Fenamiphos Transport, Transformation, and Degradation in a Highly Weathered Soil

C. C. Truman, R. A. Leonard, A. W. Johnson

Abstract. *Fenamiphos, a nematicide used on corn and sorghum, quickly oxidizes into two metabolites which have similar activities and toxicities, yet are more mobile and persistent than the parent compound. Given the soil and climatic conditions of the southeastern U.S., fenamiphos and its metabolites could be transported from the application site and contaminate off-site water bodies. A three-year study was conducted to evaluate (1) degradation and transport of the fenamiphos parent (F_p) and its metabolites (sulfoxide, F_x, and sulfone, F_o) from a 0.34 ha field site, and (2) the utility of the GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model in describing system response and simulating pesticide transport. Each year, fenamiphos was applied at 6.7 kg ha^{-1} a.i., broadcast and incorporated into the upper 100 mm soil layer before planting each crop. Concentrations of fenamiphos and its metabolites were determined from soil samples taken within the root zone at 50 mm intervals to a depth of 300 mm and from subsurface tile outflow at selected times throughout each sweet corn (Zea mays L.) and hybrid pearl millet (Pennisetum glaucum (L.) R. Br.) growing season. The GLEAMS model was used to simulate runoff, lateral subsurface flow (LSF), and F_p, F_x, and F_o losses from the Cowarts loamy sand. An average of 6 and 21% of the total rainfall + irrigation was measured as runoff and LSF, respectively. GLEAMS model simulations were correlated with measured runoff (R^2 = 0.81) and LSF (R^2 = 0.89). Field half-lives ($t_{1/2}$) were determined by comparing observed concentrations in soil by depth and time to those simulated with the GLEAMS model. Average $t_{1/2}$ values from measured field data were 5, 28, and 14 days for F_p, F_x, and F_o, respectively. For the three-year study, about 6.2% of the total amount of applied fenamiphos ($F_{tot} = F_p + F_x + F_o$) was measured in LSF, while less than 0.1% of the applied fenamiphos was measured in surface runoff. F_x was the dominant compound measured and simulated in the root zone and LSF, with 70 to 99% of measured F_{tot} being F_x. Calibration of the GLEAMS model provided fit of the field data that indicated (1) F_p dissipated rapidly while the two metabolites (F_x and F_o) formed (average F_p $t_{1/2}$ = 5.5 d); (2) $t_{1/2}$ values for all compounds remained relatively constant during 1987 and 1988, then numerically decreased in 1989; (3) coefficient of transformation (CT) values for F_x and F_o decreased from 1987 to 1989; and (4) CT values describing transformational changes from F_p to F_x were greater than those describing transformational changes from F_x to F_o. Decreases in $t_{1/2}$ and CT values for F_p, F_x, and F_o with continued use over the three-year study is characteristic of enhanced microbial degradation.*

Keywords. *Model applications, Subsurface flow, Soil and water quality, GLEAMS, Metabolites.*

Soils in the southeastern Coastal Plain of Georgia have sandy surfaces and distinct subsurface horizons with varying textures capable of initiating lateral shallow subsurface flow. Climatic conditions contribute to a high incidence of crop pests, therefore, production of economic yields on these soils requires a variety of pesticides, many of which are mobile and can contaminate surface waters, near-surface (perched) water tables, and groundwater. Understanding the transport and movement of these pesticides in different agricultural production systems is needed in order to retain more of the pesticide in the root zone to control the target pest and minimize pesticide amounts leaving a field and contaminating off-site water supplies.

Fenamiphos is a nonvolatile, organophosphate insecticide/nematicide that is applied to corn and sorghum in the Southeast. Once applied to soil, the parent fenamiphos (F_p) quickly oxidizes to fenamiphos sulfoxide (F_x), which in turn, slowly oxidizes to fenamiphos sulfone (F_o), (Leonard, et al., 1988; Davis et al., 1993, 1994). Activities and toxicity of both metabolites are similar to the parent chemical (Waggoner and Khasawinah, 1974), however, F_x and F_o are more mobile and persistent in soils than the F_p (Bilkert and Rao, 1985; Ou and Rao, 1986).

Given the soil and climatic conditions of the Southeast, fenamiphos (and metabolites) transport out of the application zone could occur leading to contamination of shallow groundwater. Objectives of this study were to evaluate degradation and transport of fenamiphos and its metabolites from a 0.34 ha field site and the utility/accuracy of the GLEAMS model in describing system response and simulating fenamiphos (and metabolites) transport.

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MATERIALS AND METHODS

For three years (1987-1989), fenamiphos (Nemacur 15G) [ethyl-3-methyl-4-(methylthio) phenyl (1-methylethyl) phosphoramidate] was applied at 6.7 kg ha^{-1} a.i., broadcast and incorporated into the top 100 mm soil layer in the spring of each year immediately before planting sweet corn (*Zea mays* L.) cultivar Merit, and in the summer of each year to a following crop of hybrid pearl millet (*Pennisetum glaucum* (L.) R.Br.). Fenamiphos application dates were 25 March 1987, 8 July 1987, 21 March 1988, 24 June 1988, 16 March 1989, and 27 June 1989.

The 0.34-ha field plot (Watershed Z), located in Tifton, Georgia, consists of a Cowarts loamy sand (fine-loamy, siliceous, thermic *Typic Kanhapludult*) which commonly occurs on 0 to 8% slopes, and is derived from Miocene sediments. Cowarts loamy sand is a deep, well-drained soil, with a moderately permeable profile, and has low to medium water holding capacity. It has about 0 to 5% clay in the surface A_p horizon (300-450 mm thick), with clay content generally increasing with depth to about 45% clay in lower argillic horizons. Average K_{sat} values for B_t, B_{tv}, and BC subsurface horizons were 3.2×10^{-2}, 1.7×10^{-2}, and 5.2×10^{-3} mm s^{-1}, respectively (Shaw et al., 1997). Maximum K_{sat} value determined for a BC horizon was 5.0×10^{-4} mm s^{-1}. Vertical water movement is restricted at the B_{tv}/BC interface resulting in lateral subsurface flow (LSF). Organic matter content is about 1% in the surface horizon resulting in low adsorptive capacity for pesticides.

