

Effect of Moisture on Sorption and Biodegradation of Carbofuran in Soil

Daniel R. Shelton*[†] and Timothy B. Parkin[‡]

Pesticide Degradation Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Building 050, BARC-West, Beltsville, Maryland 20705, and National Soil Tilth Laboratory, Agricultural Research Service, U.S. Department of Agriculture, 2150 Pammel Drive, Ames, Iowa 50011

Rates of biodegradation of soluble and sorbed [*carbonyl*-¹⁴C]carbofuran as well as evolution of ¹⁴CO₂ were monitored in soils incubated at moisture contents ranging from 20% (-0.4 bar) to 7.5% (-15 bar). Rates of biodegradation were comparable at -0.4 and -0.8 bar but decreased with diminishing moisture content. Concentrations of soluble carbofuran initially decreased and sorbed carbofuran increased as adsorption occurred, followed by losses of both soluble and sorbed carbofuran due to biodegradation. *K_d* values increased over the course of incubations but at progressively slower rates with decreasing soil moisture, suggesting that rates of degradation of carbofuran in soil solution exceeded rates of desorption at higher, but not lower, soil moistures. *K_d* values in previously air-dried (abiotic) soils increased, suggesting that partitioning into less accessible binding sites had occurred. These data indicate that soil moisture may affect rates of biodegradation either directly by inhibition of microbial activity or indirectly by affecting substrate bioavailability.

INTRODUCTION

Numerous studies have documented the ability of soil microorganisms to utilize pesticides as a carbon and energy source, either by the demonstration of mineralization in soil (release of ¹⁴CO₂ from labeled pesticides) or by the isolation of pure or mixed cultures through enrichment techniques. Clearly, the existence of indigenous soil microorganisms capable of utilizing pesticides as growth substrates indicates that repeated use of such pesticides could lead to enhanced rates of biodegradation and a subsequent loss of efficacy. This phenomenon has been observed with several classes of pesticides, including the thiocarbamate herbicides (Wilson, 1984; Moorman, 1988; Bean et al., 1988; Talet et al., 1989), the *N*-methylcarbamate insecticides (Felsot et al., 1981, 1985; Harris et al., 1984; Chapman et al., 1986; Read, 1987; Turco and Konopka, 1990), and the organophosphate insecticides (Racke and Coats, 1987, 1988). A recent overview of research is provided by Racke and Coats (1990).

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) has been used extensively since the late 1960s as a soil insecticide for control of the corn rootworm (*Diabrotica* spp.). Generally, granular carbofuran (Furadan) is banded at the time of planting and must be present for 3-5 weeks until the corn rootworm larvae hatch (Felsot et al., 1981). By 1975, farmers in the Midwest were reporting poor control of the corn rootworm using carbofuran. Because of past instances of developed resistance to organochlorine insecticides by *Diabrotica* spp., Felsot et al. (1981, 1982, 1985) investigated the relative roles of corn rootworm resistance vs enhanced rates of biodegradation as mechanisms for loss of efficacy. They observed that, although some populations of corn rootworm had developed a low level of resistance, the primary cause for lack of efficacy was enhanced rates of carbofuran degradation in fields with a history of carbofuran use. Subsequently, other investigators have demonstrated

that the treatment of soils with carbofuran can lead to enhanced rates of metabolism (Harris et al., 1984; Chapman et al., 1986; Camper et al., 1987; Read, 1987; Turco and Konopka, 1990).

Rates of pesticide biodegradation in soil are a function of multiple factors including population densities and activity of pesticide-degrading microorganisms, pesticide bioavailability, and soil parameters (Racke et al., 1990). Karns et al. (1986) and Chaudhry and Ali (1988) have reported the isolation of bacteria that rapidly hydrolyze carbofuran, utilizing the resulting methylamine as a sole source of carbon, nitrogen, or both. Chaudhry and Ali also isolated bacteria that could utilize the ring of the intact parent compound as a sole carbon source. Ramanand et al. (1988) have reported the isolation of a bacterium that mineralizes the aromatic moiety of both carbofuran and its hydrolysis product, 7-phenol (2,3-dihydro-2,2-dimethyl-7-benzofuranol).

In addition to adapted microbial populations, rapid degradation also requires bioavailability of the pesticide. Bioavailability refers to the concentration or fraction of pesticide in soil solution readily accessible by soil organisms. Unfortunately, this term has been used to describe both the dissolution of pesticides from formulations and the partitioning of dissolved pesticides between soluble and sorbed phases. Partitioning and dissolution are distinctly different physical/chemical phenomena, described by different kinetic equations. For purposes of this study, bioavailability refers exclusively to the partitioning of carbofuran between soil solution and soil surfaces.

