

**ADSORPTION, DESORPTION, SOIL MOBILITY AND AQUEOUS PERSISTENCE
OF FENSULFOTHION AND ITS SULFIDE AND SULFONE METABOLITES**

KEY WORDS: fensulfothion, adsorption, desorption, persistence

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ABSTRACT

Soil/water interactions with the insecticide fensulfothion and its sulfide and sulfone metabolites are described. Adsorption to, and desorption from four soils were studied. There was a general inverse relationship between water solubilities of the three chemicals and their adsorption K values. Order of adsorption was f.sulfide > f.sulfone > fensulfothion. Adsorption K values correlated significantly with soil organic content. Desorption of fensulfothion and the sulfone were similar whereas the less soluble sulfide desorbed to a lesser extent. To facilitate comparison of desorption tendencies of the three compounds a desorption index was developed. Mobilities through the soils were directly related to the water solubilities of the three chemicals. Mobilities in decreasing order were - fensulfothion > f.sulfone > f.sulfide. Persistence of fensulfothion was similar in both sterile and non-sterile natural water - about 50% remaining at the end of the 16 wk experiment. Under reducing conditions fensulfothion disappeared from water in 8-12 wk with almost complete conversion to the sulfide.

INTRODUCTION

The disposition of pesticides in the environment is determined by a number of factors of which physical and chemical properties of the pesticides and their interaction with soil and water are among the most important. The soil is a vast repository for pesticide residues since many pesticides are applied directly to soil, while foliar applications and spray drift also contribute pesticide residues and degradation products. Pionke and Chesters' emphasized the importance of adsorption by soil in stabilizing pesticides against loss by volatilization, leaching, or microbial degradation. We report here on adsorption by and desorption from sediments in aqueous soil systems, mobility through soils and persistence in water of the insecticide fensulfothion and two of its metabolites. Fensulfothion is an important soil insecticide - in Ontario, Canada, it is recommended for insect control on corn, onions, rutabagas and cole crops. In soils, fensulfothion (a sulfoxide) is oxidized to its sulfone^{2,3}. Benjamini *et al.* included the sulfide in reports on chemistry and toxicology⁵ of fensulfothion. All three compounds were included in our study, i.e. fensulfothion sulfide, fensulfothion, and fensulfothion sulfone.

MATERIALS AND METHODS

Adsorbents. Three soils and a stream sediment (the latter included with the mineral soils), the properties of which are shown in Table 1, were used as adsorbents. After collection the soils were air-dried, passed through a 2 mm sieve, thoroughly mixed, and stored in bulk containers until used.

Compounds. Fensulfothion was purified according to previous methods⁶ and was 99+% pure. Fensulfothion sulfone was re-crystallized from methanol at -20°C. Fensulfothion sulfide was 95.2% pure. The three chemicals were supplied by the Mobay Chemical Corp., Kansas City, MO. The water solubility values (Table 2) for fensulfothion and

TABLE 1
 Characteristics of the Soils and Stream Sediment Used.

	Percent				pH*
	sand	silt	clay	organic matter	
Plainfield Sand	91.5	1.5	7	0.7	6.9
Big Creek Sediment	71	22	7	2.3	6.5
Bondhead Sandy Loam	77	15	8	3.9	6.9
Muck Soil	52	34	14	36.7	6.3

* measured in 0.01 M CaCl₂(20 ml to 10 g soil).

f.sulfone were reported earlier and the value for f.sulfide was determined using the same technique.

Adsorption Studies. Batch-type adsorption experiments, details of which have been described⁸ were used to generate adsorption data. Triplicate one-gram soil samples in 30-ml aliquots of aqueous insecticide solution (at five different concentrations) were tumbled for 18 hr at 20±1.5°C for equilibration prior to centrifugation and sampling.

