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Nonbiological Degradation of the Herbicide Metribuzin in Manitoba Soils

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The herbicide metribuzin (4-amino-6-t-butyl-3-methylthio-1,2,4-triazin-5(4H)-one) is effective in the control of broad leafed and grassy weeds encountered in the growing of potatoes (ZIMDAHL, 1971; KOLBE and ZIMMER, 1972), soybeans (COLBE and SCHRADER, 1973) and tomatoes (FORTINO and SPLITTSTOESSER, 1974). In Manitoba, experimental trials have shown that metribuzin has the tendency, under some circumstances, to persist in the soil causing injury to sensitive subsequent crops[2,3].

Degradative loss of herbicides in soil can take place by chemical or biological means. HYZAK and ZIMDAHL (1972) have suggested that non-biological degradation of metribuzin in soil may be the most important mode of breakdown following application to San Luis sandy loam. Later work by HYZAK and ZIMDAHL (1974) suggests that degradation of metribuzin in soil is an approximately first order phenomenon at 5°, 20°, and 35°C yielding a linear plot of log (residual metribuzin) vs time. Their results show no induction period following application of metribuzin.

Several variables have been suggested to influence metribuzin persistence in Canadian prairie soils; e.g., temperature, organic matter content, and adsorption properties of soils. HYZAK and ZIMDAHL (1974) show that degradation of metribuzin in soil increases with temperature, and increased degradation in the field in Almasippi very fine sandy loam has been shown by WEBSTER and REIMER (1976a) to correspond to temperature increases in the soil. The latter two variables, however, are characteristics of specific soil types, and attention was turned in this study to an evaluation of the influence of four Manitoba soils on non-biological degradation of metribuzin.

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[2] STOBBE, E.H. 1973. Department of Plant Science, University of Manitoba, private communication.

[3] BOWDEN, B.A. 1973. Chemagro Ltd., Winnipeg, Manitoba, private communication.

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MATERIALS AND METHODS

Soil Preparation

Samples of four Manitoba soils (Table 1), Newdale clay loam, Stockton sandy loam, Almasippi very fine sandy loam, and Red River clay (approx. 37g) in 125 ml erlenmeyer flasks stoppered with non-absorbent cotton plugs were sterilized at 124° and 15 psi (1.02 atm) (wet cycle) for 20 min on three successive days and dried at 110° for 24 hr. The success of the sterilization procedure was established by inoculating Tryptic Soy Agar plates with sterilized and unsterilized soil and incubating them for 48 hr at room temperature.

Twelve samples of each soil sterilized by the above procedure, were fortified at 1.8 and 18 ppm metribuzin; sufficient metribuzin dissolved in 1 ml sterilized distilled water was added to each sample and shaken gently by hand. Six sterilized samples of each soil were used as controls. All samples were maintained at 15° in the dark in a humidity controlled chamber. The moisture levels in the soils studied were approximately equivalent being a combination of hygroscopic moisture plus the water added during the fortifiation step. No water was added during the incubation step.

TABLE 1

Properties of Manitoba Soils Used in Degradation Study

Soil Type	pH at day 0	pH at day 53	Sand %	Silt %	Clay %	O.M.*
Red River clay	7.4	6.9	1.7	48.1	50.3	8.6
Newdale clay loam	6.3	6.4	40.6	29.0	30.5	4.7
Almasippi very fine sandy loam	6.9	6.6	83.4	4.8	11.8	3.5
Stockton sandy loam	6.6	6.8	82.2	7.4	10.5	2.4

*O.M. - organic matter

Extraction and Analysis

Samples of each treatment level for each soil type were extracted at 0, 7, 14, 25, 35, 53, and 64 days from the time of fortification using a soxhlet extraction procedure. The time zero samples were fortified at 0.5, 2, 10, and 25 ppm metribuzin and allowed to stand overnight in the dark at 15° prior to extraction.

The entire sample in each case was extracted with 300 ml 20% aqueous methanol for 4 - 8 hr using a soxhlet apparatus. The extract solution was filtered through glass fibre filter paper under reduced pressure following evaporation of the methanol on a rotary evaporator at 40°. The aqueous filtrate was made up to 60 ml with water and the herbicide compounds partitioned into chloroform. The chloroform layer was extracted with 0.1 N NaOH to remove metabolites (THORNTON and SCHUMANN, 1972) and washed with water, and the chloroform removed on a rotary evaporator at 40° using benzene (2 X 20 ml) to remove final traces of water. The residue in 1 ml benzene was analyzed by GLC; injection volume, 2 µl; recovery, 95%; retention time, 2.78 min.

