Bentazon Degradation in Soil: Influence of Tillage and History of Bentazon Application

Stephen C. Wagner,*,† Robert M. Zablotowicz,† Lewis A. Gaston,† Martin A. Locke,† and Jim Kinsella‡

Southern Weed Science Laboratory, Agricultural Research Service, U.S. Department of Agriculture, P.O. Box 350, Stoneville, Mississippi 38776, and BASF Agronomic Development Center, Lexington, Illinois

Laboratory studies determined the fate of bentazon (3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide) in soil as affected by tillage and history of application. Bentazon degradation in two soils from Mississippi and three soils from Illinois under conventional-tillage (CT) and no-tillage (NT) (3−18 years) with varying histories of bentazon application (0−9 applications) was studied. The half-life (DT_{50}) for bentazon degradation ranged from 4.6 to 49.5 d; half-lives for NT of the two soils with the longest history of bentazon application were lower than those for CT. Half-lives for soils with no bentazon history were 3−11-fold higher than bentazon half-lives of those previously exposed to bentazon. Dissipation of bentazon was accompanied with increases in nonextractable material. Methylbentazon was the most consistently observed metabolite (1.7−5.8% applied ^{14}C after 48 d). Bentazon mineralization ranged from 12% to 18% applied after 48 d and 2% to 3% applied after 22 d for bentazon history and nonhistory soils, respectively. Patterns of mineralization were affected by tillage in the two of the five soils with the longest bentazon history.

Keywords: *Herbicide; bentazon; no-tillage; herbicide degradation*

INTRODUCTION

Bentazon is a postemergence herbicide used to control broadleaf weeds and sedges in soybeans. It controls many problem weeds in soybeans including velvetleaf (*Abutilon theophrasti* Medic.), jimsonweed (*Datura stramonium* L.), common cocklebur (*Xanthium strumarium* L.), common lambsquarters (*Chenopodium album* L.), and common ragweed (*Ambrosia artemisiifolia* L.) (Weed Science Society of America, 1994).

Bentazon is not readily adsorbed by soil. Abernathy and Wax (1973) found that bentazon was not readily adsorbed by 12 Illinois soils, presumably due to its high water solubility and strong anionic character. However, a 30 d exposure in soil significantly reduced leaching of bentazon (Huber and Otto, 1994).

Metabolic transformations of bentazon in soil have been described. Otto et al. (1979) reported that bentazon is biodegraded mainly by the hydroxylation of the 6- or 8-position of the phenyl ring to form 6-OH-bentazon or 8-OH-bentazon (Figure 1). It is difficult to identify these metabolites because both are further metabolized rapidly. Within 24 h, hydroxylated bentazons are incorporated as insoluble, bound residues on humic and fulvic acids. Another metabolite often formed is 2-amino-*N*-isopropylbenzamide (AIBA; Otto et al., 1979; Huber and Otto, 1994). AIBA can be hydrolyzed to anthranilic acid, which is readily catabolized by many soil microorganisms or used in tryptophan synthesis (Huber and Otto, 1994).

Bentazon is degraded microbially in the soil environment at a moderate rate. Lysimeter experiments on bentazon by Kordel et al. (1991) showed its half-life ranged from 24 to 65 d. Huber and Otto (1994) reported half-lives of bentazon from 4 to 21 d at five different field sites in Germany and from 3 to 19 d at six different sites in the United States.

Crop residue management (CRM) is defined as any tillage and planting system that utilizes practices maintaining a portion of the previous crop's residue on the soil surface. These include no-till, ridge-till, and mulch-till. CRM offers many improvements in soil quality and sustainability including moisture conservation, improved tilth, increased organic matter content, and improved water quality (Carter, 1993; Schertz, 1994). No-till practices may affect herbicide degradation patterns in soil (Locke and Harper, 1991b; Levanon et al., 1994; Reddy et al., 1995).

The fate of bentazon in soils under long-term conventional-till (CT) and no-till (NT) systems with or without history of bentazon application has not been documented. Therefore, we determined bentazon degradation in five soils with varying histories of tillage and bentazon application.

