JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Effect of Organic Manure on Sorption and Degradation of Azoxystrobin in Soil

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Information on pesticide degradation and factors influencing are important in predicting the levels of pesticide remaining in soils and allow assessment of potential risk associated with exposure. The present study reports the sorption and degradation of azoxystrobin [methyl (*E*)-2-{2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl}-3-methoxyacrylate] in a sandy loam soil. The fungicide was moderately sorbed, and the Freundlich adsorption parameter K_f (1/*n*) values in natural and 5% compost-amended soils were 9.31 and 13.72, respectively. Sorption showed hysteresis with 32.5 and 14.7% of sorbed fungicide desorbed from the natural and 5% compost-amended soils, respectively. Azoxystrobin was more persistent in the aerobic soil than the anaerobic soil with half-life values of 107.47 and 62.69 days, respectively. Amendment of compost (5%) to the soil enhanced the degradation of fungicide, and the respective half-life values in aerobic and anaerobic soils were 73.39 and 38.58 days, respectively. Azoxystrobin acid was recovered as the only metabolite of azoxystrobin degradation in soils. Both sunlight and UV light affected the persistence of azoxystrobin with fungicide degraded at a faster rate in UV light than in sunlight. Soil acts as a screen and slows the fungicide degradation under sunlight and UV light.

KEYWORDS: Azoxystrobin; sorption; degradation; organic manure; flooded; nonflooded

INTRODUCTION

Plant protection has become a key component of modern intensive agriculture, in which high-yielding crop varieties are highly susceptible to disease and pest attack. However, the presence of pesticides in environmental components has grown in the past few years and has become an intensive and burning issue of discussion. Thus, the fate of xenobiotics has become a major concern in defining the quality of our environment (*1*). Soil is the major sink for the bulk of the globally used pesticides. A pesticide reaching the complex and dynamic soil system is acted upon by an interplay of physical, chemical, and biological forces. All of these forces play an important role in deciding the fate of pesticides in soil. Information on the pathways of pesticide degradation and the factors influencing them is important in predicting the levels of pesticide remaining in soils and allows assessment of potential risk associated with the exposure.

The fate of a pesticide in soil is affected by many factors, namely, soil constituents, micro-organisms, environmental factors, moisture status, sorption, and properties of the soils. Availability of pesticide in soil solution is a prerequisite for the availability of pesticide for degradation, biological action, and transport. Adsorption−desorption phenomenon determines, to a great extent, the availability of soil-applied pesticide in solution phase by affecting the partitioning of pesticide in water and soil particles (*2*).

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Azoxystrobin [methyl (*E*)-2-{2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl}-3-methoxyacrylate], a strobilurin fungicide, is a broad spectrum, systemic, and soil-applied fungicide (**Figure 1**). It has been approved for use on more than 80 different crops representing over 400 crop/disease systems (*3*). It controls both foliar and soil-borne diseases such as downy and powdery mildew and early and late blight and pathogens such as *Sclerotinia*, *Alternaria*, *Pythium*, *Ascochyta*, and *Rhizoctonia* on many crops. Azoxystrobin has been shown to be moderately to highly toxic to aquatic organisms when used at the rates proposed for canola, grapes, and turf grass.

Information of azoxystrobin fate in the environment is mainly restricted to registration documents, which suggest that azoxystrobin degrades slowly in soils with half-lives of 54−135 days in aerobic soils and 36−45 days in anaerobic soils (*4*). The adsorption coefficient (K_d) values for azoxystrobin in different soil types ranged between 2.1 and 36 μg g^{-1}, and sorption decreased with increase in the soil pH. Joseph (*5*) reported that in nonsterile soils maintained under aerobic conditions the half-

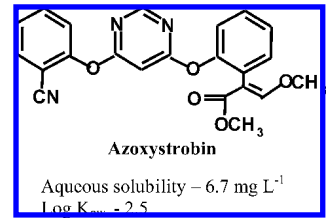

Figure 1. Chemical structure of azoxystrobin.