Desorption Studies. The four soil adsorbents were spiked at 5.0 µg/g (oven dry basis) using a hexane:acetone (95:5 v/v) solvent. The treated soil was thoroughly mixed on a jar roller while evaporating off the solvent. Triplicate one-gram treated samples were weighed into 150 ml Corex centrifuge bottles having tin-foil lined screw caps. Moisture determinations were made on the original soil and on the spiked soil to account for moisture removed during evaporation of the solvent. Subsamples of the treated soils were analysed to confirm insecticide treatment rates and to account for any degradation. Thirty-ml aliquots of distilled water were added to each centrifuge tube containing the spiked soil sample, and the tubes were shaken on a wrist-action shaker for 18 hr. After equilibration, the samples were centrifuged at 8000 x g for 0.5 hr prior

to removing a 25-ml aliquot for insecticide analysis. A 25-ml aliquot of distilled water was added back to the centrifuge tube to initiate the second desorption cycle. Four such cycles were completed for each insecticide-soil combination.

Two automated gas-liquid chromatographs (GC) were used for analysis of adsorption and desorption samples (triplicate injections) as reported previously⁷. All samples were injected as aqueous methanol mixtures (70% water, 30% methanol v/v) and the standards were of the same solvent composition. Alkali-flame ionization detectors were used to detect the three compounds. The glass columns, 0.76 m x 2 mm I.D. were packed with 100/120 mesh A.W. DMCS Varaport 30 coated with 10% OF-1 and operated at 200°C.

Mobility Studies. The apparatus used to study insecticide mobility in soils and sediment has been described⁹. Basically, the treated soil (chemicals applied in hexane solution) was held in a glass cylinder set in sand contained in a Buchner funnel. Weights of soil and treatment levels were: sand, 10 g @ 2 ppm; sediment or sandy loam, 8 g @ 2.5 ppm; and organic soil 4 g @ 5 ppm. These weights gave ca. equal volumes of the soils and the treatment levels resulted in equal starting amount of the insecticides. Two liters of distilled water were drawn through the treated soil by suction and collected as ten 200 ml fractions. The fensulfothion and its metabolites were extracted from the fractions in a separatory funnel using chloroform. Chloroform was evaporated from an aliquot and the residue taken up in 10% acetone in hexane for analysis by GC. For analysis of fensulfothion and f.sulfone a 1.2 m x 2 mm I.D. column was operated at 200°C. Liquid phase was 10% QF-1 Chromosorb W AW DMCS 80/100 mesh. Detection was by electron capture. The f.sulfide was assessed on a 1.83 m x 2 mm I.D. column operated at 170°C. Liquid phase was 3% OV 101 + 4.5% OV 210 on the above Chromosorb support. Detection was by alkali flame ionization (1:1 KBr:Rb₂SO₄).

Persistence in Water.

Natural water. Fensulfothion, or its sulfide or sulfone, dissolved in chloroform, was pipetted into 1-liter screw cap glass bottles, and the solvent was allowed to evaporate. One liter of natural water pH 7.2-7.5 from the Holland Marsh, Ontario, drainage system¹⁰ was added to each of the flasks which were then incubated at 20°C in the dark. The initial concentration of fensulfothion, f.sulfide or f. sulfone in the water was 5 mg/liter.

Sterilized natural water. The natural water was batch sterilized by autoclaving in 4-liter beakers. One ml of chloroform containing 0,5 mg fensulfothion (or sulfide or sulfone) was pipetted into sterile 230 ml screw cap glass bottles and the solvent allowed to evaporate. One hundred ml of sterilized natural water were added and the bottles were capped and stored at 20°C in darkness. All operations with sterile bottles and water were performed in an environmental air control cabinet.

At 0 day and at 1, 2, 4, 8, 12 and 16 wk intervals, 20 ml aliquots were removed and extracted with 20 ml of chloroform in 50-ml separatory funnels. To avoid contamination, samples of sterile natural water for analysis were taken from previously unopened bottles at each sampling date - once opened the bottles and contents were discarded. The chloroform extracts were analyzed by gas chromatography as described under Mobility Studies.