Watershed Z is instrumented for sampling and measurement of surface and subsurface flow (fig. 1). Surface runoff from this plot can be significant when rainfall patterns create high antecedent water conditions. Surface runoff was directed through a 0.30 m type-H flume equipped with a water-level recorder. Lateral subsurface flow moves downslope along the aquitard to an interceptor subsurface drain tile about 1 m below the soil surface and directed through a V-notch weir equipped with a water-level recorder. Rainfall was measured with a digital raingauge located adjacent to the field plot.

Soil samples were taken at selected times during the growing seasons at depths of 0 to 100, 10 to 500, 50 to 1000, 100 to 1500, 150 to 2000, 2000 to 2500, and 2500 to 3000 mm. During periods of drainage, water (grab) samples were obtained on a daily basis. All samples were extracted by appropriate procedures which included adding water (250 mL) samples and soil (50 g) samples to a methanol solvent, shaking the mixture and filtering, then evaporating, and finally dissolving each sample in acetone. Extracted samples were then analyzed for F_p, F_x, and F_o using high pressure liquid chromatography (HPLC), with selected samples (~20%) being confirmed by gas chromatography (GC). Detection limits with HPLC for all forms of fenamiphos were 1 μg kg^{-1}.

MODEL DESCRIPTION

The GLEAMS model was developed to evaluate chemical losses in runoff and sediment from field-size areas including pesticide leaching below the root zone, and to provide relative comparisons among different management-climate-soil-pesticide conditions (Leonard et al., 1987, 1988).

GLEAMS consists of four major components: hydrology, erosion, pesticides, and nutrients (N and P). The hydrology component uses daily precipitation inputs along with soil and crop characteristics to compute a soil water balance in the root zone. Precipitation is partitioned between runoff and infiltration using a modification of the USDA, SCS (1972) curve number method (Williams and Nicks, 1982). Water in excess of storage is routed through the root zone, and total amount of percolation leaving the root zone is calculated. Computational soil layers (minimum of 3 and maximum of 12 with variable thickness) are used to route water and pesticides. The surface layer thickness is constant and assumed to be 10 mm. Soil evaporation and plant transpiration are estimated with a modified Penman equation (Ritchie, 1972).

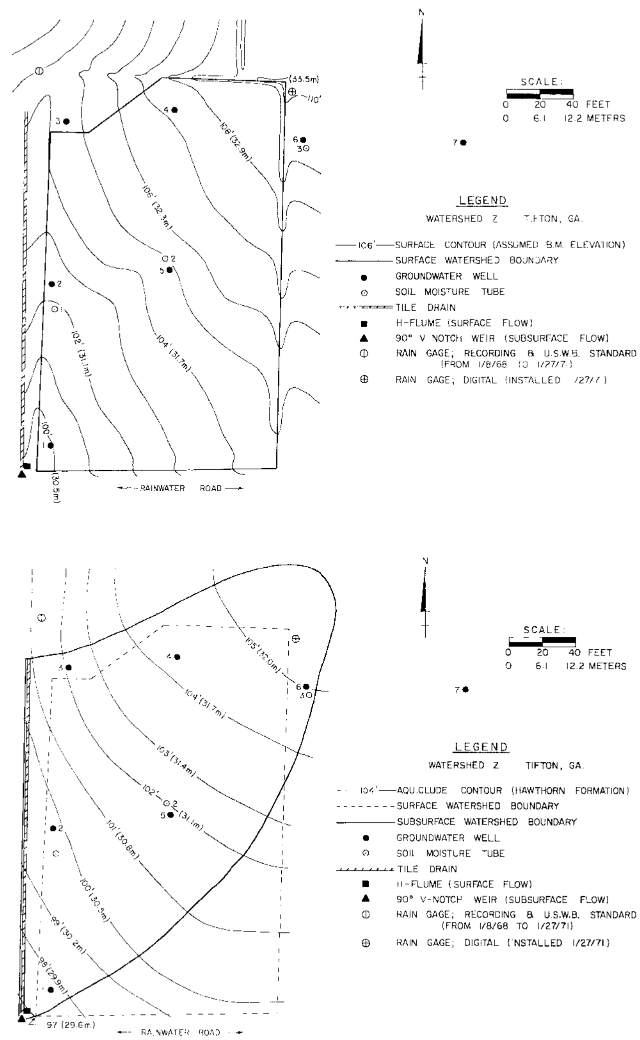


Figure 1–Topographic and physical features of the 0.34 ha field site.

The erosion component uses the modified Universal Soil Loss Equation (Wischmeier and Smith, 1978) for storm-by-storm simulation of rill and interrill erosion in overland flow areas (Foster et al., 1980). Channel and pond elements are used to estimate transport or deposition in field delivery systems to estimate sediment yield at the edge of fields. Sediment is routed with runoff by particle size (Foster et al., 1985) which allows for calculation of sediment enrichment ratios and simulation of adsorbed pesticide transport.

The pesticide component estimates pesticide concentrations and mass transported in runoff, attached to sediment, and in water moving within and through the root zone. Each day pesticides are partitioned among runoff, sediment, infiltration/percolation, foliar washoff, upward movement of pesticides, plant uptake, and pesticide degradation into metabolites (Leonard et al., 1988). Pesticides are partitioned between water and soil using K_{oc} and organic carbon content of each soil layer. Pesticides move downward with percolating water coupled with the storage-routing of the hydrology component and upward with water gradients created by evaporation. Pesticide degradation is described by first-order kinetics. Pesticide $t_{1/2}$ may be input for each soil horizon, or a single value may be used for entire root zone. Up to 10 pesticides can be simulated simultaneously with multiple applications each year of any one or all pesticides. Applications may be surface sprays, soil incorporated, injected, aerial sprays, or by chemigation (Leonard et al., 1989).