10.1021/jf802716f CCC: $40.75
Published on Web 01/06/2009

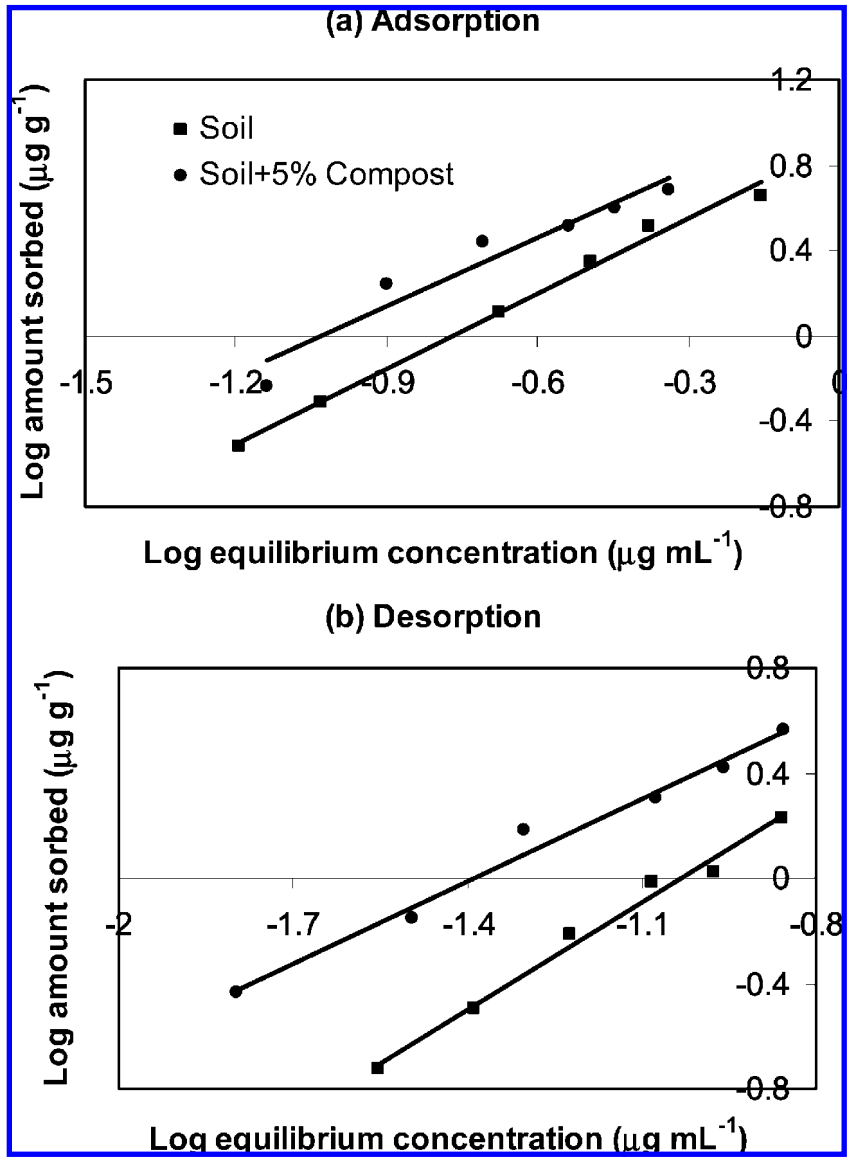

Figure 2. Freundlich adsorption (**a**) and desorption (**b**) isotherms for azoxystrobin in soils.

life of azoxystrobin ranged between 8 and 12 weeks and that azoxystrobin acid was recovered as the major metabolite. In sterile soil, too, significant degradation of azoxystrobin was observed, suggesting that the photolytic degradation of azoxystrobin is an important means of fungicide dissipation in the natural environment; therefore, a much shorter half-life of 14 days was obtained for azoxystrobin under field conditions. Bending et al. (*6*) studied the degradation of azoxystrobin in a sandy loam and a clay loam soil. The degradation rate correlated well with the soil pH, sorption coefficient, and microbial biomass. Degradation of azoxystrobin was mainly by co-metabolism.