RESULTS

Adsorption Studies. Adsorption data for fensulfothion, f.sulfide and f. sulfone were plotted using the Freundlich equation

$$x/m = KC^{1/n}, \quad \text{or} \quad \log x/m = \log K + 1/n \log C$$

where x = nanomoles of compound adsorbed, m = adsorbent weight, K is a constant, 1/n is the slope of log-log plot and C = equilibrium concentration in nanomoles/ml. Adsorption parameters 1/n (slope) and K (ordinate intercept) are shown in Table 2.

TABLE 2

Adsorption and Solubility Parameters for Fensulfothion, F.sulfide and F.sulfone in Four Soils (20°).

	F.sulfide		Fensulfothion		F.sulfone	
	1/n	K ^(a)	1/n	K ^(a)	1/n	K ^(a)
Plainfield Sand	0.903	24.53	0.973	1.46	1.120	0.970
Big Creek Sediment	1.001	57.88	1.081	3.49	0.844	8.78
Bondhead Sandy Loam	0.941	79.80	0.822	8.39	0.993	8.73
Muck Soil	0.708	748.6	0.871	59.92	0.797	147.8
Solubility						
µg/ml	3.70	2000		74.6		
nanomoles/ml	12.65	6485		230.		

^(a) units of K = nanomoles /g

K values are often used to express relative estimates of adsorption (the greater the K value, the greater is the adsorption). With exception of Plainfield sand, the K values of the three compounds decreased in the following order: f.sulfide > f.sulfone > fensulfothion. For Plainfield sand, the fensulfothion K value was slightly greater than that of the f.sulfone, but because the fensulfothion slope value was less than that for f.sulfone, the isotherms intersected at 16.63 nanomoles/ml. Above this concentration, f.sulfone exhibited greater adsorption than fensulfothion on Plainfield sand.

K values for the three chemicals and four soils varied considerably. Organic matter (O.M.) appeared to have a definite relationship with K values. Regression equations of K values on percent O.M. were derived for each insecticide in the four soils. All correlation coefficients were highly significant ($r \geq 0.999$, 0.01 level, 2 degrees of freedom) indicating a close correspondence between O.M. content and insecticide

adsorption. Sharom *et al.*⁹ reported a similar high correlation between adsorption K values of a number of insecticides and O.M. content of several mineral and organic soils.

Desorption Studies. Four desorption cycles were completed to determine the relative ease with which the three insecticides desorbed from the four soils (Figure 1). In each soil the desorption tendencies of fensulfothion and f.sulfone were similar, whereas the least soluble f.sulfide desorbed to a lesser extent.

