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Comparative Adsorption, Desorption, and Mobility of Dipropetryn and Prometryn in Soil

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Adsorption-desorption isotherms with dipropetryn [2-(ethylthio)-4,6-bis(isopropylamino)-s-triazine] and prometryn [2,4-bis(isopropylamino)-6-(methylthio)-s-triazine] were determined using six adsorbent materials possessing a wide range in cation exchange capacities (CEC), percent organic matter (OM), clay levels, and pH values. Dipropetryn and prometryn adsorption-desorption isotherms showed increasing adsorption with increasing clay content, cation exchange capacity, and organic matter levels, and decreasing pH values. With all adsorbents, more dipropetryn was adsorbed than prometryn. After eight successive desorption extractions, more di-

propetryn than prometryn remained adsorbed. Soil thin-layer chromatography was used to evaluate herbicide mobility. Fluometuron [1,1-dimethyl-3-(α,α,α -trifluoro-*m*-tolyl)urea], a more mobile herbicide, was included as a standard. Dipropetryn showed less movement in the soil than prometryn or fluometuron, with fluometuron showing the greatest movement. As CEC, percent OM, and clay content decreased, herbicide mobility increased for all three herbicides. Soil mobility of dipropetryn and prometryn correlated well with adsorption-desorption isotherm parameters.

Prometryn [2,4-bis(isopropylamino)-6-(methylthio)-s-triazine], a *methylthio-s-triazine*, has been used in cotton (*Gossypium hirsutum* L.) for weed control for a number of years. Its use on sandy soils has frequently resulted in crop injury. Dipropetryn [2-(ethylthio)-4,6-bis(isopropylamino)-s-triazine], an *ethylthio-s-triazine*, is a new herbicide being evaluated for weed control in cotton grown on sandy soils. Initial reports indicate that this ethylthio analog may be less phytotoxic to cotton than the methylthio analog.

Herbicide adsorption by the soil matrix has been used by many investigators to explain different herbicide phytotoxicity levels for various soils (Scott and Weber, 1967). Adsorption characteristics of the *s-triazines* have been shown to be affected by soil organic matter content (Harris and Warren, 1964; Scott and Weber, 1967; Talbert and Fletchall, 1965), soil pH (Harris and Warren, 1964; Swanson and Dutt, 1973; Weber et al., 1965), clay content and type (Scott and Weber, 1967; Talbert and Fletchall, 1965; Weber et al., 1965), soil temperature (Harris et al., 1968; Harris and Warren, 1964; Talbert and Fletchall, 1965), as

well as charcoal (Weber et al., 1968) and type of exchange resins (Harris and Warren, 1964; Scott and Weber, 1967; Weber et al., 1965). Harris et al. (1968) and Harris and Warren (1964) have shown a lack of correlation between water solubility and adsorption for three similar chloro-*s-triazines*. Scott and Weber (1967) have shown that adsorption on organic materials correlated well with phytotoxicity. When the adsorption of several *s-triazines* was evaluated using a given adsorbent, prometryn was shown to be adsorbed in larger quantities (Gilmour and Coleman, 1971).

Herbicide mobility in the soil is, in part, a factor which influences the effectiveness of a herbicide. The extent to which herbicides move in the soil is directly related to the adsorption-desorption characteristics of each herbicide with the soil. Davidson et al. (1972) have shown that the nonsingularity between herbicide adsorption and desorption was responsible for the shape of the total herbicide concentration distribution in the soil. The nonsingularity tends to decrease the maximum herbicide solution concentration as well as increase the length of soil profile over which the distribution occurs. This skewing of the concentration distribution noted for fluometuron [1,1-dimethyl-3-(α,α,α -trifluoro-*m*-tolyl)urea], picloram (4-amino-3,5,6-trichloropicolinic acid), and prometryn in a water-

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Table I. Chemical and Physical Properties of Soils and Amended Soils

Soils and amendments	%				CEC ^a	pH
	Sand	Silt	Clay	OM		
Quartz sand	100	0	0	0.0	0.4	5.6
Cobb sand	93	4	3	0.6	3.8	7.3
Eufaula fine sandy loam	76	14	10	1.5	5.9	6.4
Teller fine sandy loam	58	23	19	1.3	8.6	5.7
Cobb sand + 2% muck	93	4	3	2.1	9.0	5.3
Brewer clay loam	27	45	29	2.8	13.5	5.8
Port silty clay	16	42	42	1.8	17.9	6.3
North Carolina muck				42.3	40.8	3.6

^a Milliequivalents/100 g.