Bioavailability is a function of water solubility and adsorption/desorption equilibria which are controlled by chemical structure and soil organic matter content (Rao and Davidson, 1980). Studies by Ogram et al. (1985) and Speitel et al. (1988) strongly suggest that only material dissolved in soil solution is available for metabolism. Sorbed material may be metabolized but only after desorption has occurred. Therefore, pesticides that are readily bioavailable, i.e., higher water solubility and/or rapid rates of desorption, may be more susceptible to enhanced rates of metabolism.

* Address correspondence to this author.

[†] Pesticide Degradation Laboratory.

[‡] National Soil Tilth Laboratory.

Soil parameters such as pH, aeration, nutrient availability, presence of inhibitors, and soil moisture can have dramatic effects on rates of biodegradation. Although all soil parameters are subject to some degree of spatial and temporal variability, soil moisture probably exhibits the most dramatic fluctuations over space and time. Fluctuations in soil moisture may effect rates of biodegradation directly by altering the physiological status of the microorganisms or indirectly by affecting the bioavailability of the substrate compound.

The purpose of this study was to correlate rates of carbofuran metabolism with bioavailability as a function of soil moisture. Specifically, the goals of this research were (1) to assess rates of degradation of carbofuran as a function of soil moisture, (2) to investigate the partitioning of carbofuran between soluble and sorbed phases as a function of soil moisture, and (3) to assess the effect of drying and wetting on the partitioning and degradation of carbofuran in soil.

MATERIALS AND METHODS

Chemicals. The radiolabeled carbofuran solution used in all experiments was prepared by mixing 10 g of Furadan 15G granules thoroughly in 100 mL of water to produce a saturated solution of carbofuran. The solution was filtered through tightly packed glass wool to remove macroscopic particles of carbofuran and inert ingredients. The final concentration was approximately 400 $\mu\text{g/mL}$ carbofuran and 100 $\mu\text{g/mL}$ 7-phenol; 9 μCi ($3.33 \times 10^6 \text{ Bq}$) of [*carbonyl*- ^{14}C]carbofuran (purified by preparative TLC, 98%) was added to give ca. $2.0 \times 10^6 \text{ dpm/mL}$ carbofuran solution.

The [*carbonyl*- ^{14}C]carbofuran and 7-phenol were gifts from FMC Corp. (Princeton, NJ). Furadan (15G) was obtained from a commercial source.

Soils. The soil for these experiments (obtained from the South Farm of the Beltsville Agricultural Research Center) was a Hattboro silt loam (Typic Fluvaquents, fine-loamy, mixed, monoacid, mesic) with 1.5% organic matter and pH of 6.05. Surface soil (0–10 cm) at field capacity was collected between the corn rows and stored at 4 °C until used. The field had been planted in corn the previous 3 years with granular carbofuran (Furadan 15G) applied at a rate of 2.0 lb of active ingredient/acre. Previous work had indicated that this soil had an active population of carbofuran-hydrolyzing microorganisms (Parkin et al., 1991).

The soil moisture/water potential relationship was established by incubating three 20-g aliquots of soil overnight in a ceramic plate extractor (Soil Moisture Corp., Santa Barbara, CA) and determining moisture content at 110 °C.

Incubations. For moist soil experiments ca. 1100 g of soil, which had been sieved through a 5 mm mesh screen, was placed onto a 3- or 15-bar ceramic plate, thoroughly moistened, placed in a ceramic plate extractor, and allowed to equilibrate for 48 h at 40 (–0.4), 80 (–0.8), 160 (–1.6), 340 (–3.4), 700 (–7.0), or 1500 kPa (15.0) (bar) corresponding to a moisture content of ca. 20%, 17.5%, 15%, 12.5%, 10%, or 7.5% respectively. Ten milliliters of a radiolabeled carbofuran solution was applied to 1000 g of soil with an atomizer to yield a final concentration of 4 μg of carbofuran and 33.3 Bq (2000 dpm) [*carbonyl*- ^{14}C]carbofuran/g of wet soil. Three 30-g aliquots of treated soil were placed in 125-mL flasks and attached to a semiautomated incubation apparatus (Shelton and Parkin, 1989) and incubated at 26 °C. Three 10-g aliquots were dried overnight at 110 °C for soil moisture determination. The remaining soil was placed in a 2-L beaker, covered, and incubated at 26 °C. The moisture content of soils decreased by ca. 2% over the course of incubations.

For the air-dried soil experiment, soil was air-dried for 72 h (final moisture content 0.9%) and crushed and sieved through a 2 mm mesh screen (Turner and Isensee, 1969). Separate 850-g batches of soil were treated as follows: (1) one batch was sprayed with 10 mL of carbofuran solution and allowed to remain in an air-dried state for 2 weeks, and then 150 mL of tap water was added via a slurry technique (Shelton and Parkin, 1989) or (2) 150 mL of tap water was added to the soil using a slurry technique

just prior to the addition of 10 mL of carbofuran solution. The final water potential was –0.6 bar.

