

Adsorption and Desorption of Flupropacil on Various Soils

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The adsorption and desorption of flupropacil [1-methylethyl 2-chloro-5-[3,6-dihydro-3-methyl-2,6-dioxo-4-(trifluoromethyl)-1(2*H*)-pyrimidinyl]benzoate] were studied on four soils (sand, sandy loam, loamy sand, clay) of different physicochemical properties. The flupropacil adsorption and desorption data fit the Freundlich equation. Flupropacil was found to adsorb little to any of the four soil types tested, indicating it may be a potential leacher. The adsorption constant, K_a , ranged from 0.26 for sand to 2.56 for clay soil, while n varied from 0.92 to 1.14. The desorption constants ranged from 1.70 for sand to 6.26 for clay soil, and n varied from 1.03 to 1.23.

Keywords: *Flupropacil; adsorption; desorption*

INTRODUCTION

The fate and mobility of pesticides in the environment are important in predicting their leaching potential through soil and their movement to and dispersion in aquatic sites (Bailey and White, 1970; Hance, 1980; Swann and Eschenroeder, 1983; Saltzman and Yaron, 1986). Mobility of pesticides is dependent upon the properties of the chemical and the media in which they are dispersed, as well as the environmental conditions (Hamaker, 1975; Weber, 1977). Flupropacil is a potential uracil herbicide, and no published information is available on its mobility in soils under either laboratory or field conditions. The adsorption and desorption of flupropacil on four different soils were conducted following U.S. EPA guidelines (Hitch, 1982) for registering pesticides.

MATERIALS AND METHODS

Test Substance. [2-¹⁴C-pyrimidine]Flupropacil (Figure 1) was synthesized at ChemSyn Science Laboratories (Lenexa, KS) and had a radiochemical purity of $\geq 98\%$ and a specific activity of 30 mCi/mmol. Nonlabeled flupropacil (purity $>96\%$) was synthesized at Uniroyal Chemical (Middlebury, CT). Standard solutions of [¹⁴C]flupropacil and nonlabeled flupropacil were prepared in acetone at 3 and 10 ppm, respectively. The water solubility of flupropacil is 27.5 ppm at 25 °C.

Test Soils. Four soils (sand, sandy loam, loamy sand, clay) differing widely in their physicochemical characteristics (Table 1) were used in this study. The soils were collected from 0–15 cm-depth. All soils were air-dried at room temperature, sieved (2-mm mesh), and stored at room temperature prior to their use in the study. The soils were classified by Agvise Laboratories (Northwood, ND) following USDA soil characterization. The soil textural (percent sand, silt, and clay) analysis was determined according to the hydrometer method (Black, 1965). The soil organic matter was determined according to the Walkley–Black method (Nelson and Sommers, 1982). The bulk density (disturbed soil) and percent soil moisture were determined as described by Black (1965). The cation exchange capacity (CEC) was

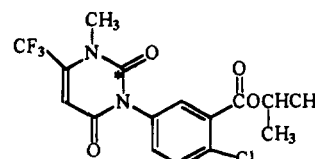


Figure 1. Structure of flupropacil showing the position of the radiolabel (*).

determined by summing the cations along with the hydrogen (Brown and Warncke, 1988). The soil pH was determined from a soil/water (1:1) suspension (Black, 1965; Nelson and Sommers, 1982). The water holding capacity at 0.33 bar was determined by measuring the moisture remaining when saturated soil was placed under 0.33 bar of pressure (Black, 1965; Nelson and Sommers, 1982).

Radioassay. Total radioactivity in solutions was analyzed directly by a Beckman LS3801 liquid scintillation counter (LSC) using Scint-A (Packard Instrument Co.) cocktail. Soil samples were combusted in an R. J. Harvey oxidizer (Hillsdale, NJ), and the released ¹⁴CO₂ was trapped in oxosol (National Diagnostics, Manville, NJ) scintillation fluid and analyzed by LSC.

HPLC and TLC Analysis. Standard solutions of flupropacil were analyzed by high-performance liquid chromatography (HPLC) and thin layer chromatography (TLC) for verifying the radiopurity of the test substance. The adsorption and desorption solutions containing the highest concentration of radioactivity from each soil type were also analyzed by HPLC and TLC to show the integrity of the test substance in solution following each of the two phases of the study.