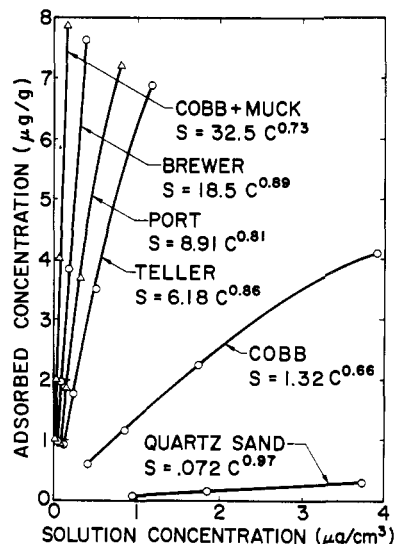


Figure 1. Equilibrium adsorption isotherms for dipropetryn and various soils.

saturated soil was attributed primarily to the nonsingularity between the adsorption and desorption processes (Davidson and McDougal, 1973). Helling (1971a-c) and Helling and Turner (1968) using soil thin-layer chromatography showed that prometryn was the least mobile of the s-triazines studied. Harris et al. (1968) have also shown s-triazines to be rather immobile with prometryn being the least mobile.

Although there has been considerable research on the

soil activity of the chloro- and methylthio-s-triazine herbicide analogs, little information is available on the relationship to them of the newly developed ethylthio analog (dipropetryn). Previous research has concentrated on adsorption, but it is now realized that the rate and degree of desorption from a colloidal surface are also important in determining herbicide mobility and persistence. The pur-

Table II. Freundlich Equation Parameters for Adsorption of Dipropetryn and Prometryn^a

Herbicide	Soil type											
	Cobb sand + 2% muck		Brewer clay loam		Port silty clay		Teller fine sandy loam		Cobb sand		Quartz sand	
	K	1/N	K	1/N	K	1/N	K	1/N	K	1/N	K	1/N
Dipropetryn	32.5	0.73	18.5	0.89	8.91	0.81	6.18	0.86	1.32	0.86	0.07	0.97
Prometryn	28.9	0.79	9.95	0.83	4.90	0.76	3.49	0.80	0.66	0.77	0.07	-0.54

^a Correlation coefficients were 0.99 for all adsorption isotherms except prometryn on quartz sand which was 0.72.

Table III. Freundlich Equation Parameters for Desorption of Dipropetryn and Prometryn

Soil type	Values	Herbicide							
		Dipropetryn rates, µg/g				Prometryn rates, µg/g			
		1	2	4	8	1	2	4	8
Cobb sand + 2% muck	K	0.88	2.10	5.65	11.04	0.84	1.63	4.25	11.20
	1/N	-0.02	0.02	0.12	0.16	-0.03	-0.05	0.04	0.21
	Corr. coeff.	0.40	0.20	0.62	0.93	0.69	0.39	0.35	0.69
Brewer clay loam	K	1.48	4.04	6.78	10.90	3.02	4.02	5.70	8.74
	1/N	0.14	0.29	0.31	0.35	0.39	0.39	0.38	0.45
	Corr. coeff.	0.82	0.97	0.89	0.94	0.79	0.92	0.90	0.97
Port silty clay	K	3.42	4.40	6.97	8.57	2.57	4.29	4.98	6.20
	1/N	0.45	0.44	0.51	0.46	0.46	0.58	0.54	0.49
	Corr. coeff.	0.91	0.96	0.96	0.97	0.92	0.93	0.96	0.97
Teller fine sandy loam	K	2.94	4.85	5.43	6.67	2.16	3.09	3.51	4.24
	1/N	0.51	0.63	0.56	0.58	0.53	0.66	0.63	0.61
	Corr. coeff.	0.94	0.97	0.99	0.98	0.99	0.99	0.99	0.99
Cobb sand	K	1.11	1.30	1.67	2.01	0.60	0.66	0.69	0.86
	1/N	0.65	0.59	0.57	0.59	0.51	0.68	0.70	0.69
	Corr. coeff.	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99