All extracts were analyzed using a Tracor Microtek MT 200 gas chromatograph fitted with a Melpar flame photometric detector operating in the sulfur mode (324 nm filter). A 1.8 m X 4 mm i.d. pyrex silanized column was packed with 80-100 mesh Chromosorb W HP coated with 3% OV 225. Temperatures: inlet, 235°; column, 220°; detector, 220°. Flow rates: N_2 carrier, 100 ml/min; H_2, 150 ml/min; O_2, 25 ml/min; air, 20ml/min. Injection volume, 1 ul.

A standard curve showed log (response) vs log (ng metribuzin)^2 was linear over a range of 3-150 ng metribuzin. The minimum detectable level was 1 ng metribuzin. Time zero samples served as extraction efficiency checks, and standards of metribuzin were injected regularly to correct for daily variation in response.

The moisture level and the pH of each soil at each sampling time was determined.

RESULTS AND DISCUSSION

Under the sterile conditions used, metribuzin concentration decreased slowly in all soils. HYZAK and ZIMDAHL (1974) have described the first order nature of metribuzin degradation in San Luis sandy loam. The half order nature of metribuzin degradative loss at -37° in stored samples of Almasippi very fine sandy loam has been reported by WEBSTER and REIMER (1976). The character of degradation of metribuzin in sterilized soil is difficult to determine. Results of this investigation using

sterile soil were thus examined for consistency with half order and first order kinetics (Figures 1 and 2).

Given half order or first order kinetics, the rate constants, k, can be calculated (HAMAKER, 1972) and are tabulated with computed "half lives"[4] in Table 2.

If c = concentration of herbicide in ppm dry weight soil at time t, then the equations for "half lives" will be as follows:

Half order:

$$t_{\frac{1}{2}} = \frac{2(c_o^{\frac{1}{2}} - (\frac{c_o}{2})^{\frac{1}{2}})}{k}$$

First order:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

It can be seen from Table 2 that rate constants and half lives differ with soil type. It appears from Table 2 that first order kinetics best describe the process of degradation of metribuzin in sterile soil in that k approaches a constant for each soil type except Almasippi. Half lives are longer in each case for the higher treatment level, however, suggesting that in fact the true order of these reactions is somewhat less than first order with respect to herbicide concentration (cf. HAMAKER, 1972).

It is interesting to note the marked difference between the rate constants for Newdale soil and those for the other three soils. Newdale soil has neither the most organic matter nor the most clay, (Table 1) two important soil constituents which have been implicated in adsorption phenomena (e.g., HAMAKER and THOMPSON, 1972) which can influence degradation rate. Newdale soil pH was lowest for the four soils and did not change appreciably during the course of the study (Table 1). The pH change appears, however, to have little effect on the extent of degradation; although pH change over the degradation period considered was negative for Red River and Almasippi soils, it was positive for Stockton soil. Newdale soil rate constants have relatively low correlation factors (Table 2); however, it is quite clear that there is a difference in rate constant for Newdale soil. A comparison of these rate constants with those of HYZAK and ZIMDAHL (1974) for degradation of metribuzin due to all causes in soil at field capacity indicates (Figure 3) that much of this degradation may proceed under relatively dry conditions in sterilized soil. The exact reason for the difference encountered with Newdale soil has not yet been determined.

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[4]"Half life" here refers to time for 50% loss of herbicide and, unlike the half life, for a true first order reaction is dependent to some extent on concentration of herbicide (HAMAKER, 1972).

TABLE 2

Rate Constants and Half Lives at 15°

SOIL TYPE	TREATMENT LEVEL (ppm)	FIRST ORDER k = -m ($\times 10^{-3}$)	FIRST ORDER r value	FIRST ORDER $t_{1/2}$ (days)	HALF ORDER k = -2m ($\times 10^{-3}$)	HALF ORDER value	HALF ORDER $t_{1/2}$ (days)
Red River	1.8	6.84	0.97	101	8.32	0.97	94
	18.	6.44	0.99	108	25.46	0.99	98
Newdale	1.8	1.99	0.62	348	2.52	0.62	312
	18.	1.64	0.64	423	6.52	0.64	381
Almasippi	1.8	7.49	0.84	93	9.52	0.83	83
	18.	3.70	0.97	187	14.34	0.98	174
Stockton	1.8	6.05	0.81	115	7.72	0.81	102
	18.	5.59	0.95	124	22.36	0.94	111