Extraction and Analysis. Periodically, three 25-g aliquots of soil were removed from the beaker after mixing and squeezed in a Carver Press at 20 000–30 000 psi (Isensee and Walsh, 1971). The water pressed from the soil was immediately collected with a Pasteur pipet and centrifuged in a 2-mL glass vial for 2 min in a Beckman microcentrifuge (setting of 10). The supernatant was collected and weighed; 0.5 or 1.0 mL of supernatant was combined with 10 mL of Beckman Ready-Solv scintillation cocktail and counted in a Beckman Model LS 5000TD liquid scintillation counter. The remaining supernatant was frozen until analysis by HPLC. The resulting soil pellet was pulverized with a hammer and extracted with 50 mL of 80% methanol/20% water for 1 h with a wrist action shaker. The soil was allowed to settle overnight, and 2.5 mL of extract was combined with 7 mL of cocktail and counted as previously described. The extraction efficiency was assumed to be constant (100%) over the course of incubations.

Concentrations of carbofuran and its hydrolysis product, 7-phenol, were monitored with a Waters HPLC system (Waters Inc., Milford, MA) consisting of two 600A pumps, a Maxima 820 system controller, a 712 Wisp autosampler, and a radial compression module with a Perkin-Elmer LC-95 UV-visible variable-wavelength detector set at 210 nm. Separations were achieved using a radially compressed cartridge (C-18 Nova-Pak; 4 μm) with a mobile phase of 50% methanol/50% dilute H_3PO_4 (pH 2); the flow rate was 2.0 mL/min.

Evolution of $^{14}\text{CO}_2$ was monitored by periodically flushing the headspace of soil flasks into 6 mL of 0.5 N NaOH trapping solution as previously described (Shelton and Parkin, 1989). Three milliliters of trapping solution was combined with 7 mL of cocktail and counted.

Calculations. Percent soluble carbofuran was calculated according to the formula

$$\left[\frac{\text{dpm/mL of soil solution} \times \text{total mL of water/25 g of soil}}{\text{initial dpm/25 g of soil}} \right] \times 100$$

Percent sorbed carbofuran was calculated according to the formula

$$\left[\frac{\text{dpm in soil pellet} - (\text{dpm/mL of soil solution} \times \text{mL of water in soil pellet})}{\text{initial dpm/25 g of soil}} \right] \times 100$$

Apparent distribution or partition coefficients were calculated from the equation $K_d = (\theta/\rho) - \theta$ (Osgerby, 1973), where $K_d = (\mu\text{g of carbofuran/g of soil}) / (\mu\text{g of carbofuran/mL of soil solution})$, ρ is the proportion of pesticide in soil solution, and θ is the fractional moisture content of soil (g of water/g of soil).

$^{14}\text{CO}_2$ production data were evaluated using the general saturation model of Morgan et al. as described by Parkin et al. (1991). Parameter estimates were obtained for the model by nonlinear regression (PCNONLIN, Statistical Consultants, Inc., Lexington, KY) using the Nelder-Mead simplex algorithm for minimizing the sum of squared residuals.

RESULTS

Dissipation of soluble and sorbed [*carbonyl*- ^{14}C]carbofuran was monitored in soil incubated at initial moistures of 20% (–0.4 bar), 17.5% (–0.8 bar), 15% (–1.6 bar), 12.5% (–3.4 bar), or 10% (–7.0 bar) moisture (Figures 1–5); data are not shown for 7.5% moisture (–15.0 bar) because recoveries of pore water (<0.1 mL) were insufficient for analysis. Evolution of $^{14}\text{CO}_2$ at each water content was monitored in separate flasks. Rates of degradation were comparable at 20% (–0.4 bar) and 17.5% (–0.8 bar) moisture with greater than 97% degraded within 14 days and $^{14}\text{CO}_2$ recoveries of 90%; rates decreased with diminishing moisture content until only 7% of $^{14}\text{CO}_2$ was recovered after 5 weeks of incubation at 7.5% (–15.0 bar) moisture. The time required for 50% of $^{14}\text{CO}_2$ to be evolved (DT-50%) was 6.7 ± 0.1 (–0.4 bar), 6.9 ± 0.1 (–0.8

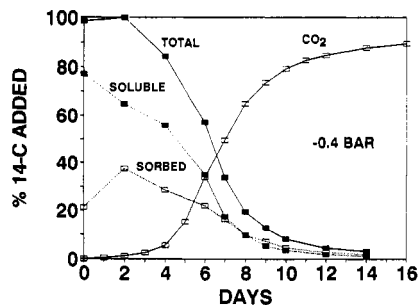


Figure 1. Disappearance of soluble, sorbed, and total (soluble plus sorbed) carbofuran as well as evolution of $^{14}\text{CO}_2$ as a function of soil water potential (-0.4 bar).

