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## ARTICLES

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### Penetration of Volatile Carbon-14 Residues into the Aerial Parts of Plants Grown Adjacent to or in [<sup>14</sup>C]Fonofos- or [<sup>14</sup>C]Carbofuran-Treated Soils

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The potential vapor absorption by plant greens of volatile <sup>14</sup>C compounds from soils treated with [<sup>14</sup>C]fonofos or [<sup>14</sup>C]carbofuran was investigated. Oats or peas were grown in insecticide-free soil adjacent to insecticide-treated soil or directly in the insecticide-treated soil. Some experiments were conducted in such a way that volatile <sup>14</sup>C compounds released from the insecticide-treated soil could be removed, thus preventing their contact with plant greens. Both [<sup>14</sup>C]fonofos and [<sup>14</sup>C]carbofuran in soils were to some extent broken down to <sup>14</sup>CO<sub>2</sub>. After its release into the air, some of this <sup>14</sup>CO<sub>2</sub> was absorbed by the aerial parts of plants that grew in untreated soil adjacent to insecticide-treated soil or directly within insecticide-treated soil. Since the major portion of radiocarbon in plant greens was water soluble, it appears that the <sup>14</sup>CO<sub>2</sub> picked up from the air was photosynthesized into water-soluble products. Only the smallest fraction of radiocarbon recovered from plants grown adjacent to or in [<sup>14</sup>C]fonofos-treated soil was benzene soluble and represented less than 0.5% of the total soil-applied <sup>14</sup>C. This radiocarbon was primarily associated with noninsecticidal metabolites. The addition of cow manure to [<sup>14</sup>C]-carbofuran-treated soil resulted in an increased production of <sup>14</sup>CO<sub>2</sub> and in an increased presence of water-soluble radiocarbon within the aerial plant parts.

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Not long after the introduction of synthetic pesticides for agricultural pest control, accumulation of some of these chemicals in soils was demonstrated, particularly with insecticides (Chisholm et al., 1951; Fleming, 1951; Lichtenstein, 1957). At the same time, health-related questions were raised in regard to the potential contamination of edible parts of crop plants that had grown in insecticide-contaminated soils. Since chlorinated hydrocarbon insecticides are barely water soluble, it was not anticipated at that time that any significant amounts of insecticides could be translocated via the root system into other plant parts. However, specially designed field experiments conducted during the period 1954-1958 showed that "lindane, DDT, and aldrin were absorbed into crops, the degree being dependent on the crop, the soil type in which the crop had grown, the insecticide, and its concentration within the soil. Carrots not only absorbed more insecticide than any other crop, but in the case of lindane concentrations in these carrots were greater than occurred in the soil" (Lichtenstein, 1959). Research conducted on plant root absorption of pesticides, except herbicides, was reviewed subsequently by Nash (1974). Although it had been established that aerial parts of plants grown in insecticide-contaminated soil can contain insecticide residues, relatively little research had been conducted concerning the possibility of leaf contamination by insecticide vapors. To eliminate pick up of lindane vapors by leaves, Lichtenstein and Schulz (1960) grew peas in insecticide-free sand, which was kept in glass jars surrounded by lindane-treated sand (Figure 1B). In addition, peas were grown in lindane-treated sand whose surface either had been covered with aluminum foil or was left uncovered (Figure 1A). Colorimetric analyses of these pea greens did not show evidence of absorption of lindane vapors through

the leaf cuticle. Ten years later, Nash and Beall (1970), however, reported that "the major environmental source of DDT (dichlorodiphenyltrichloroethane) residues in soybean plants arises from vapor movement from contaminated soil surfaces. In contrast, the presence of dieldrin, endrin, and heptachlor results primarily from root uptake and translocation through stems to leaves and seeds". In the 1962 Ph.D. thesis by Fuhr and the resulting publication by Sauerbeck and Fuhr (1966), it was stated that "10-30% of radiocarbon found in plant shoots originated from root-fixed <sup>14</sup>CO<sub>2</sub>". Anderegg and Lichtenstein (1981) demonstrated that the amounts of <sup>14</sup>CO<sub>2</sub> evolved within closed systems from fallow [<sup>14</sup>C]phorate-treated soil were nearly double of that determined when oats had grown in these soils, thus indicating that the <sup>14</sup>CO<sub>2</sub> evolved primarily from the soil rather than from the plants and that a fixation and assimilation of <sup>14</sup>CO<sub>2</sub> into photosynthetic products had probably taken place within the oats. In experiments with soil-applied herbicides, Fuhr and Mittelstaedt (1983) reported that "part of the radiocarbon in experimental plants may result from an assimilation of the <sup>14</sup>CO<sub>2</sub> released via the soil air". Experiments conducted in our laboratory with oats grown under bell jars in insecticide-free soil but in proximity to [<sup>14</sup>C]phorate-treated soil showed that the aerial parts contained 3% of the soil-applied radiocarbon, which only could have reached the leaves in vapor form.

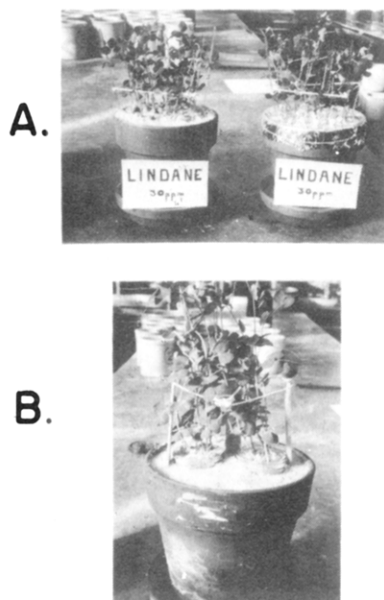
Studies described in this report were designed to investigate the route of contamination of the aerial parts of plants with <sup>14</sup>C compounds after the plants had grown in insecticide-free soil but in proximity to insecticide-treated soil or after growing directly in insecticide-treated soils. The test compounds used were [<sup>14</sup>C]fonofos and [<sup>14</sup>C]-carbofuran.

#### MATERIALS AND METHODS

**Chemicals.** [U-phenyl-<sup>14</sup>C]Fonofos (Dyfonate) (sp act. = 22.16 mCi/mM), nonradioactive fonofos, and its po-

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**Figure 1.** (A) Peas growing in noncovered and covered lindane-treated sand. (B) Peas growing in untreated sand within glass jars, surrounded by lindane-treated sand (Lichtenstein and Schulz, 1960).

tential metabolites (oxygen analogue of fonofos, thiophenol, diphenyl disulfide, methyl phenyl sulfone, and 2- or 3- or 4-hydroxymethyl phenyl sulfone) were obtained from Stauffer Chemical Co., Mountain View CA. [*carbonyl- $^{14}\text{C}$* ]Carbofuran (sp act. = 2.56 mCi/mM) and nonradioactive carbofuran were obtained from FMC Corp., Middleport, NY. [ $^{14}\text{C}$ ]Fonofos or [ $^{14}\text{C}$ ]carbofuran were diluted with the respective nonradioactive insecticide before their addition to soil.