Input requirements for GLEAMS include daily rainfall volumes, crop and management parameters, intrinsic soil physical and chemical properties with depth, soil detachment and transport parameters, and pesticide properties. Output data include runoff, sediment, and percolation amounts, pesticide masses in runoff, sediment, and percolation. Output frequency can be by day, month, or year.

Model Application

Fenamiphos degradation occurs through oxidative reactions producing sulfoxide (F_x) and sulfone (F_o) metabolites. Fate of F_x and F_o are of equal interest compared to F_p because they possess nematicidal activity and potentially leach to groundwater. F_x and F_o are significantly more mobile than F_p based on published values of the adsorption coefficients, K_{oc}, of 240, 40, and 45, for F_p, F_x, and F_o, respectively (Lee et al., 1986). Consecutive first-order reactions are presented in figure 2.

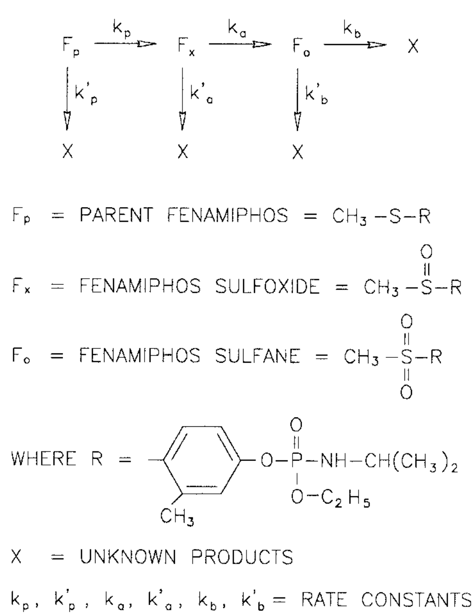


Figure 2–First-order reactions describing the breakdown of the Fenamiphos parent (F_p) into f. sulfoxide (F_x) and f. sulfone (F_o).

To simulate fate and transport of F_x, F_o, and F_p, GLEAMS computes daily concentrations in each soil layer by:

$$P_t = P_{t-1} \exp(-k_p) \quad (1)$$

$$A_t = CT_p\, P_{t-2} \exp(-k_p) + A_{t-1} \exp(-k_a) \quad (2)$$

$$B_t = CT_a\, A_{t-2} \exp(-k_a) + B_{t-1} \exp(-k_b) \quad (3)$$

where P, A, and B are concentration of the parent, first metabolite, and second metabolite, respectively, and k_p, k_a, and k_b are rate constants ($0.693/t_{1/2}$). Note that time (t) is omitted since t = 1 for a daily time increment. Also, coefficients of transformation (CT) are ratios of the product of interest, F_x or F_o, to all other products formed during F_p degradation, thus representing the fraction oxidized in each step. CT values range from 0 to 1, and may be numerically defined as:

Table 1. Measured and simulated water budgets for a 0.34 ha field plot

Year	Month	Rainfall + Irrigation (mm)	Surface Runoff Measured (mm)	Surface Runoff Simulated (mm)	Lateral Subsurface Flow Measured (mm)	Lateral Subsurface Flow Simulated (mm)
1987	Jan.	257.3	46.4	14.9	182.8	144.5
	Feb.	198.1	34.8	18.3	98.3	109.9
	Mar.	111.8	1.2	2.6	65.5	37.9
	Apr.	110.7	6.3	16.6	21.8	64.7
	May	167.1	1.6	14.8	0.15	54.8
	June	125.5	0.0	8.4	0.005	0.0
	July	74.4	0.0	0.9	0.0	0.0
	Aug.	162.6	3.3	10.2	8.5	0.0
	Sept.	167.6	16.1	17.2	15.6	0.0
	Oct.	0.0	0.0	0.0	0.0	0.0
	Nov.	104.1	4.5	7.6	0.0	0.0
	Dec.	58.4	0.1	1.9	0.0	0.0
	SUM	1537.6	114.3	113.6	392.7	411.7
1988	Jan.	152.4	4.8	3.5	44.8	55.8
	Feb.	167.6	20.6	21.3	52.0	76.1
	Mar.	210.8	27.2	18.6	62.4	75.7
	Apr.	218.4	41.2	46.6	30.7	104.5
	May	162.6	2.4	9.1	0.7	0.0
	June	147.3	0.5	8.9	0.0	0.0
	July	114.3	2.5	12.9	0.0	21.6
	Aug.	101.6	0.4	1.7	0.0	0.0
	Sept.	187.9	2.4	25.4	65.0	9.6
	Oct.	53.3	0.5	1.9	0.0	0.0
	Nov.	27.9	0.1	0.0	0.0	0.0
	Dec.	38.1	0.0	0.0	0.0	0.0
	SUM	1582.2	102.6	149.9	255.6	343.3
1989	Jan.	43.2	0.0	0.0	0.0	0.0
	Feb.	71.1	0.1	6.6	0.0	0.0
	Mar.	132.1	0.2	7.7	3.3	0.0
	Apr.	147.3	1.6	14.7	0.0	39.2
	May	220.9	4.8	24.7	8.1	72.4
	June	251.5	21.9	21.1	65.5	30.3
	July	129.5	12.9	9.2	30.8	45.6
	Aug.	40.6	0.1	0.0	0.0	0.0
	Sept.	33.0	0.0	0.0	0.0	0.0
	Oct.	53.3	0.1	2.5	0.0	0.0
	Nov.	63.5	0.8	0.1	0.0	0.0
	Dec.	180.3	5.7	18.8	40.1	32.5
	SUM	1366.3	48.2	105.5	147.8	220.0

Table 2. Measured fenamiphos parent (F_p), f. sulfoxide (F_x), and f. sulfone (F_o) concentrations (mg kg^{-1}) remaining within each soil depth for selected sampling times over the three-year study