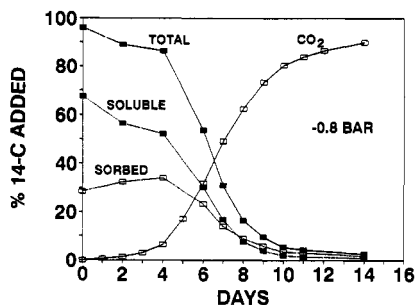


Figure 2. Disappearance of soluble, sorbed, and total (soluble plus sorbed) carbofuran as well as evolution of $^{14}\text{CO}_2$ as a function of soil moisture potential (-0.8 bar).

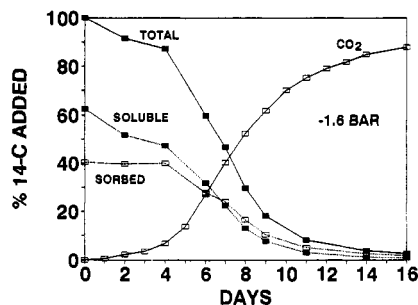


Figure 3. Disappearance of soluble, sorbed, and total (soluble plus sorbed) carbofuran as well as evolution of $^{14}\text{CO}_2$ as a function of soil moisture potential (-1.6 bar).

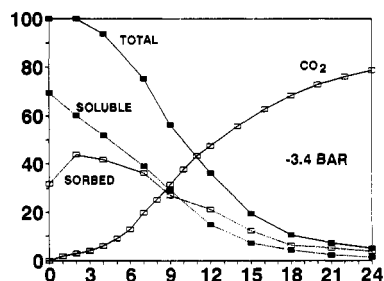


Figure 4. Disappearance of soluble, sorbed, and total (soluble plus sorbed) carbofuran as well as evolution of $^{14}\text{CO}_2$ as a function of soil moisture potential (-3.4 bar).

bar), 7.5 ± 0.1 (-1.6 bar), 11.6 ± 0.4 (-3.4 bar), and 21.7 ± 2.6 days (-7.0 bar).

Initial partitioning of carbofuran between soluble and sorbed phases (measured after 1–2 h) varied from a ratio of approximately 80:20 to 60:40. Levels of soluble carbofuran decreased and sorbed carbofuran increased over the next 2–5 days until the ratio of soluble to sorbed carbofuran varied from 50:50 to 65:35, after which time both soluble and sorbed carbofuran decreased. Significant evolution of $^{14}\text{CO}_2$ ($>10\%$) was not observed until after 4–5 days of incubation.

K_d values, calculated for each of the sampling points,

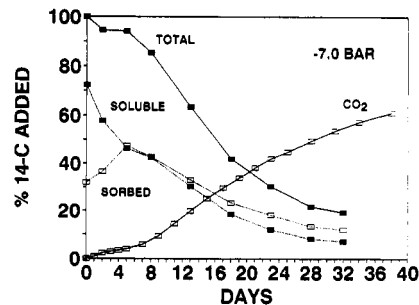


Figure 5. Disappearance of soluble, sorbed, and total (soluble plus sorbed) carbofuran as well as evolution of $^{14}\text{CO}_2$ as a function of soil moisture potential (-7.0 bar).

were initially low in all incubations (<0.10) but increased over the next 2–5 days (Table I). At higher moisture levels (-0.4 and -0.8 bar) K_d values continuously increased to 0.32–0.36. The same general phenomenon was observed at intermediate moisture levels (-1.6 and -3.4 bar), although K_d values increased progressively slower. At -7.0 bar K_d values were constant at 0.10–0.13.

Initial concentrations of carbofuran in soil solution generally increased as moisture content decreased (Figure 6). Pore water carbofuran concentrations after 2 days were 16.0 (-0.4 bar), 15.5 (-0.8 bar), 18.1 (-1.6 bar), 21.2 (-3.4 bar), and 25.5 $\mu\text{g}/\text{mL}$ (-7.0 bar). Initial recoveries of 7-phenol were 0.5 $\mu\text{g}/\text{mL}$ but were generally nondetectable (<0.1 $\mu\text{g}/\text{mL}$) at other sampling dates.

The addition of carbofuran to air-dried soil 2 weeks prior to or at the time of wetting had no discernible effect on the kinetics of adsorption or partitioning between soluble and sorbed phases (Figure 7). K_d values were 0.12–0.13 after 2 days but increased to 0.16–0.17 (statistically significant at $p \leq 0.01$) as the distribution between soluble and sorbed phases approached a ratio of ca. 50:50. Evolution of $^{14}\text{CO}_2$ was 7% after 3 weeks of incubation.