Table IV. Adsorption-Desorption of Dipropetryn and Prometryn by Five Soils

Soil type	Herbicide							
	Dipropetryn				Prometryn			
	Initial herbicide concn, $\mu\text{g/g}$							
	1	2	4	8	1	2	4	8
Cobb sand + 2% muck								
Initial ads.	0.99	1.98	3.94	7.87	0.99	1.97	3.92	7.80
Solution concn	0.01 ^a	0.02	0.06	0.13	0.01	0.03	0.08	0.20
Ads. after 8 ext.	0.95	1.90	3.78	7.51	0.94	1.87	3.69	7.29
Total des.	0.04	0.08	0.16	0.36	0.05	0.10	0.23	0.51
% des.	3.90	3.90	4.10	4.50	4.20	5.00	5.90	6.50
Brewer clay loam								
Initial ads.	0.96	1.93	3.84	7.62	0.94	1.87	3.69	7.31
Solution concn	0.04	0.07	0.16	0.38	0.06	0.13	0.31	0.69
Ads after 8 ext.	0.87	1.72	3.40	6.64	0.79	1.51	2.94	5.66
Total des.	0.09	0.21	0.44	0.98	0.15	0.36	0.75	1.65
% des.	9.90	10.90	11.50	12.90	16.50	19.20	20.40	22.60
Port silty clay								
Initial ads.	0.94	1.86	3.68	7.22	0.89	1.73	3.40	6.53
Solution concn	0.06	0.14	0.32	0.78	0.11	0.27	0.60	1.47
Ads. after 8 ext.	0.79	1.50	2.92	5.56	0.66	1.25	2.33	4.38
Total des.	0.15	0.36	0.76	1.66	0.23	0.48	1.07	2.15
% des.	16.00	19.20	20.50	22.90	26.10	27.90	31.50	32.80
Teller fine sandy loam								
Initial ads.	0.89	1.77	3.50	6.84	0.84	1.61	3.09	6.08
Solution concn	0.11	0.23	0.50	1.16	0.16	0.39	0.91	1.92
Ads. after 8 ext.	0.66	1.27	2.45	4.55	0.52	0.89	1.64	3.10
Total des.	0.23	0.50	1.05	2.29	0.32	0.72	1.45	2.98
% des.	26.30	28.40	30.00	33.50	38.20	44.90	46.80	49.00
Cobb sand								
Initial ads.	0.60	1.15	2.25	4.09	0.45	0.74	1.30	2.60
Solution concn	0.40	0.85	1.75	3.91	0.55	1.26	2.70	5.40
Ads. after 8 ext.	0.20	0.39	0.76	1.31	0.13	0.13	0.19	0.38
Total des.	0.40	0.76	1.49	2.78	0.32	0.61	1.11	2.22
% des.	67.10	66.50	66.20	68.10	70.80	83.00	85.50	85.30

^a Concentration is $\mu\text{g}/\text{cm}^3$.

pose of this research was to evaluate and compare the adsorption and desorption characteristics of the two thio-s-triazine classes of herbicides, using six adsorbent materials. Since sorption activities influence herbicide movement in the soil, the relative mobility of the herbicides was evaluated utilizing soil thin-layer chromatography.

MATERIALS AND METHODS

Adsorption-desorption characteristics of dipropetryn and prometryn were determined for four naturally occurring Oklahoma soils, an amended soil and quartz sand. The chemical and physical properties of these soils and various adsorbents are given in Table I.

