Methylcarbamate Inhibition of Phenylcarbamate Metabolism in Soil

D. D. Kaufman, P. C. Kearney, D. W. Von Endt, and D. E. Miller

Bioassays of treated soil indicated that the insecticidal N-methyl-carbamates: 1-naphthyl (I), *O*-isopropoxyphenyl (II), 4-dimethylamino-*m*-tolyl (III), 6-chloro-3,4-xylyl (IV), and 4-dimethylamino-3,5-xylyl *N*-methylcarbamate (V) but not 2,6-*di*-tert-butyl-*p*-tolyl N-methylcarbamate (VI) increased the herbicidal persistence of isopropyl *m*-chlorocarbanilate (CIPC). Soil pH, soil type, time of treatment, and methylcarbamate concentration did not significantly affect this interaction in soil systems. The microbial degradation of CIPC was inhibited by I in soil perfusion studies. An explanation for these phenomena was found in enzymatic studies, conducted with a purified enzyme isolated from CIPC degrading soil microorganisms. Enzymatic hydrolysis of CIPC was inhibited by I, II, III, IV, and V, but not by VI. Kinetic studies revealed that methylcarbamates are competitive inhibitors of the phenylcarbamate hydrolyzing enzyme. Failure of VI to cause inhibition was attributed to steric hindrance by the two *ortho*-substituted tertiary-butyl groups.

Microbial degradation of pesticides has received considerable attention. Little attention, however, has been given to the fate of pesticides when two or more are concurrently present in the soil. A combination of several herbicides, insecticides, nematocides, and fungicides may be applied to the soil in a single growing season. New problems involving the degradation or persistence of pesticides may thus arise when several pesticides or their residues are present in the soil together. Previously we reported (Kaufman, 1965; Kaufman and Kearney, 1966, 1967; Kaufman and Sheets, 1965) several pesticide interactions in which the microbial decomposition of one pesticide was inhibited or retarded in the presence of a second pesticide. Of particular interest was the observation that the microbial degradation of the phenylcarbamate herbicide CIPC (isopropyl *m*-chlorocarbanilate) was inhibited in the presence of several methylcarbamate insecticides (Kaufman and Kearney, 1966, 1967; Kaufman and Sheets, 1965). Detailed kinetic studies in purified *in vitro* systems revealed that methylcarbamates are competitive inhibitors of the phenylcarbamate hydrolyzing enzyme produced by soil microorganisms (Kaufman and Kearney, 1966, 1967).

Interactions in terms of plant response have been noted for herbicide mixtures (Colby and Feeny, 1967), herbicide–insecticide mixtures (Adachi *et al.*, 1966; Bowling and Hudgins, 1966; Hacskaylo *et al.*, 1964; Swanson and Swanson, 1968), and for fungicide–herbicide mixtures (Nash, 1967; Nash and Harris, 1969). Application of 3′,4′-dichloropropionanilide (propanil) and carbamate or phosphate insecticide mixtures results in injury to rice (*Oryza sativa* L.) plants. No injury occurs when either propanil or the insecticides are applied alone. Injury or death of cotton (*Gossypium hirsutum* L.) seedlings occurred when combinations of systemic phosphate insecticides and 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea (diuron) or 3-(*p*-chlorophenyl)-1,1-dimethylurea (monuron) were applied to the soil. Research to explain the nature of these interaction responses remains to be done. The purpose of this investigation was to examine the mechanism of methylcarbamate inhibition of phenylcarbamate biodegradation by soil microorganisms, and to determine some of the soil parameters affecting this reaction.

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MATERIALS AND METHODS

Technical grade CIPC (97%), 1-naphthyl N-methylcarbamate (I, 99.85%), *O*-isopropoxyphenyl N-methylcarbamate (II, 98%), 4-dimethylamino-*m*-tolyl N-methylcarbamate (III, 100%), 6-chloro-3,4-xylyl N-methylcarbamate (IV, 97%), 4-dimethylamino-3,5-xylyl N-methylcarbamate (V, 97%), and 2,6-*di*-tert-butyl-*p*-tolyl N-methylcarbamate (VI, 797%) were used in all experiments.

The persistence of CIPC-methylcarbamate combinations in soil was determined by bioassay methods in greenhouse tests. Air-dry soil samples (300 g) were weighed into 3-½ in. plastic pots without drainage holes. Soil applications were established by distributing 1.0 ml volumes from appropriate acetone stock solutions over the dry soil surface. All chemicals were applied individually. The soil was thoroughly mixed after evaporation of the acetone. Untreated soil receiving equivalent amounts of acetone served as controls. All soils were then watered to field capacity and maintained moist and near constant temperature (28° C) throughout the test period. Four replications were used for each experimental variable. At intervals of 0, 2, 4, 8, 16, 32, 64, and 128 days, a complete set of pots (four replicates × treatments) were bioassayed for CIPC residues with oats (variety Markton) as the assay plant. Oat seedlings were harvested after a 3-week growing period, and the fresh weight was expressed as percent of the untreated controls. Chemical and physical properties of the soils used in this investigation are presented in Table I.

The effect of several methylcarbamate insecticides on the persistence of CIPC in Hagerstown silty clay loam was determined by using the methods outlined above. CIPC was applied at the rate of 5 ppm, whereas II, III, IV, V, and VI were applied at molar equivalents to I, which was applied at 1 ppm. Treatments included each methylcarbamate and CIPC alone, and each methylcarbamate in combination with CIPC.

