Degradation of Terbutol in Soils from Turfgrass and Drainage Basins on Golf Courses

Toshinari Suzuki,*,† Kumiko Yaguchi,† Taichiro Nishima,† and Tetsuya Suga‡

Tama Branch Laboratory, Tokyo Metropolitan Research Laboratory of Public Health, 3-16-25 Shibazaki-cho, Tachikawa, Tokyo 190, Japan, and Department of Clinical Biochemistry, Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

Degradation of terbutol (2,6-di-*tert*-butyl-4-methylphenyl *N*-methylcarbamate) in soils from turfgrass (*Zoisia japonica*) and drainage basins on golf courses was investigated. Terbutol was decomposed in soils from turfgrass by 50% after 180 days, whereas decomposition in soils from drainage basins was 50% after 360 days. In soils autoclaved at 120 °C for 20 min or with reduced oxygen supplement, the rates of terbutol degradation decreased markedly. Degradation of terbutol results in the oxidation of the 4-methyl group, N-demethylation, and hydrolysis of the carbamate ester linkage. The major degradation products were 4-COOH-, NH_2-, and 4-COOH-NH_2-terbutol, BHT, and 4-COOH-BHT. Only trace amounts of oxidative intermediates of the 4-methyl group of terbutol and BHT were detected.

Keywords: *Terbutol; 2,6-di-tert-butyl-4-methylphenyl N-methylcarbamate; soil; degradation*

INTRODUCTION

Terbutol (2,6-di-*tert*-butyl-4-methylphenyl *N*-methylcarbamate) is a pre-emergence phenyl carbamate herbicide. A commercially available herbicide, Azak, containing terbutol (40%) and (2-methyl-4-chlorophenoxy)acetohydrazine (30%), has been used on golf courses in Japan for controlling crabgrass, goosegrass, and broadleaf weeds in turfgrass (*Zoisia japonica*) on fairways and in the rough and is applied at a rate of about 0.8 g/m^2.

We have investigated water pollution caused by insecticides, fungicides, and herbicides in ground water and drainage from golf courses in Tokyo. Terbutol and its degradation products were detected at ppb concentrations in drainage and ground water at golf courses even after 1 or 2 years following terbutol application (Suzuki et al., 1995). However, herbicides such as asulam, mecoprop, simazine, and benefin used to treat golf courses had dissipated from the drainage within a few months and were not detected in the ground water. In order to determine the behavior of terbutol applied on golf courses, degradation in the soil or grass and permeation in drainage and ground water from the soil had to be investigated.

The objectives of this study were to determine the rate of degradation and the degradation pathway in soils under different laboratory conditions. The persistence of several herbicides used on golf courses was also investigated.

EXPERIMENTAL PROCEDURES

Materials. Terbutol (2,6-di-*tert*-butyl-4-methylphenyl *N*-methylcarbamate), asulam (methyl [(4-aminophenyl)sulfonyl]-carbamate), mecoprop (2-(4-chloro-2-methylphenoxy)propionic acid), simazine (2-chloro-4,5-bis(ethylamino)-1,3,5-triazine), benefin (*N*-butyl-*N*-ethyl-α,α,α-trifluoro-*p*-toluidine), and dithiopyr (*S*,*S*-dimethyl-2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinecarbothioate) were purchased from GL Science, Tokyo, Japan. 2,6-Di-*tert*-butyl-4-methylphenol (BHT), 2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol (4-CH_2OH-BHT), and 2,6-di-*tert*-butyl-4-formylphenol (4-CHO-BHT) were obtained from Tokyo Chemical Industry, Tokyo. 2,6-Di-*tert*-butyl-4-carboxyphenol (4-COOH-BHT) was provided by Aldrich Chemical Co., Milwaukee, WI. 2,6-Di-*tert*-butyl-4-formylphenyl *N*-methylcarbamate (4-CHO-terbutol), 2,6-di-*tert*-butyl-4-(hydroxymethyl)phenyl *N*-methylcarbamate (4-CH_2OH-terbutol), 2,6-di-*tert*-butyl-4-carboxyphenyl *N*-methylcarbamate (4-COOH-terbutol), 2,6-di-*tert*-butyl-4-methylphenyl carbamate (NH_2-terbutol), and 2,6-di-*tert*-butyl-4-carboxyphenyl carbamate (4-COOH-NH_2-terbutol) were prepared by the previous methods (Suzuki et al., 1995).