Adsorption of these herbicides was determined by mixing a solution of ¹⁴C-labeled herbicide with soil in a 1:1 by weight ratio at $26 \pm 2^\circ$. Screw cap Pyrex tubes (25 × 150 mm) with Teflon-lined plastic caps were used for the herbicide solution and soil mixture. Unlabeled technical grade herbicide was added to the radioactive herbicide solution in order to obtain an appropriate counting rate and still provide a specified maximum herbicide concentration. Herbicide solutions of 1, 2, 4, and 8 ppm were made up in 0.01 N CaCl₂. Duplicate 10-g samples of soil on an oven-dried basis were added to 10 ml of the appropriate herbicide solution. The tubes containing the soil and herbicide solution were shaken for 12 hr on a horizontally set wrist action shaker. Preliminary experiments had shown

that 12 hr was sufficient time for soil-herbicide adsorption equilibrium. After shaking, the tubes were centrifuged at 1000g for 10 min at 26° . Duplicate 500- μl samples were transferred from each tube into scintillation vials containing 15 ml of scintillation fluid. The scintillation solution consisted of 120 g of naphthalene, 4 g of 2,5-diphenyloxazole (PPO), and 50 mg of 1,4-bis-2-(5-phenyloxazolyl)benzene (POPOP) made to 1-l. volume with *p*-dioxone.

Desorption was determined on the same samples used for adsorption, but was not determined on the quartz sand. Desorption was achieved by removing a known quantity of the supernatant from the centrifuged samples and then replacing the removed liquid with herbicide-free 0.01 N CaCl₂ solution. Eight successive desorption extractions were made. On the first, second, and third through eighth desorption extractions, 3, 4, and 5 ml of supernatant were removed, respectively, for a total of 37 ml. Duplicate 500- μl samples of supernatant at each extraction interval were placed in a scintillation vial and counted. To resuspend the soil after centrifugation, a vibrating stirrer was used. Prior to each desorption extraction the samples were shaken for 12 hr at $26 \pm 2^\circ$.

The mobility of dipropetryn in soil was determined using the soil thin-layer chromatography procedure described by Helling (1971a-c) and Helling and Turner (1968). Fluometuron was included as a standard because of its known mobility while prometryn represented a less

Table V. Herbicide Movement in Soil Using Soil Thin-Layer Chromatography

Soil type	R_f value for Herbicide		
	Dipro-petryn	Pro-metryn	Fluo-meturon
Brewer clay loam	0.03i ^a	0.08i	0.41e
Cobb sand + 2% muck	0.07i	0.12h	0.46de
Port silty clay	0.14h	0.20g	0.50d
Teller fine sandy loam	0.16gh	0.26f	0.80b
Eufaula fine sandy loam	0.17gh	0.27f	0.62c
Cobb sand	0.45de	0.63c	0.95a

^a Numbers followed by the same letter are not significantly different at the 5% level according to Duncan's New Multiple Range Test; C.V. = 9.58.

mobile herbicide. The natural soils and the amended soil used in the adsorption-desorption study were also used for soil thin-layer chromatography. In addition to these soils, Eufaula fine sandy loam was included. All soils were passed through a 420- μ screen and mixed with distilled water until moderately fluid. Soil thin-layer plates were made by using a conventional thin-layer chromatography plate-making apparatus. Duplicate 20 \times 20 cm plates were coated with a 1-mm thick layer of each of the natural and amended soils except for the Port silty clay which was only 0.5 mm thick. No binding agents were used with these soils. The plates were air dried at 25° for 6 days. Radioactive herbicide solutions, 2 μ l (0.02 μ Ci), were spotted in duplicate 1.5 cm from the bottom of each plate. A line was etched 10 cm above the spots to prevent any water movement above 10 cm. After spotting, the plates were placed in a conventional thin-layer chromatography tank using water as the solvent system. The lower 0.5 cm of each plate was then immersed in water. When the water front reached the 10 cm etched line the plates were removed and air dried for 24 hr. The plates were covered with a plastic wrap and placed in contact with X-ray film (Kodak NS2T) for 8 days. After exposure, the film was developed and the herbicide movement measured.

RESULTS AND DISCUSSION

For equilibrium conditions, several investigators (Bailey and White, 1970; Davidson and McDougal, 1973) have reported that the relationship between the solution and adsorbed phases of an organic pesticide can be described with the Freundlich equation:

$$S = KC^{1/N} \quad (1)$$

where S is the adsorbed concentration (μ g/g), C is the solution concentration (μ g/cm³), K is the distribution coefficient, and N is a constant that varies with the chemical and adsorbent. Equilibrium adsorption and desorption isotherms for dipropetryn and prometryn were described reasonably well by the Freundlich equation. The Freundlich equation values for adsorption are shown in Table II and for desorption in Table III.