MATERIALS AND METHODS

Soils Used. Samples from CT and NT plots of five different soils were used in this study (Table 1). These included three soils from Illinois with varying histories of bentazon application, Drummer silty clay loam (fine-silty, mixed, mesic, Typic Endoaquoll), Miami silt loam (fine-silty, mixed, mexic, Typic Hapludalf), and Saybrook silt loam (fine-silty, mixed, mexic, Typic Argiudoll), and two soils from Mississippi with either 8 years or no history of bentazon application, Dundee silt loams (fine-silty, mixed, thermic Aeric Ochraqualf). Soils were sampled from the upper 7.5 cm, passed through a 2 mm sieve, and stored at 4 °C. Biological characteristics of the Drummer, Miami, and Dundee (bentazon history) soils were previously described (Reddy et al., 1995).

Mineralization of Bentazon. Mineralization of bentazon in each soil was examined in soil biometer flasks (250 mL; Bellco Glass Inc., Vineland, NJ) as described by Bartha and Pramer (1965). Twenty-five grams (oven-dried weight equivalent) of each soil was placed in a biometer flask and treated with bentazon to attain a final concentration of 2.5 $\mu g\ g^{-1}$ of soil and 134.4 Bq g^{-1} of ^{14}C-ring labeled bentazon (BASF; 98% radioactive purity; specific activity, 4.0 g mBq^{-1}) g^{-1} of soil. Labeled and unlabeled bentazon were dissolved in water and

† U.S. Department of Agriculture.
‡ BASF Agronomic Development Center.

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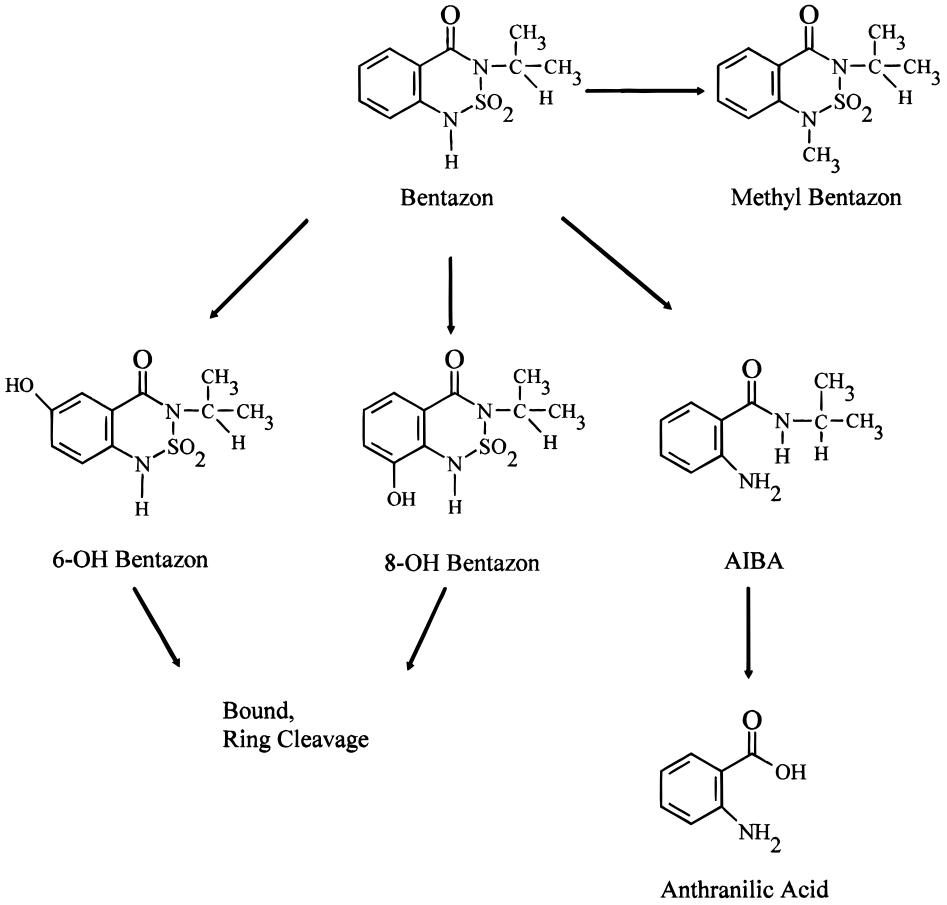

Figure 1. Metabolic pathway of bentazon in soil as proposed by Huber and Otto (1994) and methylation of bentazon.