Degradation in Soil. Soils from turfgrass (*Z. japonica*) and drainage basins on a golf course in Tokyo were used for the experiments. Turfgrass soils were taken in March 1994 by core sampler at two points on the fairway from 0 to 5 cm and combined. At the fairway terbutol was applied at a concentration of 320 mg/m^2 in May 1991. Turfgrass and thatch in soils were removed by a sieve with 2 mm mesh. Drainage basin soils were ladled at two points, mixed, and sieved with 2 mm mesh. Properties of soils were as follows: turfgrass soil, pH 6.8, maximum water-holding capacity 63%, organic matter 9.9%, fine sand 62.3%, silt 15.8%, clay 21.9%; drainage basin soil, pH 6.0, maximum water-holding capacity 113%, organic matter 7.0%, fine sand 52.7%, silt 27.6%, clay 19.7%. Soils samples (20 g of dry weight) were placed in 120-mL amber narrow-mouth jars (51 mm o.d. × 110 mm height) for treatment. The soil from turfgrass was added with distilled water and adjusted to 60% of field capacity, and soil from the drainage basin was covered with a 1-cm layer of distilled water. The jars containing the soils from the turfgrass and the drainage basin were sealed with aluminum foil or silicone rubber as described in Table 1. After the samples were preincubated in the dark at 25 °C for 2 weeks, 50 μL of 1.2 mg/mL terbutol in dimethyl sulfoxide was added to each soil. The samples were mixed by rolling the jars and were incubated in the dark at 25 °C. In the case of normal oxygen supplement, water sterilized with a membrane filter (pore size 0.22 μm) was added at intervals of 2 weeks to maintain the moisture conditions. The contents of each jar were assayed initially and at 30, 90, 180, and 360 days after the application of terbutol. Degradation in turfgrass soils for asulam, mecoprop, benefin, simazine, and dithipyr was determined under the same

* Author to whom correspondence should be addressed.

† Tokyo Metropolitan Research Laboratory of Public Health.

‡ Tokyo College of Pharmacy.

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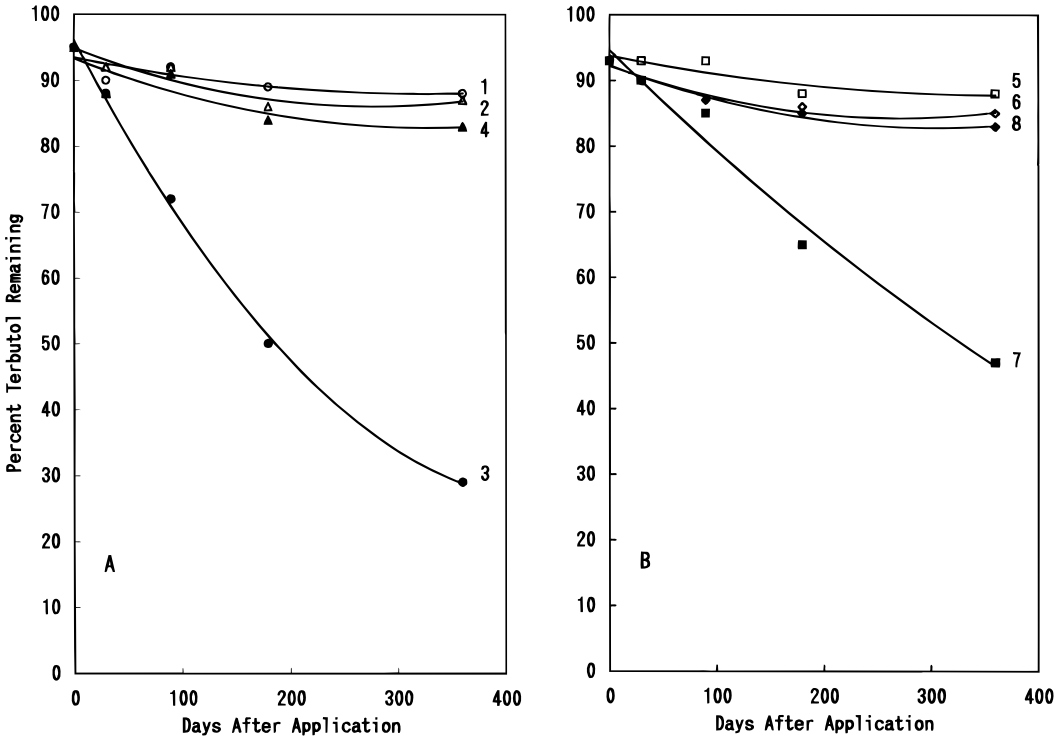