DISCUSSION

The partitioning of pesticides between soluble and sorbed phases is defined by the distribution coefficient (K_d). Distribution coefficients have traditionally been determined using soil slurry techniques. Values for carbofuran, collated by Rao and Davidson (1988), were $K_d = 1.05$ ($\text{CV} = 111.8\%$) and $K_{oc} = 29.4$ ($\text{CV} = 30.0$), while K_d values using analytical grade carbofuran at 1.0 $\mu\text{g}/\text{mL}$ with this soil were 0.36–0.49 (personal communication, Dr. Charles Helling, Tropical Plants Laboratory, Beltsville Agricultural Research Center). These values are higher than the equilibrium K_{ds} obtained in this study, $K_d = 0.12$ –0.17, $K_{oc} = 16$ –22. We suspect that this is due to the fact that (1) soil slurry techniques result in the maximization of available sorptive sites and (2) adsorption studies are generally conducted with technical or analytical grade pesticides to minimize interferences from formulating agents. Neither of these conditions is true in field soils where all sorptive sites are probably never available for sorption and where formulating agents may, depending on their chemical structure, affect distribution coefficients (Smith and Bayer, 1967). Our incubations were conducted with field moist soils and used aqueous solutions of Furadan 15G (simulating dissolved granular carbofuran) in an attempt to obtain estimates of partitioning and rates of biodegradation as consistent with in situ rates as is possible in a laboratory setting.

Concentrations of soluble carbofuran were determined by extracting pore water from soil using hydraulic pressure. Similar methods for obtaining samples of soil solution for pesticide analysis have been previously described: a

Table I. Effect of Soil Moisture on Partitioning of Carbofuran between Soluble and Sorbed Phases with Time

days	K_d value ^a				
	-0.4 bar	-0.8 bar	-1.6 bar	-3.4 bar	-7.0 bar
0	0.06 (0.04) ^b	0.07 (0.01)	0.10 (0.01)	0.06 (0.01)	0.04 (0.01)
1					
2	0.11 (0.03)	0.10 (0.01)	0.11 (0.01)	0.09 (0.01)	0.06 (0.01)
3					
4	0.10 (0.01)	0.11 (0.01)	0.12 (0.01)	0.10 (0.01)	
5					
6	0.12 (0.01)	0.13 (0.01)	0.13 (0.02)		
7	0.18 (0.01)	0.14 (0.01)	0.15 (0.01)	0.11 (0.01)	
8	0.19 (0.01)	0.19 (0.01)	0.18 (0.04)		0.10 (0.01)
9	0.26 (0.03)	0.26 (0.01)	0.19 (0.01)	0.11 (0.02)	
10	0.26 (0.03)	0.28 (0.03)			
11		0.36 (0.03)	0.23 (0.03)		
12	0.31 (0.03)			0.16 (0.01)	
13					0.10 (0.01)
14	0.32 (0.04)	0.36 (0.01)	0.33 (0.05)		
15				0.19 (0.01)	
16			0.31 (0.06)		
17					
18				0.17 (0.03)	0.11 (0.01)
19					
20					
21				0.26 (0.02)	
22					
23					0.13 (0.01)
24				0.29 (0.03)	
28					0.13 (0.01)
32					0.13 (0.01)

^a $K_d = (\mu\text{g of carbofuran/g of soil}) / (\mu\text{g of carbofuran/mL of soil solution})$. ^b (Standard deviation).

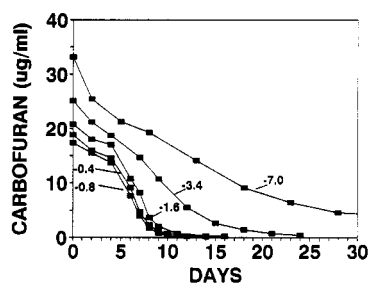


Figure 6. Concentration of carbofuran in soil solution over time as a function of soil water potential (bar).

modified drill press (Goetz et al., 1986), air pressure (Scott and Lutz, 1971; Hance and Embling, 1979), and centrifugation (Dao and Lavy, 1978). The use of a hydraulic press is conceptually identical to these other techniques; however, we feel that it is preferable due to the speed at which samples can be processed. The advantage of this approach is that partitioning of pesticides between soluble and sorbed phases can be directly related to degradation kinetics under field moisture conditions.

Effect of Soil Moisture on Microbial Activity. The effect of soil moisture content or soil water potential on rates of degradation of organic matter in general (Wilson and Griffin, 1975; Sommers et al., 1981) and pesticides in particular (Lichtenstein and Schulz, 1964; Getzin, 1968; Meikle et al., 1973; Walker, 1978; Chapman et al., 1986) is well documented. Decreasing levels of soil moisture have consistently been observed to retard or inhibit rates of microbial metabolism, although the pattern or degree of inhibition is dependent upon the substrate, microbial process, or nature of the microflora being studied. In this study, rates of carbofuran degradation were comparable at -0.4 and -0.8 bar with >97% metabolized within 2 weeks. Rates of degradation became progressively slower with decreasing soil moisture until the rate of hydrolysis was negligible at -1.6 bar. Conversely, concentrations of soluble carbofuran (after 2 days) increased from 15.5 (-0.8 bar) to 25.5 $\mu\text{g/mL}$ (-7.0 bar) with decreasing soil moisture.