Soil Depth (mm)	1987 1 April (6)*	1987 9 April (14)	1987 28 April (33)	1987 22 June (88)	1988 5 April (14)	1988 20 April (29)	1988 28 April (37)	1989 28 March (8)	1989 6 April (17)	1989 17 April (28)	1989 3 May (44)
					F_p (mg kg^{-1})						
0-100	0.63(10)†	0.35(37)	0.11(13)		0.81(44)	0.29(26)	0.13(23)	1.79(34)	0.38(10)	0.09(35)	0.15(34)
100-500	1.24(52)	0.48(46)	0.15(65)	0.09(45)‡	1.01(69)	0.14(37)	0.19(36)	3.20(9)	1.48(12)	0.23(81)	0.16(59)
500-1000	0.67(42)	0.34(66)	0.05(44)	0.13(60)	0.33(42)	0.16(8)	0.11(14)	1.83(19)	0.89(13)	0.28(57)	0.19(60)
1000-1500	0.27(44)	0.06(27)	0.00(0)	0.06(75)	0.10(38)	0.04(38)	0.06(0)	0.25(68)	0.14(76)	0.59(29)	0.03(65)
1500-2000	0.00(0)	0.10(0)	0.00(0)	0.02(0)	0.00(0)	0.02(0)	0.00(0)	0.00(0)	0.00(0)	0.22(0)	0.00(0)
2000-2500	0.00(0)	0.00(0)	0.07(0)	0.09(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)
2500-3000	0.00(0)	0.00(0)	0.00(0)	0.06(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)
Total§	1.65	0.77	0.21	0.26	1.12	0.31	0.29	4.00	1.83	0.45	0.29
					F_x						
0-100	0.90(24)	1.07(9)	0.67(0)		1.57(41)	0.32(30)	0.09(4)	2.97(47)	1.05(20)	0.21(36)	0.14(36)
100-500	1.59(21)	1.42(29)	0.91(15)	0.27(76)‡	1.39(48)	0.17(18)	1.86(13)	1.86(5)	1.45(11)	0.31(19)	0.26(58)
500-1000	2.03(10)	1.36(26)	0.37(0)	0.13(0)	1.08(36)	0.20(24)	0.90(60)	1.58(14)	1.16(16)	0.43(23)	0.11(16)
1000-1500	1.60(17)	1.07(245)	0.49(63)	0.21(36)	0.58(40)	0.49(94)	0.05(31)	0.63(43)	0.67(29)	0.23(46)	0.14(61)
1500-2000	0.77(64)	1.04(23)	0.47(60)	0.27(87)	0.19(26)	0.34(99)	0.03(58)	0.10(3)	0.20(19)	0.10(73)	0.09(12)
2000-2500	0.27(10)	0.89(20)	0.43(54)	0.33(42)	0.19(85)	0.80(62)	0.02(50)	0.00(0)	0.08(49)	0.08(30)	0.07(16)
2500-3000	0.00(0)	0.74(14)	0.46(42)	0.27(90)	0.21(97)	0.13(86)	0.04(80)	0.05(0)	0.00(0)	0.03(35)	0.09(0)
Total	4.90	5.16	2.46	1.14	4.49	1.17	0.24	3.56	2.79	0.93	0.59
					F_o						
0-100	0.25(43)	0.18(0)	0.19(7)		0.17(34))	0.04(30)	0.05(17)	0.10(54)	0.12(23)	0.02(70)	0.02(0)
100-500	0.31(33)	0.52(99)	0.20(38)	0.17(21)‡	0.13(29)	0.05(46)	0.05(86)	0.05(0)	0.06(20)	0.02(36)	0.02(0)
500-1000	0.27(17)	0.17(35)	0.19(53)	0.11(0)	0.17(33)	0.05(17)	0.05(71)	0.06(12)	0.06(8)	0.02(39)	0.02(33)
1000-1500	0.26(30)	0.28(27)	0.12(79)	0.15(48)	0.15(43)	0.07(19)	0.05(74)	0.06(50)	0.08(34)	0.02(50)	0.08(89)
1500-2000	0.20(47)	0.28(44)	0.14(69)	0.20(54)	0.13(19)	0.07(40)	0.04(78)	0.04(0)	0.04(53)	0.00(0)	0.02(0)
2000-2500	0.40(97)	0.15(29)	0.15(76)	0.15(42)	0.06(3)	0.09(8)	0.04(31)	0.04(0)	0.02(37)	0.02(64)	0.02(0)
2500-3000	0.20(69)	0.15(0)	0.12(56)	0.15(23)	0.19(96)	0.06(8)	0.05(49)	0.00(0)	0.01(53)	0.01(84)	0.00(0)
Total	1.29	1.18	0.73	0.72	0.67	0.31	0.22	0.20	0.23	0.09	0.13

* Days after pesticide application.
† Values in parentheses are coefficients of variation.
‡ A 0 to 50 mm sample.
§ Totals = kg ha^{-1}.

$$CT_p = k_p/(k'_p + k_p) \quad \text{and} \tag{4}$$

$$CT_a = k_a/(k'_a + k_a) \tag{5}$$

Other selected input parameters used in the GLEAMS model simulations were drainage area (0.34 ha), curve number (84) rooting depth (120 cm), and slope (3.6%).

Results and Discussion

Hydrology Data

Monthly rainfall plus irrigation amounts and observed and simulated runoff and lateral subsurface flow (LSF) amounts are presented in table 1. Monthly and annual rainfall patterns and amounts for the three-year period are within the range of values normally received in Tifton, Georgia. Average annual rainfall in Tifton is about 1250 mm. About 7.5, 6.5, and 3.5% of the total rainfall (rainfall + irrigation) was lost as runoff for 1987, 1988, and 1989, respectively. Total rainfall lost as LSF was 35.5, 16.2, and 10.8% during the same corresponding years. Hubbard and Sheridan (1983) and Knisel et al. (1991) reported an average of 6.5% of rainfall was lost as runoff and 25% of the rainfall was lost as LSF over a 10-year period (1969-1978).

