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Accelerated Degradation of Fenamiphos and Its Metabolites in Soil Previously Treated with Fenamiphos

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Abstract: The degradation of fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone was determined in a greenhouse experiment using autoclaved and nonautoclaved soil from field plots treated or not treated with fenamiphos. Fenamiphos degradation and formation of fenamiphos sulfoxide was faster in nonautoclaved soil than in autoclaved soil. In nonautoclaved soil, previous exposure to fenamiphos was associated with increased rate of degradation of fenamiphos sulfoxide. Fenamiphos total toxic residue degraded more rapidly in nonautoclaved soil previously exposed to fenamiphos than in nonautoclaved soil never exposed to fenamiphos. This accelerated degradation was due to more rapid degradation of fenamiphos sulfoxide and appears to be biologically mediated.

Key words: accelerated degradation, degradation, enhanced degradation, fenamiphos, fenamiphos sulfone, fenamiphos sulfoxide, metabolite, microbial degradation, nematicide, nematode, pesticide degradation.

Pesticides may be degraded in soil through chemical, physical, and biological mechanisms (19). The degradation products (metabolites) of pesticides have been implicated in creating soils capable of accelerated degradation of the parent compound (4,6,10,14,20,21,23). Repeated application of the parent compound can also lead to enhanced degradation of degradation products (1,3,15,18).

Fenamiphos (ethyl 3-methyl-4-(methylthio)phenyl (1-methylethyl)phosphoramidate) is an organophosphorus nematicide with low volatility. In soil, fenamiphos is quickly oxidized to fenamiphos sulfoxide, which is then oxidized more slowly into fenamiphos sulfone (8,9,11,12). Fenamiphos sulfone phenol, which is formed by the hydrolysis of fenamiphos sulfone, also has been detected during fenamiphos degradation in soil (11), but fenamiphos phenol and fenamiphos sulfoxide phenol were not detected in that experiment, and fenamiphos sulfone phenol was not included in the measurement of total toxic residue. Fenamiphos total toxic residue (TTR) is defined herein as the sum of fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone. Fenamiphos TTR declines more rapidly in soils that have been exposed previously to fenamiphos (11,13), but individual degradation rates for fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone have not been examined adequately. Loss of nematicidal efficacy has been reported for soil treated repeatedly with fenamiphos, but this loss of efficacy was not linked to the accelerated degradation of the nematicide (7). This study examines the degradation of fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone in soil from a field with documented loss of fenamiphos efficacy. Soil previously treated with fenamiphos and soil from the same field never treated with fenamiphos were used to determine if the rates of degradation were affected by previous nematicide application.

Materials and Methods

Soil was collected from field plots (Tifton loamy sand [fine–loamy, siliceous, thermic Plinthic Paleudults]; 84% sand, 9% silt, 7% clay, 1% organic matter; pH 6.0–6.7) in October and December 1992 for two runs of a greenhouse experiment to determine if the rates of fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone degradation were affected by previous nematicide application. Soil was collected separately for each run from plots in the same field to which fenamiphos had been applied four times over two years and from plots to which fenamiphos had never

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been applied. This field was planted to cotton–wheat–peanut and cotton–wheat–cotton crop rotations in 1991 and 1992. Fenamiphos was applied through chemigation (in 3 mm water) at 6.7 kg a.i./ha to one-half of the plots prior to planting cotton (12 June 1991), before planting wheat (10 December 1991, 8 December 1992), and again before planting peanut and cotton (18 June 1992). Soil collected in December 1992 was collected before the application of fenamiphos. The remaining half of the plots were not treated with fenamiphos. Soil was passed through an 850-μm-opening sieve to remove rocks and debris.