Adsorption isotherms for dipropetryn and six adsorbents are shown in Figure 1. Cobb sand plus 2% muck showed the greatest amount of adsorption and quartz sand the least adsorption. This same trend was apparent with prometryn (Table II); however, the amount of adsorption was consistently less than dipropetryn. Prometryn adsorption on quartz sand was so low that reliable values of K and $1/N$ were not obtained (Table II). A linear relation ($1/N = 1$) between equilibrium adsorbed and solution concentrations was not obtained for any herbicide-soil combination studied.

When comparing the adsorption of dipropetryn and pro-

metryn to these adsorbents (Table IV), dipropetryn was more highly adsorbed than prometryn except with quartz sand which showed little if any adsorption. When looking at the distribution coefficients (Table II), with the exception of the Cobb sands, the K values for dipropetryn are generally twice as large as the K values for prometryn. Table IV shows the actual amounts of herbicide adsorbed and the equilibrium solution concentrations.

When comparing the adsorbents, the general trend is for more adsorption of both herbicides with increasing cation exchange capacity or organic matter levels and decreasing soil pH. Table I shows the chemical and physical properties of natural soils and amended soil used in this study. Port silty clay had a higher cation exchange capacity than Brewer clay loam, but showed less adsorption of both dipropetryn and prometryn. Port silty clay had a pH of 6.3 while Brewer clay loam had a pH of 5.8. A probable explanation for this would be that Port silty clay had 1% less organic matter than the Brewer clay loam, although the pH values were also different. Cobb sand plus 2% muck showed the greatest amount of adsorption of both herbicides while it had only 2.1% organic matter and a cation exchange capacity of 9.0. It should be noted that Cobb sand plus 2% muck had the lowest pH and it was an amended soil rather than a natural weathered soil. The North Carolina muck which was added had a very low pH (3.6) and a high cation exchange capacity (40.8 mequiv/100 g). The adsorption of dipropetryn and prometryn by these adsorbents, with their varied cation exchange capacities, pH values, and organic matter contents requires that all three factors must be considered. However, regardless of the responsible factor, dipropetryn was more highly adsorbed than prometryn.

As shown in Tables III and IV, less dipropetryn than prometryn was desorbed after any given extraction. The adsorbents showing the greatest amount of adsorption also showed the least amount of desorption. Approximately 4% of the dipropetryn adsorbed by the Cobb sand plus muck was desorbed, while approximately 65% of the adsorbed dipropetryn was desorbed from the Cobb sand after eight extractions. An increase in the percent of dipropetryn and prometryn desorbed was noted as the herbicide rates increased. This would be expected based upon the shape of the adsorption isotherms ($1/N < 1.0$).

The desorption distribution coefficients were not constant for a given herbicide and soil (Table III) but increased as the adsorbed herbicide concentration prior to desorption increased. The $1/N$ value also was a function of the maximum quantity of herbicide adsorbed prior to desorption. These trends have been observed by van Genuchten et al. (1974) and Swanson and Dutt (1973) for picloram and atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine]. An analytic expression for the desorption distribution coefficient was derived by van Genuchten et al. (1974) by assuming an average $1/N$ value for desorption. The analytic expression was:

$$K_{des} = K_{ads} N_{ads}/K_{des} S_{max}^{(1-N_{ads}/N_{des})} \quad (2)$$

where the subscripts des and ads refer to adsorption and desorption parameters (Freundlich equation) and S_{max} is the adsorbed herbicide concentration prior to desorption. The assumption that N_{ads}/N_{des} was constant was reasonable (van Genuchten et al., 1974). Equations 1 and 2 were used by van Genuchten to describe picloram movement through a water saturated soil.

