

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/216763397>

# Trifluralin Degradation under Microbiologically Induced Nitrate and Fe(III) Reducing Conditions

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · AUGUST 2000

Impact Factor: 5.33 · DOI: 10.1021/es9912473

CITATIONS

37

READS

48

5 AUTHORS, INCLUDING:



Jason Tor

Hampshire College

11 PUBLICATIONS 504 CITATIONS

SEE PROFILE



Michelle Wander

University of Illinois, Urbana-Champaign

52 PUBLICATIONS 1,428 CITATIONS

SEE PROFILE



Sims Jerry

University of Illinois, Urbana-Champaign

57 PUBLICATIONS 1,525 CITATIONS

SEE PROFILE

# Trifluralin Degradation under Microbiologically Induced Nitrate and Fe(II) Reducing Conditions

JASON M. TOR,<sup>†,‡</sup> CAIFEN XU,<sup>‡</sup>  
JOSEPH M. STUCKI,<sup>‡</sup>  
MICHELLE M. WANDER,<sup>‡</sup> AND  
GERALD K. SIMS<sup>\*,§</sup>

*Department of Natural Resources and Environmental Sciences, University of Illinois, 1102 South Goodwin Avenue, Urbana, Illinois 61801, and United States Department of Agriculture Agricultural Research Service, 1102 South Goodwin Ave, Urbana, Illinois 61801*

Trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)-benzenamine] ranks among the most commonly used herbicides in the United States. The compound persists under most environmental conditions, yet it is rapidly transformed under certain anaerobic conditions. In this study, the fate of trifluralin in anoxic environments and the contribution of Fe(II) to its anaerobic degradation have been investigated. Trifluralin was rapidly degraded under anaerobic conditions in a range of soils representing typical agricultural usage in the Midwest. The presence of nitrate or oxygen suppressed trifluralin degradation. Degradation rate increased under iron-reducing conditions, and the addition of trifluralin appeared to promote reoxidation of extractable Fe<sup>2+</sup>. Transformation of trifluralin under iron-reducing conditions apparently involved the soil solid phase and was not limited by bioavailability. In a soil-free aqueous system, no reaction of trifluralin with dissolved Fe<sup>2+</sup> was detected in the presence or absence of kaolinite clay under anoxic conditions. Reduced but not oxidized or reoxidized forms of purified ferruginous smectite (sample Swa-1) catalyzed rapid transformation (72% of applied in 30 h) of trifluralin to polar products with a concomitant reoxidation of structural Fe in the clay. Results indicate that, as for other nitroaromatics, trifluralin is subject to reaction with Fe(II) associated with the minerals in anoxic environments.

## Introduction

Trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine] has been used since 1963 for control of a variety of weeds in agronomic and horticultural crops. In 1995 over  $6.5 \times 10^6$  kg of trifluralin was used in the United States (1). At 25 °C, the compound has limited water solubility (0.3 mg/L), moderate volatility (vapor pressure:  $9.5 \times 10^{-3}$  Pa), and a high  $K_{oc}$  (log  $K_{oc}$  = 5.07) for a herbicide (2). Trifluralin is essentially immobile toward leaching, can be transported offsite via volatilization, or may move with particulate

material in surface runoff. The environmental fate of trifluralin has been extensively reviewed by Grover et al. (3). Trifluralin undergoes photolysis readily and is subject to various abiotic and biologically mediated transformations in the environment. Metabolites detected have been attributed to common reaction mechanisms, such as reduction of the nitro groups to amines, especially in anaerobic environments (3, 4). Willis et al. (5) reported accelerated trifluralin degradation at redox potentials between 150 and 50 mV, whereas degradation was slower in the absence of O<sub>2</sub> at higher redox potentials. Similar results were reported by Crawford (6) in an experiment with river sediments in which trifluralin degradation and iron reduction were delayed in the presence of nitrate. The labile nature of trifluralin in mildly reducing environments is recognized by the manufacturer, as the product label discourages application of the material to soils that are wet or periodically flooded, due to reduced herbicidal efficacy.

That Fe(II) can serve as an electron donor in the reduction of nitroaromatic compounds has been well documented (7, 8). On the basis of observations of accelerated trifluralin degradation and accumulation of reduced transformation products under apparently Fe(III)-reducing conditions (50–150 mV), it is plausible that anaerobic transformation of the compound is facilitated by reduced iron. To the best of our knowledge, Fe<sup>2+</sup> has not been implicated in the degradation of trifluralin in flooded soils. The major objectives of this experiment were to examine factors that control trifluralin degradation in anoxic environments and to assess the contribution of reduced Fe to the anaerobic degradation of trifluralin. Soil incubations emulated temporarily flooded upland soils and utilized initially aerobic conditions. Reaction of trifluralin with dissolved Fe<sup>2+</sup> was examined in the presence and absence of kaolinite clay. The potential for transformation of trifluralin by structural Fe(II) in smectite SWa-1 was also examined.