Table 1. Tillage, Bentazon Application History, and General Characteristics of Soils Used in the Study

soil	previous crop	tillage system (years)	bentazon history (years)	pH[a]	POC[b] (%)
Dundee silt loam (history)	soybean	CT	8	5.67	1.31
	(continuous)	NT (9)	8	5.41	1.53
Drummer silty clay loam	soybean	CT	6	4.52	1.89
	(rotated with corn)	NT (16)	6	6.25	4.80
Miami silt loam	soybean	CT	7	6.45	1.78
	(rotated with corn)	NT (18)	7	6.85	3.06
Saybrook silt loam	corn	CT	1	5.01	1.77
	(rotated with soybean)	NT (4)	1	6.31	2.04
Dundee silt loam (nonhistory)	cotton	CT	0	5.79	0.87
	(continuous)	NT (3)	0	5.60	1.02

[a] 1:1 soil:0.01 M $CaCl_2$. [b] Percent organic carbon determined by the modified Mebius method (Nelson and Sommers, 1982).

added to each soil to attain the concentrations and counts indicated above with a moisture content of 33% (w/w; approximate field capacity for soils studied).

The experiment was conducted at 25 °C for 48 d. Side arms of each biometer flask were filled with 10.0 mL of 1.0 N NaOH to trap evolved CO_2. The NaOH was replaced every 3 d with fresh NaOH. To determine $^{14}CO_2$, 1 mL aliquots of the NaOH samples were added to 15 mL of ScintiSafe Plus 50% scintillation cocktail (Fisher Scientific, Pittsburgh, PA) and counted on a liquid scintillation counter (Packard TriCarb 4000 series, Packard Instruments Co., Meriden, CT). Initially, there were eight replicates of each soil/tillage combination, but four replicates were sacrificed at 12 d after application to determine bentazon degradation. The experimental design was a randomized complete block design. The remaining biometer flasks (four replicates of each soil/tillage treatment) were terminated at 48 d as described below to determine bentazon degradation.

Bentazon Degradation. Bentazon and metabolites were extracted from each soil at 6, 12, and 48 d after initiation of the experiment. In order to determine bentazon degradation at 6 d without requiring additional biometer flasks, four additional replicates of each soil/tillage treatment were set up in 250 mL Nalgene centrifuge bottles as described above and extracted after 6 d of incubation. Each soil was shaken with 60 mL of 80:20 methanol:0.01 M $CaCl_2$ in 250 mL centrifuge bottles for 18 h. After the soils were centrifuged for 15 min, 5860*g*, the supernatant was decanted, and the soils were resuspended in 40 mL of 80:20 methanol:0.01 M $CaCl_2$ and shaken for 4 h. Each soil was centrifuged again, and the supernatant was combined with the first supernatant. Subsequently, each soil was extracted three more times with 40 mL of 80:20 methanol:0.01 M $CaCl_2$ (less than 0.6 Bq mL^{-1} was detected in the final extract).

The pooled first and second methanolic extracts of each soil were evaporated in a centrifuge evaporator (Speed Vac Plus, Savant Instruments, Inc., Farmingdale, NY) to about 10% original volume; 100 mL of distilled deionized water was added to the remaining solution. After shaking for 1 h to ensure equilibration, the pH was adjusted to 2.0 with 1 N HCl. Each aqueous solution was eluted through a C-18 SPE column (J. T. Baker, Inc., Phillipsburg, NJ) to trap bentazon and metabolites in this solution. Bentazon and metabolites were eluted with 3 mL of methanol and stored at 4 °C until thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC) analysis could be performed.

Methanol extracts were analyzed for bentazon and metabo-

Table 2. Recovery of [^{14}C]Bentazon and Metabolites from Soils (of [^{14}C]Bentazon Applied) As Affected by Soil, Tillage, and Time after Application