Figure 1. Degradation of terbutol in soils: (A) turfgrass soil and (B) drainage basin soil. Numbers refer to Table 1.

Table 1. Treatment and Incubation Conditions of Soils and Generation of Gas in the Jar

soils	no.	autoclave treatment[a]	oxygen supplement[b]	detection by odor,[c] time after terbutol addition (days) 0	30	90	180	360
turfgrass	1	+	normal	−	+	+	+	+
	2	+	reduced	−	+	+	+++	++
	3	−	normal	−	−	−	−	−
	4	−	reduced	−	+	+	−	−
drainage basin	5	+	normal	−	+	+	+	−
	6	+	reduced	−	+	+	+++	+
	7	−	normal	−	−	−	−	−
	8	−	reduced	−	+	+	+	−

[a] +, soil samples were autoclaved at 120 °C for 20 min; −, no treatment. [b] Normal, jar was covered with aluminum foil; reduced, jar was sealed with silicone rubber. [c] −, Odorless; +, slight; ++, medium; +++, strong smell like sulfur-containing compounds.

conditions as those for terbutol shown in Table 1, no. 3. Duplicate samples from each treatment were extracted and analyzed.

Extraction and Determination. A soil sample was transferred to a 150-mL centrifugation tube and extracted three times with 50 mL of acetone by vigorously shaking, sonicating, and centrifuging at 3000 rpm for 10 min, respectively. The acetone solution was filtered and the filtrate concentrated to 20 mL in a rotary evaporator at 40 °C. For terbutol and its neutral degradation products, simazine, benefin, or dithiopyr, a 10-mL acetone solution was added to 100 mL of 5% sodium chloride and extracted twice with 10 mL of dichloromethane. The dichloromethane was dehydrated with anhydrous sodium sulfate and evaporated to dryness under a stream of nitrogen. The residue was dissolved in acetone−*n*-hexane (25:75) and analyzed by GC/MS according to the previous methods (Suzuki et al., 1995). For the acidic degradation products of terbutol, asulam, or mecoprop, a 10-mL acetone solution was added to 100 mL of 0.1 N HCl and extracted twice with 10 mL of dichloromethane. The dichloromethane was dehydrated with anhydrous sodium sulfate and evaporated to dryness under a stream of nitrogen. The residue was subjected to methylation with diazomethane and analyzed by GC/MS (Suzuki et al., 1995).