Garau et al. (*7*) studied the photodegradation of azoxystrobin both in the greenhouse and in the field, in the absence and presence of tomato epicuticular wax. Azoxystrobin degraded at a faster rate in the field ($t_{1/2}$ = 0.9 h) than in the glasshouse ($t_{1/2}$ = 6.0 h) when no wax was used. However, in the presence of wax the $t_{1/2}$ values of azoxystrobin in the field and glasshouse were 9.6 and 8.9 h, respectively. The study suggested that waxes have a better screening effect than the glass. Azoxystrobin has been registered in India for rice cultivation; however, no information is available on azoxystrobin sorption and degradation behavior under Indian tropical conditions. Therefore, the present study reports the degradation and sorption behavior of azoxystrobin in a sandy loam soil of northern India.

MATERIALS AND METHODS

Soil. Soil used in the study was collected from the experimental farm of the Indian Agricultural Research Institute, New Delhi, India. The soil was collected from the 0−15 cm soil profile, air-dried, ground to pass through a 2 mm sieve, and stored in plastic bags at room temperature. The physicochemical characteristics of the soil determined by standard methods were pH 7.9 measured at a 1:1.25 soil to water ratio; organic carbon, 0.39, measured by using the Walkley and Black method (*8*); and mechanical fractions sand 54.4%, silt 23.3%, and clay 22.3%, measured by employing the Bouyoucos hygrometer method (*9*).

The cow manure was obtained locally. The physicochemical characteristics of the manure included a pH of 6.3 and an organic carbon content of 23.5%. The total carbon, nitrogen, and hydrogen contents of manure were determined by elemental analysis and were 25.2, 9.8, and 2.8%, respectively.

Chemicals. An analytical grade sample of azoxystrobin (96.2% purity) was supplied by the Rallis India Ltd. The solvents and other reagents used were of analytical grade and were purchased locally from Merck Specialties Private Ltd., Mumbai, India.

Sorption−Desorption Studies. Adsorption isotherms for azoxystrobin in soils were obtained by batch equilibration method. Soil

samples (10 g) and a 0.01 M $CaCl_2$ solution of azoxystrobin (50 mL) were mixed in 60 mL glass-stoppered test tubes. This treatment was labeled T-0. To study the effect of compost amendment on azoxystrobin sorption, soil samples amended with 5.0% compost (10 g) were used, and this treatment was labeled T-1. The initial concentration of azoxystrobin ranged between 0.25 and 1.5 μg mL^{-1}, and each concentration was replicated three times. For each treatment, blanks, without soil, were also used as control. Samples were equilibrated on an end-over-end shaker for 24 h (preliminary studies indicated that equilibration for 24 h was sufficient to attain equilibrium; results not shown here). After 24 h of equilibration, the soil−water suspension was centrifuged at 6000 rpm for 15 min. Azoxystrobin was quantified in the supernatant by GC. The amount of azoxystrobin sorbed was calculated from the difference between the initial and final solution concentration. The mass balance calculations indicated that azoxystrobin was stable during the equilibration period, and there was no sorption of azoxystrobin on the glass surface.

Desorption of azoxystrobin was studied in the same soil as used for the adsorption. After adsorption, the supernatant was decanted and was replaced with 50 mL of fresh 0.01 M $CaCl_2$ solution. The soil−water suspension was again shaken on an end-over-end shaker for 24 h and centrifuged. Azoxystrobin was analyzed in the supernatant by GC. The amount of azoxystrobin desorbed was calculated by subtracting the amount of fungicide in the entrapped solution after the adsorption experiment from the solution concentration measured after the desorption experiment. Only one desorption was performed for each sample.

Degradation Studies. *Effect of Aerobic and Anaerobic Conditions.* Portions (10 g) of soils in sterilized glass test tubes (200 mm × 25 mm) were supplemented with sterile distilled water to obtain nonflooded (60% water-holding capacity) and flooded (soil/water ratio of 1:1.25, w/v) soil conditions. These treatments were labeled T-0, NF, and T-0, F, respectively. Prior to the addition of azoxystrobin, flooded soils were incubated at 28 ± 1 °C to allow the development of anaerobic conditions. Azoxystrobin (20 μg) was added to the soils in 0.1 mL of acetone. The tubes were closed with cotton plugs and then incubated at 28 ± 1 °C in the dark. Moisture was maintained by adding the required amount of water at weekly intervals, and at periodic intervals, duplicate samples were removed for analysis by gas−liquid chromatography (GC) and high-performance liquid chromatography (HPLC).