HPLC analyses were performed using a Shimadzu HPLC system (Shimadzu Scientific Instruments, Inc., Columbia, MD). The column (C₁₈) was a 25 cm × 4.6 mm Zorbax ODS (Mac-MOD Analytical Inc., Chadds Ford, PA) column preceded by a Zorbax ODS 3 cm × 4.6 mm guard column. The mobile phase contained 60% buffered water (0.025 M triethanolamine at pH 4.0 using formic acid) and 40% acetonitrile, by volume. The flow rate was 2 mL/min. Radioactivity in the samples was quantified by a Ramona 5-LS radioactivity monitor (Raytest, Pittsburgh, PA). The nonlabeled flupropacil was detected using a UV detector at 254 nm.

Two-dimensional TLC analysis was performed on 20 × 20 cm silica gel plates (60F254, E. Merck) using

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Table 1. Soil Characterization

soil characteristic	soil type			
	clay	sand	loamy sand	sandy loam
source	Mississippi	Maryland	Connecticut	California
series	Sharkey	Sassafras	Paxton	Hesperia
horizon	A	A	A	A
clay mineralogy	smectite illite	kaolinite chlorite	chlorite illite kaolinite	illite
texture				
% sand	20	90	76	60
% silt	28	4	18	32
% clay	52	6	6	8
% organic matter	3.1	0.6	5.3	0.7
pH	5.6	6.1	6.6	6.2
% soil moisture at 0.33 bar FMC	35.4	8.0	33.8	15.9
cation exchange capacity (mequiv/100g)	26.8	3.0	14.2	6.2
bulk density (g/ml)	1.15	1.53	1.11	1.45

toluene/tetrahydrofuran (60:5 v/v) as the solvent for the first dimension and hexane/ethyl acetate (60:40 v/v) as the second-dimension solvent. Radioactivity on the TLC plates was detected using an Ambis radioanalytical scanner (Ambis Systems Inc., San Diego, CA), and nonlabeled flupropacil was visualized under a UV lamp at 254 nm.

Adsorption. Adsorption of flupropacil was determined by mixing 4 g of each soil (moistened to 75% at 0.33 bar soil moisture content using water) with 20 mL of 0.01 M calcium acetate solution at 0 (control samples), 0.38, 0.93, 1.85, 9.29, and 17.85 ppm of [2-¹⁴C-pyrimidine]flupropacil in 50-mL Teflon centrifuge tubes. Duplicate samples were used for each concentration. The samples were equilibrated for 3 h at 25 ± 1 °C using an Eberbach shaker at 175–200 rpm. A preliminary study at 10 ppm of [¹⁴C]flupropacil in 0.01 M calcium acetate solution was conducted up to 48 h for each soil type, to establish the soil/solution ratio and equilibration time and to determine if flupropacil was adsorbing to the test container. Following equilibration, each soil/solution mixture was centrifuged (IEC centrifuge) at 1500 rpm for 15 min. The supernatant from each sample was decanted, and duplicate 100-μL aliquots of the supernatant were analyzed by LSC. The concentration of flupropacil adsorbed (*x/m*) to the soil was determined by combusting duplicate aliquots of the adsorbed soil.

Desorption. Following adsorption, desorption of [2-¹⁴C-pyrimidine]flupropacil was determined by adding 20 mL of fresh 0.01 M calcium acetate solution without any flupropacil to each sample. The samples were then shaken for 3 h at 175–200 rpm at 25 ± 1 °C and centrifuged at 1500 rpm for 15 min. The supernatant from each sample was decanted, and duplicate 100-μL aliquots of the supernatant were analyzed by LSC. The concentration of flupropacil in the soil following desorption was determined by combustion of the desorbed soil.

Calculations. The adsorption and desorption coefficients of flupropacil were calculated using the Freundlich equation

$$x/m = K_d C_e^{1/n} \quad \text{or} \quad \log x/m = \ln K_d + 1/n(\ln C_e)$$

where *x/m* is the concentration of the adsorbate per unit amount of adsorbent (μg g⁻¹), *C_e* is the aqueous phase equilibrium concentration in μg mL⁻¹, *K_d* is the Freundlich sorption constant, and *n* is a constant. The values of ln *C_e* vs ln *x/m* were plotted for adsorption and desorption. The constants *K_d* and *n* were determined from the slope (1/*n*) and intercept (ln *K_d*) of the resultant straight line by linear regression.

