JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Degradation and Adsorption of Fosthiazate in Soil

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Adsorption and degradation behavior of a pesticide in soil has a strong effect on its environmental fate as well as efficacy for pest control. Fosthiazate is an organophosphate compound that is currently under development as a nonfumigant nematicide. In this study, we evaluated adsorption and degradation kinetics of fosthiazate in three U.S. soils with different properties. Adsorption of fosthiazate in mineral soil was negligibly weak but appeared to increase with soil organic matter (OM) content. The half-life ($T_{1/2}$) of fosthiazate ranged from 0.5 to 1.5 months in nonsterile soils but was prolonged to 1−3 months after sterilization. Degradation of fosthiazate in soil appeared to be caused by both chemical and microbial transformations. The persistence of fosthiazate generally decreased with increasing soil pH, but increased with increasing soil OM and clay contents. This results suggest that fosthiazate may have an enhanced leaching potential in acidic soils with low OM content, and its efficacy in high pH soils may not last as long as in neutral soils because of faster degradation.

KEYWORDS: Adsorption; degradation; fosthiazate; leaching; methyl bromide alternatives; nematicide

INTRODUCTION

Fumigant nematicides have historically played an important role in the management of soil-borne parasitic nematodes. However, owing to their negative health effects and potential for polluting air and/or groundwater, most fumigant nematicides, including ethylene dibromide (EDB), 1,2-dibromo-3-chloropropane (DBCP), and methyl bromide, have been, or will soon be, banned in the United States and in many other countries. With the phase out of methyl bromide, it is anticipated that there will be a great need for chemical and nonchemical alternatives for managing nematodes and other soil-borne pests (*1*). In addition, the implementation of the 1996 Food Quality Protection Act is expected to reduce the number of currently registered nonfumigant nematicides in the U.S. due to the requirements of rigorous and extensive cumulative risk data.

Fosthiazate ((*RS*)-*S*-*sec*-butyl-*O*-ethyl 2-oxo-1,3-thiazolidin-3-ylphosphonothioate) is a relatively new nonfumigant, organophosphate nematicide (*2*). Studies in field plots have shown that fosthiazate exhibits similar efficacy as other nonfumigant nematicides against a wide range of plant parasitic nematodes, such as root-knot nematodes (*Meloidegyne* spp.), cyst nematodes (*Globodera* spp.), and root lesion nematodes (*Pratylenchus* spp.) (*2*−*10*). It also has systemic activity against various species of insects and mites on the foliar part (*2*). Fosthiazate has been on the market in Japan since 1993 and is currently registered for use on potatoes for controlling cyst nematodes in the U.K. (*2*, *4*, *8*).

The persistence and adsorption capacity of a pesticide determine its potential for causing adverse environmental effects, e.g., contamination of groundwater, as well as its efficacy for pest control. Understanding of degradation and adsorption as a function of soil type will also allow adjustment of pesticide application rate for different soils (*11*). Essentially no published data are currently available on degradation and adsorption of fosthiazate in soil. Therefore, the present study was undertaken to evaluate the adsorption and degradation behavior of fosthiazate in three different soils. Rate of degradation and adsorption were correlated with soil properties to identify the controlling factors. The mechanism of degradation was further explored through comparative experiments using sterilized and nonsterile soils.

MATERIALS AND METHODS

Chemicals. A formulation of fosthiazate (**Figure 1**) containing active ingredient at 900 g L^{-1} (Syngenta Crop Protection, Greensboro, NC) was purified by eluting through a 50-cm silica gel column (particle size 63−200 mesh; Selecto Scientific, GA) with ethyl acetate and hexane to obtain the analytical standard of the pesticide. The purity of the fosthiazate standard was determined to be >98% by HPLC and GC analysis. Other chemicals used in this study were all of analytical or HPLC grade.

Soils. Three soils with different physical and chemical properties were used in the study (**Table 1**). Soil samples were collected from the 0−20 cm surface layer from two sites in California and one site in Minnesota. Arlington sandy loam was taken from a turfgrass plot at the Agricultural Experiment Station near the University of California, Riverside campus. The San Emigidio sandy loam was collected from the University of California South Coast Research and Extension Center in Irvine, CA. The Waukegan clay loam was collected from

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10.1021/jf049094c CCC: $27.50
Published on Web 09/04/2004

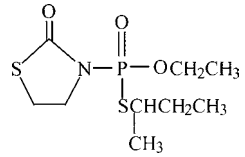

Figure 1. Chemical structure of fosthiazate.