Lakeland sandy loam was used to determine the effect of pH on the CIPC-I interaction. pH levels of 5 and 6 were established by addition of varying amounts of powdered $Al_2(SO_4)_3 \cdot nH_6O$, whereas $CaCO_3$ was used to establish neutral and alkaline (pH 8) conditions. After pH adjustment, each of the treated soils was incubated at field capacity in the greenhouse for 2 weeks to permit pH equilibration. The soils were then air-dried, potted, and treated with 5 ppm CIPC, or 1 ppm I, or both, watered to field capacity, and bioassayed at regular intervals.

Table I. Chemical and Physical Properties of Soils

Soil	pH	Cation Exchange Capacity (meq/100 g)	Moisture, Field Capacity	Organic Matter	Percentage Sand	Silt	Clay
Hagerstown silty clay loam	7.5	8.8	21.1	2.26	17.0	50.6	32.4
Lakeland sandy loam	6.4	3.0	8.7	0.9	76	13	11
Montalto clay	5.9	8.4	22.2	1.5	26	27	47
Muck	5.0	165.3	51.5	74.9	...	...	...
Ruston sandy loam	5.1	3.4	21.1	1.82	75	8	17
Wehadkee silt loam	5.6	10.2	23.7	1.93	15	60	25

Table II. Persistence of CIPC, I, and CIPC-I Combinations in Autoclaved and Nonsterile Hagerstown Silty Clay Loam

Soil Treatment	Chemical Treatment	Fresh Weight of Oats: % of control from planting day 0	4	8	16	32	64	128
Nonsterile	CIPC	28.3	25.1	55.8	74.5	99.4	98.7	103.5
	I	83.0	94.5	100.9	96.4	97.7	94.6	103.5
	CIPC-I	13.2	8.7	9.6	21.6	36.7	52.2	103.5
Autoclaved	CIPC	29.1	27.0	18.2	27.6	26.2	27.0	25.1
	I	85.4	100.9	92.3	94.5	95.6	95.4	94.5
	CIPC-I	13.6	9.6	11.2	12.0	10.9	9.2	8.7

The effect of soil type on the CIPC-I interaction was determined with Lakeland sandy loam, Montalto clay, Hagerstown silty clay loam, Ruston sandy loam, and Wehadkee silt loam. Samples of each soil were treated as in preceding experiments with 5 ppm CIPC or 1 ppm I, or both, watered to field capacity, and bioassayed at regular intervals. The effect of I application rate and application time on CIPC persistence was determined in Hagerstown silty clay loam. I application rates of 1, 2, and 4 ppm were applied alone and in combination with CIPC (5 ppm) as in the former experiment. In the latter experiment I (1 ppm) was applied to a large number of soil samples. At subsequent intervals of 0, 2, 4, and 8 weeks, CIPC (5 ppm) was applied to a portion of the original control and I-treated soil samples. These samples were then bioassayed at 0, 8, 16, and 32 day intervals.

The persistence of CIPC, I, and CIPC-I combinations in nonsterile and sterile soils was compared using the procedures outlined above. Soil sterilization was accomplished by autoclaving the soil in 300 g (air-dry) quantities in covered glass storage dishes for 2 hr at 15 lb/in.^{2} pressure, at 121° C. Chemical treatment and initial watering of autoclaved soil was accomplished using aseptic techniques. Autoclaved, treated soils were kept covered and maintained in the greenhouse until planting time, when the covers were removed. No attempt at maintaining soil sterility was made after planting. CIPC and I application rates were 5 ppm and 1 ppm, respectively, in treated soils.

A soil perfusion technique (Kaufman, 1966) was used to enrich muck soil with mixed microbial populations capable of degrading CIPC, and to determine the effect of I on the enrichment process. Each perfusion unit initially contained 10 g (air dry) of muck soil treated with 125 mg of CIPC. Soil receiving only CIPC was perfused with 250 ml of distilled water, whereas soil receiving the combined CIPC-I treatment was perfused with 250 ml distilled water containing 1 or 10 ppm I. An untreated perfused soil served as a blank. CIPC degradation was determined by daily colorimetric measurement of chloride ion in 2 ml samples of the soil perfusate (Iwasaki *et al.*, 1952: Kaufman and Kearney, 1965).

We demonstrated earlier (Kaufman and Kearney, 1965) that CIPC is degraded by an adaptive enzyme system obtained from pure cultures of *Pseudomonas striata* Chester. Therefore, studies were initiated to determine whether I might be an inhibitor of the phenylcarbamate hydrolyzing enzyme when CIPC was used as a substrate. Procedures for culturing and harvesting the organism and isolation and purification of the enzyme have been previously described (Kearney, 1965; Kearney and Kaufman, 1965). Partially purified enzyme, obtained from the 30 to 65% $(NH_4)_2SO_4$ fraction of sonicated cells, was used in all inhibition studies. Enzyme assays were conducted for 20 min at 30° C, and activity determined by measuring 3-chloroaniline production colorimetrically (Pease, 1962). Assay solutions contained 2.5 ml of CIPC (1 μmole), 0.4 ml 0.1 *M* tris (tris-[hydroxymethyl]aminomethane) buffer pH 7.0, and 0.1 ml of protein preparations. Since the enzyme exhibits activity over a wide pH range, all assay solutions were buffered at pH 7.0 to prevent alkaline hydrolysis of the methylcarbamates. II, III, V, and VI were also tested as possible inhibitors of the enzyme.