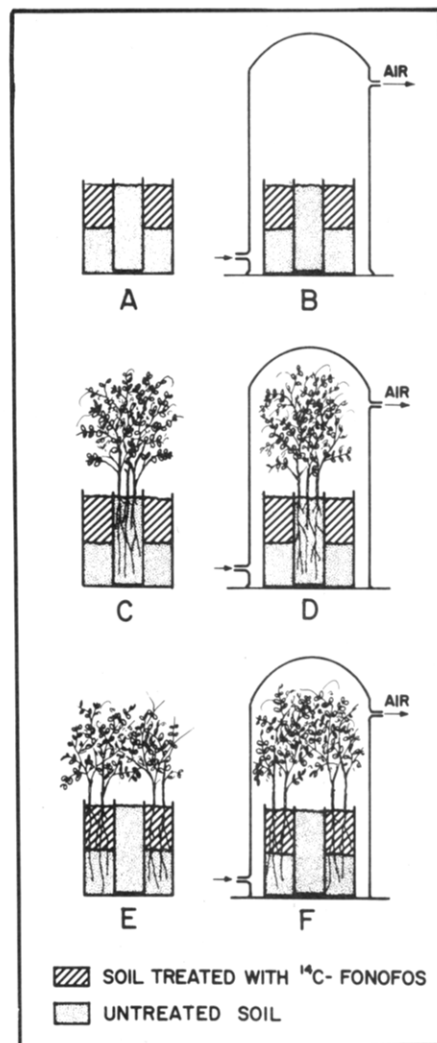
**Solvents.** Acetone, benzene, chloroform, ethyl acetate, hexane, pentane, dioxane, methyl-Cellosolve, and dichloromethane were redistilled before use. Methanol, toluene, diethyl ether, and ethanolamine were of analytical grade.

**Soils.** A Plano silt loam soil (4.7% organic matter, 5% sand, 71% silt, and 24% clay, pH 6.0), free of insecticide residues, was collected at the University of Wisconsin Experimental Farm near Madison. A Plainfield sand (0.6% organic matter, 93.4% sand, 3.6% silt, 3% clay, pH 5.6), free of insecticide residues, was collected in Adams County, Wisconsin. These soils were stored in a moist condition at  $22 \pm 2^\circ\text{C}$  prior to use. In experiments with [ $^{14}\text{C}$ ]fonofos a mixture of 2 parts of loam and 1 part of sand soil was used, while experiments with [ $^{14}\text{C}$ ]carbofuran were conducted with the loam soil.

**Cow Manure.** Cow manure, obtained from the University of Wisconsin dairy barn, was air-dried at room temperature, ground to a fine powder, and stored at  $4^\circ\text{C}$  before use.

**Soil Treatment.** The 2:1 loam-sand soil mixture was screened and treated as described (Lichtenstein et al., 1978) with [ $^{14}\text{C}$ ]fonofos to yield concentrations of 4 ppm. In experiments with [ $^{14}\text{C}$ ]carbofuran, loam soil was screened and treated with the insecticide at 4.5 ppm. Aliquots of freshly treated soils were removed and extracted to determine the actual soil application level. This level was then used as the initially applied dose from which all later data were calculated. More details are presented for each experiment under Experimental Procedures.

**Plants.** Pea seeds (*Pisum sativum*-Alaska wilt resistant) and oat seeds (*Avena sativa*) were purchased from a local dealer. The seeds were pregerminated for 72 hours



**Figure 2.** Experimental setup for growing plants in untreated soil but surrounded by  $^{14}\text{C}$ -insecticide-treated soil (C, D) or in  $^{14}\text{C}$ -insecticide-treated soil (E, F). A, C, and E = open systems. B, D, and F = closed systems to facilitate trapping of volatile  $^{14}\text{C}$  compounds.

between wet paper towels in glass dishes before planting in the insecticide-treated or untreated soils.

**Extraction and Analyses.** In experiments with [ $^{14}\text{C}$ ]fonofos soils and plant roots were combusted to  $^{14}\text{CO}_2$  to determine the total  $^{14}\text{C}$  content as described by Flashinsky and Lichtenstein (1974). Plant greens were extracted and analyzed by liquid scintillation counting (LSC), thin-layer chromatography (TLC) and autoradiography as described by Lichtenstein et al. (1982). In experiments with [ $^{14}\text{C}$ ]carbofuran, soils and plants were extracted and analyzed as described by Koepe and Lichtenstein (1982). Polyurethane traps for lipid-soluble volatiles were extracted with hexane.  $^{14}\text{CO}_2$  evolving from the plant-soil system was trapped in a KOH trap and analyzed and verified as described by Walter-Echols and Lichtenstein (1978).

#### EXPERIMENTAL PROCEDURES

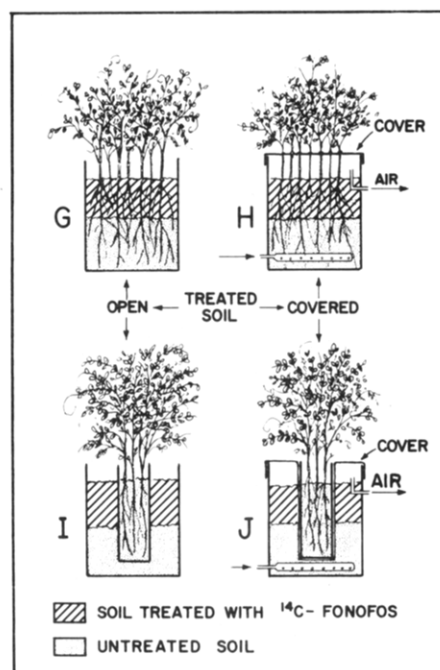
**Release of  $^{14}\text{CO}_2$  and Uptake of  $^{14}\text{C}$  Compounds by Plants from [ $^{14}\text{C}$ ]Fonofos-Treated Soil.** Experiments were conducted to evaluate the source and identity of  $^{14}\text{C}$  compounds recovered from the aerial parts of peas or oats grown in or adjacent to [ $^{14}\text{C}$ ]fonofos-treated soil. The experimental setup (Figure 2) consisted of round cardboard cartons (10-cm height, 8.5-cm diameter) with a glass vial (10-cm height, 4-cm diameter) inserted in the center of

each carton. This glass vial was filled with 100 g (dry weight) of untreated soil. In addition 200 g (dry weight) of untreated soil was placed in ringlike form on the bottom of each carton around each vial. Another 200 g (dry weight) of soil, previously treated with [ $^{14}\text{C}$ ]fonofos (0.73  $\mu\text{Ci}$ ) at 4 ppm, was then placed within the carton on top of the ringlike untreated soil layer. To test if plant greens grown in insecticide-free soil would pick up  $^{14}\text{C}$  compounds from surrounding insecticide-treated soil, 5 pea or 20 oat seedlings were grown within the inner untreated soil (Figure 2C) for 14 days at  $25 \pm 1^\circ\text{C}$  under Gro-Lux lamps on a 16-h photoperiod. To collect  $^{14}\text{CO}_2$  and lipid-soluble volatile compounds evolving from the insecticide-treated soil, plants were also grown as described above but were covered with bell jars (Figure 2D) as described by Anderegg and Lichtenstein (1981). To determine the fate of [ $^{14}\text{C}$ ]fonofos-derived radiocarbon in fallow soils, experiments without plants were conducted as shown in Figure 2.