The treatments, arranged in a 2 × 2 factorial, were 1) soil with a history of fenamiphos applications and soil with no history of fenamiphos application, and 2) autoclaved or not autoclaved. Two lots of soil, one from each fenamiphos history and each weighing 11.34 kg (≤5% moisture), were autoclaved at 121 C and 103.4 kPa for 30 minutes, and two similar lots of soil remained unautoclaved. Fenamiphos 15G (227 mg) was mixed with each of the four 11.34-kg lots of soil (3 ppm active ingredient concentration). Soil (100 cm^3) was placed into 266-ml polystyrene containers. Seven containers were set up for each of the six replications (randomized complete blocks) of each treatment. Cups were covered with four layers of moistened cheesecloth to impede desiccation and subsequent loss of microbial activity, and soil moisture was maintained at ca. 20% without leaching. Average temperatures in the greenhouse were 17.4 C minimum and 31.6 C maximum for the first run and 18.9 C minimum and 27.3 C maximum for the second run.

One polystyrene container was removed from each replication following application of fenamiphos at 0, 1, 2, 4, 7, 9, and 14 days in the first run, and 0, 1, 2, 5, 7, 9, and 14 days after fenamiphos application in the second run. Both runs were 14 days in duration. Fifty grams of moist soil (20% moisture) was collected for chemical analysis.

Fenamiphos and its two metabolites, fenamiphos sulfoxide and fenamiphos sulfone, were extracted from soil samples by methanol extraction. The 50-g soil samples were mixed from 50 ml methanol and the flasks were sealed and shaken on a platform-type shaker for 2 hours. Contents of the flasks were allowed to settle for 5 minutes before being passed through a Büchner funnel with glass fiber filter paper (1.2-μm pore size) under 500-mm-Hg vacuum. The filtrate was then passed through a 0.45-μm-pore polyvinyl difluoride syringe filter and collected in HPLC vials.

HPLC analysis was used to determine fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone concentrations. HPLC analysis utilized a C18 column, 55% acetonitrile–45% water mobile phase with a 1.3-ml/minute flow rate, a detector set at 225-nm with a 15-nm bandwidth for fenamiphos sulfoxide and fenamiphos sulfone (approximate retention times of 1.8 and 2.3 minutes) and at 250-nm with a 15-nm bandwidth for fenamiphos (approximate retention time of 4.4 minutes). HPLC calibration standards included mixtures of fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone solutions with concentrations of each compound at 0, 2.5, or 5.0 μg/ml. Peak heights were measured manually and used to determine chemical concentration. Because of the 50-g soil samples contained 10 g water, which would dilute the 50 ml methanol extraction solvent, the chemical concentrations measured by HPLC were adjusted by a factor of 1.2 to give the actual concentration of chemicals in the soil samples.

Statistical analysis included factorial analysis of variance with relevant contrasts at each sampling time (16). General linear models procedures were used to fit least-squares regression curves to the data sets. All differences reported herein are significant at the $P = 0.05$ level unless otherwise indicated.

Results and Discussion

Because fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone have nema-

ticidal properties (22), the accelerated degradation of any of these compounds could reduce efficacy of the nematicide. The accelerated degradation of fenamiphos TTR has been documented (11,13). The data presented herein further characterize the accelerated degradation of fenamiphos TTR in soil taken from a field that had previously shown loss of efficacy following repeated application of fenamiphos (7).

The predominant component of TTR at the beginning of each run was fenamiphos, which began immediately to degrade into fenamiphos sulfoxide. Fenamiphos degradation and the formation of fenamiphos sulfoxide were faster in nonautoclaved soil than in autoclaved soil. This indicates that fenamiphos degradation is biologically mediated. Because fenamiphos sulfoxide began to degrade as soon as it was formed, the amount extracted at each sampling time depended on the rate of formation relative to the rate of degradation.