All experiments reported herein were repeated two to four times.

RESULTS

Oat seedling bioassays of CIPC, I, and CIPC-I treated soils indicated that CIPC persisted in autoclaved soil but not in nonsterile soil (Table II). The addition of I to CIPC treated soil increased CIPC persistence from 4–32 days to 64–128 days in nonsterile soil. I alone displayed some phytotoxicity to oat seedlings, and some increased phytotoxicity was noted when CIPC-I combinations were compared to CIPC alone. Phytotoxicity of CIPC, I, and CIPC-I combinations remained relatively constant in autoclaved soil throughout the experimental period.

With the exception of VI, all of the methylcarbamate pesticides increased the persistence of CIPC in soil experiments (Table III). VI did not affect the persistence of CIPC in soil. Some variation was observed in the ability of I, II,

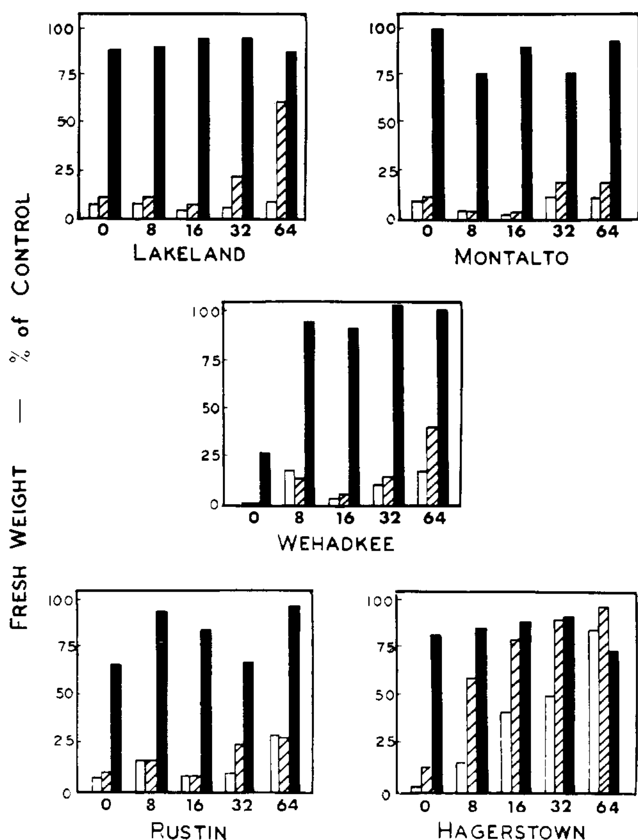

Figure 1. Effect of soil type on CIPC-I interaction at indicated assay periods (days)

Solid box = I; open box = CIPC + I; crossed box = CIPC

III, IV, and V to increase CIPC persistence in soil. I, however, appeared to be the most effective methylcarbamate for increasing CIPC persistence. In other similar experiments not reported here, I was effective in increasing CIPC persistence from 8–16 days to 128 days under greenhouse conditions.

Soil type and pH had little effect on the CIPC-I interaction (Figures 1 and 2, respectively). CIPC persistence varied with soil type (Figure 1). In general, the results indicate that persistence of CIPC alone in soil followed the order of Montalto > Ruston > Wehadkee > Lakeland > Hagerstown. I increased CIPC persistence in three (Lakeland, Wehadkee, and Hagerstown) of the five soils examined. The duration of this particular experiment (64 days) was insufficient to determine whether or not the effect would be observed in the two remaining soils (Montalto and Ruston). CIPC alone was unusually persistent in these two soils. Soil pH also had little effect on the CIPC-I interaction (Figure 2). Although

Table III. Effect of Several Methylcarbamate Pesticides on the Persistence of CIPC in Soil

Chemical combined with CIPC	Fresh Weight of Oats: % of Control from Planting Day				
	4	8	16	32	64
CIPC, alone	14.6	80.7	99.5	96.1	100.0
I	7.5	14.4	39.1	65.8	89.2
II	22.8	37.4	90.6	100.0	100.0
III	9.9	22.4	69.8	100.0	100.0
IV	14.0	27.8	46.4	102.0	105.0
V	14.0	29.4	72.9	102.4	103.8
VI	18.1	100.0	93.2	96.6	100.0

