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Binding of "Persistent" and "Nonpersistent" ^{14}C-Labeled Insecticides in an Agricultural Soil

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The extractability and formation of bound ^{14}C-labeled residues in an agricultural loam soil were investigated with the "nonpersistent" insecticides [^{14}C]methylparathion and [^{14}C]fonofos (Dyfonate) and with the "persistent" insecticides [^{14}C]dieldrin and *p,p'*-[^{14}C]DDT. With [^{14}C]methylparathion only 7% of the applied radiocarbon was extractable 28 days after soil treatment, while ^{14}C-bound residues amounted to 43% of the applied dose. With [^{14}C]fonofos, however, still 47% of the applied dose was extractable and 35% of the applied radiocarbon was bound. Only a fraction of the radiocarbon extracted from [^{14}C]methylparathion treated soil was associated with the parent compound, while extractable ^{14}C-labeled residues from the other insecticide-treated soils were primarily due to the presence of the parent compounds. Smaller amounts of soil-bound residues had been formed with the "persistent" insecticides, amounting after 28 days to only 6.5% of the applied [^{14}C]dieldrin and to 25% of the applied *p,p'*-[^{14}C]DDT, while 95 and 72%, respectively, were still recovered by organic solvent extraction. They differed from the organophosphorus compounds in their relatively low binding properties and their high extractability from soils. Contrary to results with [^{14}C]parathion, the mechanism of binding of [^{14}C]fonofos was not dependent on the presence of soil microorganisms. At higher application rates of the insecticides, relatively less radiocarbon was bound, possibly due to saturation of binding sites. Bound residues were found to be either nontoxic to fruit flies or of drastically reduced insecticidal activity. The significance of the formation of insecticide bound residues in soils in reassessing persistence of pesticides is discussed.

During the last three decades of extensive use, insecticides were referred to as either "persistent" or "nonpersistent". In most cases, those insecticide residues which could be extracted from soils or plant material by conventional methods long after they had been applied were the "visible" ones and therefore considered to be "persistent" insecticides. The use of ^{14}C-labeled insecticides, however, has made it possible to detect unextractable ^{14}C-labeled residues by combusting the insecticide contaminated material, after exhaustive extraction, to $^{14}CO_2$. The presence of these bound ^{14}C-labeled residues changed our thinking about "persistent" or "nonpersistent" insecticides, as indicated in a recent publication from our laboratory by Katan et al. (1976). They found that the total radiocarbon (extractable and bound) recovered 28 days after treatment of an agricultural loam soil with [^{14}C]parathion still amounted to 80% of the applied dose. Of this, 35% was extractable and associated with parathion and 45% was bound. It was also found that these bound residues were a product of soil microorganism activity and were primarily amino derivatives of parathion. The production of bound residues in soil was also shown with propanil (Bartha, 1971), fonofos (Flashinski and Lichtenstein, 1974b), and others.

In view of these findings, further studies were conducted in our laboratory with silt loam soil which has been used for both field and laboratory studies with a variety of insecticides during the last 18 years. To obtain additional insight into the phenomenon of extractable and bound residues, investigations were conducted with the "nonpersistent" organophosphorus insecticides, [^{14}C]-methylparathion, [^{14}C]parathion, and [^{14}C]fonofos, and the "persistent" chlorinated hydrocarbon compounds, [^{14}C]-dieldrin and *p,p'*-[^{14}C]DDT.

EXPERIMENTAL SECTION

Materials. [*ring*-^{14}C]Methylparathion (sp act. 2.83 μCi/mg), [*ring*-^{14}C]parathion (sp act. 2 μCi/mg), and *p,p'*-[*ring*-^{14}C]DDT (sp act. 2.09 μCi/mg) were purchased from Amersham-Searle, [*ring*-^{14}C]fonofos (Dyfonate) (sp act. 1.78 μCi/mg) and [*ethoxy*-^{14}C]fonofos (sp act. 1.74 μCi/mg) were obtained from the Stauffer Chemical Company, and [^{14}C]dieldrin (labeled in all positions adjacent to chlorines) (sp act. 2.95 μCi/mg) was obtained from the Shell Development Company. The radiopurity of these insecticides was at least 99% after purification by thin-layer chromatography. A small amount of [^{14}C]DDE was isolated from the originally supplied

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[^{14}C]DDT. Solvents used were anhydrous methanol and redistilled acetone and benzene.