Fenamiphos residue was not detected in soil prior to the addition of nematicide to the 11.34-kg lots. The level of fenamiphos present immediately after granular fenamiphos was mixed into the soil (0 days) did not differ among the four treatments in either run of the experiment. At all subsequent sampling times, less fenamiphos was recovered from nonautoclaved soil than from autoclaved soil (Figs. 1A, 2A). Seven days after application in the second run, more fenamiphos was recovered from nonautoclaved soil with no fenamiphos history than from nonautoclaved soil with fenamiphos history. No other differences were detected between nonautoclaved soils in either run. In general, autoclaved soil with fenamiphos history was not different from autoclaved soil without fenamiphos history; differences were observed 14 days after application in the first run and 5 days after application in the second run, but there was no consistent pattern of differences.

Fenamiphos sulfoxide levels could not be determined at 0 days in the first run because these peaks were obscured in the HPLC analysis. A history of fenamiphos application did not affect the level of fenamiphos sulfoxide extracted from autoclaved soil in the first run (Fig. 1B), but less fenamiphos sulfoxide was extracted from autoclaved soil with a fenamiphos history than from autoclaved soil with no fenamiphos history 9 and 14 days after application in the second run (Fig. 2B). The amount of fenamiphos sulfoxide extracted from nonautoclaved soils generally increased with time (Figs. 1B, 2B).

In nonautoclaved soils, a history of fenamiphos application resulted in lower levels of fenamiphos sulfoxide than was extracted from soil without fenamiphos history. The lower levels detected from days 4–14 in both runs indicated that the rate of fenamiphos sulfoxide degradation was faster in soil with a history of fenamiphos application. In nonautoclaved soil in the second run, the rate of fenamiphos degradation was slightly faster in soil with a history of fenamiphos application than in soil with no fenamiphos history, but, as in the first run, the amount of fenamiphos sulfoxide extracted was less from soil with a history of fenamiphos application than from soil without fenamiphos history.

Fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone can be hydrolyzed to fenamiphos phenol, fenamiphos sulfoxide phenol, and fenamiphos sulfone phenol (12). Studies that examined the formation of these products found no fenamiphos phenol and little fenamiphos sulfone phenol (11,12). One study (12) found small amounts ($\leq$⅙ the amount of fenamiphos sulfoxide) of fenamiphos sulfoxide phenol during the first 14 days (the length of our runs) but the other study (11) found none. Because such small amounts of fenamiphos sulfoxide phenol have been reported during the first 14 days of fenamiphos degradation, if any is to be found at all, it seems unlikely that the hydrolysis of fenamiphos sulfoxide played an important role in our study.