Table 2. Concentration (Parts per Million) of Flupropacil following Adsorption and Desorption

soil	initial concn of [¹⁴ C]flupropacil				
	0.38 μg/mL	0.93 μg/mL	1.85 μg/mL	9.29 μg/mL	17.85 μg/mL
MS clay					
<i>C_e</i> (Ads) ^a	0.25	0.63	1.25	6.29	12.90
<i>x/m</i> (Ads) ^b	0.76	1.77	3.20	9.74	29.52
<i>C_e</i> (Des) ^c	0.05	0.12	0.23	1.07	2.12
<i>x/m</i> (Des) ^d	0.39	0.85	1.62	7.02	12.00
MD sand					
<i>C_e</i> (Ads)	0.37	0.91	1.82	8.88	17.69
<i>x/m</i> (Ads)	0.10	0.27	0.43	2.19	7.95
<i>C_e</i> (Des)	0.01	0.02	0.05	0.20	0.63
<i>x/m</i> (Des)	0.03	0.09	0.12	0.53	1.07
CT loamy sand					
<i>C_e</i> (Ads)	0.26	0.69	1.40	7.15	14.95
<i>x/m</i> (Ads)	0.59	1.33	2.76	12.27	20.85
<i>C_e</i> (Des)	0.05	0.12	0.23	0.99	1.81
<i>x/m</i> (Des)	0.30	0.65	1.19	4.49	8.69
CA sandy loam					
<i>C_e</i> (Ads)	0.36	0.90	1.79	8.81	17.69
<i>x/m</i> (Ads)	0.12	0.30	0.57	2.53	4.99
<i>C_e</i> (Des)	0.01	0.03	0.06	0.29	0.55
<i>x/m</i> (Des)	0.04	0.09	0.16	0.71	1.40

^a Concentration of [¹⁴C]flupropacil in solution following adsorption. ^b Concentration of [¹⁴C]flupropacil in soil following adsorption. ^c Concentration of [¹⁴C]flupropacil in solution following desorption. ^d Concentration of [¹⁴C]flupropacil in soil following desorption.

The sorption constant (*K_d*) was also expressed in terms of the soil organic carbon content using the equation

$$K_{OC} = (K_d \times 100)/\%OC$$

where *K_{OC}* is the sorption coefficient based on soil organic carbon content and % OC is the organic carbon content of the soil. The organic carbon content of the soil was calculated by dividing the organic matter content by 1.7.

RESULTS AND DISCUSSION

Results obtained from the Freundlich equations are provided in Tables 2 and 3 and Figure 2.

The adsorption of flupropacil in general increased with increasing soil organic matter; however, flupropacil adsorbed very little to any of the four soils tested. The *K_d* (adsorption) values were 0.26 for Maryland (MD) sand, 0.33 for California (CA) sandy loam soil, 1.95 for Connecticut (CT) loamy sand, and 2.56 for Mississippi (MS) clay. It has been shown by several authors (Goring, 1962; Bailey and White, 1970; Briggs, 1973, 1981; Hamker and Thompson, 1972) that organic matter is the major soil component responsible for adsorption