Effect of Organic Manure. To quantify the effect of organic amendments on the persistence of azoxystrobin, the following experiment was performed. Soils samples (10 g), flooded and nonflooded, with 5% cow manure, were prepared as mentioned in the previous section, and these treatments were labeled T-1, F, and T-1, NF, respectively. The soils were incubated at 28 ± 1 °C, and at regular intervals, duplicate samples were removed for extraction and analysis by GC and HPLC.

Effect of Sunlight and UV Light. The effect of light on the degradation of azoxystrobin was studied by using a thin film (without and with soil) technique. A thin film of azoxystrobin was prepared by dispensing 1.0 mL of acetone solution (10 μg mL^{-1}) of azoxystrobin to glass Petri plates (5 cm diameter). Samples were left for 10 h for evaporation of acetone at room temperature. One set of samples was exposed to UV light (254 nm), and another set was exposed to sunlight (8 h a day). The samples (in duplicate) were withdrawn at regular intervals and extracted thoroughly with acetone (2 × 2 mL). The samples were centrifuged at 10000 rpm for 10 min and were analyzed by GC.

Soil thin layer plates were prepared from a suspension of 1 g of soil and 2 mL of distilled water in a Petri plate (5 cm diameter). The plates were left to dry at room temperature for 24 h. Azoxystrobin (10 μg) in 1 mL of acetone was applied to the soil thin films as mentioned above. One set of samples was exposed to UV light, and another set was exposed to sunlight. The samples (in duplicate) were withdrawn at regular intervals, extracted, and analyzed by GC.

Azoxystrobin Extraction and Analysis. Soil samples were transferred to a 150 mL stoppered conical flask, and 20 mL of ethyl acetate and 5 g of anhydrous sodium sulfate were added. The samples were equilibrated on a rotary shaker for 1 h. The ethyl acetate fraction was transferred to a 250 mL beaker, and soil was extracted again in a similar manner. A total of three extractions were performed, and ethyl acetate fractions were pooled together. The ethyl acetate fraction was evaporated to dryness at room temperature, and residues were redissolved in 10 mL of acetone. The fungicide residues in acetone were quantified by a Hewlett-Packard (Palo Alto, CA) gas chromatograph, model 3840, equipped with a Ni^{63} electron capture detector (ECD) and fitted with a HP-1 column [10 m (l) × 0.50 mm (i.d.) × 2.53 μm film thickness]. The operating conditions were as follows: oven temperature, 270 °C; injector temperature, 300 °C; detector temperature, 300 °C; carrier gas (nitrogen) flow rate, 45 mL min^{-1}.

Azoxystrobin residues in water samples were extracted using ethyl acetate. The sample (25 mL) in a 100 mL separating funnel was extracted with 30 mL of ethyl acetate. The ethyl acetate fraction was transferred to a 250 mL beaker, and the water fraction was extracted again in a similar manner. A total of three extractions were performed, and ethyl acetate fractions were pooled together. The organic solvent was dried over anhydrous sodium sulfate and evaporated to dryness at room temperature. The fungicide residues were redissolved in 5 mL of acetone. The fungicide residues in acetone were quantified by GC and HPLC.

Samples were analyzed for azoxystrobin acid using HPLC. One milliliter of sample in acetone was evaporated to dryness at room temperature, and residues were redissolved in 2 mL of acetonitrile. A Hewlett-Packard instrument (series 1100) equipped with a degasser, quaternary pump, and diode array detector (DAD) connected with a Rheodyne injection system was used for analysis. The stationary phase consisted of Lichrospher on a C-18 stainless steel column [250 mm × 4 mm (i.d.)]. Wavelength for UV detection was 220 nm. Mobile phase was acetonitrile and acidic water (0.1% orthophosphoric acid) (70:30, v/v) at the rate of 1 mL min^{-1}.