soil type[a]	time (d)	tillage system[b]	CO_2 (%)	extractable (%)			nonextractable (%)	total (%)
				bentazon	methylbentazon	others		
Dundee	6	CT	2.5 a[c]	67.6 a	1.1 a	3.4 a	23.3 b	97.9 a
silt loam (8)	6	NT	2.6 a	41.5 b	2.7 a	2.7 a	40.3 a	89.8 b
	12	CT	6.0 a	33.9 a	2.6 b	5.8 a	45.9 b	94.1 a
	12	NT	5.4 b	15.1 b	6.7 a	6.7 a	57.5 a	90.7 a
	48	CT	17.3 a	2.8 a	3.3 b	3.2 a	64.7 a	91.1 a
	48	NT	12.3 b	3.5 a	4.5 a	3.5 a	62.9 a	86.8 a
Miami	6	CT	1.9 b	73.1 a	0.0 a	2.4 a	17.2 b	94.6 a
silt loam (8)	6	NT	3.1 a	57.7 b	0.0 a	3.4 a	28.7 a	92.9 a
	12	CT	4.0 b	57.4 a	0.6 a	3.6 a	25.8 b	90.6 a
	12	NT	6.1 a	40.5 b	0.9 a	4.0 a	39.4 a	91.0 a
	48	CT	13.9 b	12.9 a	1.9 a	2.6 a	53.4 b	84.8 b
	48	NT	17.6 a	8.6 a	1.7 a	2.1 a	59.9 a	89.9 a
Drummer	6	CT	1.4 b	60.4 a	1.8 a	3.4 a	27.5 a	94.5 a
silty clay loam (7)	6	NT	2.5 a	57.4 a	0.4 a	1.9 a	28.9 a	91.1 a
	12	CT	3.7 b	36.2 a	1.7 a	6.2 a	42.6 a	90.3 a
	12	NT	5.2 a	42.0 a	0.9 a	2.4 a	38.2 a	88.6 a
	48	CT	14.4 a	4.4 a	5.8 a	3.0 a	62.3 a	90.0 a
	48	NT	14.4 a	5.0 a	3.1 a	1.9 a	60.6 a	85.0 b
Saybrook	6	CT	1.5 b	67.6 a	2.1 a	2.4 a	20.5 a	93.9 a
silt loam (1)	6	NT	2.3 a	67.8 a	0.0 b	1.5 a	21.4 a	92.8 a
	12	CT	3.3 b	45.1 a	4.4 a	5.9 a	34.4 a	93.1 a
	12	NT	4.9 a	44.1 a	1.3 a	8.7 a	32.5 a	90.8 a
	48	CT	14.4 a	5.2 b	4.8 a	4.7 a	58.9 a	87.9 a
	48	NT	15.5 a	7.1 a	2.7 b	2.7 b	58.8 a	86.8 a
Dundee	7	CT	1.2 a	83.6 b	0.0	0.0	9.6 a	94.5 a
silt loam (0)[d]	7	NT	1.0 a	87.0 a	0.0	0.0	8.1 a	96.3 a
	14	CT	1.9 a	77.7 b	0.0	0.0	16.0 a	95.8 a
	14	NT	1.6 b	81.9 a	0.0	0.0	13.6 b	97.3 a
	22	CT	2.7 a	71.1 b	0.0	0.0	19.9 a	94.4 a
	22	NT	2.3 b	76.7 a	0.0	0.0	15.2 b	94.3 a

[a] Years of bentazon history in parentheses. [b] CT = conventional-tillage, NT = no-tillage. [c] Means within a soil and time (d) followed by the same letter are not significantly different (LSD, $\alpha = 0.05$). [d] Gaston et al. (1996).

lites using TLC (J. K. Lee, personal communication, 1994). Each sample was spotted on a silica gel plate (250 μm thick; 3.3 cm preabsorbent layer) and developed with 60:10:5:1 benzene:dioxane:isopropyl alcohol:formic acid (v:v:v:v) for 10 cm. Bentazon and metabolites were quantified on each chromatogram with a BioScan System 200 imaging scanner (Bioscan, Inc., Washington, DC). Compounds were identified by comparing R_f values to values obtained for the following standards: 6-hydroxy bentazon, 8-hydroxybentazon, bentazon, anthranilic acid, AIBA, and methylbentazon (Chem Service, West Chester, PA; R_f values were 0.28, 0.28, 0.35, 0.44, 0.75, and 0.94, respectively).