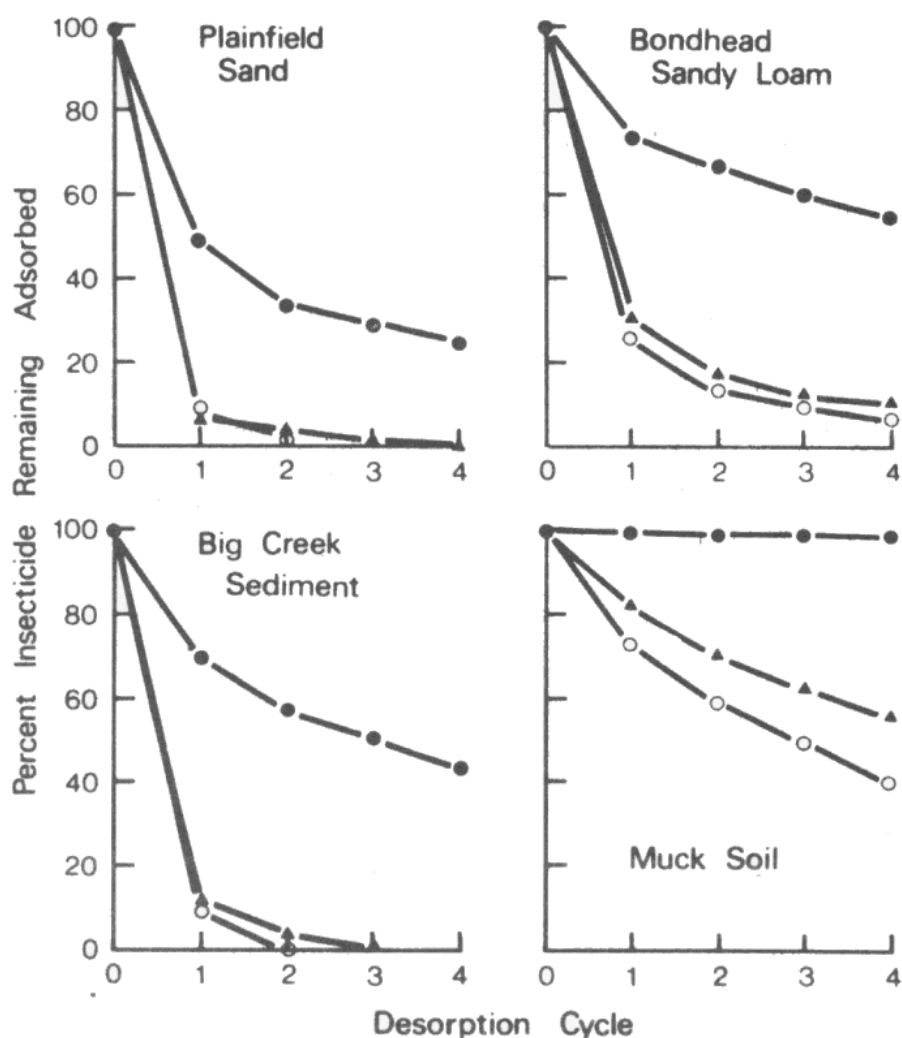


FIGURE 1. Desorption of fensulfothion(o-o), fensulfothion sulfide (●-●) and fensulfothion sulfone (Δ - Δ) from four soils.

To facilitate comparison of desorption tendencies of the three compounds, a desorption index (D.I.) was developed. It is a weighted mathematical expression favoring the amount of desorption in the early desorption cycles. Maximum desorption would have a D.I. value of 100 and the minimum would be zero.

$$D.I. = \sum_{D=1}^{D=N} \left[\frac{N+1-D}{N} \right] \left[\frac{\% \text{ Remaining}_{D-1} - \% \text{ Remaining}_D}{D-1} \right]$$

where N is the total number of desorption cycles and D is the desorption cycle number. The D.I. values (Table 3) indicate that fensulfothion desorbed to a slightly greater extent than the f.sulfone in the three mineral soils, with a larger difference being exhibited in the muck soil, perhaps reflecting the more soluble nature of fensulfothion. In all cases f.sulfide desorbed least from the soils.

Regression equations of D.I. on percent O.M. of the soil showed a highly significant relationship ($r \leq 0.990$, 0.01 level, 2 degrees of freedom) for both fensulfothion and f.sulfone but not for the f.sulfide ($r = 0.925$). The goodness of fit of the D.I. vs O.M. data to the regression equation improved considerably if the muck soil data was not

TABLE 3

Desorption Index (D.I.) Values for Fensulfothion, F.sulfide and F.sulfone in Four Soils.

	F.sulfide	Fensulfothion	F.sulfone
Plainfield Sand	65.4	96.9	96.5
Big Creek Sediment	44.8	97.7	95.9
Bondhead Sandy	36.4	86.9	83.4
Muck Soil	0	44.4	32.0

included with the mineral soils for evaluation. However, there were too few soil data points to do this since the reduced degrees of freedom considerably increased the " f " value required for significance.