Table 1. Sorption Constants of Azoxystrobin in Natural (T-0) and 5% Compost-Amended (T-1) Soils

soil	K_f	1/n	R^2	K_d (μg g^{-1})	R^2
			Adsorption		
T-0	7.96	1.17	0.992	6.87	0.997
T-1	12.70	1.08	0.933	10.27	0.959
			Desorption		
T-0	24.99	1.35	0.986	13.12	0.978
T-1	27.98	1.04	0.984	25.23	0.983

Table 2. Effect of Soil Conditions on Degradation Constants and Half-Life of Azoxystrobin

treatment	K_{obs} (day^{-1})	$t_{1/2}$ (days)	R^2
flooded (T-0, F)	−0.0048	62.69	0.963
nonflooded (T-0, NF)	−0.0028	107.47	0.987
flooded + 5% compost (T-1, F)	−0.0078	38.58	0.952
nonflooded + 5% compost (T-1, NF)	−0.0041	73.39	0.962

RESULTS AND DISCUSSION

Sorption Studies. The adsorption data for azoxystrobin in natural (T-0) and 5% compost-amended (T-1) soils were fitted to the Freundlich adsorption equation

$$\log x/m = \log K_f + 1/n \log C_e \quad (1)$$

where x is the amount of azoxystrobin adsorbed (μg), m is the weight of the soil (g), C_e is the equilibrium concentration of azoxystrobin (μg mL^{-1}), and K_f and 1/n are the constants. The Freundlich constant K_f (intercept) represents the amount of azoxystrobin adsorbed at an equilibrium concentration of 1 μg mL^{-1}. The constant 1/n (slope) is the measure of the intensity of sorption and reflects the degree to which sorption is a function of azoxystrobin concentration. Adsorption isotherms and Freundlich adsorption parameters are presented in **Figure 2** and **Table 1**. The values of correlation coefficient were high (R^2 > 0.933), indicating that the Freundlich adsorption equation satisfactorily explained the results of azoxystrobin sorption in

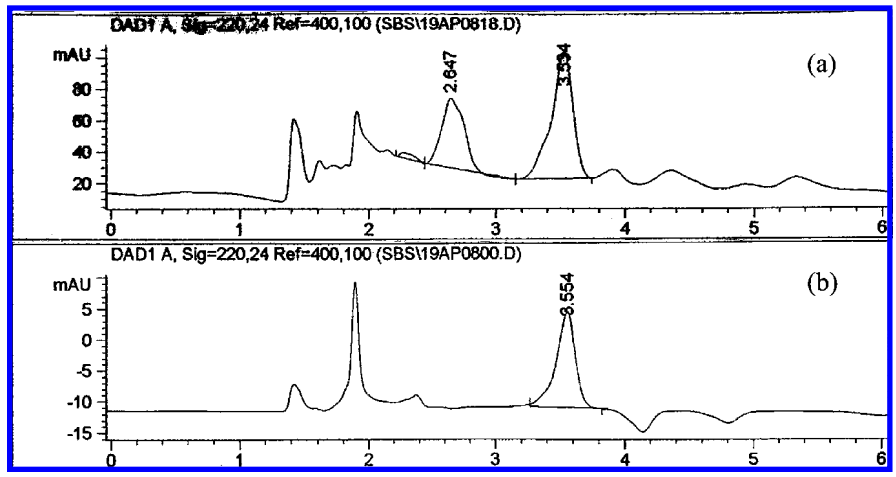

Figure 3. HPLC chromatogram of (**a**) soil samples indicating formation of azoxystrobin acid in 5% compost-amended soil (T-1, F) and (**b**) standard azoxystrobin.

Table 3. Azoxystrobin Acid Produced during the Degradation of Azoxystrobin in Soils

	azoxystrobin acid (detector response in mV)			
days	T-0, F	T-1, F	T-0, NF	T-1, NF
60	269.8 (17.9)[a]	380.6 (11.3)	263.6 (9.6)	293.8 (8.9)
90	766.0 (22.6)	1050 (15.7)	612.8 (12.5)	548.0 (16.8)
120	1076 (32.4)	1357 (22.5)	1095 (20.6)	1019 (19.9)

[a] Values in parentheses are the mean error values.