HPLC was used to confirm results obtained in the TLC methods. Fifty microliters of each methanol extract was injected into a Waters Model 510 HPLC instrument (Millipore Inc., Milford, MS) equipped with an Alltima column (250 mm $\times$ 4.6 mm column packed with Alltima C18, 5 μm polymer; Alltech Associates Inc., Deerfield, IL). The column was subjected to the following gradient for 20 min (1 mL min^{-1} mobile phase): 6 min at 50:50% water acidified to pH 2.0 with acetic acid:acetonitrile, 8 min at 30:70% pH 2.0 water:acetonitrile, and 8 min at 50:50% pH 2.0 water:acetonitrile. Compounds were detected with a UV detector (250 and 225 nm), a fluorescence detector (228 nm ex and 433 nm em), and a beta ram radioactivity detector (INUS Systems Inc., Tampa, FL). Bentazon and metabolites were identified in each sample by comparing retention times (t_R) to values obtained for anthranilic acid, 6-hydroxybentazon, 8-hydroxybentazon, AIBA, bentazon, and methylbentazon (t_R values were 4.5, 5.0, 5.0, 5.2, 5.8, and 9.0 min, respectively). All compounds except 6- and 8-hydroxybentazon emitted fluorescence under conditions described above. RAD-HPLC analysis for quantification of the 6- and 8-hydroxybentazon and AIBA was difficult due to similar t_R's. However, strong fluorescence of AIBA allowed us to confirm its presence in samples.

After extraction of bentazon and metabolites, the soil samples were air-dried to determine nonextractable compounds. Duplicate subsamples (0.2 g) of each soil sample were mixed with 0.3 g of cellulose and combusted using a Packard Oxidizer 306 instrument (Packard Instruments Co., Meriden, CT). The $^{14}CO_2$ released during combustion was trapped in Carbo-Sorb and Permafluor (Packard Instruments Co., Meriden, CT) and counted on a liquid scintillation counter.

Statistical Analysis. Analysis of variance of the treatments was determined with the PROC GLM program of SAS (SAS Institute, Inc., 1989). Means were separated at $\alpha = 0.05$ using Fisher's least significant difference test. In addition, parameters for mineralization and degradation were derived using the PROC NLIN program of SAS.

RESULTS AND DISCUSSION

Mineralization of Bentazon. A moderate degree of bentazon mineralization, indicated by $^{14}CO_2$ evolution, was observed in both NT and CT treatments of all soils studied except the Dundee silt loam with no bentazon history (Table 2). There was no lag phase of $^{14}CO_2$ evolution at the onset of the experiment, indicating immediate bentazon metabolism by soil microflora. For bentazon history soils, mineralization of this herbicide after 6 d ranged from 1% to 3% of the applied ^{14}C and remained linear for the first 15−24 d of incubation (Figure 2).

Differences were observed between CT and NT treatments in the Miami, Saybrook, and Dundee history soils (Figure 2; Table 2). Mineralization of bentazon was significantly higher in NT than in CT Miami (18% versus 14% after 48 d) during all sample periods. In the Saybrook soils, significantly greater mineralization occurred in NT compared to CT for the first 42 d. Increases in plant residue in the NT soils, resulting in higher levels of organic matter (Table 1), may have enhanced microbial populations present in these soils, thus increasing the potential for bentazon mineralization. Although the Drummer NT soil had 2.5-fold

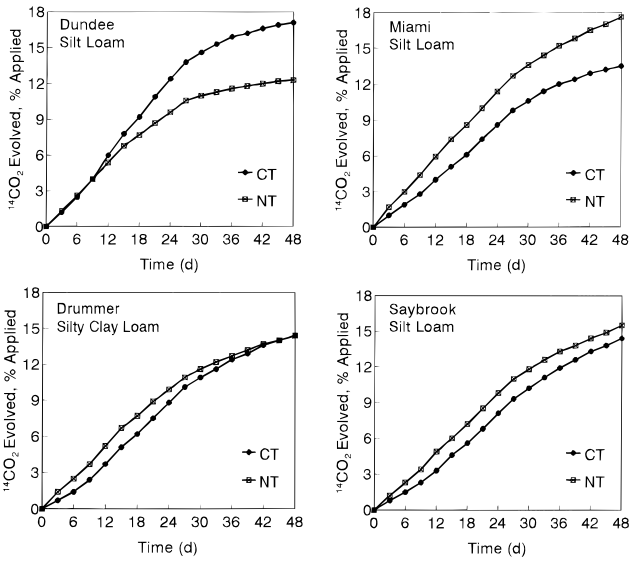

Figure 2. Effect of tillage on bentazon mineralization in Dundee, Miami, Drummer, and Saybrook soils with a history of bentazon application. Statistical analyses of selected days are presented in Table 1.

greater organic carbon content than the CT soil, the rate of bentazon mineralization was similar under both tillage treatments (Figure 2; Table 2). Because the Drummer CT soil had a much lower pH than the NT treatment, conditions may have been more favorable for fungal degradation of bentazon.