Experiments as depicted in Figure 2E,F were conducted to compare root absorption of [ $^{14}\text{C}$ ]fonofos-derived radiocarbon with vapor absorption by leaves. Twenty pea or 80 oat seedlings were planted in the outer ring of [ $^{14}\text{C}$ ]fonofos-treated soil and grown for 14 days at  $25 \pm 1^\circ\text{C}$  and under Gro-Lux lamps on a 16-h photoperiod. Air was passed continuously through each of the closed systems at a flow rate of 100 mL/min.

All experiments were conducted in duplicate. At the end of the plant growing period, each system was dismantled, and plant greens were extracted and analyzed as described. Plant roots and insecticide-treated and untreated soil were analyzed by combustion procedures.

**Effects of the Removal of  $^{14}\text{CO}_2$  from [ $^{14}\text{C}$ ]Fonofos-Treated Soil on the Presence of  $^{14}\text{C}$  Compounds in Plant Greens Grown in or Adjacent to Insecticide-Treated Soil.** Preliminary data obtained from experiments in our laboratory had indicated that  $^{14}\text{CO}_2$  released from  $^{14}\text{C}$ -insecticide-treated soil might be the source of  $^{14}\text{C}$  compounds recovered later from the aerial parts of the plants. Experiments were therefore conducted to eliminate contact of plant greens with  $^{14}\text{CO}_2$  that originated from [ $^{14}\text{C}$ ]fonofos-treated soil. As shown in Figure 3 (G and H) peas were grown in the insecticide-treated soil, whose surface had been tightly covered, and also in non-covered insecticide-treated soil that served as controls. To accomplish this, 400 g (dry weight) of untreated soil was placed into each of four polyurethane containers (12.5-cm height, 9-cm diameter). After that, 400 g (dry weight) of soil treated with [ $^{14}\text{C}$ ]fonofos (0.91  $\mu\text{Ci}$ ) at 4 ppm was placed on top of the insecticide-free soil in each of the four containers. Two of these containers (Figure 3H), fitted previously with an air-inlet tube at the bottom and an air-outlet tube just above the soil surface, were used to remove  $^{14}\text{CO}_2$  from these systems. The air-outlet tube was connected to a polyurethane filter to trap lipid-soluble radiocarbon and to a 0.1 N KOH trap for  $^{14}\text{CO}_2$  collection. Air was passed continuously through these systems at 100 mL/min. The top of each of these two containers was sealed tightly with a plastic Petri dish through which 22 holes (5-mm diameter) had been drilled previously. Twenty pea seedlings were then planted through 20 holes, and two rubber stoppers were inserted in the 2 remaining holes. The remaining opening around each plant stem and the cover were carefully closed with plastic putty. Plants were then grown in the insecticide-treated soil for 21 days at  $25 \pm 1^\circ\text{C}$  under Gro-Lux lamps on a 16-h photoperiod. The initial weight of each container was maintained through the growing period by adding tap water through



**Figure 3.** Effect of the removal of  $^{14}\text{CO}_2$  from [ $^{14}\text{C}$ ]fonofos-treated soil (H and J) on the presence of  $^{14}\text{C}$  compounds in the aerial parts of plants grown in insecticide-treated soil (G and H) or in untreated soil but surrounded by insecticide-treated soil (I and J).

the two remaining holes, whose rubber stoppers could be removed for watering purposes.

In each of the uncovered soils in the two remaining containers (Figure 3G) 20 pea seedlings were planted and grown as controls for 21 days as described above. The initial weight of each container was maintained by adding water as necessary during the growing period. At the end of the incubation period, pea greens were extracted and analyzed for their radiocarbon content. TLC, autoradiography, and LSC of the organic solvent extracts of pea greens were also performed. Pea roots and treated and untreated soils were analyzed by combustion procedures as described.

In an additional series of experiments peas or oats were grown in insecticide-free soil but were surrounded by insecticide-treated soil as shown in Figure 3 (I and J). In duplicate tests, 5 pea seedlings or 20 oat seedlings were planted in 300 g (dry weight) of insecticide-free soil contained within glass vials (10-cm height, 4-cm diameter). These vials were placed in the center of each of two polyurethane containers (12.5-cm height, 9-cm diameter), surrounded by a bottom ring layer of 300 g (dry weight) of untreated soil onto which a ring of 300 g (dry weight) of [ $^{14}\text{C}$ ]fonofos (1.33  $\mu\text{Ci}$ ) treated (4 ppm) soil had been placed. To prevent pick up of volatile radiocarbon from the insecticide-treated soil, this treated soil was covered with plastic wrap (Figure 3J). Air between the soil surface and below the plastic cover was removed by means of a constant air flow (100 mL/min) that was passed through a polyurethane and a 0.1 N KOH trap. For control purposes, two additional experiments were setup as described above, except the insecticide-treated soil was not covered with plastic material and no air was passed through the soil (Figure 3I). In all experiments, peas were grown for 14 days and oats for 11 days under the conditions described above. After determination of the initial weight of each of the four containers, tap water was added to keep this weight. Loss of water from the covered soils was replaced with a syringe. Holes thus made in the plastic cover were later closed with Scotch tape. At the end of the experi-

Table I. Release of  $^{14}\text{CO}_2$  and Uptake of  $^{14}\text{C}$  by Peas from [ $^{14}\text{C}$ ]Fonofos-Treated Soil<sup>a</sup>

	$^{14}\text{C}$ recovered, % of applied to soil <sup>a</sup>					
	no plants in soil		peas grown in soil for 14 days			
	A, <sup>d</sup> open <sup>e</sup>	B, closed <sup>f</sup>	surrounded <sup>b</sup>		[ $^{14}\text{C}$ ]fonofos <sup>c</sup>	
		C, open	D, closed	E, open	F, closed	
$^{14}\text{CO}_2$ <sup>g</sup>		2.99 ± 0.2		2.01 ± 0.1		1.08 ± 0.0
pea greens						
benzene <sup>h</sup>			0.01 ± 0.01	0.06 ± 0.01 <sup>m</sup>	0.49 ± 0.02	0.12 ± 0.01 <sup>i</sup>
water <sup>h</sup>			0.01 ± 0.01	1.06 ± 0.12 <sup>i</sup>	1.83 ± 0.21	2.00 ± 0.25
bound <sup>h</sup>			0.01 ± 0.01	0.21 ± 0.03 <sup>m</sup>	0.52 ± 0.13	2.46 ± 0.13 <sup>i</sup>
total (G)			0.03 ± 0.02	1.33 ± 0.10 <sup>i</sup>	2.84 ± 0.33	4.58 ± 0.37 <sup>m</sup>
total/g			0.01 ± 0.01	0.53 ± 0.03 <sup>i</sup>	0.24 ± 0.03	0.36 ± 0.04 <sup>m</sup>
pea roots (R)			0.00	0.09 ± 0 <sup>k</sup>	17.51 ± 1.3	16.72 ± 0.7
total (G + R)			0.03 ± 0.02	1.42 ± 0.03 <sup>k</sup>	20.35 ± 1.0	21.30 ± 0.3
soils						
treated <sup>i</sup>						
U	67.47 ± 0.5	84.42 ± 0.1 <sup>k</sup>	70.29 ± 0.1	87.96 ± 1.3 <sup>i</sup>	68.85 ± 4.8	67.77 ± 1.7
L	28.70 ± 0.3	11.03 ± 0.8 <sup>i</sup>	25.33 ± 0.5	7.28 ± 0.8 <sup>k</sup>	7.70 ± 3.0	8.06 ± 0.6
total	96.17 ± 0.8	95.45 ± 0.8	95.62 ± 0.4	95.24 ± 0.6	76.55 ± 1.9	75.83 ± 1.2
untreated <sup>j</sup>	0.02 ± 0	0.41 ± 0.03 <sup>i</sup>	0.02 ± 0	0.37 ± 0.02 <sup>i</sup>	0.0	0.10 ± 0 <sup>k</sup>
total	96.19 ± 0.9	98.85 ± 0.9	95.67 ± 0.4	99.04 ± 0.8 <sup>m</sup>	96.90 ± 1	98.31 ± 0.8