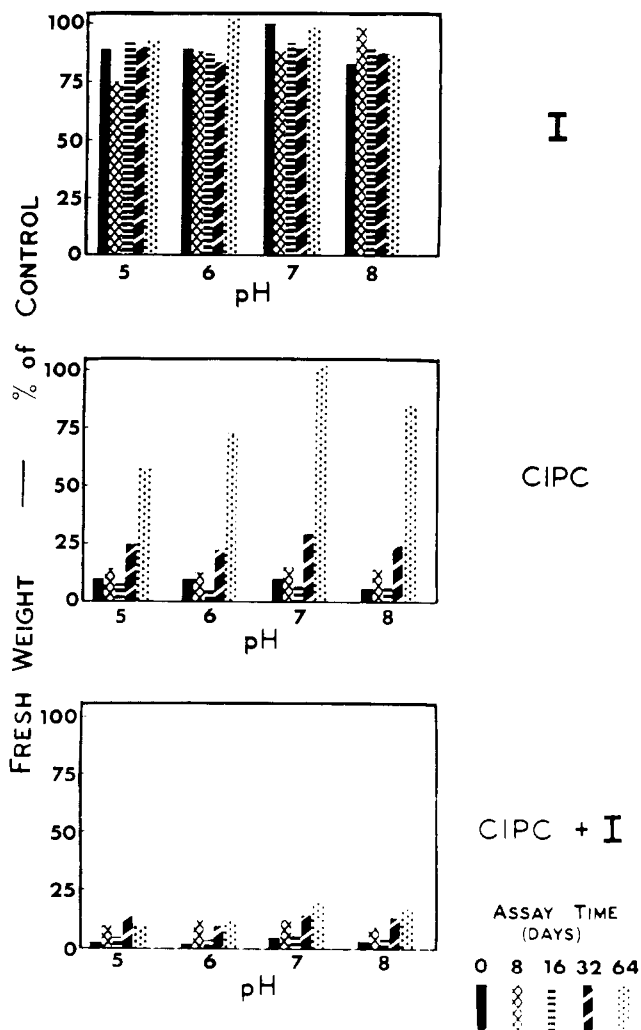

Figure 2. Effect of soil pH on CIPC-I interaction in Lakeland sandy loam

CIPC disappeared most rapidly in soil at pH 7.0, I increased the persistence of CIPC at all soil pH levels.

CIPC persistence in Hagerstown silty clay loam did not increase with increased I application rates (Figure 3). Persistence of CIPC alone was 16 to 32 days, whereas in the presence of I, CIPC persisted more than 64 days. No increased effect due to increased I concentrations was noted, however. The CIPC-I interaction effect was still detectable when CIPC was applied to I-treated soil 8 weeks after the I had been applied (Table IV). The interaction effect, however, was not

Table IV. Effect of CIPC Application Time on CIPC: I Interactions

CIPC Application Times[a]	Treatment	Fresh Weight of Oats: % of Control from Planting Day			
		0	8	16	32
0	CIPC	28.3	27.6	62.3	98.7
	CIPC + I	13.2	12.0	33.0	52.2
2	CIPC	13.9	43.4	101.1	98.9
	CIPC + I	10.2	12.6	17.5	62.2
4	CIPC	26.8	72.3	93.3	100.0
	CIPC + I	11.8	20.3	32.7	73.4
8	CIPC	32.5	70.4	90.3	103.5
	CIPC + I	16.2	31.6	58.7	100.5

[a] Weeks, after I applied.

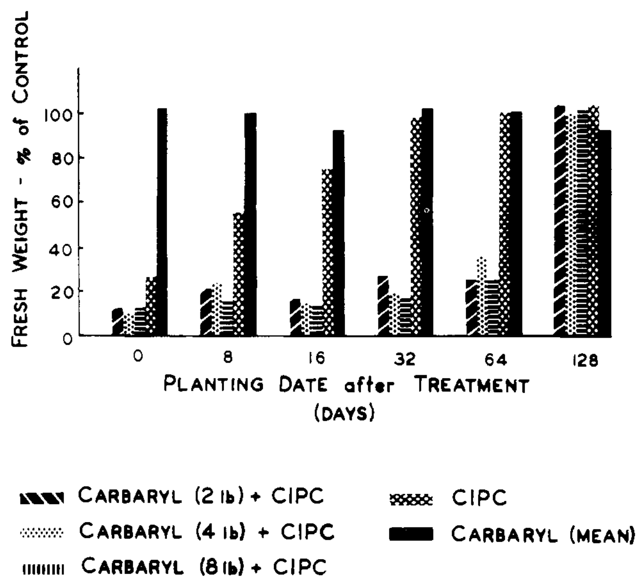

Figure 3. Effect of I concentration on CIPC (10 lb) persistence in Hagerstown silty clay loam

as pronounced at 8 weeks as it was at the 0, 2, and 4 week intervals.

Further investigations in soil perfusion systems revealed that I inhibits the microbial degradation of CIPC by mixed populations of soil microorganisms. I concentrations of 1 and 10 ppm increased the persistence of CIPC in soil perfusion units from 8–10 days to 24–30 days (Figure 4). No difference in this effect was observed with increased I concentrations. At these concentrations under pure culture conditions, I did not effect growth of *Pseudomonas striata* Chester, as measured turbidimetrically. 1-Naphthol, a suspected I degradation product, did not inhibit microbial degradation of CIPC in soil perfusion systems.