The clay and organic matter content present in each soil appeared to significantly influence the amount of herbicide desorbed from the soil matrix. The shape of the desorption isotherms also appeared to be influenced by the presence of organic matter. The desorption isotherms for the dipropetryn and prometryn in Cobb sand plus muck and Brewer clay loam were nearly flat ($1/N \approx 0.0$) at the low herbicide concentrations. This suggests that the her-

bicide was firmly attached to the adsorbent and difficult to remove. Some of the herbicide may also be irreversibly adsorbed by the adsorbent. The significance of a nonsingularity between adsorption and desorption and the persistence of biological activity of the herbicide in the soil has not been studied. The nonsingularity does prevent the herbicide from moving through the soil as a "bell-shaped" pulse and reduces the herbicide solution concentration behind the downward moving herbicide front.

The mobility of dipropetryn, prometryn, and fluometuron in each soil, as determined by soil thin-layer chromatography is shown in Table V. The differences in the mobility of these herbicides in various soils are apparent. Dipropetryn moved the least and fluometuron moved the most. In general, as the cation exchange capacity, organic matter, and clay levels decreased, the mobility of all three herbicides increased. There was a good relationship between the parameters from the adsorption isotherms and herbicide mobility. Soils showing the highest amounts of adsorption showed the least herbicide mobility. The R_f values for prometryn using the soil thin-layer plate technique were similar to the R_f values for prometryn reported by Helling (1971b) and Helling and Turner (1968).

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Action of Weak Bases upon Aflatoxin B₁ in Contact with Macromolecular Reactants

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Radiolabeled aflatoxin B₁ added to corn grain flour, when treated with ammonia at 25–50° for periods of 3–30 days, binds covalently and preferentially to corn protein fractions and water-soluble components. In the presence of base, results indicate that two types of associations can occur between the aflatoxin and macromolecular substrate. A reversible type of association results from opening the lactone ring of the B₁ molecule in basic media and can lead to electrostatic and/or hydrogen bonding interactions with substrate.

The irreversible or covalent interaction between B₁ and substrate does not visibly alter the spectral properties of the primary B₁ chromophore (365-nm absorbance). The affixation of this chromophore to much larger molecules in the presence of weak bases implicates the dihydrofuran ring system of B₁ as the site of B₁ interaction. A marked reduction or complete loss of toxicity in certain corn fractions containing the primary B₁ chromophore is further evidence indicating the dihydrofuran ring system to be the site of interaction.

The problems associated with and proposed methods of detoxifying aflatoxin-contaminated agricultural commodities have been reviewed (Goldblatt, 1969). In a recent review of the toxicity and carcinogenicity of aflatoxins, Wogan (1973) points out that accumulated evidence indicates that aflatoxin B₁ has two functional groups, the dihydrofuran segment and the lactone-pentanone ring systems, responsible for B₁ biological activity.

From the chemical standpoint, it was Coomes et al. (1966) who first presented evidence that the lactone ring is quite reactive, readily opening upon refluxing B₁ in water. This reaction in neutral medium is in contrast to that under acidic conditions generally used to add 1 mol of water to the double bond of the terminal furan rings (Andrellos and Reid, 1964). Using ammonium hydroxide at elevated temperatures and pressures, Lee et al. (1974) were able to detoxify a portion of B₁ by removing the carbonyl of the lactone ring, but such drastic treatment did not completely destroy all of the B₁ aflatoxin.

In the work to be presented, ¹⁴C-labeled aflatoxin B₁ preparations were employed to show that low levels of ammonia as ammonium hydroxide (≤2.0 g of NH₃/100 g of flour) caused the irreversible binding of B₁ to corn flour components. Based upon extractability with various solvents after acidification of the basic reaction mixture, in addition to gel permeation chromatography of certain preparations, we established that the binding occurs preferentially with the major protein fractions and water-soluble materials of corn. This conclusion is further supported by the observed low level of interaction between B₁ and starch which is the predominant macromolecular component of corn. We further observed that the reaction between B₁, ammonia, and corn flour could produce water-soluble products which were teratogenic to chick embryos. But, the active products were isolated only from reaction mixtures artificially contaminated at very high levels of toxin (1 mg/g of flour). Water extracts of ammonia-treated whole corn flour (from naturally contaminated corn initially containing 1200 μg of B₁/kg) and corn germ isolate (7000 μg of B₁/kg) contained no substance teratogenic to chick embryos.

With the alkaline form of DEAE-cellulose serving as the source of base, changes occurring in the fluorescence emis-

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