## Materials and Methods

**Experimental Design.** The experiment consisted of five separate studies. An initial study was performed to determine whether the relationship between trifluralin degradation rate and redox regime was sufficiently reproducible among soils to merit further investigation. Changes in trifluralin degradation kinetics were measured as flooded soils (16 soils with a range of properties) in biometers progressed from nitrate-reducing to iron-reducing conditions. In that study, NO<sub>3</sub><sup>−</sup> concentration in the floodwater was measured daily until it was no longer detectable (<1.0 mg/kg of soil). After depletion of NO<sub>3</sub><sup>−</sup> (1–16 d), half of the biometers were extracted for analysis of Fe<sup>2+</sup> and trifluralin as described below. Remaining biometers were then incubated an additional 21 d, after which they were again extracted for Fe<sup>2+</sup> and trifluralin analyses. A more detailed kinetic study was then performed using two of the 16 soils above (S10 and S11). The kinetic study differed from the initial study in that both flooded and aerobic treatments were included, and Fe(II) as well as trifluralin were determined at 3, 7, 10, 16, 21, 28, and 43 d of incubation. The effect of a carbon source (2 mM ethanol) on Fe<sup>3+</sup> reduction and trifluralin degradation in soils S8 and S16 was examined in the same manner as the kinetic study, with sampling for Fe<sup>2+</sup> and trifluralin occurring at 2, 4, 7, 12, 19, 26, and 33 d. The extent of Fe<sup>3+</sup> reduction was measured in the presence and absence of trifluralin after 11, 18, and 46 d of incubation in soil S15. The final studies, described in detail below, examined the potential for exchangeable Fe<sup>2+</sup> adsorbed onto kaolinite clay and structural Fe(II) in SWa-1

\* Corresponding author phone: (217)333-6099; fax: (217)333-5251; e-mail: gk-sims@uiuc.edu.

<sup>†</sup> Present address: Department of Microbiology, University of Massachusetts, Amherst, MA.

<sup>‡</sup> University of Illinois.

<sup>§</sup> United States Department of Agriculture Agricultural Research Service.

**TABLE 1. Site Characteristics and Selected Properties of Surface 15 cm of Soils<sup>a</sup>**

soil	pH	texture (g (kg of soil) <sup>-1</sup> )			respiration (kg ha <sup>-1</sup> d <sup>-1</sup> )	soil organic C (g (kg of soil) <sup>-1</sup> )
		sand	silt	clay		
1	6.9	21	423	556	40	22.9
2	6.4	15	355	630	120	17.9
3	6.6	20	470	509	39	17.8
4	6.5	103	420	476	57	21.7
5	6.4	190	373	438	63	8.2
6	6.1	167	372	461	69	23.0
7	6.7	40	447	513	67	22.6
8	6.1	43	474	335	60	16.5
9	6.7	116	478	407	48	17.7
10	5.7	124	446	430	33	17.4
11	6.4	54	358	588	54	8.6
12	6.2	40	463	497	31	7.1
13	6.4	58	425	516	25	8.7
14	7.2	38	441	521	30	6.5
15	6.2	51	393	556	57	11.5
16	6.5	60	241	700	53	19.9

<sup>a</sup> Soil pH was determined with a 1:1 soil:water ratio. Texture (sand, silt, clay) was determined using the hydrometer method (9). Organic carbon was determined by dry combustion (10). Respiration was performed in the field by a sealed chamber method using headspace analysis.

smectite to catalyze transformation of trifluralin. All studies were conducted using a minimum of three replicates.

**Chemicals.** Uniformly ring-labeled [<sup>14</sup>C]trifluralin (specific activity =  $5.48 \times 10^8$  Bq mmol<sup>-1</sup>) was obtained from Sigma Chemical Company, St. Louis, MO. Unlabeled trifluralin (chemical purity = 99%) was obtained from Chem Service, West Chester, PA. Organic solvents and water were Optima grade (Fisher Scientific, Pittsburgh, PA).

**Soil.** During the spring of 1996, 16 soils from farms throughout Illinois were collected to a depth of 15 cm, placed in polyethylene bags, and transported on ice. All samples were passed through a 4-mm screen, homogenized, and stored at 5 °C until needed. Chemical, physical, and biological properties of the soils are listed in Table 1.