<sup>a</sup> [ $^{14}\text{C}$ ]Fonofos (0.74  $\mu\text{Ci}$ ) was mixed with 200 g of soil (dry weight) at 4 ppm and placed on top of 200 g (dry weight) of untreated soil (Figure 2), both surrounding a center core of 200 g (dry weight) of insecticide-free soil. Results are averages of duplicated tests. <sup>b</sup> Pea plants were grown in insecticide-free soil but were surrounded by [ $^{14}\text{C}$ ]fonofos-treated soil (Figure 2C, D). <sup>c</sup> Pea plants were grown in the outer ring of insecticide-treated soil (Figure 2E, F). <sup>d</sup> Capital letters A-F refer to Figure 2. <sup>e,f</sup> Plants were grown in open systems (e) or in soils under bell jars (f). <sup>g</sup>  $^{14}\text{CO}_2$  trapped in 0.1 N KOH. <sup>h</sup> Benzene and water extracted phases of pea greens. Bound = unextractable  $^{14}\text{C}$ . <sup>i,j</sup> U = upper insecticide-treated soil layer and L = lower untreated soil layer, both surrounding a glass vial that contained the (j) inner untreated soil core. <sup>k-m</sup> Results obtained with closed systems are significantly different from those obtained with comparable open systems at the 0.1% (k), 1% (l), and 5% (m) levels (Student's *t* test).

ments, plant greens were extracted and analyzed by LSC. Since only pea or oat greens from control experiments with noncovered soils contained measurable amounts of radiocarbon, TLC, autoradiography, and LSC could be performed with the benzene extraction phases of these plant greens. Plant roots and insecticide-treated and untreated soils were analyzed by combustion procedures.

**Effects of Cow Manure on the Production of  $^{14}\text{CO}_2$  from [ $^{14}\text{C}$ ]Carbofuran-Treated Soil and on the Pickup of Volatile  $^{14}\text{C}$  Compounds by the Aerial Parts of Oats.** Studies conducted previously in our laboratory had shown that the production  $^{14}\text{CO}_2$  from [ring- $^{14}\text{C}$ ]carbofuran in soil was significantly increased when cow manure was added to this soil (Koeppel and Lichtenstein, 1984). We also had observed that the amounts of  $^{14}\text{CO}_2$  produced from [ $^{14}\text{C}$ ]carbofuran-treated soil were significantly greater when [carbonyl- $^{14}\text{C}$ ]carbofuran rather than [ring- $^{14}\text{C}$ ]carbofuran was used. It was for these reasons that the present studies were conducted with [carbonyl- $^{14}\text{C}$ ]carbofuran and cow manure in soil in order to produce the maximum amounts of  $^{14}\text{CO}_2$  for potential pick up by the aerial parts of oat plants. Four duplicate experiments were conducted in closed systems with a Plano silt loam. The experimental setup was the same as depicted in Figure 2B,D, except that [ $^{14}\text{C}$ ]carbofuran was used. In all eight cartons the center glass vial contained 115 g (dry weight) of untreated soil, while the surrounding ring of soil consisted of a lower layer of 170 g (dry weight) of untreated soil with an upper layer of 85 g (dry weight) of soil previously treated with [carbonyl- $^{14}\text{C}$ ]carbofuran (0.77  $\mu\text{Ci}$ ) at 4.5 ppm. Two duplicate experiments (four tests) were conducted with insecticide-treated soil that had also been mixed with cow manure (3.8 g of dry weight)/85 g of soil and two duplicate experiments (four tests) with soil treated only with the insecticide, thus serving as controls for the effects of cow manure.

To study the potential pick up of insecticide-derived  $^{14}\text{CO}_2$  by plants, 15 oat seedlings were planted in the inner untreated soil in each of four glass vials, of which two were surrounded by insecticide-treated soil plus cow manure and two with insecticide-treated soil only. Finally, each of the

eight cartons (four with cow manure and four without) was covered with a bell jar and connected to polyurethane and 0.1 N KOH traps as described above. During the 14-day incubation period, air was purged continuously through the system at 100 mL/min. Experiments were conducted at  $25 \pm 1$  °C under Gro-Lux lamps on a 16-h photoperiod. At the end of the incubation period, plant tops, roots, the inner core of untreated soil, and all the soil surrounding the glass vials were extracted and analyzed by LSC as described.

## RESULTS AND DISCUSSION

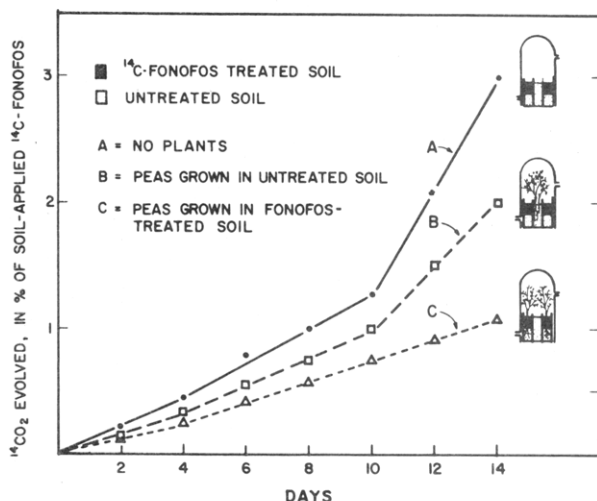
**Release of  $^{14}\text{CO}_2$  and Uptake of  $^{14}\text{C}$  Compounds by Plants from [ $^{14}\text{C}$ ]Fonofos-Treated Soil.** Results obtained from experiments conducted in open or closed systems with soils and pea plants grown either in insecticide free or in insecticide-treated soils are summarized in Table I. The amounts of  $^{14}\text{CO}_2$  trapped from the insecticide-treated soil (Figure 2B,D,F) were largest in the absence of plants, constituting 3% of the soil-applied radiocarbon, smallest where plants had been grown within the insecticide-treated soil (1% of soil-applied radiocarbon), and in between these two values (2% of soil-applied radiocarbon) when plants were grown in untreated soil that was surrounded by [ $^{14}\text{C}$ ]fonofos-treated soil. These differences are significant at the 1% or 2% level (Student's *t* test). Differences observed in the trapping of  $^{14}\text{CO}_2$  over the 2-week incubation period (Figure 4) became most noticeable during the second week when plants had developed more leaf material and, therefore, could pick up more  $^{14}\text{CO}_2$ .

