated applications were made May 17, 1955, when the plants were 4 inches tall.

Table I. Dalapon Residue in Empire Bird's-foot Trefoil from Fall and Spring Applications, Ithaca, N. Y.

Date of Treatment	Dalapon, Lb./Acre	Total Days between Last Treatment and Harvest	Dalapon[a] Residue, P.P.M.
Oct. 3, 1955 (dormant)	10	255	8 8
	15	255	10 20 36 1310
May 24, 1956	10	22	1250
	15	22	1750 660
Oct. 3, 1955, and May 24, 1956	5 + 5	22	685 575
	10 + 10	22	1000

[a] All data corrected for blanks.

Table II. Effects of Rate of Dalapon Applied in Spring and Fall (Albany County, N. Y.)

(Harvested August 1, 1957)

Dalapon, Lb./Acre	Corrected Dalapon Residue, P.P.M.[a] Treated 10/8/56, 3 inches tall, 300 days between treatment and harvest	Treated 5/17/57, 4.5 inches tall, 77 days between treatment and harvest
1.5	11.8	9.5
3.0	4.5	23.7
4.5	2.7	33.3
6.0	8.8	82.0
7.5	7.1	37.5
9.0	13.3	59.1

[a] All data corrected for blanks.

Residue samples were taken July 27, 1955, and handled in the same manner as at Location 1.

Experiment 2. To compare the residue values from fall, spring, and fall plus spring treatments of dalapon, a second experiment was initiated in Ithaca, N. Y., on a 6-year-old stand of Empire bird's-foot trefoil (Table I). All treatments were applied with the equipment used in Experiment 1, Location 1. The bird's-foot trefoil plants at the time of spring application were approximately 10 inches tall. All treated plots and untreated strips were harvested for hay on June 14, 1956; samples were taken for residue analysis and handled in the manner described.

Experiment 3. Grass control studies on seed yield conducted simultaneously with the residue studies showed definite advantages for the use of low rates of dalapon. High rates of application led to serious broad-leaved weed problems arising when the grasses were removed. Consequently, two experiments were established to determine the effect of low rate and time of application on grass control on bird's-foot trefoil seed production. Samples for residue studies were taken from these experiments as well.

Dalapon, Lb./Acre	Corrected Dalapon Residue,[a] P.P.M.
5	48 33 51
10	132 139
20	239

[a] Blank value of 7 p.p.m. used to correct data.

A field of Empire bird's-foot trefoil for seed production located in Albany County, N. Y., was used to determine crop residues resulting from low rates of dalapon applied in either the fall or spring. The rates of dalapon ranged from 0 to 9 pounds per acre with increments of 1.5 pounds. Fall applications were made October 8, 1956, to 3-inch-tall bird's-foot trefoil, and spring applications were made May 17, 1957, when the plants had approximately 4.5 inches of new spring growth. Ten gallons of water were used at the 1.5-pound rate, with an increase of 10 gallons for each increase in concentration up to 60 gallons at the 9-pound rate. The experimental plots, which were harvested for seed August 1, 1957, were sampled at that time for residue analysis. Twenty-five pounds of forage from each plot were air-dried for from 48 to 72 hours. The samples were then ground, packed in plastic bags, and sent to the Cornell Residue Laboratory for analysis (Table II).

Experiment 4. A fourth experiment was set up at the Cornell Agronomy Department Farm, Ithaca, N. Y., to determine the effect of stage of growth and rate of dalapon application on dalapon residue in bird's-foot trefoil. A 3-year-old stand of Viking bird's-foot trefoil was treated with two rates of dalapon: 2.5 and 5 pounds per acre, in 30 gallons of water per acre at three different stages of growth: September 3, 1956, when the plants had 5 to 6 inches of recovery growth following second cutting; April 20, 1957, when the bird's-foot trefoil was still dormant; and on May 7, 1957, when the plants had 4 to 5 inches of new spring growth. The experimental plots were harvested for seed August 13, 1957, and residue samples were collected and handled as before (Table III).