**Soil Incubation.** Incubations were performed using serum bottle biometers (120 mL) containing 15 g of field moist soil and 20 mL of deoxygenated water. Just prior to flooding, [UL-ring-<sup>14</sup>C]trifluralin was added in 30  $\mu$ L of methanol to each microcosm to produce a final concentration of 0.65 mg/kg of soil with a specific activity of  $1.18 \times 10^7$  Bq mol<sup>-1</sup> (prepared by diluting the stock with unlabeled trifluralin). To the biometer was then added a CO<sub>2</sub> trap consisting of a 12  $\times$  75 mm disposable culture tube containing 2 mL of 0.2 M NaOH and fitted with a polyurethane foam plug (PUF) to trap labeled volatiles. The microcosm headspace was flushed with N<sub>2</sub>, immediately crimp sealed with a butyl stopper, and incubated in the dark at  $25 \pm 3$  °C. Microcosms and trifluralin stock solutions were protected from light to avoid photodecomposition, and syringes were purged with nitrogen to avoid oxygen intrusion into the biometers.

**Sample Preparation.** Destructive sampling of biometers was accomplished by removing the tube containing the base trap and PUF plug, followed by agitating the biometer for 1 min, and transferring contents to a 50-mL Teflon centrifuge tube. The solid and liquid phases of the soil slurry were then separated by centrifugation (15 min, 15000g). Volatilized trifluralin was determined by direct liquid scintillation spectrometry (LSS) analysis of PUF plugs (11). Quantification of <sup>14</sup>CO<sub>2</sub> in NaOH traps was accomplished by direct LSS. Biosafe II (Research Products International, Mt. Prospect, IL) was used for LSS with the exception of flow analysis described below.

Aqueous samples were removed and filtered (PVDF, 0.2  $\mu$ m), and pH was determined prior to further analysis. Labeled

H<sup>14</sup>CO<sub>3</sub><sup>-</sup> in the aqueous phase was determined by loss of radioactivity following treatment of an aliquot (1 mL) with saturated BaCl<sub>2</sub> to precipitate dissolved CO<sub>2</sub> as BaCO<sub>3</sub>. An additional aliquot (1 mL) of the water phase was extracted in a 4.0-mL vial with 2.0 mL of hexane:ethyl acetate (97:3) on a reciprocating shaker for 1 h. The organic layer was collected for analysis of trifluralin and transformation products.

Soil was extracted in a Teflon centrifuge tube with 20 mL of hexane:ethyl acetate (97:3) on a reciprocating shaker for 24 h. Extracts were centrifuged (5000 g) for 5 min, and the supernatant retained for analysis of trifluralin and transformation products.

**Analysis of Trifluralin and Transformation Products.** Aqueous and extractable trifluralin and transformation products were quantified after separation by solid-phase extraction (SPE) on 100-mg silica cartridges (Alltech, Deerfield, IL). After the extracts (1.0 mL) were loaded onto the cartridges, hexane:ethyl acetate (97:3) was used to quantitatively elute trifluralin into a 20-mL scintillation vial. Polar metabolites were then eluted from the column with 2.5 mL of methanol. <sup>14</sup>C-Labeled trifluralin and metabolites were determined via LSS. The procedure was possible due to the large difference in polarity between trifluralin and its transformation products (4). Confirmation of the SPE method for incubated samples containing transformation products was accomplished by HPLC (Hewlett-Packard, Waldbronn, Germany) using a 250 mm  $\times$  5 mm, 10  $\mu$ m particle size C<sub>18</sub> column (Alltech, Waukegan, IL), with radioactivity detection employing a Packard flow scintillation analyzer and Ultima-Flo LSS cocktail (Packard Instruments, Meriden, CT). Separation was achieved with a linear acetonitrile:water gradient in which the solvent ratio changed from 55:45 (acetonitrile:water) to 100:0 over a 10-min period, followed by a 5-min isocratic period (100% acetonitrile). At a flow rate of 1 mL/min, trifluralin had a reproducible retention time of 10.1 min in this system.

**Analyses of Nitrate and Ferrous Iron.** Nitrate was determined by adapting the method of Vendrell and Zupancic (12) to a microtiter plate. A 50- $\mu$ L aliquot of sample was added to a 96-well plate (Corning No. 25860, Corning, NY) and evaporated to dryness at 38 °C. After being dried, 10  $\mu$ L of salicylic acid reagent (5% in 18 M H<sub>2</sub>SO<sub>4</sub>) was added to each well, and the plate was agitated for 10 min. After being cooled, 238  $\mu$ L of 1.7 M NaOH was added to each well; the plate was again agitated; and after allowing 30 min for color development, absorbance was measured at 410 nm with a Model UV900HDI plate reader (Bio-Tek Instruments, Winooski, VT).