Peas grown in insecticide-free soil (Table I, "surrounded") contained soil-applied radiocarbon although they had no physical contact with the  $^{14}\text{C}$ -insecticide-treated soil. The only possibility of leaf contamination could, therefore, have only occurred in vapor form, most probably in the form of  $^{14}\text{CO}_2$ . This is also supported by the finding that plants grown in untreated soil under bell jars contained 1.42% (1.33% in leaves, 0.09% in roots) of the applied radiocarbon. When, the amounts of  $^{14}\text{CO}_2$  trapped (2% of soil-applied radiocarbon) are added to this,

**Table II.** [ $^{14}\text{C}$ ]Fonofos and Metabolites Recovered from Plant Greens Grown in Insecticide-Free Soil but "Surrounded" by [ $^{14}\text{C}$ ]Fonofos-Treated Soil or Grown Directly in Insecticide-Treated Soil ([ $^{14}\text{C}$ ]Fonofos)

compd <sup>a</sup>	$R_f$	$^{14}\text{C}$ recovered from plant greens, % of all benzene-soluble <sup>e</sup> radiocarbon							
		peas grown in soil				oats grown in soil			
		surrounded		[ $^{14}\text{C}$ ]fonofos		surrounded		[ $^{14}\text{C}$ ]fonofos	
		C, b open <sup>c</sup>	D, closed <sup>d</sup>	E, open	F, closed	C, open	D, closed	E, open	F, closed
fonofos	0.69	0.0	10.0	0.6	2.3	0.0	19.1	1.8	12.6
F-oxon	0.30	1.8	1.9	7.9	6.4	0.0	12.0	6.0	9.6
MPSO <sub>2</sub>	0.40	0.0	5.5	45.3	18.7	0.0	0.0	42.7	28.9
PS, TP	0.78	0.0	0.0	31.1	52.5	0.5	0.0	11.7	5.9
others	0.18	0.0	0.0	0.3	0.1	0.0	0.0	0.4	2.2
unknown 1	0.60	0.7	0.6	0.8	3.4	0.1	0.3	3.8	4.0
unknown 2	0.50	0.0	0.1	0.1	0.9	0.1	0.0	0.9	1.3
unknown 3	0.00	97.5	81.9	13.9	15.7	99.3	68.6	32.7	35.5

<sup>a</sup> Determined by TLC separation and LSC. F-oxon = fonofos-oxon; MPSO<sub>2</sub> = methyl phenyl sulfone; PS = diphenyl disulfide; TP = thiophenol; others = trace amounts of 2- and/or 4-hydroxyphenyl methyl sulfone. <sup>b</sup> Capital letters C–F refer to Figure 2. <sup>c,d</sup> Plants grown (C) in open systems or (d) in soils under bell jars ("closed"). <sup>e</sup> Data for all benzene-soluble  $^{14}\text{C}$  in peas are presented in Table I. Comparable data obtained with oats, expressed in percent of soil-applied  $^{14}\text{C}$ , are 0.01% ("surrounded—open"), 0.22% ("surrounded—closed"), 0.34% ("[ $^{14}\text{C}$ ]fonofos—open"), and 0.30% ("[ $^{14}\text{C}$ ]fonofos—closed").

**Figure 4.** Amounts of  $^{14}\text{CO}_2$  trapped over a 2-week period from [ $^{14}\text{C}$ ]fonofos in soils without plants (A) or with plants (B and C).

a total of 3.4% is obtained that is similar to the amount of  $^{14}\text{CO}_2$  trapped (3% of soil-applied radiocarbon) in the absence of plants.

Plants grown within [ $^{14}\text{C}$ ]fonofos-treated soil (Table I, "[ $^{14}\text{C}$ ]fonofos") contained a total of 20–21% of the soil-applied  $^{14}\text{C}$ , most of it (17% of applied) in the plant roots. The finding that in these experiments only 1% of the soil-applied  $^{14}\text{C}$  was trapped as  $^{14}\text{CO}_2$  is to some extent related to an increased leaf absorption of  $^{14}\text{CO}_2$  by the 20 pea plants growing in the outer ring as opposed to only 5 that could be grown in the untreated soil within the inner vial (Figure 2D). Pea greens grown in closed systems contained significantly larger amounts of  $^{14}\text{C}$  compounds than those grown in open systems. It appears that the restricted ventilation in the closed system made absorption of volatile  $^{14}\text{C}$  compounds more feasible. Of the total radiocarbon recovered from pea greens, 33–80% were in water-soluble form (Table I). These substances could, to a large extent, have been formed by fixation of  $^{14}\text{CO}_2$  into water-soluble photosynthetic products.

Untreated soils within the inner vials of each experimental setup contained significant amounts of  $^{14}\text{C}$ , primarily in studies with closed systems. This contamination also must have occurred due to vapors. The amounts of radiocarbon recovered from the insecticide-treated soils ranged from 95 to 96% of the originally applied [ $^{14}\text{C}$ ]fonofos except in experiments where plants had been grown directly within the outer ring of insecticide-treated soil.

In this latter case only 76% of applied  $^{14}\text{C}$  was recovered at the end of the experiments from these soils.

Experiments as described above were also conducted with oats. Since results were rather similar to those reported for peas, no special table is presented for oats.

The majority of  $^{14}\text{C}$  compounds recovered from both pea and oat leaves were in water-soluble form, while in most cases benzene-soluble radiocarbon represented the smallest fraction. To obtain information about the identity of these benzene-soluble compounds, the organic extraction phases were subjected to analyses by TLC, autoradiography, and LSC. Standard reference compounds, mentioned under Chemicals above and in Table II, were used for comparison purposes. With the exception of fonofos and its oxygen analogue (fonofos-oxon), all the other compounds have been found not to be insecticidal to house flies (Liang and Lichtenstein, 1980). As shown in Table I, the amounts of benzene-soluble  $^{14}\text{C}$  compounds recovered from pea greens grown in untreated soil ("surrounded") were rather small and amounted to only 0.01% ("open") and 0.06% ("closed") of the [ $^{14}\text{C}$ ]fonofos applied to the outer ring of soil. For oats these figures were 0.01% and 0.22%, respectively. Data in Table II show that 69–99% of these benzene-soluble  $^{14}\text{C}$  compounds recovered from greens of peas or oats were associated with a rather polar compound ( $R_f$  0.00), while 0.0–31.1% were associated with fonofos plus fonofos-oxon.