II, III, IV, and V were inhibitors of the CIPC-hydrolyzing enzyme from *P. striata* when examined at various dilutions of saturated solutions of each of the respective compounds (Figure 5). The exact concentration of the inhibitor in several of these solutions was difficult to obtain, since adequately sensitive colorimetric assays were not available. In

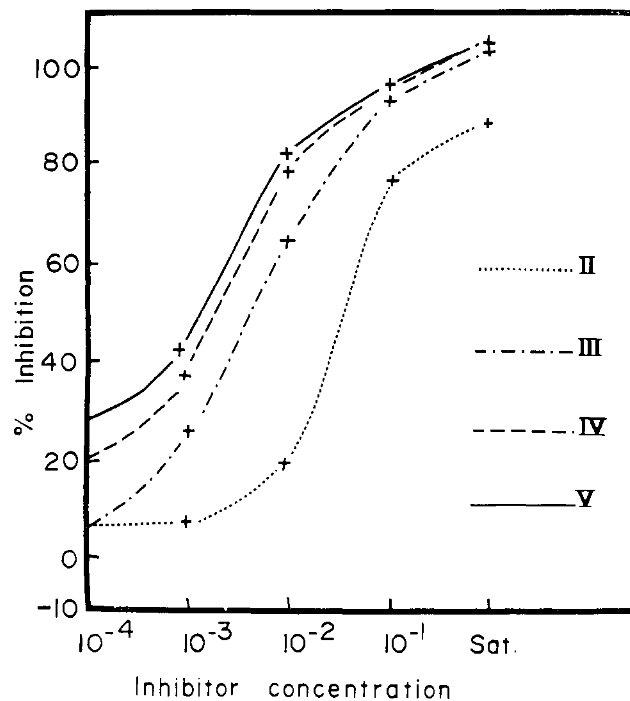

Figure 5. Effect of several methylcarbamates on enzymatic hydrolysis of CIPC

addition to the inhibitor curves for the different methylcarbamates, the substituents at different positions on the ring are also shown in the figure. I was also an effective inhibitor of the enzyme, but VI failed to inhibit at any concentration examined (Figure 6).

The low solubility of the substrate (CIPC-about 108 ppm) and the limited sensitivity of the colorimetric assay procedure for 3-chloroaniline, in the range of 1–2 μg, prevented an extensive investigation over a number of concentrations. The inhibition of the enzyme by two concentrations of I was examined over five concentrations of substrate (Figure 7), by working within the rather narrow limits allowed by solubility of the substrate and by using an extended light path for the colorimetric procedure. A plot of these data, according to

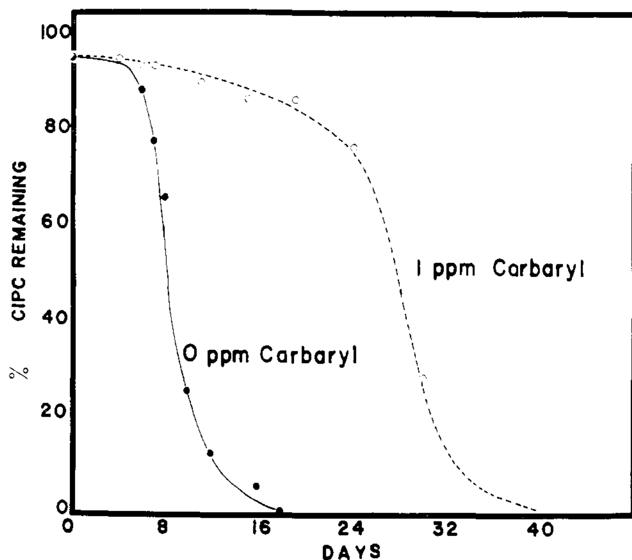

Figure 4. Effect of I on microbial decomposition of CIPC in perfused muck soil

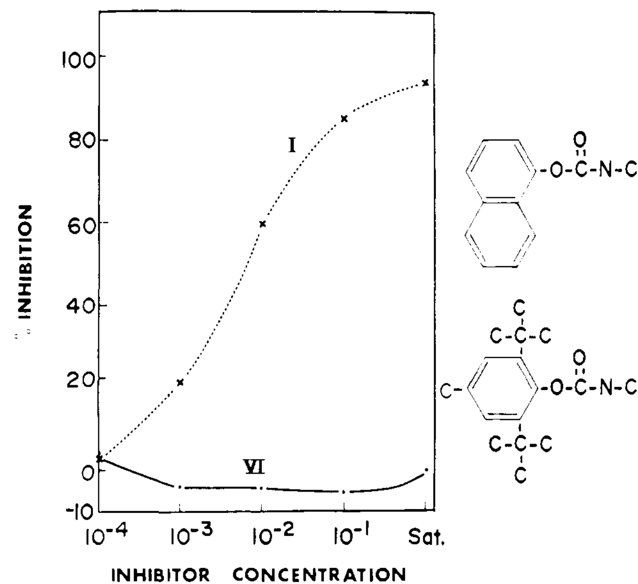

Figure 6. Effect of I and VI on enzymatic hydrolysis of CIPC

the Lineweaver-Burke method, shows that I is a competitive inhibitor of the CIPC-hydrolyzing enzyme system. The apparent dissociation constant for the enzyme-substrate complex is K_m, approximately 8.4×10^{-6}M, whereas that for the enzyme inhibitor complex was K_i, approximately 4.3×10^{-9}M, indicating that a very minute amount of I is needed to inhibit the enzyme.

DISCUSSION

Microbial degradation of several carbamate pesticide combinations was studied under greenhouse and laboratory conditions. CIPC disappeared rapidly from a nonsterile soil, but was more persistent in soil when applied in combination with certain methylcarbamate pesticides. Continued persistence of CIPC or CIPC-I combinations in autoclaved soil implicates the role of soil microorganisms in the CIPC degradation process. Kinetic studies indicated that methylcarbamates were competitive inhibitors of the phenylcarbamate hydrolyzing enzyme produced by soil microbes. The methylcarbamate inhibition of CIPC degradation in perfused muck soil, known to have a mixed population of CIPC-degrading microorganisms (Kaufman and Kearney, 1965) demonstrates the applicability of this observation to mixed populations of soil microorganisms. This conclusion is further substantiated by the bioassay results obtained in other similarly treated soil types.