Table III. Effects of Stages and Rates of Application on Dalapon Residue in Viking Bird's-foot Trefoil (Ithaca, N. Y.)

(Harvested August 13, 1957)

Date of Application Stage of Growth	Days between Treatment and Harvest	Dalapon, Lb./Acre	Corrected Dalapon Residue, P.P.M.[a]
Sept. 3, 1956 5–6 inches tall	347	2.5	0.76 0.0
		5.0	1.59 0.35
April 20, 1957, dormant	116	2.5	0.42 7.13
		5.0	7.57 13.12
May 7, 1957, 4–5 inches tall	98	2.5	6.21 7.42
		5.0	14.08 14.84

[a] All data corrected for blanks.

Analysis Procedure. The analyses were made at The Dow Chemical Co. laboratory and the Cornell Pesticide Residue laboratory by the Getzendaner and Smith method (*3*).

Results and Discussion

Experiment 1, Location 1. There was a trend to higher residues from higher rates of treatment; however, the

relative magnitude of change was somewhat variable. Differential rate of growth may partially account for the discrepancy observed, as residues are reported in parts per million of dry weight. High rates of treatment have consistently resulted in slight stunting of plants for a short period, after which plants appeared to recover fully.

Crops grown on fertile soil well supplied with moisture might be expected to have a lower residue at the end of the growing season or at harvest time than those grown on poor land or without soil moisture sufficient for maximum growth. The 1955 growing season was relatively dry; however, this would not explain the differences between two rates in the same year. Some injury to the bird's-foot trefoil did occur from the 10-pound rate, at least a partial stunting which reduced the growth and would partially account for the higher parts per million based on dry weight at harvest time.

The dalapon at 20 pounds per acre caused almost immediate foliage burn, which may have resulted in absorption of a smaller proportion of dalapon. The dalapon remaining on the surface of the foliage was exposed to greater loss due to weather effects, particularly rain. Over 0.5 inch of rain fell within 2 days after applications were made.

Considering rates at the same time of application and at the same harvest date, the residues appear to be proportional to the rate.

Experiment 1, Location 2. A 10-pound application of dalapon on Empire bird's-foot trefoil from the second location resulted in a residue of 295 and 302 p.p.m. of dalapon for two replications. At this location, the soil was extremely shallow, and in the extremely dry season (1955) a greater residue occurred than at Location 1. The poorer growth at Location 2 probably resulted in a greater residue in terms of parts per million at the same rate of application. The application date was 24 days later than at Location 1; although the harvesting date was 9 days later, there was less total time for growth to dilute the residue, regardless of fertility and moisture.

Experiment 2. Dalapon residues from fall and spring applications at various rates on Empire bird's-foot trefoil are presented in Table I. The differences may be explained on the basis of growth, weather, and a reduced dalapon absorption into dormant bird's-foot trefoil.

The extremely high residues from the spring applications show definitely the significance of the time interval between treatment and harvest. Twenty-two days is an extremely short time for dilution due to growth, especially at rates of 10, 15, and 20 pounds per acre. The stage of growth at the time the treatments were applied is also an important factor. It is likely that where the fall application was used, little dalapon went directly onto the bird's-foot trefoil foliage. Thus, the fall-applied dalapon which contributed to residue in the spring may have been absorbed from the soil by the roots of the plant (*4*). With the spring applications, however, a greater percentage of the dalapon was probably absorbed by the foliage, and in 22 days little extra growth had occurred to dilute the residue. Actually, such a treatment at a high rate in such a short time would probably never be used under field conditions.

Because of the residue levels obtained, repeated treatments could be as effective for control of grasses and offer less dalapon residue in the year of harvest. This would suggest the advisability of lower application rates at each time. The data in Table I suggest that the 10-pound rate of dalapon applied in the fall contributed little, if anything, to the residue at time of harvest. Similarly, although 5 pounds was not applied in the fall of 1955, most of the residue from the 5-pound rate in fall plus spring was probably due to the spring application only.