RESULTS

The incubation conditions of the soil samples and the generation of odors in the jars are listed in Table 1. In turfgrass soils autoclaved at 120 °C for 20 min, the odor of sulfur-containing compounds was detected under both normal moisture and oxygen-reduced conditions. A similar odor was undetectable in unsterilized turfgrass soils under normal oxygen conditions at all incubation times, but such an odor was detectable under oxygen-reduced conditions. The results from the drainage basin soils were similar to those from turfgrass soils. The principal constituent of the odor was identified as dimethyl sulfide by GC/MS analysis of the head space gas in the jars. Unidentified microorganisms that had survived in the soils following autoclaving very likely converted dimethyl sulfoxide, the solvent for terbutol, to dimethyl sulfide in the soil.

The decrease of terbutol in soils from the turfgrass and drainage basin is shown in Figure 1. Degradation of terbutol in unsterilized soils from the turfgrass under normal conditions was most rapid; 50% of the originally incorporated terbutol remained after 180 days, and 30% remained after 360 days. Conversely, terbutol was degraded only slightly in soils under decreased oxygen supplement with or without autoclaving, 80−88% detectable after 360 days. In soils from the drainage basin, the rate of terbutol degradation was slower than that from turfgrass soil; the residual amount of terbutol remaining after 360 days was about 50% without heat treatment and about 90% with heat treatment. The rate of terbutol degradation in the drainage basin soil was decreased significantly under conditions of reduced oxygen supplement.

The formation of degradation products after an application of terbutol is shown in Table 2. Oxidation of the 4-methyl group and N-demethylation was the major route of terbutol degradation in soils from turfgrass as evidenced by the large amount of 4-COOH-terbutol, NH_2-terbutol, and 4-COOH-NH_2-terbutol formed in comparison to the other degradation products detected.

Table 2. Time Course of Degradation Products of Terbutol in Soils[a]

	amount of terbutol and its degradation products (ng)[b]							
	turfgrass soil, time (days)				drainage basin soil, time (days)			
compound[c]	30	90	180	360	30	90	180	360
terbutol	52 600	44 100	29 810	18 800	53 000	50 000	38 920	28 000
4-CH_2OH-terbutol	ND	80	80	ND	ND	ND	50	ND
4-CHO-terbutol	ND	ND	ND	ND	ND	ND	10	ND
4-COOH-terbutol	3090	8080	13 660	5010	1080	2610	7310	8700
NH_2-terbutol	1360	2410	7200	3630	720	1210	4940	4200
4-COOH-NH_2-terbutol	320	1150	2330	2220	250	370	830	2290
BHT	40	170	210	120	50	50	90	110
4-CH_2OH-BHT	ND	10	190	ND	ND	100	180	ND
4-CHO-BHT	20	30	10	30	ND	20	30	30
4-COOH-BHT	40	110	220	350	30	20	50	290
total	57 470	56 140	53 710	30 160	55 130	54 380	52 410	43 620

[a] Unsterilized soil under normal oxygen conditions (no. 3 and 7 in Table 1). [b] Amount of terbutol and its metabolites extracted from 20 g of soil samples. ND, less than 10 ng. [c] Chemical structures refer to Figure 3.

The amount of these degradation products increased to a maximum at 180 days with a decrease thereafter. BHT, a hydrolysis product of terbutol, and 4-COOH-BHT were always detected. The range is from a low of 40 ng to a high of 350 ng. Only small amounts of oxidative intermediates, 4-CH_2OH- and 4-CHO-terbutol and 4-CH_2OH- and 4-CHO-BHT, were detected in some soil samples. The total amount of terbutol and its degradation products recovered from unsterilized soil sample under normal conditions decreased with increasing incubation time. However, the recovery of these compounds from autoclaved soil and reduced oxygen supplement was more than 95% even after 360 days. In the drainage basin soil, the degradation products were similar to that from the turfgrass soils. The amount of 4-COOH-, and NH_2-, and 4-COOH-NH_2-terbutol gradually increased up to 360 days. In the case of autoclaved soils and the soils under the conditions of reduced oxygen supplement, the total amount of terbutol and its degradation products after 360 days was more than 90%. The minor terbutol metabolites, 6-*tert*-butyl-2-[2-(1-hydroxy-2-methylpropyl)]-4-methylphenol and the corresponding *N*-methylcarbamate, appeared on rat hepatocytes (Suzuki et al., 1995) and were not detected in any soil sample.