GLEAMS model simulations of runoff and LSF are presented in table 1. Monthly simulations for the 3-yr period were correlated with measured runoff (R^2 = 0.81) and lateral subsurface flow (R^2 = 0.89). Simulated runoff and LSF sums for the three years were numerically greater than corresponding observed values, however simulated values represented well the timing and magnitude of the two flow types. In 1989, simulations were not as representative as expected, especially for runoff. A possible explanation for this is that rainfall during the last two months of 1988 and the first two months of 1989 were relatively low. Usually during those months, rainfall amounts are relatively large resulting in “wet” soil profiles which produce LSF and are susceptible to spring rains that generate runoff. Therefore, runoff and LSF amounts were low and rainfall normally lost to runoff and LSF restored

Table 3. Rate constants (k) and half-life ($t_{1/2}$) values for fenamiphos parent by soil depth for the top 150 mm over the three-year study

Soil Depth (mm)	1987 k	1987 $t_{1/2}$ (d)	1988 k	1988 $t_{1/2}$ (d)	1989 k	1989 $t_{1/2}$ (d)	1987-89 k	1987-89 $t_{1/2}$ (d)
0-10	–0.0639	10.8	–0.7818	8.9	–0.1488	4.7	–0.0757	9.2
10-50	–0.0751	9.2	–0.0802	8.6	–0.1330	5.2	–0.0904	7.7
50-100	–0.0969	7.2	–0.0478	14.5	–0.0943	7.3	–0.0827	8.4
100-150	–0.1170	5.9	–0.0272	25.5	–0.1073	6.5	–0.0759	9.1

Table 4. Measured fenamiphos parent (F_p), f. sulfoxide (F_x), and f. sulfone (F_o) amounts (kg ha^{-1}) remaining in the top 300 mm of soil for selected times over the three-year study

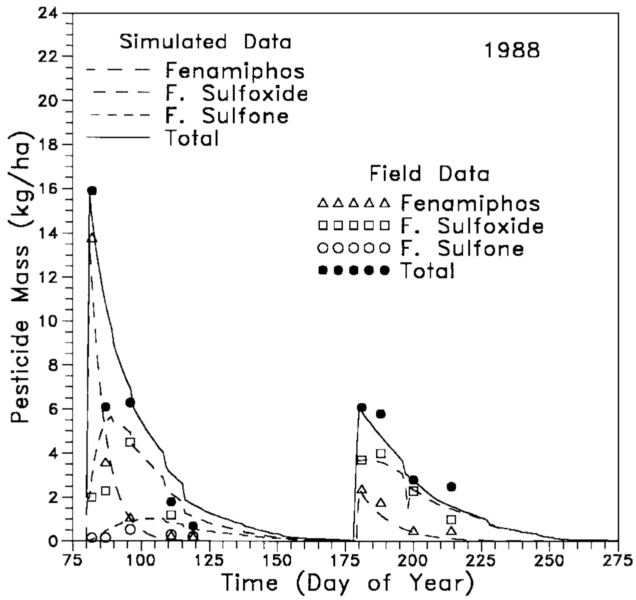
Year	Appli-cation	Day of Year	Days After Appli-cation	F_p (kg ha^{-1})	F_x (kg ha^{-1})	F_o (kg ha^{-1})	F_{tot}† (kg ha^{-1})
1987	1	087	2	5.2	4.7	ND	9.9
		091	6	1.7	4.9	1.2	7.8
		099	14	0.8	5.2	1.1	7.1
		118	33	0.2	2.4	0.7	3.4
		173	88	ND	1.1	0.6	2.2
	2	191	1	4.7	4.1	ND	8.8
		195	5	3.4	2.6	ND	5.9
		202	12	1.1	4.6	0.4	6.1
		217	27	0.7	2.5	0.7	3.9
1988	1	082	1	13.8	2.0	0.2	15.9
		087	6	3.6	2.3	0.2	6.1
		096	14	1.1	4.5	0.6	6.3
		111	29	0.3	1.2	0.3	1.8
		119	37	0.2	0.2	0.2	0.7
	2	181	1	2.4	3.7‡		6.1
		188	8	1.8	4.0		5.8
		200	20	0.5	2.3		2.8
		214	34	0.5	1.0		2.5
1989	1	079	1	15.1	1.6	0.1	16.7
		087	8	4.0	3.6	0.2	7.7
		096	17	1.8	2.7	0.2	4.9
		107	28	0.5	0.9	0.1	1.5
		123	44	0.2	0.6	0.1	1.0
	2	180	1	10.4	3.6	0.1	14.1
		184	5	1.9	0.8	0.1	2.9
		199	20	0.5	0.2	0.3	0.9
		216	37	0.9	0.1	0.1	1.0

† $F_{tot} = F_p + F_x + F_o$.
‡ Numbers represent $F_x + F_o$.
ND No Detection.

soil water throughout the profile. Percentages of total rainfall lost as simulated runoff were 7.4, 9.5, and 7.7% for 1987, 1988, and 1989, respectively. Like measured data, percentages of total rainfall lost by LSF were larger than that for runoff at 26.8, 21.7, and 16.1%, respectively, for the corresponding three-year period. Knisel et al. (1991) reported similar simulated results. Rainfall amounts lost as simulated runoff ranged from 4.8 to 8.1% (average = 6.4%) and rainfall amounts lost as simulated LSF ranged from 12 to 35% (average = 26%).