Mineralization of bentazon was significantly higher in CT than in NT Dundee soil with bentazon history (17% vs 12% after 48 d; Figure 2, Table 2). These results are similar to those of Locke and Harper (1991b) who found that over 20% of metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] applied to a Dundee soil (collected from the same experimental plots) was mineralized after 140 d in the CT soil, while less than 5% was mineralized in the NT soil. In a related study (Locke and Harper, 1991a), the addition of soybean residue to a Dundee silt loam significantly reduced the metribuzin mineralization. In this case metribuzin and/or metabolites seemed to be immobilized in plant residues and/or microbial biomass, thereby reducing the mineralization rate.

Increased mineralization of certain herbicides has been observed in certain NT compared to CT soils. Levanon et al. (1994) reported that atrazine was mineralized more rapidly in soils under NT than those under CT. Higher mineralization rates in NT soils were related to increased populations and activities of soil microorganisms. Zablotowicz et al. (1993) observed a more rapid mineralization of ring- and carboxyl-labeled 2,4-D in NT Miami, Drummer, and Saybrook soils compared to CT soils. Reddy et al. (1995) found that microbial populations and activities of Drummer, Miami, and Dundee soils under NT were significantly higher than those observed in corresponding CT soils. Increased initial mineralization of bentazon in NT treatments of Miami and Saybrook soils differed from the results of Reddy et al. (1995) who did not observe a tillage effect on chlorimuron [ethyl 2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-benzoate] mineralization. However, tillage did affect patterns of chlorimuron metabolite formation.

Repeated applications of bentazon in the Dundee soils enhanced mineralization (Table 2). The CT and NT soils with 8 year histories of this herbicide exhibited a 5−6-fold greater mineralization of bentazon, compared to that of soils with no history. These data suggest adaptation of a microbial community capable of mineralizing bentazon in soils receiving repeated applications of bentazon. Similar results were found by Dowler et al. (1987) and Skipper et al. (1986) for the carbamothioates butylate, EPTC, and vernolate. Fournier et al. (1993) demonstrated that increasing doses of 2,4-D enhanced populations of microorganisms capable of using the herbicide as a carbon source, thereby stimulating rapid degradation of 2,4-D after a second application.

Degradation of Bentazon. Dissipation of bentazon in the first 12 d was more rapid in both the Dundee and Miami soils under NT compared to CT (Table 2). After 12 d only 15.1% of the bentazon applied to the Dundee NT soil was recovered versus 33.9% in the CT soil. In the Miami soil, 40.5% of the applied bentazon remained in the NT soil, compared to 57.4% in the CT soil after 12 d. After 48 d, the recoveries from CT and NT were not significantly different in both Miami and Dundee soils.

There were no differences in persistence of bentazon due to tillage for the Drummer and Saybrook soils. In the Drummer soils, bentazon levels decreased at the same rate, from 60% after 6 d to 5% after 48 d. As in the assessment of mineralization, the lower pH of the Drummer CT soil could have favored fungal metabolism of bentazon. Otto et al. (1979) reported oxidative metabolism of bentazon by several species of soil-born fungi. This might mask the influence of organic matter content among tillage regimes on bentazon degradation in the Drummer soils. Bentazon levels in both CT and NT Saybrook soils decreased from 68% of that applied after 6 d to about 6% after 48 d. Bentazon persisted longest in the Dundee soils with no history of bentazon application. After 22 d, 71 and 77% of the applied bentazon remained in the CT and NT soils, respectively. Long-term persistence of bentazon in this nonhistory soil is further evidence that bentazon biodegradation is enhanced by repeated application of this herbicide. Because bentazon is typically absorbed by weed foliage instead of roots (Weed Science Society America, 1994), enhanced degradation of this herbicide in soil should not affect its potential for weed control. However, accelerated degradation should minimize the potential for detrimental environmental effects.