The anticholinesterase (Metcalf and Fukuto, 1965) and amidase (Frear and Still, 1968; Swanson and Swanson, 1968) activity of certain methylcarbamate pesticides is well known. The esterase-amidase-like activity of the phenylcarbamate hydrolyzing enzyme has also been reported (Kearney, 1965; Kearney and Kaufman, 1965). The methylcarbamate inhibition of the phenylcarbamate hydrolyzing enzyme is therefore not surprising. I, II, III, IV, and V were all effective inhibitors of phenylcarbamate degradation in both laboratory and greenhouse experiments. *Ortho*-substituted methylcarbamates have low mammalian toxicity (Metcalf and Fukuto, 1965; Haubein and Hansen, 1965), but vary in their anticholinesterase activity (Kaeding *et al.*, 1965). *Ortho*-substituents which severely restrict rotation of the carbamate group reduce activity drastically (Kaeding *et al.*, 1965). Failure of VI to inhibit CIPC degradation in this investigation was, therefore, attributed to steric hindrance caused by the two *ortho*-substituted tertiary-butyl groups.

The CIPC-I interaction effect was still detectable in Hagerstown silty clay loam when CIPC was applied to I treated soil 8 weeks after I had been applied. At first glance, this observation could indicate a greater persistence of I, at least in some soils, than has heretofore been recognized. Back (1965) reported the half-life of I in soil to be about 1 week. Although such figures are not specifically applicable to all soil types, extrapolation of this value with the I application rates most commonly used in this investigation (2 lb/A or 1 ppm) reveals that even after 8 weeks the concentration of I theoretically remaining in the soil is still far in excess of that needed for inhibition in *in vitro* enzyme studies. In view of the extremely low I levels capable of inhibiting CIPC degradation in enzyme or soil perfusion experiments, it is quite probable that lower levels (<2 lb/A) of I would be sufficient to effect an increase of CIPC persistence in soil systems. This phenomenon would also explain the apparent lack of effect of soil pH on the CIPC-I interaction. The susceptibility of carbamates, particularly methylcarbamates, to alkaline hydrolysis is well known. The effectiveness of low I levels in increasing CIPC persistence may have precluded this observation.

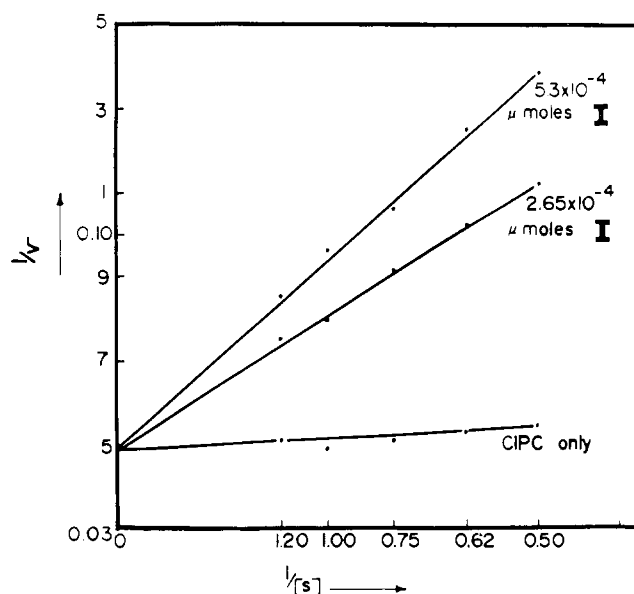

Figure 7. Kinetics of I inhibition of CIPC enzyme

The herbicide propanil (3′,4′-dichloropropionanilide) is selective in rice (McRae *et al.*, 1964) because enzymatic hydrolysis to 3,4-dichloroaniline and propionic acid (Frear and Still, 1968) inactivates the herbicide. Combinations of propanil and I result in injury to rice plants not observed when either chemical is applied alone (Adachi *et al.*, 1966). This effect results from the inactivation of the propanil hydrolyzing enzyme by I (Adachi *et al.*, 1966; Frear and Still, 1968), thus permitting the herbicide propanil to remain phytotoxic to rice. A similar response has been observed in degradation of monuron in cotton plants treated with methylcarbamate insecticides (Swanson and Swanson, 1968). Throughout the present investigation we noted that some increased phytotoxicity to oat seedlings frequently resulted from application of the methylcarbamate-phenylcarbamate combinations to soil (Figures 1, 2, 3, and Tables II, III, and IV). This phenomenon was also observed when barley was used as the assay plant. I alone displayed some degree of phytotoxicity to oats when applied to soil. The question could arise, therefore, whether the observed interaction actually represents an increased CIPC persistence in soil or an increased sensitivity of oats to CIPC in the presence of I, which enables the assay detection of lower levels of CIPC.