The soil used was a Plano silt loam (organic matter, 4.2%; sand, 4.8%; silt, 68%; clay, 23%; pH 6.0) and was obtained from the Experimental Farm of the University of Wisconsin near Madison.

Soil Treatment. For each test, 10-g aliquots of field moist loam soil were placed into each of 15 82 × 20 mm glass vials. Measured amounts of an acetone solution of a particular insecticide were then added to each soil at 1 or 10 ppm. Soil moistures were then adjusted to 20% and were maintained at that level throughout the test. The vials were plugged with cotton and incubated in the dark at 27 ± 1 °C for 0, 7, 14, 21, and 28 days. Additional samples containing [^{14}C]DDT were also analyzed after 1 day and of [^{14}C]methylparathion-treated soils after 1, 2, and 4 days. Each triplicated experiment was repeated once.

Since previous studies in our laboratory (Katan et al., 1976) indicated that the binding of [^{14}C]parathion was a function of soil microorganisms which reduced the insecticide to bindable amino compounds, the potential involvement of soil microorganisms in the binding of [^{14}C]fonofos was investigated in this study. Experiments were, therefore, conducted with [^{14}C]fonofos-treated soils previously sterilized by autoclaving (1 h at 120 °C and 1 atm) on two successive days or by γ irradiation (45 000 rads for 70 h), which causes less alteration of the soil structure and composition. When sterile soils were used, all procedures up to the extraction were carried out aseptically; the sterility of these soils was confirmed by incubating samples in yeast extract–dextrose medium. To test the potential effects of anaerobic microorganisms, loam soil was also flooded by pipetting distilled water onto the treated sample until it was 15 mm above the soil surface. All experiments were carried out with three replicates.

EXTRACTION AND ANALYSES

At the end of the incubation periods, the soil from each vial was quantitatively transferred into a 125-ml Erlenmeyer flask and extracted three times with 75 ml of a mixture of benzene, methanol, and acetone (1:1:1) by shaking each time for 1 min. After separation of the soil and the solvent in a Büchner funnel, the combined extracts from each soil sample were concentrated at 35 °C in a rotary evaporator and adjusted to 100 ml with the same solvent mixture. Aliquots were used for liquid scintillation counting (lsc) as described (Lichtenstein et al., 1972). Preliminary studies conducted in our laboratory with [^{14}C]parathion showed that six additional extractions with various solvent mixtures, ranging in polarity from benzene to water, yielded only a total of 2.4% of the applied radiocarbon, while 56.5% still remained in the soil as bound residues. Unextractable or bound residues were, therefore, defined as ^{14}C-labeled residues remaining in soils which had been extracted three times, as is routinely done in our laboratory. To determine bound residues, three 1.5-g aliquots of the extracted soil from each vial were oxidized to $^{14}CO_2$ in a Packard Model 305 Tri-Carb sample oxidizer and subsequent liquid scintillation analyses were performed as described by Flashinski and Lichtenstein (1974a).

For analyses by gas–liquid chromatography (GLC), concentrated extracts of soils treated with [^{14}C]methylparathion, [^{14}C]parathion, or [^{14}C]fonofos were analyzed as described by Lichtenstein et al. (1973) except that a 1.8 m × 4 mm column, containing 10% DC-200 on 80–100 Chromosorb W, was used and the detector gas flow rates were 60 ml/min of hydrogen and 105 ml/min of air. Extracts containing [^{14}C]DDT or [^{14}C]dieldrin were concentrated at 35 °C on a rotary evaporator to near dryness, redissolved in benzene, adjusted to volume, and analyzed by electron-capture GLC as described (Lichtenstein and Schulz, 1970).