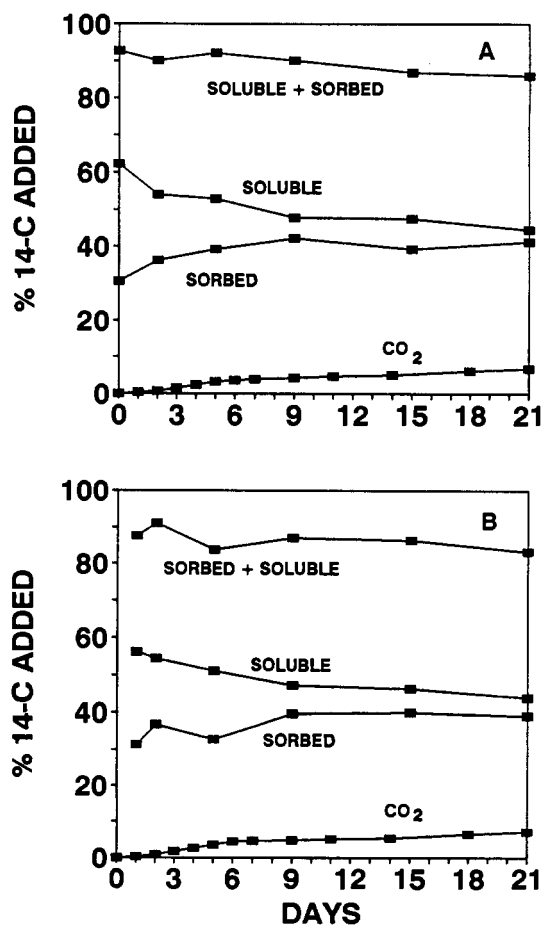


Figure 7. Fate of carbofuran in air-dried soil when applied 2 weeks prior to wetting (A) or immediately after wetting (B).

These data indicate that the primary reason for the progressive inhibition of carbofuran degradation was the relative sensitivity of the carbofuran-hydrolyzing microorganisms in this soil to desiccation, as opposed to

decreased bioavailability. Air-drying of this soil also resulted in a loss of biological activity [residual rates of hydrolysis were similar to sterile controls (Parkin et al., 1991)], suggesting that desiccation resulted in not only inhibition but also cell death. Although not all soil microorganisms are this sensitive to desiccation, these data do demonstrate that severe soil perturbations should be avoided when one is dealing with microbial processes (Pramer and Bartha, 1972).

Effect of Soil Moisture on Adsorption. At all moisture levels (except -7.0 bar) rates of carbofuran adsorption were relatively rapid reaching K_d values of 0.09–0.11 within 2 days, suggesting that the ratio of soluble to sorbed carbofuran at equilibrium is relatively constant, independent of soil moisture content. Rates of 7-phenol adsorption were very rapid with >98% bound within 2 days. At -7.0 bar rates of carbofuran adsorption were slower, with 5 days required to reach a K_d value of 0.10. Also, the addition of carbofuran to air-dried soil 2 weeks prior to the time of wetting had no discernible effect on the rate or extent of adsorption. These data indicate that rates of adsorption at lower moisture content were partially or completely depressed.

In air-dried soil, K_d values after 2 days were consistent with other incubations at comparable moisture levels (0.12–0.13); however, K_d values increased with time, approaching an equilibrium value of 0.16–0.17 after 21 days (statistically significant at $p \leq 0.01$). This observation is similar to that of McCall and Agin (1985), who studied picloram adsorption/desorption in several soils. They observed a consistent increase in K_d over a 300-day period. They also observed an initial rapid rate of desorption followed by a much slower rate. They interpreted their data as indicative of a two-step process: an initial rapid rate of adsorption to (or desorption from) "external" sites followed by a slower rate of adsorption to (or desorption from) "internal" sites. Although the absolute increase observed in K_d for carbofuran was relatively small, the percentage increase was comparable with that of picloram over the same incubation period in the majority of soils studied. However, the rapid rate of carbofuran biodegradation combined with the relatively low organic matter content probably limited sorption to internal sites in the Hatsboro soil.