The data presented in Tables II, III, IV, and Figures 1, 2, and 3 were submitted to the calculations described by Colby (1967) for determining antagonistic, additive, and synergistic responses to pesticide combinations, in an attempt to determine the possible importance of these various effects. Briefly, the plant responses to pesticides applied singly are used in calculating the "expected" responses when they are combined. The expected response (E) for a combination is obtained by dividing the product of the percent-of-control value for pesticides applied alone by $(100)^{n-1}$, where n is the number of pesticides in combination. When the observed (O) values is less than expected, the combination is antagonistic; when greater than expected, it is synergistic. When the O and E values are equal, the combination is additive.

If appropriate experiments involving a time variable are conducted and the percent-of-control data obtained are submitted to these calculations, one should be able to represent graphically any significant change occurring with time in the $E-O$ values. Theoretically, in a system such as observed in

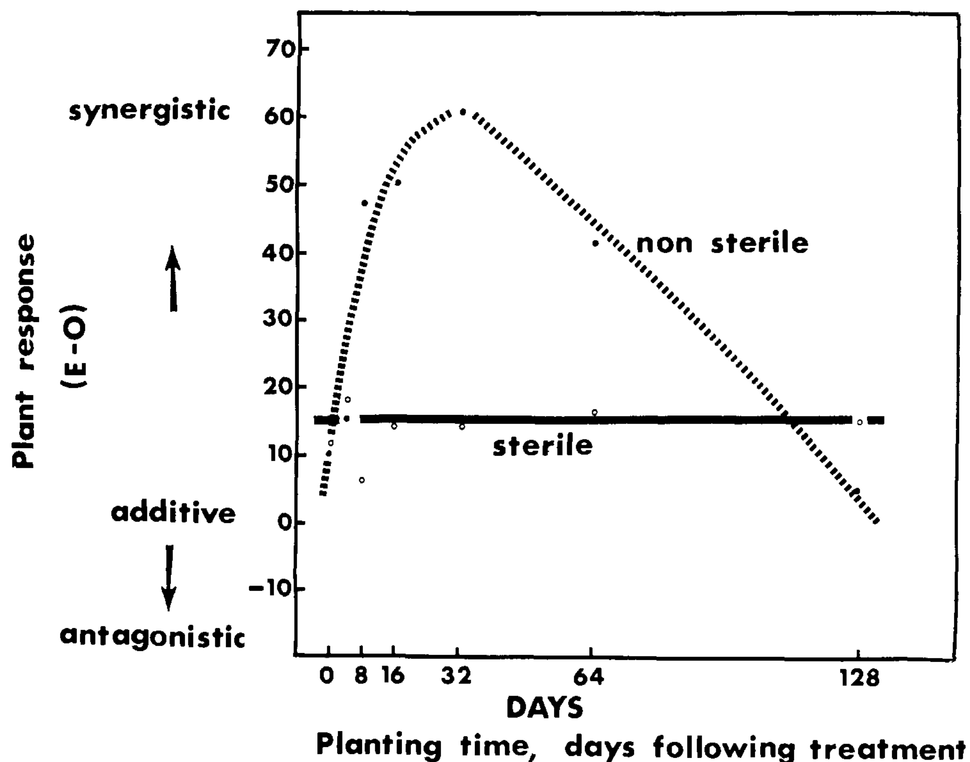

Figure 8. Response of oats to CIPC-I treatments in nonsterile and autoclaved Hagerstown silty clay loam

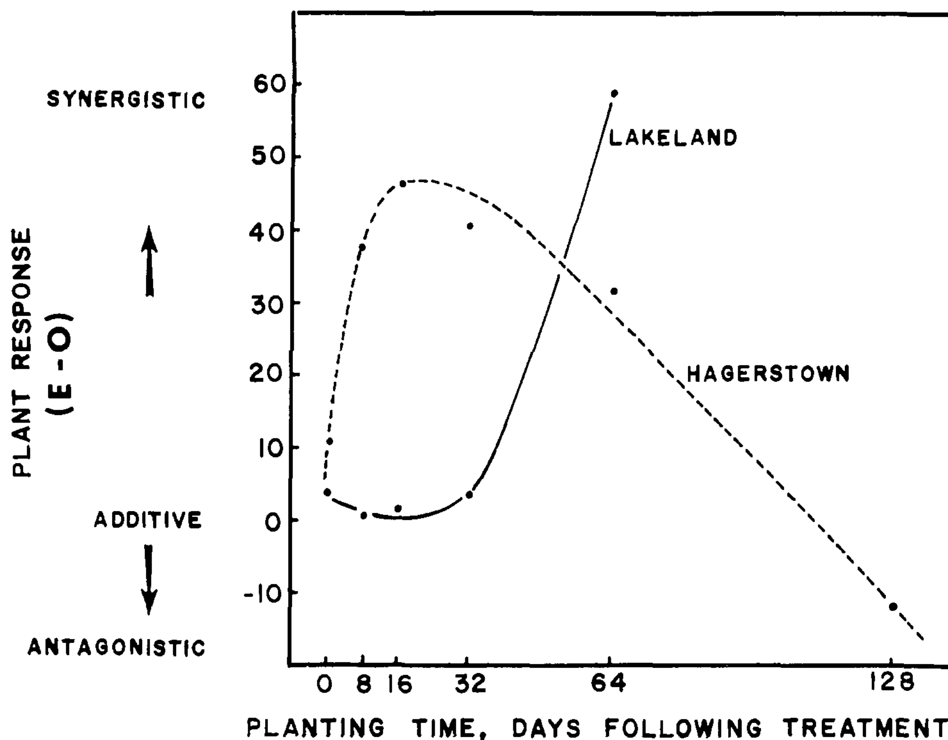

Figure 9. Response of oats to CIPC-I treatments in Lakeland sandy loam and Hagerstown silty clay loam