Bioassay Procedures. Since the bound residues could not be extracted from the soils, the problem of their potential biological activity, if any, is of interest. For this purpose, fruit flies (*Drosophila melanogaster*, Meigen) were exposed to aliquots of extracted soils that contained ^{14}C-bound residues. Soil samples, previously treated at 10 ppm with [^{14}C]methylparathion or [^{14}C]fonofos, were incubated at 27 ± 1 °C for 1 or 3 weeks, respectively. The soils were then extracted as described and the amounts of bound radiocarbon were determined. Fifty flies were then introduced into each of three bioassay jars containing 4 g of extracted soil (Edwards et al., 1957). Mortality counts were performed at intervals over a 72-h exposure period.

For control purposes, fruit flies were also exposed to soils immediately after treatment with one of the insecticides at a concentration equivalent to the radiocarbon determined as "bound" in the 1- or 3-week incubated soils. To check for potential solvent toxicities, insecticide-free soils were also extracted three times as described, and then exposed to fruit flies. These latter soils, however, did not show any insect mortality over a 72-h exposure period.

RESULTS AND DISCUSSION

Methylparathion is usually referred to as considerably less persistent than parathion. Thus, Lichtenstein and Schulz (1964) determined that only 3.5% of methylparathion applied to the same loam soil could be recovered under field conditions 1 month after application, while 25% of applied parathion could still be accounted for after that time. Under laboratory conditions at 30 °C and after 12 days of incubation, methylparathion and parathion were recovered from the soil to an extent of 7 and 66%, respectively, of the applied dose. This higher "degradability" of methylparathion was later also reported by Getzin and Rosefield (1968) and by Kishk et al. (1976). If nonpersistence is, to some extent, related to nonextractability, then methylparathion could be expected to be bound to a larger degree than parathion. Figure 1A shows that this had indeed happened. (For comparison purposes, the amounts of bound [^{14}C]parathion residues as determined by Katan et al. (1976) are also shown.) In soils treated with [^{14}C]methylparathion and analyzed after 0, 1, 2, and 4 days of incubation, a relatively rapid binding of radiocarbon compounds occurred which, in turn, is reflected in the rapid decline of extractable [^{14}C]methylparathion residues. Thus, 7 days after soil treatment, only 29.2% of the applied radiocarbon was extractable while 41.2% was bound to the soil, resulting in a total recovery of 70.4% of the applied radiocarbon. At that time, however, previously determined extractable [^{14}C]parathion residues amounted to 65% of the applied dose, and only 27% was nonextractable (Katan et al., 1976). While with [^{14}C]parathion-treated soils the extractable radiocarbon was primarily associated with parathion, this was not the case with [^{14}C]methylparathion. Utilizing GLC of the soil extracts, the amounts of [^{14}C]-methylparathion were 85, 67, 44, 32, 19, and 7% and traces of the applied dose, after 0, 1, 2, 4, 7, 14, 21, and 28 days of incubation, respectively. The amounts of recovered radiocarbon, however, were considerably higher and amounted to 96, 76, 65, 45, 29, 14, 8, and 7%, respectively. This indicated that, unlike parathion, methylparathion had been metabolized to unidentified organic-soluble products. Since the total recovery of extractable and bound [^{14}C]-methylparathion derived radiocarbon amounted to only