FENAMIPHOS DEGRADATION, TRANSFORMATION, AND TRANSPORT

Mean pesticide (F_p, F_x, and F_o) concentrations measured in the 0 to 10, 10 to 50, 50 to 100, 100 to 150, 150 to 200, 200 to 250, and 250 to 300 mm soil layers for selected dates (days after application) are presented in table 2. Fall applications are not presented because only two soil depths (0-150 and 150-300 mm) were evaluated. Coefficients of variation for each mean concentration ranged from 3 to 99%. For F_p, maximum concentrations with depth for any given sampling date generally occurred



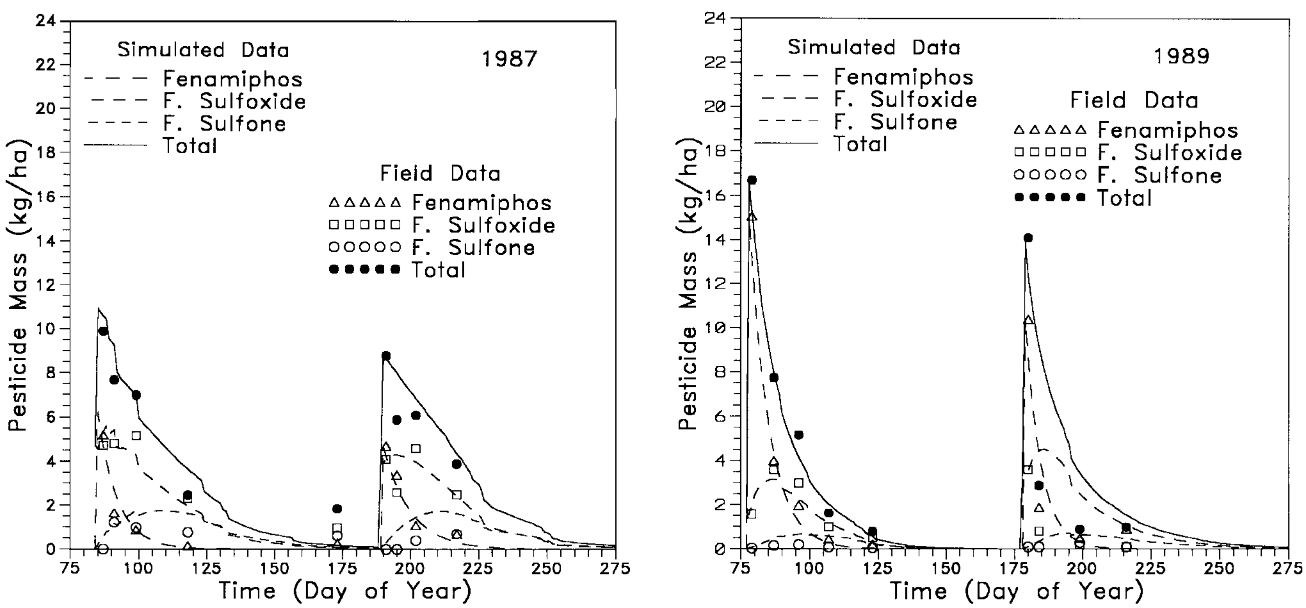


Figure 3–Simulated and measured fenamiphos parent (F_p), f. sulfoxide (F_x), and f. sulfone (F_o) amounts in the top 300 mm of soil for each application in 1987, 1988, and 1989.

in the 10 to 50 mm soil layer. Distribution of F_p for any given sampling date was influenced by degree and depth of mechanical mixing at the time of pesticide application and amount of water moving through the soil profile for later sampling times. Generally trends were less obvious with F_x and F_o for a given sampling date due to anabolic and catabolic processes affecting each metabolite.

Pesticide concentrations in each soil layer generally decreased with days after application (table 2). However, little differences were found in measured rate constants and effective $t_{1/2}$ values for F_p over the three-year period (table 3) even though F_p $t_{1/2}$ values for the 0 to 10 and 10 to 50 mm soil layers numerically decreased (10.8, 8.9, 4.7, and 9.2, 8.6, 5.2, respectively) from 1987 to 1989. Based on effective $t_{1/2}$ data for the three-year period and the lack of movement of F_p into the 150 to 300 mm soil layers, transport processes did not influence F_p persistence. Total amounts (kg ha^{-1}) in the 300 mm soil depth for each compound showed similar declining trends with time after application (table 2).

GLEAMS simulated pesticide concentrations reasonably well within each soil layer in table 2 (data not shown). Model-simulated concentration maxima, with soil depth, were similar to measured values. Both measured and simulated data indicated movement of F_x and F_o below the top 300 mm of soil; whereas, no significant movement of F_p was noted. Correlation coefficients (R^2) between measured and simulated concentrations with depth for F_p, F_x, F_o, and F_{tot} ranged from 0.85 to 0.86, 0.43 to 0.63, 0.07 to 0.40, and 0.70 to 0.79, respectively. These R^2 values are indicative of the ability of GLEAMS to simulate fate and transport of each compound. Similar results were found by Leonard et al. (1990). Acceptable simulation results were obtained with F_p and F_{tot}, while simulation results were less desirable with F_x and F_o.

Field data showing amounts of F_p, F_x, and F_o in the top 300 mm of soil with days after application are presented in table 4. Half-life values for F_p remained relatively constant from year to year, and averaged 5 d (range 6-10 d). Persistence of F_{tot} ($F_p + F_x + F_o$) generally decreased over the three-year period. Average estimated $t_{1/2}$ values from field data were 28 and 14 d for F_x and F_o, respectively (table 4). In Hawaii, Lee et al. (1986) found $t_{1/2}$ values of 2, 81, and 16 d for F_p, F_x, and F_o, respectively. In the southeastern U.S., total fenamiphos residue (parent + metabolites) $t_{1/2}$ values ranged from 14 to 21 d (Johnson et al., 1982). Ou and Rao (1986) also found that the two oxidized metabolites of fenamiphos were more persistent than the parent compound.