Mobility Study. The most water soluble compound, fensulfothion, was eluted from the mineral soils in the first few fractions (Table 4). Fensulfothion sulfone also eluted rapidly but was spread through the first six fractions. Fensulfothion sulfide, with water solubility of 3.7 ppm, did not elute to the same degree as the other two chemicals and the small amount eluted was spread through the ten fractions. The high O.M. content of the muck soil appeared to reduce slightly the total leaching of fensulfothion, relative to the mineral soils - amounts in each fraction were smaller and elution was spread through eight fractions. The percent of f.sulfone eluted through the organic soils was much less than through the mineral soils, while f.sulfide did not elute through the organic soil at all.

The regression of Mobility Factor (M.F.)⁹ on O.M. content of the soils was highly significant ($r = 0.996$, 0.01 level, 2 degrees of freedom) for both fensulfothion and f.sulfone, but not the f. sulfide ($r = 0.910$) - a result similar to that obtained with the Desorption Index.

Persistence in Water. The persistence of fensulfothion was similar in sterile and non-sterile natural water (Fig. 2) suggesting that degradation was chemical, possibly by hydrolysis, rather than microbial in nature. A similar persistence curve was obtained for fensulfothion in distilled water (not shown).

In water persistence studies of 12 organochlorine, organophosphorus and carbamate insecticides, Sharom¹¹ indicated that the "addition of insecticides in ethanol created an anaerobic environment resulting in reduction of parathion to aminoparathion." We included samples of fensulfothion in natural water containing 1% ethanol in our persistence study. Under these conditions fensulfothion was reduced relatively quickly (Fig. 2C) to f.sulfide (Fig. 2D.)

TABLE 4
 Mobility of Fensulfothion, F sulfone and F. sulfide in Four Soils.

	Percent (of applied) Leached in Fraction										Total Percent 10 Fractions	Mobility Factor (M.F.)
	1	2	3	4	5	6	7	8	9	10		
<u>Fensulfothion</u>												
Plainfield Sand	78	13	4	tr*	-	-	-	-	-	-	95	9.29
Big Creek Sediment	73	13	10	tr	-	-	-	-	-	-	96	9.27
Bondhead Sandy	70	20	tr	-	-	-	-	-	-	-	90	8.80
Muck Soil	20	17	9	10	8	7	6	5	tr	tr	82	6.17
<u>Fensulfothion Sulfone</u>												
Plainfield Sand	75	11	5	3	2	1	tr	-	-	-	97	9.27
Big Creek Sediment	63	20	6	4	2	2	1	tr	-	-	98	9.12
Bondhead Sandy	51	23	10	5	4	2	tr	-	-	-	95	8.66
Muck Soil	6	6	7	5	5	6	3	4	3	3	48	2.98
<u>Fensulfothion Sulfide</u>												
Plainfield Sand	-	6	4	3	2	2	1	tr	tr	-	22	1.33
Big Creek Sediment	-	4	2	3	2	3	2	2	2	1	21	1.19
Bondhead Sandy	-	2	5	5	8	5	2	2	1	2	32	1.84
Muck Soil	-	-	-	-	-	-	-	-	-	-	0	0

* tr = <1% f. sulfone and f. sulfide.
 = <3% fensulfothion.