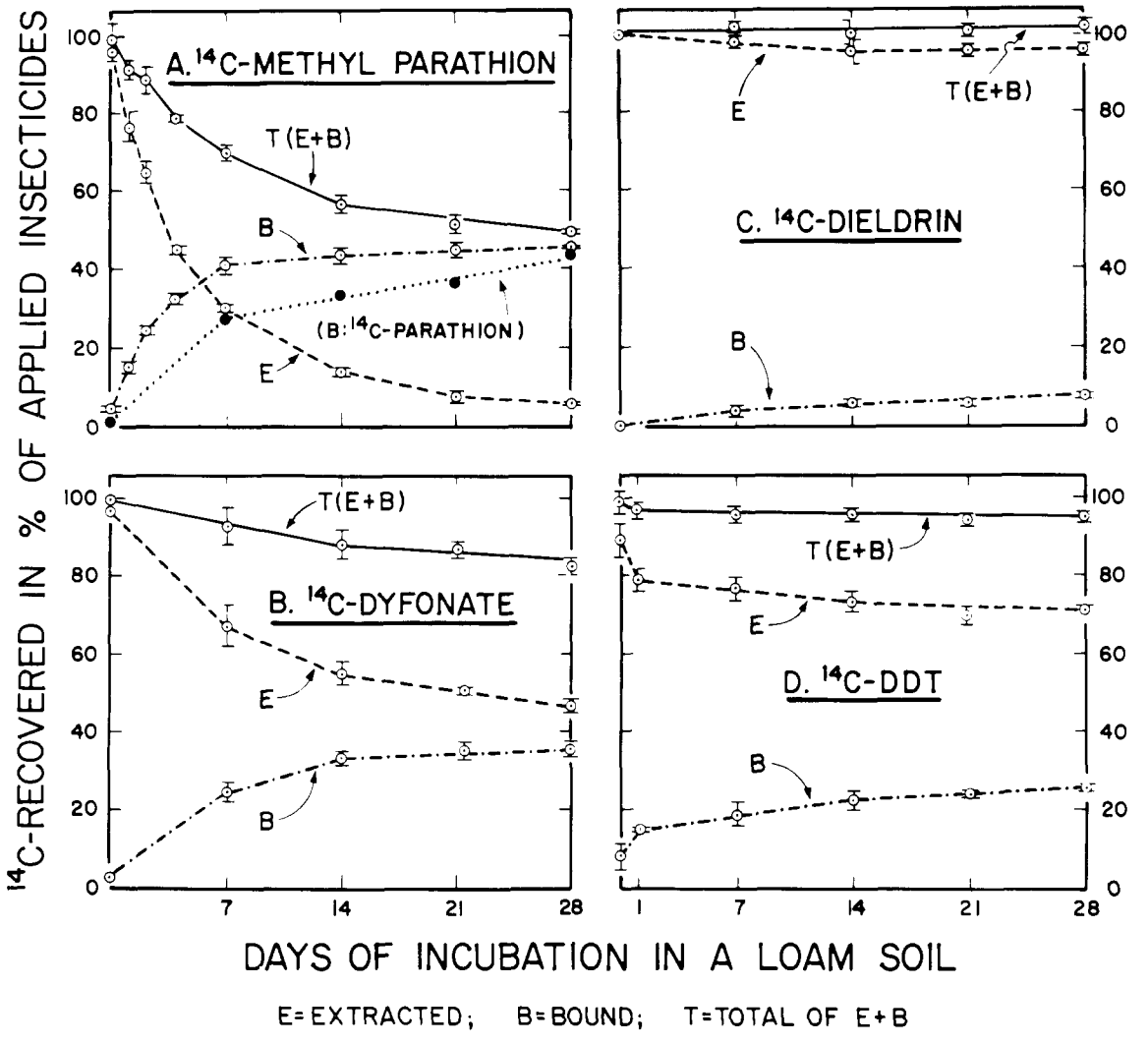

Figure 1. Binding and extractability of ^{14}C-labeled insecticides in a silt loam soil during a 28-day incubation period, after soil treatment at 1 ppm. With the exception of [^{14}C]methylparathion the amounts of extractable [^{14}C]Dyfonate (fonofos), [^{14}C]dieldrin, and [^{14}C]DDT, as determined by gas-liquid chromatography, were similar to the amounts of extractable radiocarbon. For comparison purposes, data are inserted in A for the bound residues of [^{14}C]parathion in soil (Katan et al., 1976).

50% of the applied dose after 28 days of incubation (this figure was 78% with [^{14}C]parathion), volatile materials had apparently been produced which were no longer detectable. This greater reactivity or metabolism of methylparathion could be a factor in its relatively higher soil binding properties.