Model simulations and measured field data for spring and fall applications in 1987, 1988, and 1989 of F_p, F_x, and F_o in the 0 to 300 mm soil layer are shown in figure 3. A best-fit modeling approach was taken to back calculate $t_{1/2}$ and CT values for all compounds studied, especially for F_x and F_o. Selected parameters from the GLEAMS pesticide component used in the best-fit modeling approach are presented in table 5. Measured F_p amounts remaining in certain soil layers were used to calculate effective $t_{1/2}$ values. However, the anabolic and catabolic nature of F_x and F_o does not allow accurate measure of $t_{1/2}$ values. Therefore, output from the GLEAMS model was utilized to provide a best-fit approach to backout effective $t_{1/2}$ values for these two metabolites. Also, variability in application rates occurred (note differences between target rate, 6.7 kg/ha, and actual application rates given in table 5), influencing correlations between measured and simulated results. Applications in table 5 were assumed to be the same as measured F_p amounts given in table 4 (1-2 days after application) and were used as input in GLEAMS model simulations. Better agreement was obtained between measured and simulated results if application rates given in table 5 were used compared to those with the 6.7 kg ha^{-1} target rate. Values of R^2 for comparisons between measured and simulated F_p, F_x, F_o, and F_{tot} amounts were 0.96, 0.73, 0.56, and 0.83, respectively. Calibration of the GLEAMS model to provide fit of the field data indicate that: (1) F_p dissipated rapidly while F_x and F_o formed (average $t_{1/2}$ = 5.5 d); (2) $t_{1/2}$ values of the oxidative reactions generally remained relatively constant for 1987 and 1988 then numerically decreasing for 1989; (3) coefficient of transformation (CT) values for F_x and F_o decreased from 1987 to 1989; and (4) CT values describing transformational changes from F_p to F_x were greater than those describing transformational changes from F_x to F_o. Decreases in $t_{1/2}$ and CT values for the parent and metabolite compounds with continued use over the three-year study is characteristic of enhanced microbial degradation. Enhanced microbial degradation leading to decreases in fenamiphos $t_{1/2}$ and CT values have been reported (Lee et al., 1986; Davis et al., 1993; Ou et al., 1993). Johnson and co-workers (1992) noted similar results in that during a five-year study, numbers of nematodes were lower in fenamiphos-treated plots during the first three years of the study, but were not significantly different ($P \leq 0.05$) than those in untreated/control plots during the last two years of the study. As a result, sweet corn yields increased for the first two years of the study, and

Table 5. Selected parameters from the GLEAMS pesticide component used to obtain best-fit comparisons of fenamiphos parent (F_p), f. sulfoxide (F_x), f. sulfone (F_o), and total fenamiphos (F_{tot}) remaining in the top 300 mm soil layer†

Year	Time	Parameter‡	F_p	F_x	F_o
1987	Spring	Applic. rate (kg ha^{-1})	5.2		
		$t_{1/2}$ (d)	5	16	10
		CT	1.00	0.80	
	Fall	Applic. rate	4.7		
		$t_{1/2}$	7	17	10
		CT	1.00	0.65	
1988	Spring	Applic. rate	13.8		
		$t_{1/2}$	4	16	10
		CT	0.80	0.50	
	Fall	Applic. rate	2.4		
		$t_{1/2}$	8	18	10
		CT	0.60	0.50	
1989	Spring	Applic. rate	15.1		
		$t_{1/2}$	5	11	10
		CT	0.65	0.30	
	Fall	Applic. rate	10.4		
		$t_{1/2}$	4	14	9
		CT	0.60	0.40	

† Pesticide solubility for F_p, F_x, and F_o = 400 mg L^{-1}.

‡ CT and $t_{1/2}$ are Coefficient of Transformation and half-life values.

NOTE: Partitioning coefficients (K_{oc}) for F_p, F_x, and F_o = 240, 40, and 45, respectively.

Table 6. Measured and simulated fenamiphos parent (F_p), f. sulfoxide (F_x), and f. sulfone (F_o) amounts in lateral subsurface flow

		Lateral Subsurface	Flow	F_p		F_x		F_o		F_{tot}	
Year	Month	Measured (mm)	Simulated (mm)	Measured (g/ha)	Simulated (g/ha)	Measured (g/ha)	Simulated (g/ha)	Measured (g/ha)	Simulated (g/ha)	Measured (g/ha)	Simulated (g/ha)
1987	Jan.	182.8	144.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Feb.	98.3	109.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mar.	65.5	37.9	0.0	0.0	0.0	0.7	0.0	0.1	0.0	0.8
	Apr.	21.8	64.7	0.0	0.0001	0.0	24.6	0.0	9.8	0.0	34.3
	May	0.15	54.8	0.0	0.0	0.0	18.7	0.0	20.4	0.0	39.1
	June	0.005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	July	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Aug.	8.5	0.0	0.0	0.0	180.4	0.0	0.5	0.0	180.9	0.0
	Sept.	15.6	0.0	0.1	0.0	97.2	0.0	1.5	0.0	98.7	0.0
	Oct.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Nov.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Dec.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	SUM	392.7	411.7	0.1(0.0)*	0.0001(0.0)	277.6(5.6)	43.9(0.9)	2.0(0.1)	30.3(0.6)	279.6(5.6)	74.3(1.5)
1988	Jan.	44.8	55.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Feb.	52.0	76.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mar.	62.4	75.7	1.0	0.0	7.2	0.2	0.0	0.0	8.2	0.2
	Apr.	30.7	104.5	4.2	0.0	28.6	31.9	0.0	12.1	32.8	44.0
	May	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	June	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	July	0.0	21.6	0.0	0.0	0.0	0.5	0.0	0.1	0.0	0.6
	Aug.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Sept.	65.0	9.6	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.2
	Oct.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Nov.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Dec.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	SUM	255.6	343.4	5.2(0.1)	0.0(0)	35.8(0.4)	32.7(0.4)	0.0(0.0)	12.3(0.2)	41.0(0.5)	44.9(0.6)
1989	Jan.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Feb.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mar.	3.3	0.0	0.1	0.0	0.4	0.0	0.0	0.0	0.5	0.0
	Apr.	0.0	39.2	0.0	0.0	0.0	1.3	0.0	1.0	0.0	2.3
	May	8.1	72.4	0.1	0.0	0.5	8.5	0.2	7.3	0.8	15.8
	June	65.5	30.3	0.2	0.0	2.7	0.6	1.5	0.2	4.4	0.8
	July	30.8	45.6	0.1	0.0	2.1	5.6	1.1	1.1	3.3	6.7
	Aug.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Sept.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Oct.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Nov.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Dec.	40.1	32.5	0.0	0.0	2.7	0.0	0.3	0.0	3.0	0.0001
	SUM	147.8	220.0	0.5(0.0)	0.0(0)	8.4(0.1)	16.0(0.1)	3.1(0.0)	9.6(0.1)	12.0(0.1)	25.6(0.2)

* Percent of total fenamiphos applied.

fenamiphos efficacy diminished for the last two years of the study.