Table 1. Textural and Chemical Properties of Soils Used in the Study

soil	clay (%)	sand (%)	silt (%)	OM (%)	pH
San Emigdio sandy loam	12	12.5	75.4	0.45	7.2
Arlington sandy loam	9	67	24	0.82	6.7
Waukegan clay loam	21	41	38	3.1	5.5

Rosemont, MN. The soil samples were homogenized without air-drying, and then passed through a 2-mm sieve before use. The prepared soil samples were stored in closed plastic bags at room temperature and used within one month after sampling. The mechanical composition and basic chemical properties of the test soils were analyzed using standard methods by the University of California DANR Analytical Laboratory in Davis, CA (**Table 1**).

Adsorption Experiment. 10 g of each soil (dry weight equivalent) were weighed into 50-mL propylene centrifuge tubes, and 20 mL of 0.01 M $CaCl_2$ solution containing fosthiazate at 0, 2, 5, 10, 16, or 25 μg mL^{-1} was added. The pesticide solution also contained 0.01 M NaN_3 to inhibit microbial degradation during the period of sample equilibration. Triplicate samples were prepared for each concentration. The soil samples were equilibrated at high speed on a mechanical shaker for 24 h at room temperature (20 ± 2 °C) and then centrifuged at 12 000 rpm for 15 min to separate the solution and solid phases. The supernatant was decanted and an aliquot was used for analysis by HPLC to determine the aqueous phase concentration C_w (μg mL^{-1}). The remaining soil phase was extracted by mixing with 10 mL methanol for 2 h, followed by centrifugation at 12 000 rpm. An aliquot of the extract was used for analysis on HPLC. Preliminary experiments showed that the above procedure gave recovery >75% for fosthiazate. The centrifuge tubes were individually weighed before and after the removal of the aqueous phase to estimate the amount of solution that remained in the soil after phase separation. The adsorbed concentration C_s (μg g^{-1}) was calculated from the difference between the amount of pesticide recovered after methanol extraction, and the amount remaining in the residual water. The C_w and C_s values were fitted to the Freundlich equation to estimate K_f and n, and to a linear model to estimate K_d.

Degradation Experiment. Degradation of fosthiazate was determined in an incubation experiment. 19 g of soil (dry weight equivalent) was placed in 150-mL flasks, and the soil water content was adjusted to about 60% of field holding capacity of each soil (w/w) by drying or adding deionized water. Two sets of 24 soil flasks were prepared for each soil type. One set of soil samples was autoclaved twice at 121 °C for 60 min, with a 24-h interval between the first and second autoclaving, to remove microbial activity. The second set was not autoclaved. For treatment, 50 g of oven-dried soil was treated with 10 mL of methanol solution containing fosthiazate at 500 μg mL^{-1} in a small beaker. The soil samples were placed in the fume hood overnight to allow evaporation of the methanol. After thoroughly mixing the soil using a glass rod, a 1.0-g aliquot was removed from the beaker and mixed into the previously prepared soil samples. The soil flasks were thoroughly mixed by rotating and shaking. The initial fosthiazate concentration in the soil was 5 μg g^{-1}. All flasks were covered with aluminum foil and placed in the incubator at 20 °C. The flasks were weighed periodically to check for water loss, and deionized water was added to compensate the moisture loss when necessary.

Three replicate flasks were removed from each treatment on day 0, 3, 5, 10, 18, 25, 40, and 60 d after the treatment and immediately transferred into a freezer (−21 °C) to stop the degradation. For extraction, soil samples were thawed at room temperature and then transferred to 50-mL Teflon centrifuge tubes. The soil samples were shaken with 30 mL of acetone−hexane mixture (1:1, v/v) for 1 h on a mechanical shaker and then centrifuged at 9000 rpm. The same extraction step was repeated for a total of three times, and the solvent extracts from all extractions were combined. The extracts were evaporated to dryness on a vacuumed rotary evaporator at 50 °C. The residues were recovered by rinsing the flask with 4.0 mL of acetonitrile, and an aliquot was used for analysis by HPLC. Preliminary experiments showed that the recovery was about 75% for this extraction method. The pesticide concentrations measured at the different time points were fitted to a first-order decay model to estimate the first-order rate constant k (d^{-1}) and the half-life $T_{1/2}$ (d).