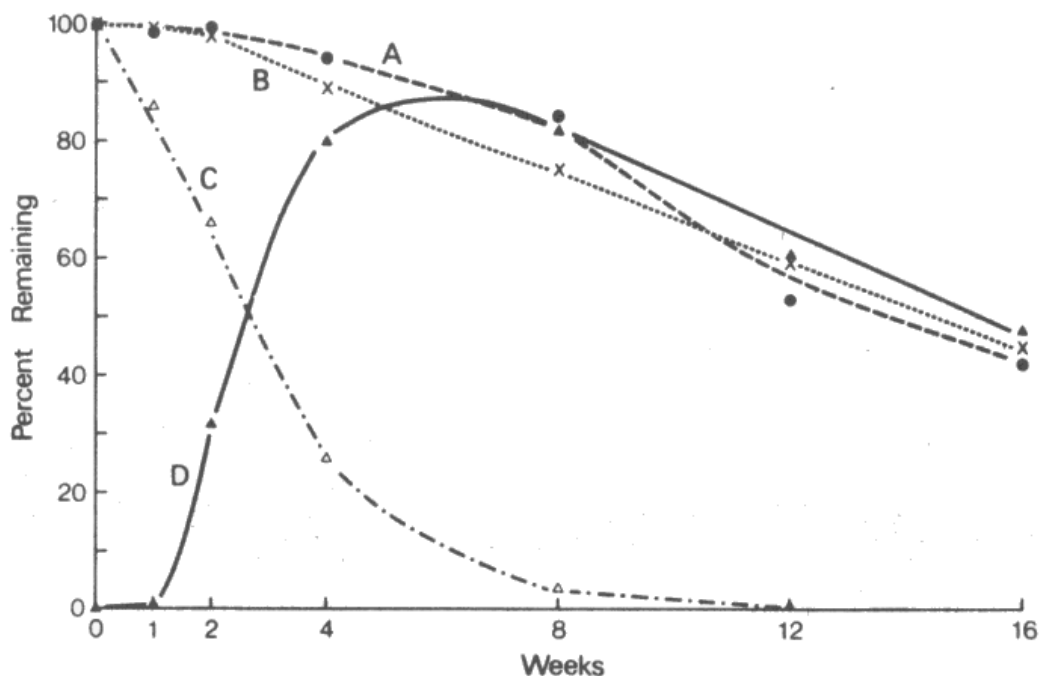


FIGURE 2. Persistence and degradation of fensulfothion in sterile (A) and non-sterile (B) natural water, and natural water plus 1% ethanol (C). Curve D represents fensulfothion sulfide produced from fensulfothion under same conditions as "C".

Calculation of percent conversion has been adjusted for molecular weight ratio. The persistence of sulfone was almost identical in the three water types (Fig. 3). The f.sulfide (Fig.4) degraded equally in the three waters, but in the non-sterile natural water there was some oxidation of f.sulfide to fensulfothion (Fig, 4D). Water pH values did not change markedly (<0.5 pH unit) throughout the experiment.

DISCUSSION

The adsorption data for fensulfothion, f.sulfide and f.sulfone indicated that there was a general inverse relationship between water solubility and K values (Table 2). However, the K values for fensulfothion and f.sulfone were not as different on mineral soils as one might expect considering the differences in water solubility (26.8 fold).