Degradation of asulam, mecoprop, simazine, benefin, and dithiopyr in turfgrass soils is reported in Figure 2. Degradation of asulam was the most rapid of the herbicides examined. The residual amount of asulam after 6 days was 30%, and sulfanilamide, one of the degradation products of asulam (Smith and Milward, 1983), was detected at a concentration of 0.17 μg/g. Mecoprop was degraded to 45% of its initial quantity after 15 days, and 4-chloro-2-methylphenol, one of the degradation products (Smith, 1985), was not detected at the detection limit of 0.03 μg/g. Simazine decreased to 30% after 60 days and to 9% within 90 days. Benefin decreased to 32% after 90 days. The degradation rate of dithiopyr was similar to that of terbutol; it remained at 81% of the initially incorporated amount after 90 days. The estimated times to 50% reduction of asulam, mecoprop, simazine, benefin, and dithiopyr were 4, 11, 39, 68, and 200 days, respectively.

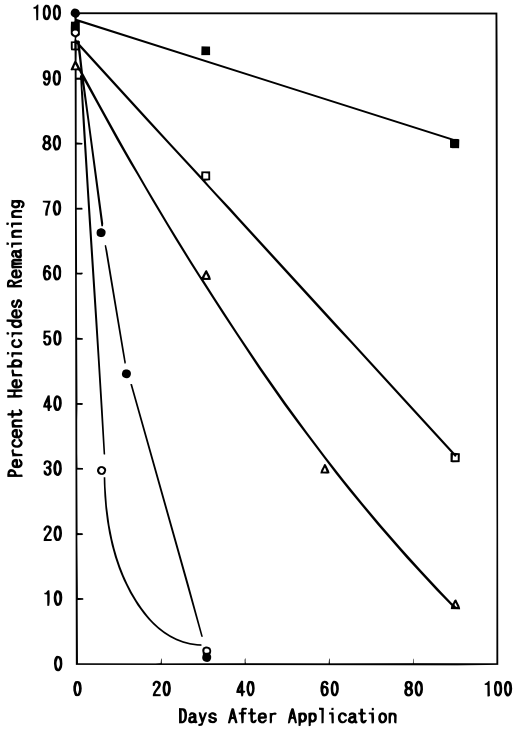

Figure 2. Degradation of herbicides in unsterilized turfgrass soil under normal conditions: (○) asulam, (●) mecoprop, (△) simazine, (□) benefin, and (■) dithiopyr.

DISCUSSION

Degradation of terbutol in soils from turfgrass and drainage basins was more rapid under normal oxygen supplement than under oxygen-reduced conditions. Autoclaving the soils at 120 °C for 20 min also reduced the rate of terbutol degradation. These results suggest that microorganisms growing under aerobic conditions may be primarily responsible for the degradation of terbutol in soil.

The major degradation products of terbutol in soils under both normal and flooded conditions were 4-COOH-, NH_2-, and 4-COOH-NH_2-terbutol, BHT, and 4-COOH-BHT. Trace amounts of the oxidative intermediates of the 4-methyl group of terbutol and BHT were also detected. The oxidative products of the *tert*-butyl group which appeared on rat hepatocytes (Suzuki et al., 1995) were not detected in any soil sample. The total amount of the compounds recovered from the soils undergoing rapid terbutol degradation decreased with increasing incubation times. These results may be due to increased binding of terbutol and/or its metabolites with soil particles to form unextractable residues (Kaufman et al., 1976) or further degradation of metabolites to volatile low molecular weight compounds such as carbon dioxide (Ogawa et al., 1976, 1977). These results indicated that metabolic transformations of terbutol in soil from turfgrass and drainage basins occurred as