The organophosphorus insecticide fonofos, often used for soil insect control, had been tested with our Plano silt loam. Under field conditions 50% of the applied insecticide was extracted from the soil 28 days after soil treatment (Schulz and Lichtenstein, 1971). Under laboratory conditions [*ethoxy*-^{14}C]fonofos or [*ring*-^{14}C]fonofos-treated soils, through which water was percolated 1, 15, and 29 days after the insecticide application, contained, after 29 days, 59.5 and 62.0%, respectively, of the applied dose as extractable fonofos residues, while 11.4 and 16.1%, respectively, were bound (Lichtenstein et al., 1972). In the present study (Figure 1B) it is also shown that 46.8% of the applied [*ring*-^{14}C]fonofos was extractable after 28 days of incubation. Results obtained for extractable radiocarbon were similar to those determined by GLC for fonofos. As with [^{14}C]methylparathion, however, increasing amounts of bound radiocarbon were noticed with time, amounting to 35.3% of the applied insecticide at the end of the incubation period. The total recovery of extractable and bound residues 28 days after soil treatment amounted to 82.1% of the applied fonofos. Additional soil samples were also treated with [*ethoxy*-^{14}C]fonofos, incubated for 14 days and extracted and analyzed as described. Results (30.0% of the applied radiocarbon bound and 54.3% extractable) were very similar to those obtained with [*ring*-^{14}C]fonofos (Figure 1B), indicating that bound residues probably contain both the ethoxy and ring moieties of the fonofos molecule.

Contrary to results obtained previously with [^{14}C]-parathion (Katan et al., 1976), the binding of [^{14}C]fonofos in soil was not related to the presence of microorganisms. Thus, 2 weeks after soil incubation, 37.0 ± 2.9% of the radiocarbon derived from [*ring*-^{14}C]fonofos was bound in control soils, 32.5 ± 1.3% in irradiated soils, 23.4 ± 2.3% in autoclaved soils, and 28.1 ± 1.8% in flooded soils. With [*ring*-^{14}C]parathion, these figures were 34.8 ± 1.2, 14.0 ± 1.4, 14.7 ± 1.1, and 66.7 ± 2.1%, respectively. Since fonofos does not contain a reducible nitro group, the mechanism of binding, as observed with parathion, could not be expected. Differences observed in the binding of [^{14}C]fonofos between irradiated and nonirradiated soils were not significant, while with autoclaved soils, probably due to the change of soil structure, significantly less ^{14}C was bound than in irradiated soils. Moreover, flooding of the soil

Table I. Insecticidal Activity of Soil Bound and Freshly Deposited Insecticide Residues in Soil[a]

Insecticide (concn, ppm)	Mode of soil contam.	% insect mortality after h of exposure to soil					
		2	3	18	24	48	72
Dyfonate (3)	Bound[b]	0	0	0	0	12 ± 2	17 ± 1
Dyfonate (3)	Fresh[c]	37 ± 5	100	100	100	100	100
Methylparathion (2.9)	Bound	0	0	0	0	4 ± 2	5 ± 3
Methylparathion (2.9)	Fresh	0	0	43 ± 7	69 ± 12	96 ± 2	96 ± 2
None[d]		0	0	0	0	0	0

[a] Test insect: *Drosophila melanogaster*, Meig. Results are means ± standard deviation of triplicated tests. [b] ^{14}C-bound residues remaining in soils after incubation with an insecticide and extraction. Concentration (ppm) is based on the amount of ^{14}C recovered by combustion. [c] Soil was treated with the insecticide at concentrations as calculated in footnote *b*, followed by immediate exposure of fruit flies to the soil. [d] Insecticide free soil after its extraction with a mixture of benzene, methanol, and acetone (1:1:1).

resulted in reduced binding of [^{14}C]fonofos, while with [^{14}C]parathion, a dramatic increase had occurred.

It appears that the binding of some insecticides to soil is related to their reactivity and rate of metabolism to bindable compounds. Therefore, more stable compounds, such as dieldrin and DDT, would be expected to be bound to soil to a lesser degree than organophosphorus compounds. Results obtained with ^{14}C-labeled dieldrin and DDT prove this point (Figure 1, C and D). With [^{14}C]-dieldrin only 6.5% of the applied radiocarbon was bound after 28 days, while 95–97% remained extractable throughout the incubation period. As shown by GLC analyses this extractable radiocarbon was associated with dieldrin.