An alternative explanation for the reduced levels of fenamiphos sulfoxide in

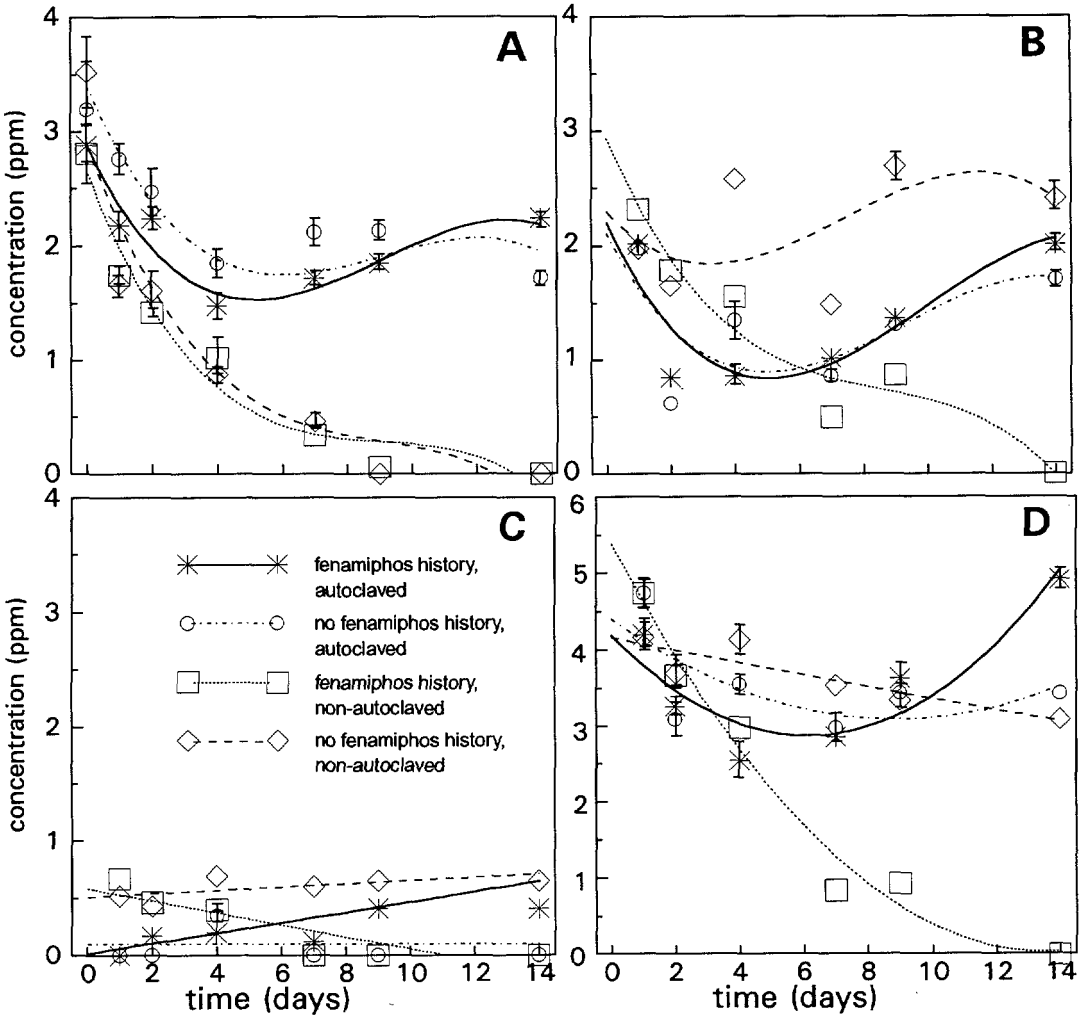

FIG. 1. Concentration of nematicidal compounds in soil for 14 days after incorporation of fenamiphos 15G (run 1). Bars represent one standard error of the mean of six replications. Error bars smaller than the data point markers are not drawn. A) Fenamiphos. B) Fenamiphos sulfoxide. C) Fenamiphos sulfone. D) Total toxic residue.

soil with a history of fenamiphos application could be that degradation may be at or near the same rate regardless of fenamiphos history, but the mechanisms or pathways of degradation may be different in soils previously treated with fenamiphos. If the pathway of degradation is changed, then fenamiphos may be degraded at the same rate but not be degraded into fenamiphos sulfoxide; and if the rate of fenamiphos sulfoxide degradation remained unchanged, then less fenamiphos sulfoxide would be extracted from soil with a history of fenamiphos application. This explanation seems unlikely, because a lag time (2,17) would be expected in fenamiphos degradation during which shifts in metabolic pathways would occur in the microorganisms responsible for fenamiphos degradation. Such a lag period did not occur.

In contrast, a lag period did occur in the degradation of fenamiphos sulfoxide in the second run. A lag period is indicated by an observable change in the degradation rate of fenamiphos sulfoxide. In nonautoclaved soil, fenamiphos degradation (and consequent fenamiphos sulfox-