Effect of Soil Moisture on Desorption. As rates of microbial metabolism accelerated within 2–6 days levels of both soluble and sorbed carbofuran decreased. The increase in apparent K_d values with time, however, indicates that concentrations of soluble carbofuran decreased more rapidly than sorbed carbofuran. On the basis of previous studies which strongly suggest that only soluble compounds are available for microbial metabolism (Ogram et al., 1985; Speitel et al., 1988) these data indicate that rates of carbofuran metabolism were faster than rates of desorption at higher moisture levels, resulting in a measurable concentration gradient. However, as rates of metabolism became progressively slower at lower moisture levels due to desiccation effects, K_d values increased progressively slower or were essentially constant (-7.0 bar), indicating that rates of biodegradation and desorption were comparable. Therefore, at higher moisture levels desorption was rate-limiting while at lower moisture levels biodegradation was rate-limiting. In contrast to distribution coefficients, which dictate only the fraction of substrate in the soluble phase available for immediate metabolism (short-term bioavailability), desorption constants dictate the rate at which pesticides in the sorbed

fraction will become available for metabolism in the future (long-term bioavailability).

In this study, rates of carbofuran biodegradation decreased as a function of decreasing soil moisture, primarily due to the inhibitory effects of desiccation on carbofuran-degrading microorganisms. In contrast, decreasing soil moistures had little or no effect on carbofuran bioavailability. Concentrations of soluble carbofuran increased and rates of adsorption decreased with decreasing soil moistures. These results are consistent with the hypotheses that rapid rates of biodegradation or enhanced degradation are dependent on both the presence of active populations of pesticide-degrading microorganisms and relatively high levels of pesticide bioavailability.

ACKNOWLEDGMENT

We thank Eton Codling and April Talcot for technical assistance.

LITERATURE CITED

- Bean, B. W.; Roeth, F. W.; Martin, A. R.; Wilson, R. G. Influence of prior pesticide treatments on EPTC and butylate degradation. *Weed Sci.* 1988, 36, 70–77.
- Camper, N. D.; Fleming, M. N.; Skipper, H. D. Biodegradation of carbofuran in pretreated and nonpretreated soils. *Bull. Environ. Contam. Toxicol.* 1987, 39, 571–578.
- Chapman, R. A.; Harris, C. R.; Harris, C. Observations on the effect of soil type, treatment intensity, insecticide formulation, temperature and moisture on the adaptation and subsequent activity of biological agents associated with carbofuran degradation in soil. *J. Environ. Sci. Health* 1986, B21, 125–141.
- Chaudry, G. R.; Ali, A. N. Bacterial metabolism of carbofuran. *Appl. Environ. Microbiol.* 1988, 54, 1414–1419.
- Dao, T. H.; Lavy, T. L. Extraction of soil solution using a simple centrifugation method for pesticide adsorption-desorption studies. *Soil Sci. Soc. Am. J.* 1978, 42, 375–377.
- Felsot, A. S.; Maddox, J. V.; Bruce, W. Enhanced microbial degradation of carbofuran in soils with histories of Furadan use. *Bull. Environ. Contam. Toxicol.* 1981, 26, 781–788.
- Felsot, A. S.; Wilson, J. G.; Kuhlman, D. E.; Steffey, K. L. Rapid dissipation of carbofuran as a limiting factor in corn rootworm (Coleoptera: Chrysomelidae) control in fields with histories of continuous carbofuran use. *J. Econ. Entomol.* 1982, 75, 1098–1103.
- Felsot, A. S.; Steffey, K. L.; Levine, E.; Wilson, J. G. Carbofuran persistence in soil and adult corn rootworm (Coleoptera: Chrysomelidae) susceptibility: relationship to the control of damage by larvae. *J. Econ. Entomol.* 1985, 78, 42–52.
- Getzin, L. W. Persistence of diazinon and zinophos in soil: effects of autoclaving, temperature, moisture, and acidity. *J. Econ. Entomol.* 1968, 61, 1560–1565.
- Harris, R.; Chapman, R. A.; Harris, C.; Tu, C. M. Biodegradation of pesticides in soil. Rapid reduction of carbonate degrading factors after carbofuran treatment. *J. Environ. Sci.* 1984, B19, 1–11.
- Isensee, A. R.; Walsh, L. M. Influence of banded fertilizer on the chemical environment surrounding the band I. Effect on pH and solution nitrogen. *J. Sci. Food Agric.* 1971, 22, 105–109.
- Karns, J. S.; Mulbry, W. W.; Nelson, J. O.; Kearney, P. C. Metabolism of carbofuran by a pure bacterial culture. *Pestic. Biochem. Physiol.* 1986, 25, 211–217.
- Lichtenstein, E. P.; Schulz, K. R. The effects of moisture and microorganisms on the persistence and metabolism of some organophosphorus insecticides in soils with special emphasis on parathion. *J. Econ. Entomol.* 1964, 57, 618–627.
- McCall, P. J.; Agin, G. L. Desorption kinetics of picloram as affected by residence time in the soil. *Environ. Toxicol. Chem.* 1985, 4, 37–44.
- Meikle, R. W.; Youngson, C. R.; Hedlund, R. T.; Goring, C. A. I.; Hamaker, J. W.; Addington, W. W. Measurement and prediction of picloram disappearance rates from soil. *Weed Sci.* 1973, 21, 549–555.