Extractable ferrous iron was determined with a modification of the Lovely and Phillips (13) ferrozine method. Each sample was extracted with 5 mL of 0.5 M HCl for 1 h in a 50-mL Teflon centrifuge tube on a horizontal shaker. The tube was centrifuged (15000g) for 10 min, and the supernatant was filtered through a GF/C glass-microfiber filter (Whatman, Maidstone, England). A 5- $\mu$ L aliquot of each extract was added to a well containing 250  $\mu$ L of color reagent prepared by dissolving ferrozine (1 g/L) in 50 mM HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid) buffered at pH 7. The plate was agitated on a vortex mixer for 30 min to allow color development, and absorbance was determined at 590 nm.

Structural Fe(II) present in SWa-1 smectite was determined after digestion in 1 mL of 48% HF and 12 mL of 3.6 M H<sub>2</sub>SO<sub>4</sub> as described by Komadel and Stucki (14) with the 1,10-phenanthroline colorimetric determination (15) scaled to microtiter plate format.

**Unextractable Radioactivity.** Unextractable radioactivity (bound residue) was determined on samples that had been previously extracted with hexane:ethyl acetate (97:3), dried (60 °C), and ground with a mortar and pestle. Unextractable

$^{14}\text{C}$ -labeled residues were quantified using combustion at 900 °C (Biological Oxidizer, OX500, R. J. Harvey Instruments, Hillsdale, NJ), and LSC of collected  $^{14}\text{CO}_2$ .

**Clay Suspensions.** Aqueous suspensions of 0.5 g of Na-saturated kaolinite and dissolved  $\text{Fe}^{2+}$  were prepared in Teflon centrifuge tubes. Three treatments were used: (a) 0.01 M NaCl, (b) 0.1 M  $\text{FeCl}_2$  (Fisher), and (c) 7.0 M  $\text{FeCl}_2$ . Kaolinite was washed three times with 2.0 M NaCl followed by three washes with one of the solutions described above. Reactions of trifluralin with smectites were examined using suspensions containing 100 mg of either oxidized, reduced, or reduced-reoxidized smectite. Reduced (using  $\text{Na}_2\text{S}_2\text{O}_4$ ) and reoxidized (using  $\text{O}_2$ ) smectites (SWa-1) were prepared from the lyophilized oxidized (unaltered) clay by the procedure of Stucki et al. (16). Solutions used with kaolinite or reduced smectite were prepared in deoxygenated, deionized water, filtered through 0.2- $\mu\text{m}$  pore diameter membrane filters (Alltech, Waukegan, IL) and maintained under an  $\text{O}_2$ -free  $\text{N}_2$  atmosphere.

Reaction mixtures were prepared from the above clay suspensions, to which was added [ $^{14}\text{C}$ ]trifluralin (0.3  $\mu\text{g}/\text{mL}$ , 9250 Bq), and 0.01 M NaCl in a total volume of 30 mL. The treated suspensions were extracted with hexane:ethyl acetate (97:3) as described above, and analyses of trifluralin and degradation products were performed on the extract.

**Statistical Analyses.** Data were subjected to statistical analysis using the SAS system (SAS Institute). Coefficients of variability (CV) were determined as the sample standard deviation expressed as a percentage of the sample mean.

## Results and Discussion

**Initial Investigation.** Soils responded similarly to flooding, resulting in decreased redox potential (Pt electrode), slight increase in pH, depletion of nitrate, and accumulation of  $\text{Fe}^{2+}$ . Nitrate declined to below 1 mg/kg of soil within 7 d for 13 of the soils and was depleted from all soils after 16 d. Accumulation of  $\text{Fe}^{2+}$  was not observed before nitrate had decreased to a concentration of less than 1 mg/L, thus the two phases of the incubation are described hereafter as nitrate-reducing and iron-reducing conditions. Several studies have shown that  $\text{Fe}^{3+}$  is not reduced in the soil as long as nitrate is present (17, 18) due to the ability of nitrate reducers to outcompete  $\text{Fe}^{3+}$  reducers (19).

Rates of trifluralin degradation among soils converged and were significantly ( $\alpha = 0.025$ ) faster (1.2-fold) and less variable under iron-reducing conditions (CV = 10.2) than under nitrate-reducing conditions (CV = 50.4). Degradation of trifluralin was not correlated ( $\alpha = 0.05$ ) with initial soil pH, respiration, or biomass under either redox regime. Though accounting for less than 1% of the total trifluralin added, trifluralin initially in solution was negatively correlated ( $\alpha = 0.05$ ;  $r^2 = 0.48$ ) with degradation kinetics, implying that bioavailability was not rate-limiting. A significant correlation ( $\alpha = 0.05$ ;  $r^2 = 0.5206$ ) was observed between degradation