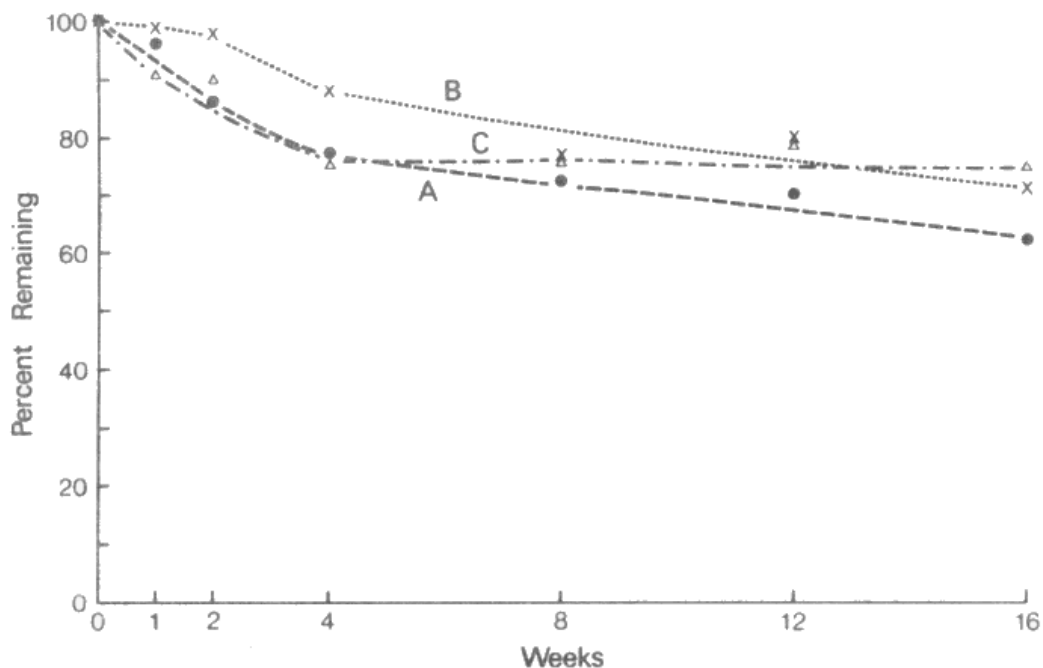


FIGURE 3. Persistence of fensulfotion sulfone in sterile (A), non-sterile (B) natural water, and natural water plus 1% ethanol (C).

This anomaly may be partially explained by the fact that fensulfotion, by virtue of its sulfoxide functional group, is a rather polar molecule. This may enhance its water solubility as well as increase its tendency to be adsorbed by hydrophilic surfaces of mineral soils. By contrast, fensulfotion was much less strongly adsorbed by the more hydrophobic muck soil than was the f.sulfone (by 2.5 fold). In all cases, the least soluble f.sulfide was most strongly adsorbed by all four soils.

There was excellent consistency among the adsorption, desorption and mobility data for the three compounds in the four soil systems. The D.I. and M.F. values for fensulfotion and f.sulfone exhibited the same close correspondence in the three mineral soils as the K values. Such agreement is to be expected since the two factors are just different approaches to measuring the tendency for compounds to be desorbed or transported through a soil.

Regression analyses showed a highly significant relationship between adsorption K values of the three compounds and O.M. content of the soils.