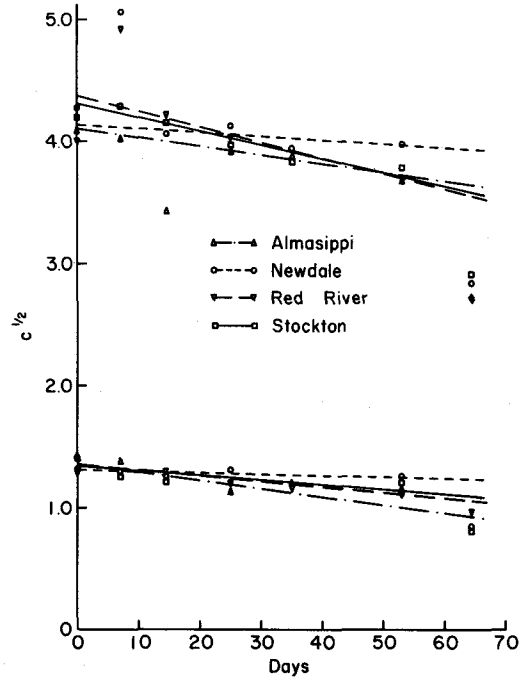

FIGURE 1. Half order plots of metribuzin degradation in four Manitoba soils at 15°.

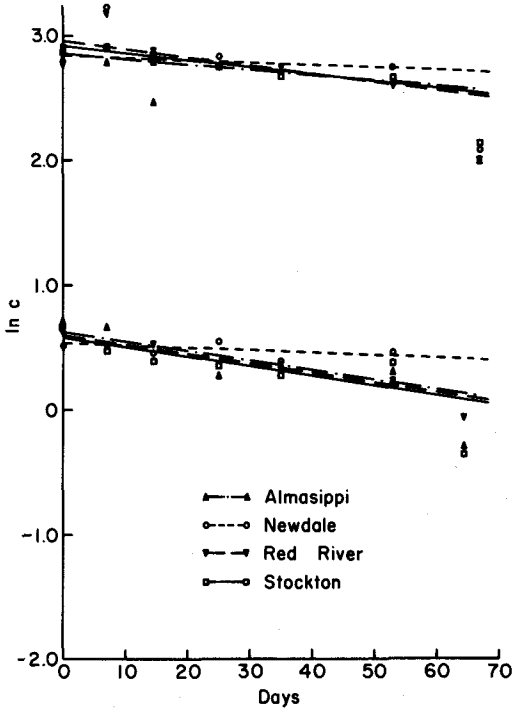

FIGURE 2. First order plots of metribuzin degradation in for Manitoba soils at 15°.

Metribuzin has been shown to undergo nonbiological degradation in four Manitoba soils under dry conditions at 15°, and the rate law describing this degradation has been shown to be somewhat less than first order. Calculated times for 50% loss (at a "normal" application rate of 1.8 ppm metribuzin) vary with soil type from approximatley 90-115 days for Red River, Almasippi, and Stockton soils to three times this period for Newdale soil. At higher application rates, half lives are somewhat longer.

ACKNOWLEDGMENTS

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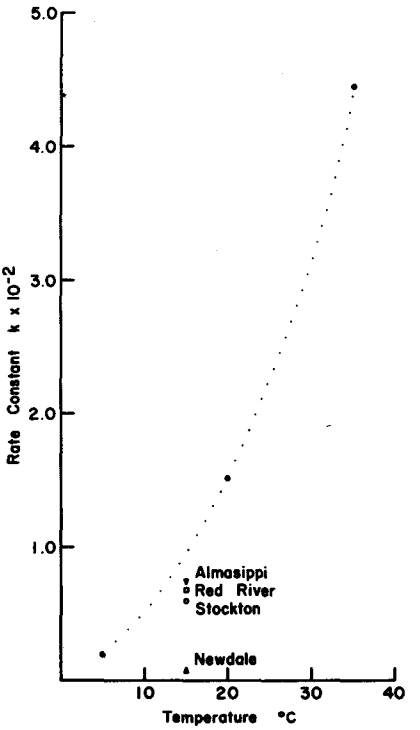

FIGURE 3. First order rate constants for the four Manitoba soils at 15° compared with values reported by HYZAK & ZIMDAHL at 5, 20, and 35° in San Luis sandy loam.

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