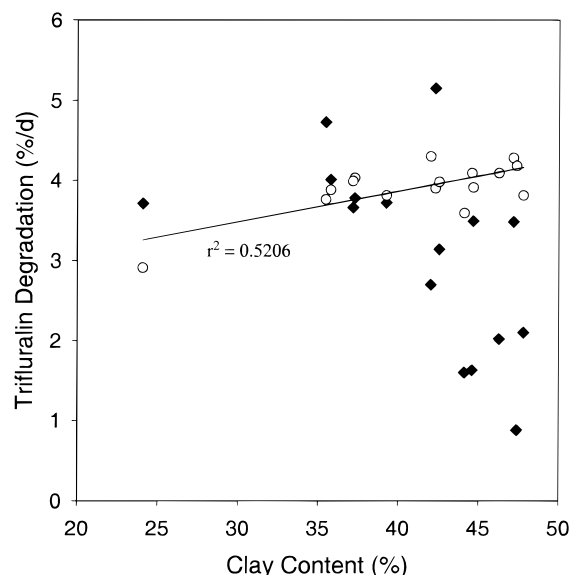


FIGURE 1. Trifluralin degradation (% of total) in the preliminary study under nitrate- (◆) and Fe(III)-reducing (○) conditions as a function of the fraction of clay-sized particles (<2  $\mu\text{m}$ ).

kinetics and the fraction of clay-sized particles only under iron-reducing conditions, suggesting a role of soil minerals in the transformation of trifluralin (Figure 1). Studies on reduction of nitrobenzenes indicate a requirement for a colloidal support, such as a clay or iron mineral in order for  $\text{Fe}(\text{II})$  to serve as a reductant (8).

On the basis of these observations, further study of the role of  $\text{Fe}^{2+}$  in trifluralin degradation was justified. Thus, we conducted a detailed study of trifluralin fate under aerobic, nitrate-reducing, and iron-reducing conditions, using a subset of the soils evaluated in the preliminary work above.

**Role of Fe(III) Reducing Conditions.** The mass balance for  $^{14}\text{C}$  in incubation studies after 10 d with soils S10 and S11 is reported in Table 2. As expected, sorbed trifluralin was the dominant form, with bound residues accumulating over time. As aforementioned, less than 1% of applied radioactivity was accounted for as aqueous phase trifluralin. Volatilization, mineralization, and accumulation of metabolites accounted for a minor proportion of the trifluralin recovered in all three redox regimes. Flooding resulted in a 50–75% decrease in volatilization losses. Under all conditions studied, soil sorption exceeded volatilization by at least 7-fold, demonstrating that PUF traps were a weaker sink for trifluralin than soil, and thus soil was not depleted of trifluralin by the PUF traps. Trends in volatilization losses were similar to previous findings with trifluralin (3). The primary fate of trifluralin was to be incorporated into unextractable bound residues. Under aerobic conditions, formation of bound trifluralin

TABLE 2. Redox Regime Effects on  $^{14}\text{C}$  Distribution 10 d after [ $^{14}\text{C}$ ]Trifluralin Application to Soil

	$^{14}\text{C}$ recovered as % of initial [ $^{14}\text{C}$ ]trifluralin <sup>a</sup>							
	soil S10				soil S11			
	oxic	nitrate reducing	iron reducing	LSD <sup>b</sup>	oxic	nitrate reducing	iron reducing	LSD <sup>b</sup>
volatilized	9.94	4.33	0.61	1.32	14.95	5.00	1.64	1.48
mineralized	0.52	0.12	0.13	0.20	0.81	0.31	ND <sup>c</sup>	0.42
aqueous $^{14}\text{C}$	0.06	0.01	0.24	0.21	0.06	0.16	1.17	0.38
metabolites	1.90	4.09	ND	0.53	3.36	5.77	ND	1.48
extractable trifluralin (sorbed)	83.32	71.86	28.47	7.63	63.72	52.75	29.50	5.60
unextractable (bound)	9.35	10.40	54.28	10.35	19.26	22.24	57.83	2.48
total recovered	105.09	90.81	83.73		102.16	86.23	90.14	

<sup>a</sup> Results are means of triplicate tests. <sup>b</sup> Least significant differences at  $\alpha$  level of 0.05. <sup>c</sup> ND, not detected.