HPLC Analysis. A method for quantitative measurement of fosthiazate in aqueous or solvent phase was developed through preliminary experiments. Briefly, fosthiazate in aqueous solution or solvent extract of soil samples was determined on an Agilent 1100-series HPLC system (Agilent Technologies, Wilmington, DE) with a variable wavelength UV detector. A reversed phase C_{18} column (5 μm, 4 × 250 mm; Hypersil ODS, Agilent) was used for the separation. The detection wavelength was 230 ± 15 nm. The mobile phase was made of methanol and water at 1:1 (v/v) ratio and the flow rate was 1.0 mL min^{-1}. The injection volume was 10 μl. Under these conditions, the retention time for fosthiazate was about 10.1 min.

Table 2. Adsorption Coefficients and Correlation Coefficient of Fosthiazate in Three Different Soils

soil	K_f	n	r^2	K_d	r^2
San Emigdio sandy loam	0.45	1.07	0.99	0.55	0.99
Arlington sandy loam	0.10	1.00	1.00	0.10	1.00
Waukegan clay loam	1.18	0.90	1.00	0.89	1.00

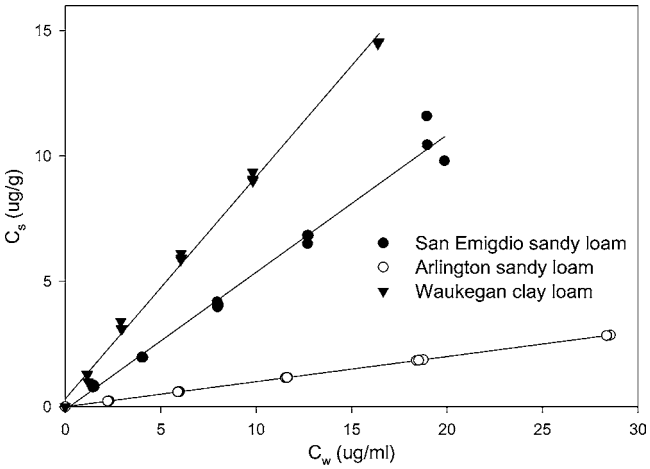

Figure 2. Fosthiazate adsorption isotherms in three different soils. Symbols are measured data and lines are fitted from a linear model.

RESULTS AND DISCUSSION

Adsorption. Adsorption of fosthiazate as a function of pesticide concentration fitted well to the Freundlich equation, and the correlation coefficient r^2 was ≥ 0.99 (**Table 2**). The Freundlich adsorption coefficient K_f ranged from 0.10 to 1.18, suggesting that fosthiazate was weakly adsorbed to the three soils for the concentration range tested in this study (**Figure 2** and **Table 2**). The nonlinearity factor n was about 1.0 (0.90−1.07), and the closeness of n to unity implies that fosthiazate displayed a linear adsorption behavior under the conditions used in this study. Adsorption isotherms were subsequently fitted to a linear relationship to estimate the linear adsorption coefficient K_d (**Table 2**). As evident from the K_d values, adsorption of fosthiazate was negligible in San Emigdio sandy loam and Arlington sandy loam and was slightly enhanced in Waukegan clay loam. The small increase in K_d for Waukegan clay loam may be attributed to the higher organic matter content in the

Table 3. First-order Degradation Rate Constants and Correlation Coefficient of Fosthiazate in Soils

soil	k (d^{-1})	$T_{1/2}$ (d)	r^2
	Nonsterile		
San Emigdio sandy loam	0.026	26.8	0.98
Arlington sandy loam	0.039	17.7	0.93
Waukegan clay loam	0.015	46.8	0.87
	Sterilized		
San Emigdio sandy loam	0.024	28.9	0.98
Arlington sandy loam	0.024	28.4	0.99
Waukegan clay loam	0.008	87.7	0.96

soil. Numerous studies have shown the dependence of adsorption of organic compounds on soil organic matter content (*12*, *13*). The K_{oc} value, or the adsorption coefficient normalized over the soil organic carbon content, was estimated to be 220 for San Emigdio sandy loam, 22 for Arlington sandy loam, and 52 for Waukegan clay loam. These K_{oc} values suggest that adsorption of fosthiazate is generally weak in soils. The weak adsorption implies that fosthiazate may have a high leaching potential, especially in light textured soils, and that adsorption will not adversely affect the efficacy of fosthiazate in different soil types. Fosthiazate was found to be effective in a wide range of soil types (*2*).