In this study, about 6.2% of the total amount of applied fenamiphos F_{tot} ($F_p + F_x + F_o$) was measured in lateral subsurface flow (table 6), while less than 0.1% of the applied fenamiphos was measured via runoff over the three-year period. F_{tot} losses were greatest in 1987 (280 g ha^{-1} or 5.6% of the total amount of applied fenamiphos), and decreased to 41 and 12 g ha^{-1} in 1988 and 1989, respectively. F_{tot} losses in 1988 and 1989 were less than 0.5% of the total amount of fenamiphos applied for each of those years. F_{tot} losses followed similar patterns as LSF. LSF volumes decreased from a maximum (393 mm) in 1987 to a minimum (149 mm) in 1989. F_x was the dominant compound found in LSF. For 1987-1989, at least 70% of F_{tot} was F_x. This result was mostly due to greater $t_{1/2}$ values for F_x (11-18 d) compared to those for F_p or F_o (table 5). As with LSF, F_x amounts were maximum in 1987 and decreased through 1988 and 1989. Also, F_x losses were influenced by rainfall timing relative to pesticide application.

The F_p and F_o losses were low, never exceeding 0.1% of the total fenamiphos applied. F_p $t_{1/2}$ values averaged 5.5 d (table 5) and very little F_p moved from the top 150 mm of soil (table 2). As a result, very little F_p was lost through LSF or runoff.

Simulated fenamiphos amounts associated with LSF are shown with corresponding measured data in table 6. GLEAMS generally underpredicted F_p amounts and overpredicted F_o amounts. For the three-year study, about 2.3% of the F_{tot} was simulated in LSF, compared to about 6.2% for corresponding measured data. As with measured data, simulated F_{tot} amounts were at a maximum in 1987 (74.3 g ha^{-1} and 1.5% of total amount of applied fenamiphos), and decreased over the three-year study. F_x was the dominant compound in simulated LSF. For any given year, greater than 60% of F_{tot} was F_x. Both simulated LSF volumes and F_x amounts decreased over the study period.

Correlation coefficients (R^2) between all measured and simulated fenamiphos amounts in LSF ranged from 0.17-0.96. Relatively poor correlations were obtained from monthly values, whereas more acceptable correlations were obtained from annual sums. Knisel et al. (1991) reported similar results for a 10-year study. Correlation differences can be attributed to how GLEAMS routes percolation below a certain soil depth which is assumed to be transported as LSF. This in turn influences timing of LSF in relation to rainfall, especially if the input for an event occurs at the end of one month and the output occurs at the beginning of the next month. Also, differences in winter and summer ET have been documented. Different ET options have been incorporated into GLEAMS to better represent ET during a year. In this study, R^2 values between annual measured and simulated LSF, F_x, and F_{tot} values were 0.95 (monthly = 0.90), 0.73 (monthly = 0.31), and 0.91 (monthly = 0.60), respectively. Confidence in annual correlations may be limited because only three (annual) data points were used to develop each correlation. However, for the three-year study, output from the GLEAMS model agreed with observed LSF, F_x, and F_{tot} data on an annual basis. Relatively poor values ($R^2 < 0.31$) were obtained for annual and monthly F_p and F_o most likely due to relatively low amounts of measured and simulated data.

Summary and Conclusions

We evaluated F_p, F_x, and F_o degradation and transport from a 0.34 ha field site and used the GLEAMS model to describe system response and simulate pesticide transport. Fenamiphos was broadcast each year at a target rate of 6.7 kg ha^{-1}. Concentrations of F_p, F_x, and F_o were determined from soil samples taken within the top 300 mm soil layer and from subsurface tile outflow. The following conclusions can be made:

1. LSF was a greater percentage (21%) of total rainfall + irrigation than was runoff (6%).
2. GLEAMS was successfully calibrated to represent field runoff and LSF losses, and pesticide amounts remaining in the 0 to 300 mm layer, expressed as effective dissipation rates and transport pathways of F_p, F_x, and F_o, respectively.
3. Simulated and field data indicated that F_p dissipated rapidly (average F_p $t_{1/2}$ = 5.5 d) while F_x and F_o formed, and $t_{1/2}$ values for all compounds remained relatively constant during the first two years of the study, then numerically decreased in 1989. Also, coefficient of transformation (CT) values for F_x and F_o decreased over the three-year period. CT values describing transformational changes from F_p to F_x were greater than those describing transformational changes from F_x to F_o. Decreases in $t_{1/2}$ and CT values for F_p, F_x, and F_o with continued use over the three-year study are characteristic of enhanced microbial degradation.
4. Over the three-year study, about 6.2% of the total amount of applied fenamiphos was measured in LSF (compared to 2.3% for corresponding simulated data); whereas, during the same study period less than 0.1% of the total amount of applied fenamiphos was measured in runoff.
5. F_x as a result of a greater $t_{1/2}$ was the dominant compound measured and simulated in the root zone and LSF, with 70 (1989) to 99% (1987) of measured F_{tot} being F_x.
6. GLEAMS generally underpredicted F_p amounts and overpredicted F_o amounts. Over the three-year period, GLEAMS simulations agreed with corresponding measured LSF, F_x and F_{tot} data on an annual basis. Simulations were relatively poor between monthly and annual measured and simulated F_p and F_o values. However, GLEAMS was used to predict concentrations in the root zone which is useful in estimating overall control by the pesticide, and runoff and leaching/drainage losses from different soil and management scenarios.

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