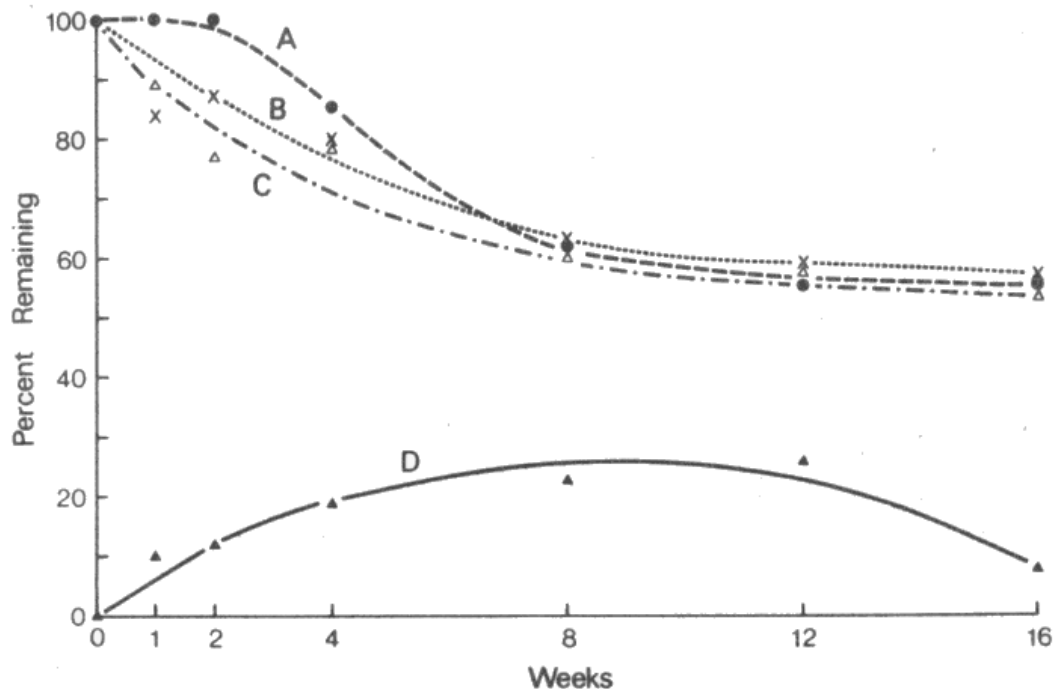


FIGURE 4. Persistence of fensulfothion sulfide in sterile (A) and non-sterile (B) natural water, and natural water plus 1% ethanol (C). Curve D shows fensulfothion produced from fensulfothion sulfide in natural water under same conditions as in curve "B".

They also showed a highly significant relationship between D.I. values and O.M. content and also between M.F. values and O.M. content (fensulfothion and f.sulfone). F.sulfone was more strongly adsorbed than fensulfothion, except on Plainfield sand, and thus exhibited less tendency to desorb and move through the soil. In Plainfield sand, fensulfothion adsorbed slightly more than f.sulfone but also tended to desorb and move in the soil as much or more than the sulfone.

Fensulfothion sulfide was adsorbed most strongly in all soils and consequently exhibited the least tendency to desorb or move. The D.I. and M.F. values were not significantly related to soil organic matter content for f.sulfide. There was an indication in the mobility experiments with f.sulfide that it was oxidizing to fensulfothion. In separate experiments to simulate field conditions, f.sulfide was eluted from treated

sandy loam which had an underlay of the same, but untreated sandy loam. Percent conversions of f. sulfide to fensulfothion without the underlayer, and with equal and double volumes of untreated underlay were 8, 21 and 33% resp. It would appear that the f.sulfide was being oxidized in its passage through the layers of untreated soil. This aspect is being investigated and will be reported later.

In natural water + 1% ethanol, (Fig. 2), fensulfothion was almost completely reduced to f.sulfide, In utilizing the ethanol, microorganisms consumed the available oxygen in the water producing anaerobic conditions¹² which resulted in reduction of fensulfothion to f.sulfide and, as reported by Sharom¹¹, for reduction of parathion to aminoparathion. In the f.sulfone persistence study (Fig, 3) there were no great differences in disappearance rates in natural water (sterile or non-sterile) or in natural water containing 1% ethanol. No fensulfothion or f.sulfide was produced from f.sulfone under the anaerobic conditions induced by addition of ethanol to natural water. This agrees with results of chemical reduction experiments in our laboratory, where treatment with zinc and hydrochloric acid produced f.sulfide from fensulfothion, but failed to reduce f.sulfone to fensulfothion, Similarly, no differences were evident in rates of degradation of f. sulfide (Fig. 4) in sterile or non-sterile natural water or in natural water containing 1% ethanol, However, in natural water (non-sterile), oxidizing conditions were sufficient to produce the fensulfothion shown in curve D of Fig. 4 (up to 26% conversion of the f.sulfide).

Fensulfothion and its sulfide and sulfone disappeared at similar rates in water, degradation being primarily chemical with little or no microbial involvement in natural water except where anaerobic conditions were induced. It is interesting to note that in all these water persistence studies there was no oxidation of fensulfothion to f.sulfone, whereas in previous soil persistence studies³, early conversion of fensulfothion to f.sulfone occurred, attaining a maximum sulfone concentration in the soil in two weeks. Possibly stronger oxidizing conditions exist in natural soil than in natural water.

The results of these and earlier³ studies suggest that fensulfothion, following soil application, is oxidized to f.sulfone, which being less soluble in water, is more strongly adsorbed by soil and therefore less subjected to leaching to ground water. If some fensulfothion were leached to ground water shortly after soil application, it would be subject to reduction to the much less soluble f.sulfide if anaerobic conditions prevailed. The f.sulfide would adsorb quite strongly to stream sediments thereby diminishing aqueous pollution. Once in stream water, our results indicate that fensulfothion would be relatively persistent, not converting to either f.sulfide or f.sulfone.

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