Greens from peas grown within the insecticide-treated soil (Table I, "[ $^{14}\text{C}$ ]fonofos") contained 0.1% and 0.5% of the soil-applied radiocarbon in benzene-soluble form. Only 14% and 16% of these organic-soluble compounds were associated with the most polar compound ( $R_f$  0.00), 8.5% and 8.7% with fonofos plus fonofos-oxon, but 71% and 76% with methyl phenyl sulfone (MPSO<sub>2</sub>) diphenyl disulfide (PS), and thiophenol (TP). With oat greens, these figures were 33% and 36%, 8% and 22%, and 35% and 54%, respectively. Data, therefore, indicate that only minute amounts of fonofos and fonofos-oxon were recovered from plant greens, primarily under conditions where plants had been grown in closed systems.

**Effects of the Removal of  $^{14}\text{CO}_2$  from [ $^{14}\text{C}$ ]Fonofos-Treated Soil on the Presence of  $^{14}\text{C}$  Compounds in Plant Greens Grown in or Adjacent to Insecticide-Treated Soil.** Pea plants were grown for 21 days in [ $^{14}\text{C}$ ]fonofos-treated soil that was covered in such a way that soil-derived  $^{14}\text{CO}_2$  could be removed and not come into contact with the aerial parts of the plants (Figure 3H). For control purposes plants were also grown in noncovered soils (Figure 3G). Results (Table III) indicate that with covered

**Table III. Effects of the Removal of <sup>14</sup>CO<sub>2</sub> from [<sup>14</sup>C]Fonofos-Treated Soil on the Presence of <sup>14</sup>C Compounds in Pea Greens Grown for 21 Days in This Soil<sup>a</sup>**

	<sup>14</sup> C recovered, % of applied to soil <sup>a</sup> for peas grown in insecticide-treated soil	
	G, <sup>b</sup> open	H, <sup>b</sup> covered
<sup>14</sup> CO <sub>2</sub> from soil <sup>c</sup>		3.97 ± 0.56
pea greens		
benzene <sup>d</sup>	0.48 ± 0.04 (9) <sup>e</sup>	0.26 ± 0.08 (13)
water <sup>d</sup>	4.45 ± 0.69 (85)	1.53 ± 0.24 <sup>i</sup> (76)
bound <sup>d</sup>	0.29 ± 0.09 (6)	0.23 ± 0.12 (11)
total (T)	5.22 ± 0.74 (100)	2.02 ± 0.44 <sup>i</sup> (100)
total/g	0.77 ± 0.02	0.55 ± 0.07 <sup>j</sup>
pea roots	1.23 ± 0.13	1.04 ± 0.07
soil		
treated U <sup>e</sup>	76.79 ± 0.13	63.21 ± 1.47 <sup>h</sup>
untreated L <sup>e</sup>	11.59 ± 0.28	20.96 ± 1.68 <sup>h</sup>
total	88.38 ± 0.41	84.17 ± 0.21 <sup>h</sup>
miscellaneous <sup>f</sup>		3.56 ± 0.20
total	94.83 ± 0.46	94.76 ± 0.85

<sup>a</sup> [*ring-<sup>14</sup>C]Fonofos (0.91 μCi) was mixed with 400 g of soil (dry weight) at 4 ppm and placed on top of 400 g (dry weight) of insecticide-free soil. Results are averages of duplicated tests. <sup>b</sup> Figure 3: G = plants grew in insecticide-treated soil that was not covered; H = plants grew through holes in a plastic lid that covered the insecticide-treated soil. <sup>c</sup> <sup>14</sup>CO<sub>2</sub> released from treated soil was collected below the plastic cover and trapped in 0.1 N KOH (Figure 3H). <sup>d</sup> Benzene and water extraction phases of pea greens. Bound = unextractable <sup>14</sup>C. <sup>e</sup> U = upper insecticide-treated soil layer. L = lower untreated soil layer. <sup>f</sup> <sup>14</sup>C recovered from polyurethane traps and tygon tubing. <sup>g</sup> Values in parentheses are % T = <sup>14</sup>C in percent of total radiocarbon recovered. <sup>h-j</sup> Results obtained with covered soils are significantly different from uncovered (open) soils at the 1% (h), 3% (i), and 5% (j) level (Student's *t* test).*

soils a total of 4% of the soil-applied radiocarbon was removed as <sup>14</sup>CO<sub>2</sub> during the 3-week growing period, while the pea greens contained only 2% of the soil-applied <sup>14</sup>C. Because of the tight soil cover, this amount could only have reached the leaves by translocation within the plant systems. When plants were grown in noncovered soils and were thus exposed to the air above the soil surface, the total amounts of radiocarbon recovered from the plant greens were more than double of that observed with plants grown in covered soils. The sum of radiocarbon removed as <sup>14</sup>CO<sub>2</sub> (4% of the soil-applied insecticide) and that found

in plant greens (2%) grown in these covered soils was similar to the amounts of <sup>14</sup>C compounds (5.2%) recovered from pea greens in control experiments. These findings indicate that a major portion of <sup>14</sup>C in the plant greens originated from soil-released <sup>14</sup>CO<sub>2</sub> and was not the result of translocation of <sup>14</sup>C compounds within the plant system.

Of the total radiocarbon recovered from pea greens grown within open or covered soils, 85% and 76% were in water-soluble form, respectively (Table III). Benzene-soluble compounds, however, represented only a minor fraction, amounting to 0.48% and 0.26% of the soil-applied radiocarbon, respectively, or to 9% and 13% of the total <sup>14</sup>C recovered from pea greens. Analyses by TLC of these organic-soluble extraction phases showed that 62% and 73% were associated with methyl phenyl sulfone, 3% and 4% with fonofos-oxon, 1% with fonofos, and 20% and 30% with an unknown substance (*R<sub>f</sub>* 0.00).

To study further the potential pick up of volatile <sup>14</sup>C compounds by plants that had no direct contact with insecticide-treated soils, peas and oats were also grown in insecticide-free soil that was surrounded by covered [<sup>14</sup>C]fonofos-treated soil (Figure 3I,J). As shown in Table IV, the amounts of <sup>14</sup>CO<sub>2</sub> removed from the covered soils and trapped were 1% and 1.2% of the soil-applied radiocarbon. On the basis of total combustion analyses, peas or oats grown in these untreated soil did not contain radiocarbon. Plants grown in insecticide-free, noncovered soils, however, contained very small amounts (0.06% with peas and 0.08% with oats) of the soil-applied radiocarbon, indicating that these amounts must have been absorbed by the plant greens in the form of volatile <sup>14</sup>C compounds. Most of the radiocarbon in the plant greens, however, was in water-soluble form. Although the amounts of benzene-soluble compounds were quite small, they could be analyzed by TLC, autoradiography, and LSC. In pea greens, 86% of these compounds were associated with an unknown compound (*R<sub>f</sub>* 0.00), 3.5% with methyl phenyl sulfone, 2.8% with fonofos-oxon, and 1.5% with fonofos. Figures for oats were 67%, 8.6%, 1%, and 1.7%, respectively. Analyses of pea or oat roots by total combustion methods did not reveal the presence of radiocarbon.