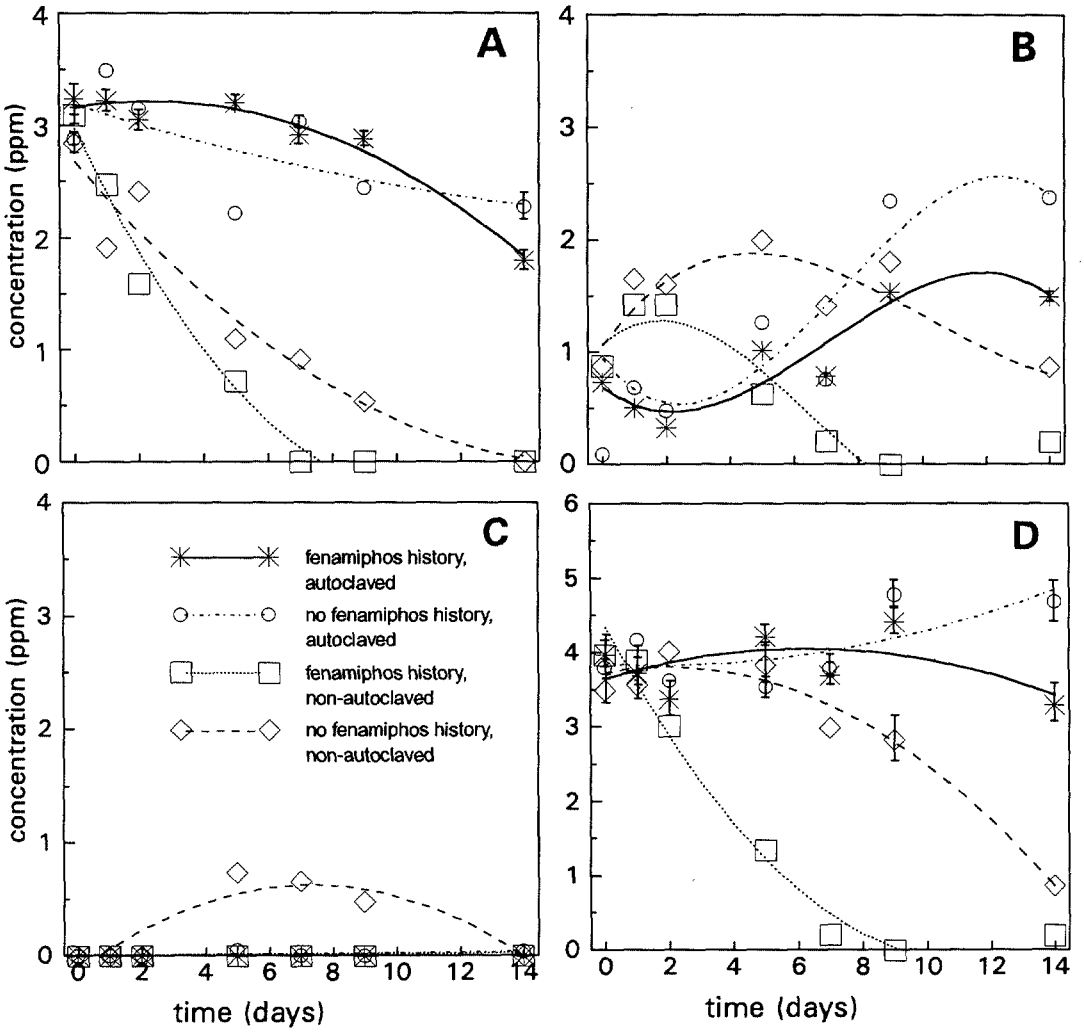

FIG. 2. Concentration of nematicidal compounds in soil for 14 days after incorporation of fenamiphos 15G (run 2). Bars represent one standard error of the mean of six replications. Error bars smaller than the data point markers are not drawn. A) Fenamiphos. B) Fenamiphos sulfoxide. C) Fenamiphos sulfone. D) Total toxic residue.