Experiment 3. Relatively low residues were obtained from the fall applications, as expected from the previous years' results. The correlation coefficient between rates and residue was 0.558 from fall applications and is insignificant. On the basis of grass control and seed yields, 5 pounds or less would bring about the necessary control. The spring applications had the same range of concentrations as the fall applications; and the residue levels obtained tended to vary according to rates used. Grass control was again sufficient at the 4.5-pound rate from the spring application. The correlation coefficient between rates and residue was 0.795 from the spring application and is significant.

Experiment 4. The data on the effect of stages and rate of application on dalapon residue in Viking bird's-foot trefoil are presented in Table III. None of the rates at any dates of application resulted in residues that exceeded 15 p.p.m. Extreme variability was found between replicate samples at each rate of application in the fall and early spring treatments. Although no reliability can be placed on absolute residue values, particularly at the two early dates of application, the data strongly suggest extremely low residue values from low application rates in the fall and spring. Relatively lower residue values from low applications of dalapon in the spring resulted with Viking (Table III) than with Empire variety of bird's-foot trefoil (Table II). This could be attributed in part to the earlier starting habit of growth of the Viking variety.

No injury due to herbicides was noticeable. The 2.5- and 5.0-pound rates per acre were effective for the control of grasses and resulted in extremely low residues of dalapon.

The data presented in these tables, although they do not give a direct measure of dilution, demonstrate that dilution due to growth can overshadow the effect of rate. The higher rates may cause some stunting, which again has a marked effect on total growth during the season. As no analyses were made in any experiments on residue and yield immediately after application and later, no data are available for direct comparison of the dilution effect. Plans are under way to evaluate the question of dilution, due to growth, of applications made at various dates and sampling periods following application.

Acknowledgment

The author acknowledges the cooperation of The Dow Chemical Co. and the Pesticide Residue Laboratory of Cornell University under the direction of D. J. Lisk in determining dalapon in bird's-foot trefoil, and of Richard M. Shibles in collecting and making available samples from his research plots on grass control in bird's-foot trefoil.

Literature Cited

(1) Barrons, K. C., McQueen, G. R., *Down to Earth* **10,** No. 3, 16 (1954).
(2) Dow Chemical Co., Midland, Mich., Dalapon Bull. **2** (1953).
(3) Getzendaner, M. E., Smith, G. E., Pesticide Residue Conference, Washington, D. C., January 1957.
(4) Holstun, J. T., Jr., Loomis, W. E., *Weeds* **4** (3), 205–17 (1956).
(5) Kerkin, A. J., Peters, R. A., *Proc. Northeast. Weed Control Conf.* **11,** 128–38 (1957).
(6) Kerr, H. D., Klingman, D. L., *Research Rept. North Central Weed Control Conf.* **12,** 119 (1955).
(7) MacDonald, H. A., Winch, J. E., Dept. of Agronomy, Cornell University, Ithaca, N. Y., Mimeo. **57-18** (February 1957).
(8) Scholl, J. M., Staniforth, D. W., *Agron. J.* **49,** No. 8, 432–5 (1957).
(9) Southwick, L., *Proc. Northeast. Weed Control Conf.* **8,** 251–6 (1954).
(10) Swezey, A. W., *Proc. Calif. Weed Conf.* **6,** 15–20 (1954).
(11) Thiegs, B. J., *Down to Earth* **11,** No. 2, 2–4 (1955).
(12) Vengris, J., *Proc. Northeast. Weed Control. Conf.* **9,** 301–3 (1955).
(13) *Ibid.*, **10,** 54–60 (1956).
(14) *Ibid.*, **11,** 143–9 (1957).

Received for review June 19, 1958. Accepted February 25, 1959. Cooperative investigations between the Department of Agronomy, New York State College of Agriculture, Ithaca, N. Y., and the Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture as Agronomy Paper No. 443.