Data reported in Table IV clearly indicate that volatile <sup>14</sup>C compounds had been picked up by the plant greens,

**Table IV. Pickup of <sup>14</sup>C by Peas and Oats Grown in Insecticide-Free Soil but Surrounded by [<sup>14</sup>C]Fonofos-Treated Soil<sup>a</sup>**

	<sup>14</sup> C recovered, % of applied to soil, <sup>a</sup> for peas or oats grown <sup>b</sup> in untreated soil			
	peas		oats	
	I, <sup>c</sup> open	J, <sup>c</sup> covered	I, open	J, covered
<sup>14</sup> CO <sub>2</sub> from soil <sup>d</sup>		1.2 ± 0.0		1.0 ± 0.0
plant greens				
greens				
benzene <sup>e</sup>	0.01 ± 0.00		0.01 ± 0.00	
water <sup>e</sup>	0.04 ± 0.01		0.07 ± 0.01	
bound <sup>e</sup>	0.01 ± 0.00		0.00 ± 0.00	
total	0.06 ± 0.00	0.0	0.08 ± 0.00	0.0
total/g	0.03 ± 0.01	0.0	0.04 ± 0.00	0.0
plant roots	0	0	0	0
soil				
treated				
U <sup>c</sup>	85.4 ± 3.3	83.4 ± 2.1	83.0 ± 0.6	83.8 ± 2.3
L <sup>c</sup>	7.3 ± 1.7	7.7 ± 0.9	5.2 ± 0.2	6.6 ± 0.6
total	92.7 ± 1.4	91.1 ± 1.3	88.2 ± 0.8	90.4 ± 3.0
untreated/ <sup>f</sup>	TR <sup>g</sup>	0	TR	0
miscellaneous <sup>h</sup>		0.13 ± 0.01		0.12 ± 0.01
total	92.8 ± 1.3	92.4 ± 1.2	88.3 ± 0.8	91.5 ± 3.0

<sup>a</sup> [*ring-<sup>14</sup>C]Fonofos (1.33 μCi) was mixed with 300 g of soil (dry weight) at 4 ppm and placed on top of 300 g (dry weight) of untreated soil, both surrounding a glass vial containing 300 g (dry weight) of insecticide-free soil. Results are averages of duplicated tests. <sup>b</sup> Oats and peas were grown for 11 and 14 days, respectively. <sup>c</sup> Figure 3: I = outer ring consisting of an upper layer (U) of treated soil and a lower layer (L) of untreated soil was not covered; J = same as I, but the treated soil was covered. <sup>d</sup> Same as footnote c in Table III. <sup>e</sup> Same as footnote d in Table III. <sup>f</sup> Untreated: the inner core of soil in which the plants were grown had not been treated with the insecticide. <sup>g</sup> TR = trace. <sup>h</sup> Same as footnote f in Table III.*

**Table V. Pickup of  $^{14}\text{C}$  by Oat Plants Grown for 14 Days in a Closed System in Insecticide-Free Loam Soil but Surrounded by [ $^{14}\text{C}$ ]Carbofuran-Treated Soil<sup>a</sup>**

	$^{14}\text{C}$ recovered, <sup>a</sup> for [ $^{14}\text{C}$ ]carbofuran-treated soil, plus			
	none, plus		cow manure, <sup>b</sup> plus	
	none, B <sup>c</sup>	oats, D <sup>c</sup>	none, B <sup>c</sup>	oats, D <sup>c</sup>
$^{14}\text{CO}_2$ <sup>d</sup>	6.43 ± 0.5	4.38 ± 0.02	24.24 ± 1.1 <sup>k</sup>	16.97 ± 0.66 <sup>k</sup>
plant tops (T)				
organic soluble <sup>e</sup>		0.32 ± 0.04		0.94 ± 0.03 <sup>k</sup>
water soluble		0.52 ± 0.01		2.60 ± 0.24 <sup>k</sup>
bound <sup>f</sup>		0.55 ± 0.05		2.12 ± 0.21 <sup>k</sup>
total		1.40 ± 0.10		5.66 ± 0.01 <sup>j</sup>
plant roots (R) <sup>g</sup>		0.45 ± 0.11		1.85 ± 0.42 <sup>j</sup>
total (T + R)		1.85 ± 0.12		7.50 ± 0.29 <sup>k</sup>
soil, untreated <sup>h</sup>	0.08 ± 0.01	0.21 ± 0.04	0.30 ± 0.07 <sup>i</sup>	0.84 ± 0.01 <sup>k</sup>
soil, treated <sup>i</sup>	96.62 ± 0.72	95.67 ± 0.48	66.77 ± 0.69 <sup>k</sup>	67.81 ± 0.48 <sup>j</sup>
organic soluble <sup>e</sup>	94.90 ± 0.67	94.06 ± 0.63	62.38 ± 0.75 <sup>j</sup>	63.33 ± 0.22 <sup>j</sup>
water soluble	0.11 ± 0.05	0.06 ± 0.04	0.72 ± 0.09 <sup>j</sup>	0.75 ± 0.21
bound <sup>f</sup>	1.61 ± 1.0	1.55 ± 0.19	3.67 ± 0.03 <sup>k</sup>	3.73 ± 0.05 <sup>k</sup>
total	103.1 ± 0.09	102.1 ± 0.04	91.33 ± 0.58 <sup>k</sup>	93.12 ± 0.30 <sup>j</sup>

<sup>a</sup> Percent of applied to outer soil: [ $^{14}\text{C}$ ]carbofuran (0.77  $\mu\text{Ci}$ ) was mixed with 85 g of loam soil (dry weight) at 4.5 ppm and placed on top of 170 g (dry weight) of untreated loam soil, both surrounding a glass vial with 115 g (dry weight) of insecticide-free soil in which the plants were grown for 14 days (Figure 2D). Results are averages of duplicated tests. <sup>b</sup> 3.8 g (dry weight) of cow manure was mixed with the upper 85 g of insecticide-treated outer soil layer. <sup>c</sup> Letters B and D refer to Figure 2, except that carbofuran was used. <sup>d</sup>  $^{14}\text{CO}_2$  trapped in 0.1 N KOH. Polyurethane traps contained less than 0.04% of soil-applied  $^{14}\text{C}$ . <sup>e</sup> Organic: total of benzene and  $\text{CH}_2\text{Cl}_2$  extraction phases. <sup>f</sup> Bound: unextractable  $^{14}\text{C}$  residues. <sup>g</sup> Results are based on total combustion. <sup>h</sup> Inner core of insecticide-free soil in which oat plants were grown. <sup>i</sup> Outer ring of soil, consisting of a top layer of [ $^{14}\text{C}$ ]carbofuran-treated soil placed on top of untreated soil (see footnote a). <sup>j-k</sup> Results obtained with soil plus cow manure are significantly different from comparable results obtained without cow manure at the 0.1% (j), 1% (k), and 5% (l) level (Student's *t* test).

most likely as  $^{14}\text{CO}_2$ , which was then utilized in the photosynthesis of water-soluble compounds.