In general, bentazon degradation proceeded with the formation of a pool of bound as well as extractable metabolites. The NT Miami soil had significantly higher levels of nonextractable ^{14}C-labeled material than the CT soils (Table 2) at every sample period. In Dundee soils with bentazon history, levels of nonextractable material in NT were 1.7- and 1.3-fold higher than that of CT after 6 d and 12 d, respectively; however, they were not significantly different at 48 d. In Miami soils, levels of nonextractable material in NT were significantly greater than those of CT at all sample dates. These results are similar to those of Locke and Harper (1991b) who found higher levels of nonextractable ^{14}C in NT than in CT soil after metribuzin application. In contrast, there were no differences of nonextractable material between the NT and CT treatments of Drummer and Saybrook soils.

In Dundee soils with no bentazon history, nonextractable material in CT soil was higher than in NT soil. Gaston et al. (1996) found higher microbial populations in this NT soil. They suggested that metabolic activity of these populations may have produced anaerobic

Table 3. Model Parameters for Bentazon Mineralization and Degradation

soil	tillage[a]	k_D (d^{-1})	k_U (d^{-1})	k_M (d^{-1})	DT_{50} (d)
Dundee	CT	0.079 ± 0.003[b]	0.100 ± 0.032	0.023 ± 0.005	8.77 ± 0.33
silt loam (history)	NT	0.104 ± 0.011	0.127 ± 0.134	0.018 ± 0.016	6.66 ± 0.70
Miami	CT	0.046 ± 0.001	0.127 ± 0.030	0.024 ± 0.005	15.07 ± 0.33
silt loam	NT	0.080 ± 0.003	0.089 ± 0.034	0.020 ± 0.006	8.66 ± 0.32
Drummer	CT	0.084 ± 0.001	0.055 ± 0.008	0.011 ± 0.001	8.25 ± 0.10
silty clay loam	NT	0.079 ± 0.003	0.112 ± 0.040	0.019 ± 0.005	8.77 ± 0.33
Saybrook	CT	0.066 ± 0.001	0.056 ± 0.004	0.012 ± 0.001	10.50 ± 0.16
silt loam	NT	0.066 ± 0.001	0.093 ± 0.016	0.019 ± 0.002	10.50 ± 0.16
Dundee	CT	0.018 ± 0.002	nd	nd	38.51 ± 4.28
silt loam (nonhistory)	NT	0.014 ± 0.002	nd	nd	49.51 ± 7.07

[a] CT = conventional-tillage, NT = no-tillage. [b] Standard error.

conditions, particularly within soil aggregates, leading to slower bentazon degradation. This could have led to less accumulation of bound material in the NT soil than in the corresponding CT soil.

The major metabolite in most of the soil extracts was methylbentazon. After 48 d of the experiment, this compound was found in all extracts, ranging from 1.7% to 4.5% of the applied ^{14}C (Table 2). These levels approached, and in some cases exceeded, the levels of bentazon remaining in the soil (i.e., Dundee CT and NT at 48 d). These results suggest that N-methylation is one step in the biotransformation of bentazon (Figure 2). Because the level of methylbentazon in soil extracts increased as the experiment progressed, it is likely that this metabolite persisted longer than others, such as AIBA and the hydroxybentazons. Gaston et al. (1995) showed that methylbentazon is highly adsorbed by soil. N-methylation occurs via a *N*-methyltransferase-catalyzed methyl transfer from *S*-adenosylmethionine (Iwan, 1976; Borchardt, 1980). Microbial methylation of the pesticide 2,4-D and pentachlorophenol has been shown to occur (Iwan, 1976).

Two bentazon metabolites, AIBA and anthranilic acid, arising from the hydrolysis of N−S bonds of the thiadiazine structure, as well as 6- and/or 8-hydroxybentazon were found in soil extracts (listed as others in Table 2). We were unable to separate the hydroxy bentazons by TLC or HPLC methods. The distribution of these metabolites in the extracts was transient, random, and not related to treatment or sampling time. Anthranilic acid and AIBA can be incorporated into humic materials by oxidative coupling reactions similar to mechanisms described by Tatsumi et al. (1994a,b). Most likely, the hydroxybentazons were quickly incorporated into the soil organic matter and thereby rendered unextractable. The appearance of these metabolites suggests that both pathways of bentazon degradation occurred; however, we were unable to ascertain the dominant pathway of degradation. Pure cultures of several genera of soil fungi (*Mucor, Penicillium, Rhizopus,* and *Trichoderma*) were found to form 6- and 8-hydroxybentazon upon exposure to bentazon (Otto et al., 1979).