With *p,p'*-[^{14}C]DDT, however, more binding was observed, in particular during the first day after soil treatment. After that, the increase in binding was slow. Indeed, binding at zero time (actually after the first 1–2 h) was unusually high, amounting to 9.7% of the applied ^{14}C as compared to 4.2, 2.7, and 0.7% for methylparathion, fonofos, and dieldrin, respectively. After 1 day, the amount of [^{14}C]DDT derived bound radiocarbon was 17.2% of the applied dose and increased by only 7.9% during the remaining 27 days. Thus, except for the initial relatively high binding of [^{14}C]DDT, which apparently was not dependent on the activity of microorganisms, the insecticide resembled dieldrin in the slow increase of binding with time, in the high recovery of total radiocarbon, and in the high persistence of the insecticide as shown by GLC. This latter analysis also showed that the extracted radiocarbon from *p,p'*-[^{14}C]DDT treated soil was primarily associated with *p,p'*-DDT. Additional soil samples, treated with [^{14}C]DDT as described, were incubated for 56 days and extracted and analyzed. However, no further increase in binding had occurred. To test whether the high initial binding of [^{14}C]DDT was related to the type of extraction solvents used, separate [^{14}C]DDT treated soil samples were extracted after 14 days of incubation with either a 1:1 mixture of hexane–acetone or with benzene–acetone (1:1). However, the amount of bound residues was similar to that obtained with the solvents mixture used throughout this study.

Although only traces of DDE were found in DDT-treated soil, the problem of its capacity to be bound to soil was investigated. For that purpose, soil was also treated with [^{14}C]DDE at 1 ppm. After 1 day of incubation, however, only 1.3% of the applied dose was bound to the soil, indicating that this DDT metabolite was not responsible for the initial relatively high binding of [^{14}C]-DDT. Porter and Beard (1968) had shown that part of the applied [^{14}C]DDT was no longer extractable after a short incubation period. Guenzi and Beard (1968) found that after 24 weeks of incubation of [^{14}C]DDT treated soil, 11% of the applied radiocarbon was detected by combustion of the previously extracted soil.

The "persistence" or "disappearance" of several chlorinated hydrocarbon insecticides in soil was also shown to be dependent on their rate of application (Lichtenstein and Schulz, 1959). Recoveries of DDT, aldrin, and lindane, expressed in percent of the applied dose, were smaller with lower application rates. To translate these 1959 findings into our knowledge today, one would assume that at lower application rates a larger proportion of the applied insecticide would be available for metabolism and binding. To study this possibility, soils were also treated at 10 ppm with *p,p'*-[^{14}C]DDT, [*ring*-^{14}C]fonofos, and [*ring*-^{14}C]-methylparathion. After an incubation of 7 ([^{14}C]-methylparathion) or 21 days, soils were extracted and analyzed as described. It was found that the amount, expressed in percent of the applied dose, of these insecticides bound to soil was indeed higher after 1-ppm application than the comparable figures obtained with soil treated at 10 ppm. These amounts for the applied dose of 1 ppm were 22.5, 33.0, and 43.2% for [^{14}C]DDT, [^{14}C]fonofos, and [^{14}C]methylparathion, respectively, while at the application of 10 ppm these figures amounted to only 15.6, 30.8, and 29.0%, respectively. Although an increase in pesticide concentrations resulted in relatively less binding, the absolute amount of bound residues was greater at the higher concentration. Since at higher application rates of insecticides to soil more binding sites might be saturated, the greater binding at lower concentrations, expressed in percent of the applied dose, could be explained.