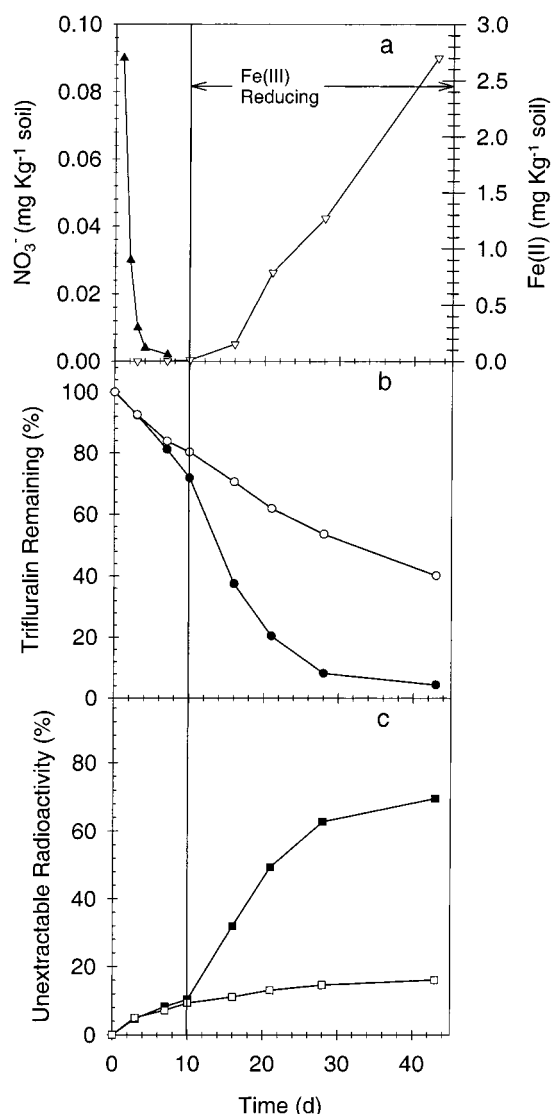


FIGURE 2. Time course for electron acceptors ( $\text{NO}_3^-/\text{Fe(II)}$ ), trifluralin degradation (% of total), and bound residue accumulation in aerobic and flooded soil (S8). (a) Loss of nitrate (▲) and accumulation of Fe(II) (▽). (b) Trifluralin loss in flooded (●) soils versus aerobic soil (○). (c) Bound residue in flooded (■) soil versus aerobic soil (□).

residues has been reported to involve metabolites rather than the parent compound (4). In this study, loss of trifluralin and accumulation of bound residues occurred with concomitant decrease in sorbed trifluralin, and both processes were

dramatically enhanced (2–5-fold) under iron-reducing conditions as compared to either aerobic or nitrate-reducing conditions. Total recovery of  $^{14}\text{C}$  ranged from approximately 83 to 105%.

As noted previously, accumulation of  $\text{Fe}^{2+}$  was observed immediately following depletion of nitrate (Figure 2a), resulting in a clear differentiation of the iron- and nitrate-reducing phases as distinct components of the incubation. In flooded soil, trifluralin dissipation exhibited biphasic kinetics with an increase in rate coinciding with the onset of  $\text{Fe}^{2+}$  accumulation (Figure 2b), suggesting a role for reduced Fe in trifluralin degradation under anaerobic conditions. Similarly, unextractable bound residues accumulated more rapidly after the appearance of  $\text{Fe}^{2+}$  (Figure 2c), perhaps due to transformation of trifluralin to reactive products or changes in the solid phase that reduced extraction recovery. The rate of trifluralin degradation did not differ between aerobic and nitrate-reducing conditions and exhibited a half-life approximately 3-fold greater than under iron-reducing regimes. The above findings were similar for both soils used.

Addition of carbon has been shown to stimulate microbial activity and promote the accumulation of  $\text{Fe}^{2+}$  in some anaerobic environments (7, 20). In the present study, addition of 2.0 mM ethanol to soils S8 and S16 resulted in a significant increase ( $\alpha = 0.05$ ) in  $\text{Fe}^{3+}$  reduction as well as degradation of trifluralin (Table 3), although ethanol had a negligible effect on the half-life (for loss of total atrazine) predicted over the 33-d study period. No conclusion can be drawn as to whether the effect of ethanol on trifluralin degradation was direct (due to stimulation of trifluralin-degrading microorganisms) or indirect (resulting from stimulation of  $\text{Fe}^{3+}$  reduction). The latter possibility, however, is supported by observations of Crawford (6), in which trifluralin was transformed upon addition to sediments that had been allowed to accumulate  $\text{Fe}^{2+}$  under reducing conditions and were then sterilized by  $\gamma$ -irradiation prior to trifluralin addition.

Addition of trifluralin ( $0.65 \mu\text{g g}^{-1}$ ) to soil S15 under iron-reducing conditions resulted in a significant decrease (up to 19% decrease) in  $\text{Fe}^{2+}$  accumulation at each sampling time, with the effect becoming less pronounced with increasing incubation time. Results of previous studies with nitrobenzenes showed that, in the presence of a mineral phase,  $\text{Fe}^{2+}$  can serve as an electron donor in the reduction of nitro groups to amines (8, 21). It is expected that  $\text{Fe}^{2+}$  would be consumed in such a reaction, thus the negative effect of trifluralin on  $\text{Fe}^{2+}$  accumulation reported here may be attributed to reoxidation of  $\text{Fe}^{2+}$  by trifluralin.