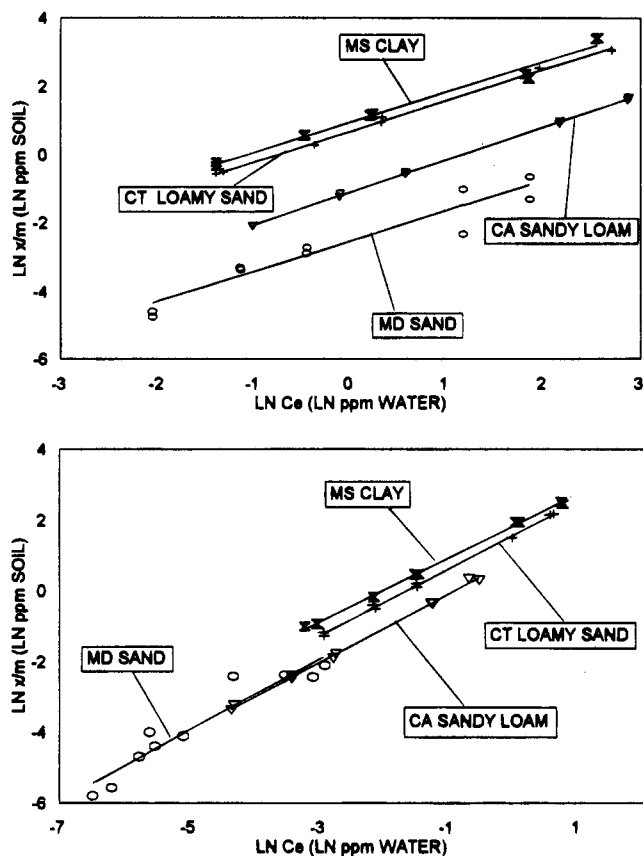


Figure 2. Adsorption (top) and desorption (bottom) isotherms of flupropacil in four soils.

Table 3. Freundlich Constants and Correlation Coefficients for Flupropacil following Adsorption and Desorption

	MS clay	MD sand	CT loamy sand	CA sandy loam
Adsorption Data				
K_{Ads}	2.56	0.26	1.95	0.33
K_{OC}	140	75	62	79
n	1.14	0.92	1.12	1.06
% OC	1.82	0.35	3.12	0.41
r	0.984	0.968	0.998	0.999
slope	0.88	1.08	0.89	0.95
Desorption Data				
K_{Des}	6.26	1.70	4.84	2.43
K_{OC}	343	482	155	589
n	1.11	1.23	1.05	1.03
% OC	1.82	0.35	3.12	0.41
r	0.998	0.982	0.998	0.998
slope	0.90	0.81	0.95	0.97

of pesticides to soil. Although the adsorption of flupropacil to all four soils tested is low, our results do indicate higher adsorption of flupropacil in general to soils with higher organic matter and CEC. The CEC measures the available exchangeable cations in the soil clay and humus (organic matter) fractions of the soil. Therefore, soils demonstrating high organic matter and to a lesser extent higher clay content exhibit higher CEC. The correlation coefficients (r) for the adsorption phase ranged from 0.9839 to 0.9997, indicating that the isotherms fit the Freundlich adsorption equation. The linearity of the slopes ($1/n$) for the four soils tested ranged from 0.88 to 1.08 in the adsorption phase, indicating that sorption is independent of the initial concentration, as seen with the herbicide thiobencarb in three Florida soils (Braverman et al., 1990).

The K_d (desorption) values were 1.70 for MD sand, 6.26 for MS clay, 4.84 for CT loamy sand, and 2.43 for CA sandy loam with good correlation coefficients (r ranging from 0.9910 to 0.9992). These desorption isotherms for flupropacil had n values ranging from 1.03 to 1.23 and are similar to the adsorption isotherms, indicating that equilibrium of flupropacil was attained and there was no hysteretic desorption process, as seen in some pesticides such as fluometuron (Hornsby and Davidson, 1973), atrazine (Swanson and Dutt, 1973), and 2,4-5 T (Van Genuchten et al., 1977).

The material balance ranged from 94.0 to 99.7%, indicating no loss of radioactivity due to either adsorption to the test container or volatilization. The linearity of the slopes ($1/n$) ranged from 0.81 to 0.97 in the desorption phase. Both HPLC and 2-D TLC analyses of the adsorption and desorption solutions from the highest concentration tested showed only flupropacil, confirming the stability of flupropacil during the experiment and also providing true Freundlich isotherms for flupropacil.

The results indicate that the adsorption of flupropacil to clay and other soil types is low, similar to that of other uracil herbicides (Haque and Coshov, 1971; Weber, 1972; Angemar et al., 1984), and that flupropacil may leach through the soil. However, the results from the controlled aerobic soil metabolism study (Vithala and White, 1995) show flupropacil to degrade with a fairly short half-life of 79 days in loamy sand soil with a moisture content of 75% at 0.33 bar and incubated at 25 ± 1 °C. The major metabolite was flupropacil acid, which accounted for up to 69% of the initially applied radioactivity at day 238. Volatile radioactivity totaled less than 0.3%, indicating that flupropacil is not volatile. Since various environmental factors affect the degradation of flupropacil under field conditions, it may not persist very long in the environment.

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