Table 4. Dissipation Constants (K_{obs}) and Half-Life ($t_{1/2}$) Values for Azoxystrobin under Sunlight and UV Light

treatment	K_{obs}	$t_{1/2}$	R^2
sunlight (soil thin film)	−0.0141	16.71 h	0.967
sunlight (thin film)	−0.0919	3.27 h	0.949
UV light (soil thin film)	−0.2291	1.31 h	0.974
UV light (thin film)	−0.0307	9.80 min	0.942

natural (T-0) and 5% compost-amended (T-1) soils, and the results were significant at 99% levels.

The slope (1/*n*) values of azoxystrobin adsorption isotherms in natural (T-0) and 5% compost-amended (T-1) soils were higher than 1, suggesting S-type isotherms (*10*). This type of isotherm is commonly found in the literature and involves the interaction of the organic compounds having polar groups with the soil and its components. These interactions are characterized by the strong competition between the water molecule and the pesticide for the adsorption sites at low pesticide concentration and/or molecular interaction between the sorbed species. In the present study azoxystrobin, which contains carbonyl group, shows S-type isotherms, indicating that the nonlinearity of the adsorption isotherm is probably due to the interaction of this group of azoxystrobin with the organic or mineral fraction of the soil.

The K_f value of 7.8 in natural soil (T-0) indicated that azoxystrobin was moderately sorbed in the sandy loam soil. Further increase in the K_f value of azoxystrobin in 5% compost-amended soil (T-1) clearly indicated that compost provided additional sites for the sorption of azoxystrobin. Both K_f and 1/*n* are important coefficients for the description of adsorption isotherms, especially in the case of nonlinear isotherms. Therefore, $K_f(1/n)$ was selected as a parameter of adsorption (*11*). The respective $K_f(1/n)$ values of azoxystrobin for treatments T-0 and T-1 were 9.31 and 13.72. The higher azoxystrobin sorption in compost-amended soils may be attributed to the increased organic carbon (OC) content of the compost-amended soil (OC contents for T-0 and T-1 were 0.39 and 1.57%, respectively). Compost application decreased the soil pH and increased the dissolved organic carbon (DOC) content of the soil. Results indicated that the increase in azoxystrobin sorption in the compost-amended soils was not on par with the increase in the soil OC content. A nearly 4-fold increase in the soil OC content resulted in an only 1.5 times increase in the azoxystrobin sorption. This may be due to the fact that a portion of azoxystrobin may be associated with the dissolved portion of the organic carbon. Application of compost can lead to a substantial amount of dissolved and colloidal organic material in the soil solution that may have an impact on the subsequent pesticide binding and transport behavior (*12*). Enhanced water solubility, decreased sorption, and enhanced transport resulting from the complexation or association of hydrophobic substances with dissolved or colloidal organic material have been clearly documented in both batch and column studies (*12, 13*). The K_d (partition coefficients) values calculated from the equation $x/m = K_dC_e$ were similar to the K_f values and were higher in the compost-amended soil.

The results of the present study are in agreement with earlier findings with other compounds, which suggested that sorption of organic compounds in soils is correlated to their organic carbon content (*14*−*18*). No literature is available on the effect of soil organic carbon content on the sorption of azoxystrobin. The partition coefficient values obtained in this study were in accordance with the values reported in the registration data and regulatory note (*4*), where the K_d value for azoxystrobin sorption in different soil types ranged between 2.1 and 36.

Results of the desorption study suggest that the amounts of azoxystrobin desorbed from natural (T-0) and 5% compost-amended (T-1) soils were 32.5 and 14.7%, respectively. This indicated that the amount of sorbed azoxystrobin retained in the soil was higher for the compost-amended (T-1) soil than for the natural soil (T-0). Thus, sorption was more irreversible in soil with higher OC content. The K_f values for azoxystrobin desorption were higher than the K_f values observed for azoxystrobin adsorption in both the soils. This clearly indicated that a considerable portion of the azoxystrobin sorbed in soil matrix was retained in the soil during desorption and that azoxystrobin sorption in soil is partially irreversible in nature.