The question of the potential biological activity of bound insecticide residues was investigated as described above by testing the insecticidal activity of bound residues from [^{14}C]fonofos and [^{14}C]methylparathion treated soils with fruit flies. Results obtained are summarized in Table I. With soils containing unextractable radiocarbon at the insecticide equivalent of 3 ppm, no mortalities were observed during a 24-h exposure period to the soil and only slight mortalities during an additional 48-h exposure period. However, with soils to which the insects were exposed immediately following the insecticide application, 50% of the flies had died within 2–3 h after fonofos application and within 18–20 h after soil treatment with methylparathion. It appears, therefore, that bound residues are not only unextractable, but they are also less active biologically.

The chlorinated hydrocarbon insecticides differed from the organophosphorus compounds in their relatively low binding properties, their high extractability from soils, and the resulting high recoveries (94–100% of applied) of the total radiocarbon, previously applied to the soil. Guenzi and Beard (1968) found that the unextractable portion of [^{14}C]DDT applied to soil was similar in both sterile and nonsterile soils. This seems to indicate that DDT is bound

either as an intact molecule (Guenzi and Beard, 1968) or in the form of one of its metabolites, other than DDE, which could be rapidly formed from DDT in the soil. Hsu and Bartha (1976) reported that bound residues of 3,4-dichloroaniline were composed of both hydrolyzable and nonhydrolyzable forms. Therefore, the nature and mechanism of the formation of soil-bound residues of different pesticides may be different.

In the future, it will be important to obtain information about the mechanism of binding of pesticides, thus possibly shedding some light on the mechanism of their potential release and the conditions at which this release might occur. Since not much information is available pertaining to the nature and the potential biological activity of the compounds that are bound, extensive research in this field is highly desirable. In view of the above findings, the expression "disappearance" and "persistence" of pesticides, so widely used during the last two decades, should be reassessed to consider the bound products.

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Laboratory Studies on the Degradation of (the Pesticide) Aldicarb in Soils

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Degradation of aldicarb samples separately ^{14}C labeled at three positions (*S*-methyl, *N*-methyl, and tertiary carbon) in Norfolk sandy loam, Lufkin fine sandy loam, and Lakeland fine sand soils has been studied under laboratory conditions. Extensive fragmentation of the aldicarb molecule was accompanied by recovery of up to 82.8% of the applied radiolabel as $^{14}CO_2$, the amount depending primarily on label position, incubation time, and soil type/pretreatment. Aldicarb sulfoxide and sulfone were the major solvent extracted metabolites. Part of the solvent unextracted radiolabel was isolated in conjunction with the humic and fulvic acid fractions of soil organic matter.

Aldicarb pesticide is used for protection of cotton, potatoes, peanuts, sugarbeets, and sweet potatoes from attack by mites, nematodes, and many other pests. Since aldicarb is soil applied its fate in soils is of particular importance. The degradation of radiolabeled aldicarb in a variety of soil types has been studied under both field (Andrawes et al., 1971; Bull, 1968; Bull et al., 1970; Coppedge et al., in press) and laboratory (Coppedge et al., in press, 1967) conditions. The field studies were performed under environmental conditions similar to those encountered in commercial application of aldicarb pesticide. However, experimental difficulties led to the loss of substantial portions of the applied radiolabel, thereby making it impossible to provide a good accounting of the pesticide's fate in soil. In laboratory studies, Coppedge et al. (1967) have shown that aldicarb is degraded by soil in a manner qualitatively similar to that under field conditions. Evidence has also been obtained (Coppedge et al., in press) that the volatile degradation product is CO_2, but this was not proven nor could much light be shed on the nature of the unextracted soil residues.

Our objective in the studies reported herein was to gain a fuller understanding of aldicarb degradation in soils. Specifically, we sought to identify conclusively the volatile portion of the degradation products and to increase our knowledge of the chemical nature of the fragments not readily extracted from soil. The use of aldicarb samples separately radiolabeled at the *S*-methyl, *N*-methyl, and tertiary carbon atoms was intended to allow inference of the degree of molecular fragmentation accompanying degradation. Figure 1 gives the radiolabel positions for aldicarb (**1**) and its major metabolites aldicarb sulfoxide (**2**) and aldicarb sulfone (**3**).

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