A first-order kinetic model provided a good description of trifluralin dissipation under each redox regime investigated. Coefficients of determination ( $r^2$ ) ranged from 0.864 to 0.999. These results are somewhat surprising for a compound with such low water solubility, as sorption would be expected to

TABLE 3. Ethanol (2 mM) Effects on  $^{14}\text{C}$  Distribution 12 d after [ $^{14}\text{C}$ ]Trifluralin Application to Soil

	$^{14}\text{C}$ recovered as % of initial [ $^{14}\text{C}$ ]trifluralin <sup>a</sup>					
	soil S8			soil S16		
	control	ethanol	$P(T-t)^b$	control	ethanol	$P(T-t)^b$
volatilized	2.90	2.65	**	3.63	2.73	**
mineralized	0.30	0.32		0.33	0.38	
aqueous $^{14}\text{C}$	0.78	0.35		1.65	2.72	
metabolites	6.36	3.79	***	3.71	3.87	
extractable trifluralin (sorbed)	42.99	30.51	***	38.85	30.55	***
unextractable (bound)	34.71	55.52	***	41.68	52.09	**
total recovered	88.04	93.14		89.85	92.34	
Fe(II) (mg (kg of soil) <sup>-1</sup> )	0.03	0.47	***	0.47	0.79	**

<sup>a</sup> Results are means of triplicate tests. <sup>b</sup>  $t$ -test significance at  $\alpha = 0.05$ , \*, 0.025, \*\*, 0.01, \*\*\*.

TABLE 4. Fe(II) in Soils with and without Trifluralin (0.65 mg (kg of soil)<sup>-1</sup>) Treatment

DAT	control	treated	P (T-t)
11	0.209	0.171	0.029
18	1.099	0.959	0.011
46	2.916	2.671	0.246

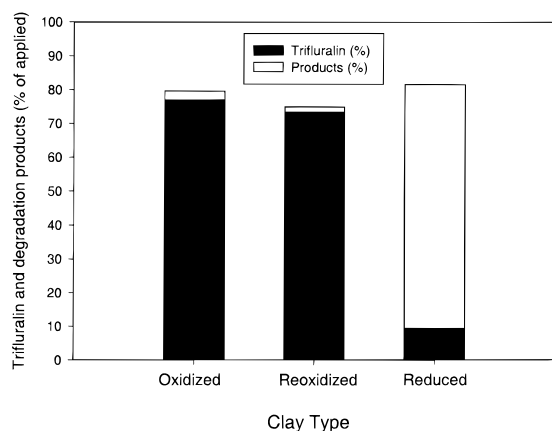


FIGURE 3. Transformation of [<sup>14</sup>C]-trifluralin (0.3 mg mL<sup>-1</sup>) by oxidized, reduced-reoxidized, and reduced SWa-1 smectite.

reduce availability and induce tailing of dissipation kinetics. Aerobic dissipation of dinitroaniline herbicides has been described with a two-compartment model due to the limited aqueous pool and slow replenishment through desorption (22). Trifluralin has been shown to resist desorption (3). The very small solution-phase pool observed here did not undergo the characteristic depletion (23) expected for an aqueous-phase transformation process involving a hydrophobic substrate supplied to the solution by desorption. Transformation occurring at the solid phase may account for these results.

**Clay Suspensions.** The potential of Fe(II) to serve as an electron donor in the transformation of trifluralin was investigated using dissolved Fe(II) in the presence and absence of kaolinite and smectite (SWa-1) bearing reduced or oxidized structural Fe. Less than 4% conversion of trifluralin to degradation products was detected after reaction with 0.0–7.0 M Fe<sup>2+</sup> for up to 11 d. Similar results were obtained when trifluralin was reacted with Fe<sup>2+</sup> (up to 7.0 M) in the presence of kaolinite. Klausen et al. (8) reported no reaction of nitrobenzenes with Fe<sup>2+</sup>, whereas immediate reduction of nitrobenzene and monosubstituted nitrobenzenes was observed when kaolinite was included. Failure of trifluralin to react with Fe<sup>2+</sup>-substituted kaolinite as previously observed for simple nitrobenzenes may be attributed to effects of the dipropylamine or trifluoromethyl functional groups.