Degradation Studies. Degradation data from all of the conditions studied fitted well to the following first-order kinetic equation: $\log(C/C_0) = -K_{obs}t$, where C_0 is the initial concentration of azoxystrobin (mg kg^{-1}), C is its concentration (mg kg^{-1}) after time t (days), and K_{obs} is the rate constant of the reaction.

Azoxystrobin was quite persistent in the sandy loam soil and was detected in all samples even up to 120 days. Soil moisture

conditions affected the degradation of azoxystrobin, and the fungicide was more persistent in the nonflooded soil than in the flooded soil. The half-life values of azoxystrobin in nonflooded and flooded soils were 107.47 and 62.69 days, respectively (**Table 2**). Application of compost to soil enhanced azoxystrobin degradation, and half-life values in flooded and nonflooded soils were 38.58 and 73.39 days, respectively. These results suggested that both compost application and flooding of the soil enhanced degradation of azoxystrobin in soils. Flooding of the soil causes anaerobiosis; therefore, soils become predominantly anaerobic in nature. Compost application to soil increases the organic carbon content of the soil and, therefore, increases soil microbial activity. Increase in soil organic carbon content also causes greater sorption of azoxystrobin (discussed in previous section) and reduces the amount of azoxystrobin in the soil solution, which is available to soil microbes for degradation. However, despite greater retention of azoxystrobin in compost-amended soil, enhanced degradation of azoxystrobin in soils can be attributed to increased soil microbial activity and more reduced soil conditions (higher redox potential). Probably, anaerobic microorganisms might be involved in the azoxystrobin degradation.

Furthermore, ethyl acetate extracts from 1- to 4-month-old soil samples were analyzed for the formation of azoxystrobin metabolite using HPLC. The HPLC chromatogram (**Figure 3**) showed a few peaks other than the parent azoxystrobin. However, the area of peak at retention time (t_R) 2.64 min increased with increase in the duration of incubation. Figures in **Table 3** represent the detector response (mV) for the metabolite in the soils [both natural (T-0) and 5% compost-amended (T-1) incubated under flooded and nonflooded conditions]. There was no detectable amount of this metabolite in samples <60 days old. The amount of metabolite was maximum in treatment T-1, F, where azoxystrobin was degraded at the fastest rate. The amount of this metabolite in soils increased with time, and the maximum amount was recovered in 120-day-old samples, suggesting that the compound was persistent in nature and was not further degraded. These results are in line with the results obtained by previous workers, which suggested that azoxystrobin was more persistent in aerobic soils than in anaerobic soils (*4*) and that azoxystrobin acid was recovered as the major metabolite of azoxystrobin degradation (*5*).

Photodegradation of azoxystrobin in the field plays an important role in the degradation of pesticides in the environment. Results of laboratory studies on degradation of azoxystrobin under sunlight and UV light are represented in **Table 4**. The study indicated that azoxystrobin was more prone to degradation under UV light than under sunlight. Soil acted as a shield and prevented photodegradation of azoxystrobin by UV light and sunlight, and the fungicide persisted for a longer time. The degradation data for azoxystrobin under UV light and sunlight were subjected to first-order kinetics, and half-life values for azoxystrobin degradation were calculated. The half-life values for azoxystrobin were higher under sunlight (3.27 h, without soil; and 16.71 h, with soil) than under UV light (9.80 min, without soil; and 1.31 h, with soil). Faster degradation of azoxystrobin in UV light than in sunlight may be due to the fact that sunlight provided a fraction of high-energy UV light compared to when sole UV light was used. Slow degradation of azoxystrobin in the presence of soil is probably due to the fact that azoxystrobin adsorbed in the soil matrix is protected from degradation by light (sunlight and UV light). Earlier, Garau et al. (*7*) reported that epiculticaular waxes have a screening effect on azoxystrobin degradation.

The present study suggests that azoxystrobin is moderately sorbed in sandy loam soil. Degradation of the fungicide was affected by soil moisture conditions, organic carbon content, and sunlight/UV light. Azoxystrobin acid was recovered as the major metabolite of azoxystrobin.

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Received for review September 3, 2008. Revised manuscript received November 27, 2008. Accepted November 28, 2008. R.K.G. is thankful to the Indian Agricultural Research Institute, New Delhi, India, for financial assistance.

JF802716F