Degradation. Dissipation of fosthiazate was followed in the soils at 20 °C. The fit of data to the first-order decay model was good for all treatments, with r^2 ranging from 0.87 to 0.99 (**Table 3**). In nonsterile soils, the most rapid degradation of fosthiazate occurred in Arlington sandy loam, and the first-order half-life $T_{1/2}$ was 17.7 d. Substantially slower degradation was observed in the Waukegan soil, with $T_{1/2}$ of 47 d (**Figure 3**a and **Table 3**). The number of soils used in this study allowed only a tentative analysis of the factors that influence the degradation rate of fosthiazate. Regression of the first-order rate constant k with soil properties showed that the rate of degradation correlated inversely with soil OM content ($r^2 = 0.58$) or clay content ($r^2 = 0.89$), but proportionally with soil pH ($r^2 = 0.49$). Previous studies have shown that pesticide degradation may be inhibited in soils with higher OM or clay content due to enhanced adsorption (*14*). Adsorption may decrease degradation by limiting the availability of the chemical to microbial or chemical transformations (*15*). Given the overall weak adsorption of fosthiazate in the test soils, effect of adsorption, if any, would be of limited importance. In other cases, soil organic matter was found to serve as an alternative source of C and N for the microorganisms involved in pesticide degradation, preventing the pesticide from being used as a nutrient source and consequently, increasing its half-life (*16*). On the other hand, studies have shown that there is often close dependence between the degradation rate of organophosphate or carbamate compounds and soil pH. The hydrolysis of the phosphate or carbamate ester bond is typically base-catalyzed and is therefore enhanced in soils with high pH (*17*). Shortened persistence has been found in high pH soils for a great number of organophosphate and carbamate compounds (*17*, *18*). Therefore, the relatively slow degradation in the Waukegan soil may be partly attributable to the soil's low pH.

Sterilization treatment generally resulted in a decrease in degradation rate, or an increase in persistence, of fosthiazate in the selected soils (**Figure 3b** and **Table 3**). The effect was statistically significant ($p < 0.05$; pair t-test) for Arlington sandy loam and Waukegan clay loam. In the Arlington soil, sterilization increased $T_{1/2}$ from 17.7 to 28.4 d, or by 60%. In the Waukegan soil, the persistence increased from 46.8 to 87.7 d,