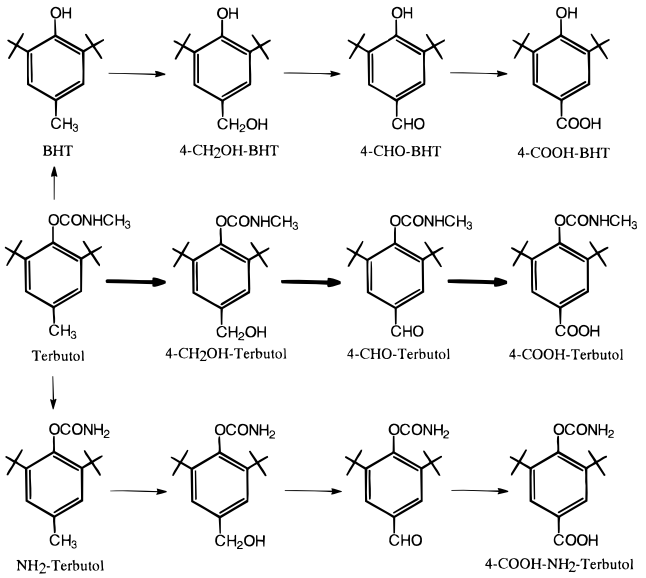

Figure 3. Proposed degradation pathways for terbutol in turfgrass and drainage basin soils.

follows: (1) oxidation of the 4-methyl group to carboxylic acid derivatives, (2) N-demethylation of the *N*-methyl group to form the corresponding carbamates, and (3) hydrolysis of the carbamate ester linkage to form the corresponding phenol. Proposed degradation pathways for terbutol in soils are given in Figure 3. Terbutol was degraded in a manner similar to that of several alkylphenyl *N*-methylcarbamates such as 2-*sec*-butylphenyl *N*-methylcarbamate and 2-isopropylphenyl *N*-methylcarbamate (Ogawa et al., 1976, 1977, respectively) in soils. In our previous report (Suzuki et al., 1995), terbutol and 4-COOH-, NH_2-, and 4-COOH-NH_2-terbutol were detected at concentrations of microgram/liter levels in drainage and ground water from golf courses on which terbutol had been applied. In addition, 4-CH_2-OH- and 4-CHO-terbutol, BHT, and 4-CH_2OH-, 4-CHO-, and 4-COOH-BHT were observed at nanogram/liter levels in some water samples. The proportions of these degradation products in water samples were in good agreement with that of the degradation products obtained by the present study.

For the degradation rate of terbutol in the field conditions, the average concentrations of terbutol in the surface soils around the sampling points in this study were 80 μg/kg in May 1993 and 35 μg/kg in May 1995. The degradation rate of terbutol in soils is slower under the field conditions than under the present laboratory conditions. The degradation rates of herbicides such as asulam and mecoprop decreased at lower temperature and moisture content (Helweg, 1993; Smith and Walker, 1977). The mean temperature and rainfall in a month around the golf course change at the range of 3−25 °C and 50−400 mm, respectively, and are less than 10 °C and 100 mm from November to March. The temperature and moisture content may have affected terbutol degradation.

Degradation of asulam, mecoprop, simazine, and benefin in soils under the same conditions as those for terbutol was more rapid than terbutol, and the degradation rate of each herbicide was similar to that of previous reports (Smith and Walker, 1977; Smith and Hayden, 1981; Walker and Blacklow, 1994; Hurto et al., 1979, respectively). Persistence of dithiopyr in this study was similar to that of terbutol, although the estimated time for a 50% reduction in detectable residues of dithiopyr under field conditions was 35 days (Schleicher et al., 1995). The rate of decrease of terbutol and its degradation products in drainage and ground water at golf courses is relatively slow compared to that of the other pesticides. One of the causes of this is the persistence of terbutol in soils from turfgrass and drainage basins.

Further investigations of permeation of these herbicides and terbutol from the soil and monitoring of the herbicides in drainage and ground water on golf courses are necessary to clarify the behavior of terbutol and the other pesticides.

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