Kinetics of Bentazon Mineralization and Degradation. Production of bound and extractable metabolites may be incorporated into a substrate mineralization model. Under the assumption that bound metabolites were not mineralized,

$$dP_E/dt = k_D S - (k_M + k_U)P_E \quad (1)$$

$$dP_U/dt = k_U P_E \quad (2)$$

$$dP_M/dt = k_M P_E \quad (3)$$

where the subscripts E, U, and M refer to extractable metabolites, unextractable metabolites, and evolved $^{14}CO_2$, respectively; P_j is mass (μmol) of metabolite(s); S is mass of bentazon; k_D, k_U, and k_M (all, d^{-1}) are first-order rate constants for bentazon degradation, metabolite binding, and mineralization, respectively; and t is time (d). Equations 1−3 may be successively solved starting with the first-order substitution $S = \exp(-k_D t)$. It was not possible to distinguish between solution and sorbed (nonbound) species by the methodology used. Therefore, these phases were pooled, and mass rather than concentration was used as the dependent variable. Bentazon exhibits negligible sorption in most soils (Abernathy and Wax, 1973). Furthermore, sorption kinetics are rapid, with little or no increase in sorption for reaction times up to 5 d (Gaston et al., 1996).

In principle, all four data sets (S, P_E, P_U, and P_M) may be used in estimating model parameters. However, since differentiation between extractable and unextractable metabolites was based on methodology, measured values for P_E and P_U may only loosely correspond to actual pools of metabolites available (or unavailable) for microbial/enzymatic degradation. Furthermore, recovery of ^{14}C was <100%, so that attempts to fit all four data sets would compromise accuracy in the description of one or more. Therefore, only data for extractable bentazon and evolved $^{14}CO_2$ were used to estimate the three parameters k_D, k_U, and k_M. These parameters were optimized by fitting eqs 1−3 to the data using a least-squares procedure. The half-life of bentazon (DT_{50}) for each soil/tillage treatment was determined by the following equation:

$$DT_{50} = -\ln(0.5)/k_D \quad (4)$$

Bentazon degradation in all 10 soils was adequately described by first-order kinetics (Table 3). The half-life of bentazon ranged from 4.59 to 49.51 d (first-order rate constants for bentazon degradation (k_D) ranged from 0.014 to 0.151 d^{-1}; Table 3). The half-lives for nonhistory Dundee NT and CT were 3−11-fold higher than bentazon half-lives of the other soils studied. This suggests that even one application of bentazon may significantly reduce the persistence of this herbicide. Only the Dundee history and Miami soils, the two soils with the longest history of bentazon application, exhibited an effect of tillage on the half-life of bentazon. Half-lives were lower in NT treatments with the greatest effect in the Miami soil, providing further evidence that history of bentazon application stimulated its degradation. Huber and Otto (1994) determined that the mean DT_{50} for bentazon was about 46 d in the laboratory and 12 d in the field (average of several field locations in Germany and the United States). Bentazon half-lives in all the soil/tillage combinations, with the exception of the Dundee nonhistory soils, were less than values

reported in laboratory studies and also similar to values reported for field experiments.

For the most part, differences in bentazon levels between NT and CT within each soil were minimal after 48 d. However, with the exception of the Dundee soil without bentazon history, bentazon levels rapidly decreased to values ranging between 15% and 57% applied 12 d after application. This suggests that the critical time period to consider the fate of bentazon is during the first 2 weeks after bentazon application (see 6 and 12 d data, Table 2). This is also the most important time period to consider the efficacy of bentazon for weed control and its environmental fate.

CONCLUSIONS

This study demonstrated that bentazon is short-lived in soils that have had previous exposure (1−2 week DT_{50}). Furthermore, soils with a long history of bentazon application have greater ability to degrade it under NT than under CT. Bentazon is primarily degraded to products that are rapidly incorporated into soil organic matter, although a significant amount is mineralized to CO_2. However, one product that persists is methylbentazon. These results provide evidence that the bentazon persistence in soils is affected by soil management practices, such as no-tillage.

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