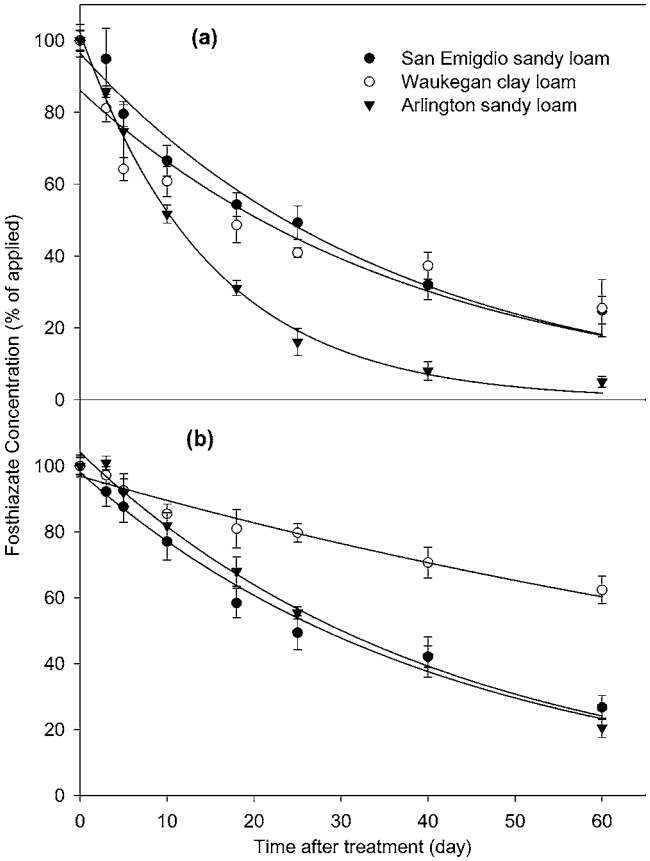

Figure 3. Degradation of fosthiazate in different soils: (*a*) nonsterilized soils; (*b*) sterilized soils. Symbols are mean values of three replicated measurements and lines are fitted from a first-order decay model. Vertical bars are standard deviations.

or by 87% (**Table 3**). The inhibition by sterilization suggests that microbial transformations partly contributed to the overall degradation of fosthiazate in the soils. Assuming that both abiotic and biotic transformations obeyed first-order kinetics, the overall degradation rate constant k may be expressed as the sum of chemical degradation rate constant k_c and microbial degradation rate constant k_b

$$k = k_c + k_b \quad (1)$$

The relatively contribution of microbial or chemical degradation to the overall degradation may be estimated from the ratio of k_b or k_c over k. In the San Emigdio soil, it was estimated that abiotic degradation was predominant, contributing to about 92% of the overall degradation. In the Arlington sandy loam, abiotic degradation accounted for about 62% of the total degradation, whereas microbial degradation contributed about 38%. The highest contribution from microbial degradation was observed in the Waukegan clay loam, where about 47% of the overall degradation was attributable to abiotic transformations. The limited contribution by microorganisms in the San Emigdio soil may be due to the very low organic matter content in the soil, because soil organic matter is known to support microbial growth. Conversely, the relatively more significant role of microorganisms in fosthiazate degradation in the Waukegan soil may be explained by the inhibited chemical degradation due to the relatively low soil pH.

Adsorption and persistence are usually the predominant factors influencing the leaching potential of a pesticide in soil. For instance, K_{oc} and 50% dissipation time (DT_{50}) have been

used in an empirical model to estimate the leaching potential of pesticides (*19*)

$$\mathrm{GUS} = \log(\mathrm{DT}_{50}) \times (4 - \log(K_{\mathrm{OC}})) \quad (2)$$

where GUS stands for groundwater ubiquity score. A chemical with GUS > 2.8 is considered of high leaching potential, while a chemical with GUS < 1.8 is defined as a low leaching candidate. Using the measured K_{oc} and $T_{1/2}$ values, the estimated GUS index was 2.4 for San Emigdio sandy loam, 3.3 in Arlington sandy loam, and 3.8 in the Waukegan clay loam. Therefore, it may be concluded that fosthiazate may leach easily through soils under conducive conditions, especially in soils with relatively low pH. However, many other factors may alter the actual dissipation rate of a pesticide under field conditions, and such factors include volatilization and photolysis, among others. The exact leaching risk of fosthiazate must therefore be investigated under field conditions.

In conclusion, this study showed that fosthiazate was weakly adsorbed in soils. The weak adsorption may facilitate leaching of fosthiazate under conditions of active water movement. Fosthiazate was degraded via both chemical and microbial pathways, and its persistence generally decreased with increasing soil pH. Therefore, it is concluded that leaching of fosthiazate may be further enhanced by low soil pH. The weak adsorption also suggests that fosthiazate may be equally effective in different types of soils. However, the dependence of its persistence on soil pH may decrease the efficacy of fosthiazate in soils of high pH. In addition, fosthiazate contains two sulfur atoms, and its transformation in soil may form sulfoxides and sulfones. As such oxidized intermediates are expected to possess biological activity similar or even greater than the parent compound, future studies must also consider the formation and fate of these metabolites.

ACKNOWLEDGMENT

The authors thank Dr. S. K. Papiernik for providing the Waukegan soil and Syngenta Crop Protection, Inc., for providing the commercial formulation of fosthiazate used in this study.

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Received for review June 3, 2004. Revised manuscript received July 2, 2004. Accepted August 2, 2004.

JF049094C