Less than 3% of applied trifluralin was recovered as degradation products after reaction with oxidized or reduced-reoxidized smectite, whereas polar products accounted for 72% of the applied radiocarbon in the presence of reduced smectite (Figure 3). The extent of reduction of the structural Fe declined from 70% of the total to less than 40% as a result of reaction with trifluralin. These data show that structural Fe(II) is a highly effective reductant for abiotic transformation of trifluralin. On the basis of transformation of simple nitroaromatics in the presence of Fe(II) on a wide range of mineral surfaces (8), Fe-bearing minerals in addition to smectites may be expected to catalyze degradation of trifluralin in anoxic environments.

Trifluralin was rapidly degraded under anaerobic conditions in a range of soils representing typical agricultural usage in the Midwest. Under iron-reducing conditions, the rate of

trifluralin degradation among soils converged, suggesting a common mechanism. The presence of NO<sub>3</sub><sup>-</sup> or O<sub>2</sub> suppressed trifluralin degradation. Degradation kinetics were faster under iron-reducing conditions, and the addition of trifluralin appeared to result in reoxidation of Fe(II). Results also indicate that transformation of trifluralin under iron-reducing conditions involves the soil solid phase and may not be limited by bioavailability. These findings in combination with observed reaction of trifluralin with structural Fe(II) in smectite suggest that, as for other nitroaromatics, the fate of trifluralin in anoxic environments includes reaction with Fe(II) associated with the mineral phase. These results have implications for remediation of trifluralin-contaminated soil or sediment and may explain deactivation of this herbicide in wet fields.

## Acknowledgments

The authors appreciate the assistance of R. F. Mitchell, University of Illinois. Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

## Literature Cited

- (1) United States Department of Agriculture. *Agricultural chemical usage, 1995 field crops survey*; National Agricultural Statistics Service, Economics Research Service: Washington, DC, 1996; Chapter 1.
- (2) WSSA *Herbicide Handbook*, 7th ed.; Weed Science Society of America: Champaign, IL, 1994.
- (3) Grover, R.; Wolt, J. D.; Cessna, A. J.; Schiefer, H. B. *Reviews of Environmental Contamination and Toxicology*; Springer: New York, 1997.
- (4) Golab, T.; Althaus, W. A.; Wooten, H. L. *J. Agric. Food Chem.* **1979**, *27*, 163.
- (5) Willis, G. H.; Wander, R. C.; Southwick, L. M. *J. Environ. Qual.* **1974**, *3*, 262.
- (6) Crawford, J. J. *Anaerobic Dissipation of Herbicides in Microbiologically-Induced Soil Redox Regimes*. Ph.D. Thesis. University of Illinois, 1997.
- (7) Heijman, C. G.; Grieder, E.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, *29*, 775.
- (8) Klausen, J.; Trober, S. P.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, *29*, 2396.
- (9) Gee, G. W.; Bauder, J. W. *Methods of Soil Analysis. Part 1*, 2nd ed.; American Society of Agronomy and Soil Science Society of America: Madison, WI, 1986.
- (10) Nelson, D. W.; Sommers, L. E. *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, 2nd ed.; American Society of Agronomy and Soil Science Society of America: Madison, WI, 1982.
- (11) Mervosh, T. L.; Stoller, E. W.; Simmons, F. W.; Ellsworth, T. R.; Sims, G. K. *Weed Sci.* **1995**, *43*, 445.
- (12) Vendrell, P. F.; Zupancic, J. *Commun. Soil Sci. Plant Anal.* **1990**, *21*, 1705.
- (13) Lovley, D. R.; Phillips, E. J. P. *Appl. Environ. Microbiol.* **1987**, *53*, 1536.
- (14) Komadel, P.; Stucki, J. W. *Clays Clay Miner.* **1988**, *36*, 379.
- (15) Stucki, J. W. *Soil Sci. Soc. Am. J.* **1981**, *45*, 638.
- (16) Stucki, J. W.; Golden, D. C.; Roth, C. B. *Clays Clay Miner.* **1984**, *32*, 350.
- (17) Patrick, W. H., Jr.; Jugsujinda, A. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1071.
- (18) Peters, V.; Conrad, R. *Soil Biol. Biochem.* **1996**, *28*, 371.
- (19) Lovley, D. R. *Microbiol. Rev.* **1991**, *55*, 259.
- (20) Lovley, D. R.; Phillips, E. J. P. *Appl. Environ. Microbiol.* **1986**, *51*, 683.
- (21) Heijman, C. G.; Grieder, E.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, *29*, 775.
- (22) Zimdahl, R. L.; Gwynn, S. M. *Weed Sci.* **1977**, *25*, 247.
- (23) Mervosh, T. L.; Sims, G. K.; Stoller, E. W.; Ellsworth, T. R. *J. Agric. Food Chem.* **1995**, *43*, 2295.

Received for review November 4, 1999. Revised manuscript received May 3, 2000. Accepted May 8, 2000.

ES9912473