ide formation) occurred at the same rate in soil with a fenamiphos history as in soil with no fenamiphos history. If the degradation rates of fenamiphos sulfoxide were the same in the two soils, then the amounts of fenamiphos sulfoxide extracted from the two soils should be the same. The amounts of fenamiphos sulfoxide extracted during the first 2 days of the second run were the same for the two soils, but beginning on day 4, the amount extracted from soil with a fenamiphos history was less than the amount extracted from soil without fenamiphos history. Therefore, the rates of fenamiphos sulfoxide degradation in the two soils were the same for the first 2 days, but after 2 days the rate was greater in soil with a fenamiphos history than in soil with no fenamiphos history; there was a 2-day lag before accelerated degradation was observed. Although a lag period is not as clearly indicated in the first run, this situation is possibly due to the lack of measurements at 0 days. This lag period probably results from the time required by microorganisms capable of de-

grading fenamiphos sulfoxide to shift metabolic pathways and subsequently reproduce.

Levels of fenamiphos sulfone were lower in autoclaved soil than in nonautoclaved soil at 1, 2, and 4 days after application in the first run (Fig. 1C). In nonautoclaved soil, less fenamiphos sulfone was extracted from soil with a history of fenamiphos application than from soil without such history at 4 days after application and all sampling dates thereafter. In the second run, the only treatment with levels of fenamiphos sulfone greater than zero was nonautoclaved soil without fenamiphos history (Fig. 2C).

Analysis of variance indicated that fenamiphos TTR concentrations did not decrease in autoclaved soil during either run. Fenamiphos TTR concentrations in nonautoclaved soil with a history of fenamiphos application declined to 0 ppm by 12 days after application in the first run (Fig. 1D) and by 9 days after application in the second run (Fig. 2D). In the second run, nonautoclaved soil with no history of fenamiphos application had reductions in TTR concentration during the experiment.

The differences between autoclaved and nonautoclaved soil suggest that fenamiphos degradation is biologically mediated, but Ashton (2) cautioned that autoclave sterilization may also affect the physical and chemical properties of a soil. Microorganisms with the ability to degrade fenamiphos and its metabolites appear to be present even in soil never treated with fenamiphos. Accelerated degradation may occur if microorganisms were conditioned by previous exposure to fenamiphos to preferentially metabolize fenamiphos or if organisms were selected for more efficient metabolism of fenamiphos, fenamiphos sulfoxide, or fenamiphos sulfone. Shifts in metabolic pathways have been reported (5). Perhaps organisms with the same degradation abilities are present in soils regardless of previous exposure to fenamiphos, but are present in greater numbers in previously treated soils. These possibilities need to be examined with additional research.

Ou (11) reported that little fenamiphos sulfone was formed as fenamiphos sulfoxide degraded in soil previously exposed to fenamiphos, but fenamiphos sulfone was formed in larger amounts in soil not previously exposed to fenamiphos. These results are consistent with the results of our study. If fenamiphos sulfoxide is degraded by a different mechanism (such as microbial metabolism) and not converted into fenamiphos sulfone in soil previously treated with fenamiphos, then one would expect to get these results. Although Ou did not discuss the relative rates of fenamiphos sulfoxide degradation, data in his graphs indicate that fenamiphos sulfoxide may have degraded faster in soil previously exposed to fenamiphos than in soil not previously exposed to fenamiphos.

The more rapid degradation of fenamiphos in nonautoclaved soil indicates that fenamiphos degradation is biologically mediated. Fenamiphos TTR is degraded more rapidly when soil has been exposed previously to fenamiphos. This accelerated degradation appears to be due primarily to an increase in the degradation rate of fenamiphos sulfoxide, a nematicidal metabolite of fenamiphos. In nonautoclaved soil, the more rapid degradation of fenamiphos sulfoxide in soil with a fenamiphos history than in soil with no fenamiphos history demonstrates that previous applications of fenamiphos can lead to more rapid degradation of the nematicide. The fact that this accelerated degradation was not observed in autoclaved soil indicates that accelerated degradation is biologically mediated. Further research is necessary to identify microorganisms involved in the accelerated degradation of fenamiphos sulfoxide.

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