**Effects of Cow Manure on the Production of  $^{14}\text{CO}_2$  from [ $^{14}\text{C}$ ]Carbofuran-Treated Soil and on the Pickup of Volatile  $^{14}\text{C}$  Compounds by the Aerial Parts of Oats.** Experiments as illustrated in Figure 2B, D were conducted with oats that grew under bell jars in untreated soil but were surrounded by either [ $^{14}\text{C}$ ]carbofuran-treated soil or by insecticide-treated soil to which cow manure had also been added. Results (Table V) obtained after a 2-week growing period indicated that substantial amounts of  $^{14}\text{CO}_2$  had been released and trapped. These amounts were 4 times larger in experiments with soils plus cow manure than with soils only. In the presence of oat plants, however, the amounts of  $^{14}\text{CO}_2$  were only 68–70% of those trapped in experiment with soils in which no oats had been grown. This reduction occurred due to an absorption of  $^{14}\text{CO}_2$  by oat greens that grew in the inner untreated soil, since in the absence of cow manure the amounts of  $^{14}\text{C}$  compounds recovered from plant greens and roots amounted to only 1.85% of the soil-applied radiocarbon. By adding to this figure the amount of  $^{14}\text{CO}_2$  trapped (4.38%), one obtains a total of 6.23%, which is similar to the  $^{14}\text{CO}_2$  trapped (6.43%) in the absence of plants.

Plants greens grown in soils mixed with cow manure contained a total of 7.5% of the soil-applied radiocarbon while 16.97% was released from this soil and trapped as  $^{14}\text{CO}_2$ , thus representing a total recovery of  $^{14}\text{C}$  compounds amounting to 24.47% of the soil-applied radiocarbon. In the absence of plants, cow manure treated soil released 24.24% of soil-applied  $^{14}\text{C}$  as  $^{14}\text{CO}_2$ , a figure nearly identical with the  $^{14}\text{C}$  recovered from plants plus  $^{14}\text{CO}_2$ . The results, therefore, clearly indicate that a substantial part of  $^{14}\text{C}$  compounds in oat greens resulted from the pickup of  $^{14}\text{CO}_2$ .

Under all experimental conditions, oat greens contained primarily water-soluble  $^{14}\text{C}$  compounds. Because of the rather small amounts of organic-soluble radiocarbon recovered from oat greens, no further analyses were performed. Although the inner soils in which all plants were grown had not been treated with the insecticide, small

amounts of  $^{14}\text{C}$  compounds were detected by combustion analyses. The outer rings of soil, previously treated with the insecticide, still contained 67–97% of the originally applied dose of radiocarbon. Of these residues, 93–98% were organic soluble, 1.6–5.5% were unextractable, and only 0.1–1.1% were water soluble. Polyurethane traps from all experiments contained less than 0.04% of the soil-applied radiocarbon.

**Conclusion.** Both [ $^{14}\text{C}$ ]fonofos and [ $^{14}\text{C}$ ]carbofuran in soils are to some extent broken down to  $^{14}\text{CO}_2$ . After its release into the air, this  $^{14}\text{CO}_2$  can be picked up by the aerial parts of plants that grew in untreated soil adjacent to insecticide-treated soil or directly within insecticide-treated soil. Since the major portion of radiocarbon in plant greens was water soluble, it appears that the  $^{14}\text{CO}_2$  picked up from the air was photosynthesized into water-soluble products. Only the smallest fraction of radiocarbon recovered from plants grown adjacent to or in [ $^{14}\text{C}$ ]fonofos-treated soil was benzene soluble and represented less than 0.5% of the soil-applied  $^{14}\text{C}$ . This radiocarbon was primarily associated with noninsecticidal metabolites. The addition of cow manure to [ $^{14}\text{C}$ ]carbofuran-treated soil resulted in an increased production of  $^{14}\text{CO}_2$  and in an increased presence of water-soluble radiocarbon within the aerial plant parts.

**Registry No.** Fonofos, 944-22-9; carbofuran, 1563-66-2.

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## Effects of Sediment Sorption and Abiotic Hydrolyses. 1. Organophosphorothioate Esters

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The kinetics of hydrolysis of selected organophosphorothioate insecticides were determined in sediment-water samples to define the role of hydrolysis in the sediment-sorbed state. Investigations with well-characterized sediments showed that the rates of neutral hydrolysis of chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate], diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate], and Ronnel [*O,O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate] are unaltered when the compounds are sorbed to sediments. For chlorpyrifos, the observed rate constants were the same in the sediment and aqueous phases and similar in magnitude to those found for natural water samples. Limited data for diazinon and Ronnel indicated similar kinetic behavior for these related compounds. Alkaline hydrolysis rates in the sediment-sorbed phase for chlorpyrifos, on the other hand, were slowed considerably relative to those in the aqueous phase. Experiments indicated that the rate of alkaline hydrolysis in the sorbed state is approximately 10 times slower than in the bulk solution.

In sediment-water systems it is generally assumed that organic compounds do not hydrolyze in the sediment-sorbed state but that the compound is in rapid equilibrium between the sediment and aqueous phases and hydrolysis occurs only through the aqueous phase (Wolfe et al., 1977). Unfortunately, detailed studies to support such assumptions have not been reported in the literature. Thus, a quantitative expression describing the hydrolytic process in sediments, coupled with a mechanistic insight about sediment effects, is needed to evaluate the fate and transport of organic compounds in sediment and soil systems.

Recent linear free energy relationships (LFER) relate the sorption of nonionic organic compounds to the organic matter associated with the sediment (Karickhoff, 1981). Thus, the question arises as to what types of reactions can occur in this organic matrix. It is anticipated that different types of reactions would be affected differently. For hydrolysis reactions, a neutral hydrolysis reaction may be affected differently than an acid- or base-mediated reaction. Furthermore, recent studies suggest that relative to some degradative processes the assumption of a fast equilibrium between the sediment and water is not always

valid (Karickhoff, 1980). Thus, the kinetics of sorption-desorption must be described and included in disappearance kinetic expressions.

Limited insight into reactions in the sorbed state is provided by studies addressing the breakdown of organophosphates and organophosphorothioates in soil systems. Unlike aqueous sediment suspensions, transport in the solid matrix of soil studies may be diffusion controlled and very slow. In soil studies, temperature, pH, moisture, and heavy metal effects have been reported (Sethunan and MacRae, 1969; Mingelgrin et al., 1977). Also, degradation is often divided into biotic and abiotic pathways by comparing sterile and nonsterile systems. In general, organophosphorus esters have been shown to undergo abiotic reactions in the soil sorbed states.

For studies of degradation of organic compounds in sediments, we selected three organophosphorothioate esters and designed experiments to test the hypothesis that hydrolysis occurred only in the aqueous phase, with no reaction of the esters in the sorbed phase. The three compounds were chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate], diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate], and Ronnel [*O,O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate], selected because of the magnitude of their sediment-water partition coefficients ( $K_p$ ) and neutral or alkaline hydrolysis rate constants. Experiments were designed to measure the rates of disappearance of these compounds in both the sediment-sorbed and the aqueous phases. Detailed studies were first carried out on

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