(Mean response of all experiments)

this investigation, where the biodegradation of one chemical is inhibited by the other, one would expect a temporary increase in the *E–O* value, followed by a decrease and eventual equalization of the values. Such an effect was obtained when we plotted the *E–O* values calculated from data listed in Table II (Figure 8). A high *E–O* value, or synergistic-type response, develops immediately and increases rapidly during the initial assay periods, but then decreases with time in the nonsterile soil. The relative constancy of *E–O* values obtained in the autoclaved soil would again reflect the role of soil microorganisms in this interaction in nonsterile soil.

The time and rate at which *E–O* values changed could be expected to vary with soil type. The mean *E–O* values from all experiments involving Hagerstown silty clay loam and

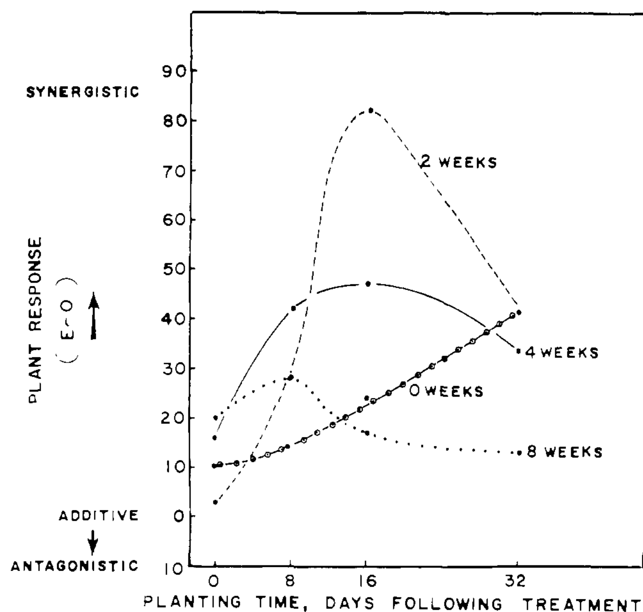

Figure 10. Effect of CIPC-application time on response of oats to CIPC-I application in Hagerstown silty clay loam

Lakeland sandy loam were also graphed (Figure 9). As before (Figure 8), the *E–O* values increased rapidly during initial assay periods, but then decreased slowly with time in the Hagerstown silty clay loam. The *E–O* values in the Lakeland sandy loam were initially low but eventually shifted to a higher value. Similar type responses were obtained with CIPC-I combinations in the Wehadkee, Ruston, and Montalto soil types (Figure 1) and with other methylcarbamate-CIPC combinations in Hagerstown silty clay loam (Table III). Experiments conducted with Lakeland sandy loam were of insufficient duration to determine whether the *E–O* values would eventually decrease. This apparent difference in initial response could be explained in terms of each soil's microbiological activity. CIPC alone was more persistent in the Lakeland soil, which has a lower microbiological activity. The greater microbiological activity of the Hagerstown soil could account for the shorter persistence of CIPC.

A similar situation was observed in the Hagerstown silty clay loam in experiments (Table IV) involving two time variables (CIPC application time, and bioassay time) (Figure 10). When these data are submitted to the recommended calculations (Colby, 1967) the initial *E–O* values increased slowly, following CIPC application (time *O*). Subsequent CIPC applications resulted in a more rapid increase in the *E–O* values but also an eventual decrease in the *E–O* values. This sequence of reactions would be typical of a situation in which the microbial activity increased at the same time the inhibitor concentration was decreasing.

The occurrence of relatively constant positive *E–O* values in autoclaved soil (Figure 8) could indicate that some synergistic effect might also be occurring within the bioassay plant. The actual mechanism and nature of this increased phytotoxicity is not clear. The synergistic interaction of certain pesticide combinations in plants may also result from the inhibition by one pesticide of metabolic processes active in degrading the other pesticide (Swanson and Swanson, 1968). Such a synergistic mechanism may be functional in oat seedlings in the presence of low CIPC concentrations. The increased persistence of CIPC by I in nonsterile soils, and the strong competitive inhibition of the phenylcarbamate hydrolyzing enzymes of soil microorganisms by I, demonstrated in this investigation, however, would preclude the possibility of additive or other synergistic effects within the assay plant as being the sole explanation for increased CIPC persistence.

The practical significance of this observation is, of course, open to question. At present, harmful occurrence of phenylcarbamate-methyl-carbamate residue combinations in soil is unlikely, in view of current agronomic uses of these chemicals. The phenylcarbamate herbicides, CIPC and IPC, are generally used as soil applied preplant, preemergence, early postemergence, or late fall and winter herbicides, whereas the methylcarbamate insecticides are foliar, applied during the growing season. Since both types of compounds are readily degraded in soil systems, the frequency of their encounter under present practices would appear limited. The deliberate combination of methylcarbamates with phenylcarbamates, acetanilides, and acylanilides for purposes of controlled persistence of biodegradable pesticides, however, holds considerable promise and is currently under wide-scale investigation in this laboratory and others.

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