- Moorman, T. B. Populations of EPTC-degrading microorganisms in soils with accelerated rates of EPTC degradation. *Weed Sci.* 1988, 36, 96-101.
- Ogram, A. V.; Jessup, R. E.; Ou, L. T.; Rao, P. S. C. Effects of sorption on biological degradation rates of 2,4-dichlorophenoxyacetic acid in soils. *Appl. Environ. Microbiol.* 1985, 49, 582-587.
- Osgerby, J. M. Processes affecting herbicide action in soil. *Pestic. Sci.* 1973, 4, 247-258.
- Parkin, T. B.; Shelton, D. R.; Robinson, J. A. Evaluation of methods for characterizing carbofuran hydrolysis in soil. *J. Environ. Qual.* 1991, 20 (4).
- Pramer, D.; Bartha, R. Preparation and processing of soil samples for biodegradation studies. *Environ. Lett.* 1972, 2, 217-224.
- Racke, K. D.; Coats, J. R. Enhanced degradation of isofenphos by soil microorganisms. *J. Agric. Food Chem.* 1987, 35, 94-99.
- Racke, K. D.; Coats, J. R. Comparative degradation of organophosphorus insecticides in soil: specificity of enhanced microbial degradation. *J. Agric. Food Chem.* 1988, 36, 193-199.
- Racke, K. D.; Coats, J. R. *Enhanced Biodegradation of Pesticides in the Environment*; ACS Symposium Series 426; American Chemical Society: Washington, DC, 1990; 302 pp.
- Racke, K. D.; Laskowski, D. A.; Schulz, M. R. Resistance of chlorpyrifos to enhanced biodegradation in soil. *J. Agric. Food Chem.* 1990, 38, 1430-1436.
- Ramanand, K.; Sharmila, M.; Sethunathan, N. Mineralization of carbofuran by a soil bacterium. *Appl. Environ. Microbiol.* 1988, 54, 2129-2133.
- Rao, P. S. C.; Davidson, J. M. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. In *Environmental Impact of Nonpoint Source Pollution*; Overcash, M. R., Davidson, J. M., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1988; pp 23-67.
- Read, D. C. Greatly accelerated microbial degradation of aldicarb in pretreated field soil, in flooded soil, and in water. *J. Econ. Entomol.* 1987, 80, 156-163.
- Scott, H. D.; Lutz, J. F. Release of herbicides from clay minerals as a function of water content: I. Kaolinite. *Soil Sci. Soc. Am. Proc.* 1971, 35, 374-379.
- Shelton, D. R.; Parkin, T. B. A semiautomated instrument for measuring total and radiolabeled carbon dioxide evolution from soil. *J. Environ. Qual.* 1989, 18, 550-554.
- Smith, L. W.; Bayer, D. E. Soil adsorption of diuron as influenced by surfactants. *Soil Sci.* 1967, 103, 328-330.
- Sommers, L. E.; Gilmour, C. M.; Wildung, R. E.; Beck, S. N. The effect of water potential on decomposition processes in soils. In *Water Potential Relations in Soil Microbiology*; Parr, J. F., Gardner, W. R., Elliot, L. F., Eds.; Special Publication 9; Soil Science Society of America: Madison, WI, 1981; pp 97-116.
- Speitel, G. E.; Lu, C. J.; Turakhia, M.; Sho, X.-J. Biodegradation of trace concentrations of substituted phenols in granular activated carbon columns. *Environ. Sci. Technol.* 1988, 22, 68-74.
- Tal, A.; Rubin, B.; Katan, J.; Aharonson, N. Fate of ¹⁴C-EPTC in a soil exhibiting accelerated degradation of carbomothioate herbicides and its control. *Weed Sci.* 1989, 37, 434-439.
- Turco, R. F.; Konopka, A. Biodegradation of carbofuran in enhanced and nonenhanced soils. *Soil Biol. Biochem.* 1990, 22, 195-201.
- Turner, B. C.; Isensee, A. R. An inexpensive soil crusher-sever. *Agron. J.* 1969, 61, 820-821.
- Walker, A. The degradation of methazole in soil. I. Effects of soil type, soil temperature and soil moisture content. *Pestic. Sci.* 1978, 9, 326-332.
- Wilson, J. M.; Griffin, D. M. Water potential and the respiration of microorganisms in the soil. *Soil Biol. Biochem.* 1975, 7, 199-204.
- Wilson, R. G. Accelerated degradation of thiocarbamide herbicides in soil with prior thiocarbamide herbicide exposure. *Weed Sci.* 1984, 32, 264-268.

Received for review November 28, 1990. Revised manuscript received June 10, 1991. Accepted August 7, 1991.

Registry No. Carbofuran, 1563-66-2.