Adsorption–Desorption of Selected Pesticides by Organic Matter and Montmorillonite

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Adsorption–desorption studies were conducted with the following pesticides: asulam (methyl sulfanilylcarbamate), butralin [4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine], dicamba (3,6-dichloro-o-anisic acid), fluometuron [1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)-urea], leptophos [O-(4-bromo-2,5-dichlorophenyl) O-methyl phenylphosphonothioate], methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione], norflurazon [4-chloro-5-(methylamino)-2-(α,α,α-trifluoro-m-tolyl)-3(2H)-pyridazinone], oxadiazon [2-$tert$-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one], profluralin [N-(cyclopropylmethyl)-α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine], prometryn [2,4-bis(isopropylamino)-6-(methylthio)-s-triazine], and TH 6040 [1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea]. Adsorbents used were soil organic matter and Ca-saturated montmorillonite. Desorbing solutions were deionized water and 1 N CaCl$_2$. Adsorption of prometryn by both adsorbents was primarily by cation exchange. Adsorption by organic matter of asulam and the nonionic compounds was in the reverse order of their water solubilities. This suggests that the mechanism of adsorption was hydrophobic bonding.

The adsorption and desorption of pesticides by soil organic matter and clay minerals are important factors affecting the fate of pesticides in the environment. Adsorption and desorption are involved in determining the ease with which pesticides move through the soil profile and their plant availability and microbial degradability and, thus, persistence.

Correlation studies have shown that the organic fraction of the soil was the single factor most highly related to herbicide activity (Sheets et al., 1962; Upchurch and Mason, 1962); as organic matter increased, herbicide activity decreased. Organic pesticides adsorb on both organic and inorganic surfaces depending upon the chemical properties of the adsorbents and adsorbates involved (Weber, 1972). Basic pesticides were strongly adsorbed by soil organic matter (Weber et al., 1969) and expanding lattice clay minerals (Weber, 1966, 1970). Acidic pesticides were adsorbed in moderate amounts on organic matter and in relatively low amounts on clay minerals and hydrous metallic oxides (Carringer, 1974; Carringer and Weber, 1974; Scott and Weber, 1966; Weber, 1972). Nonionic pesticides were adsorbed in greatest amounts by organic matter but adsorption by clay minerals was also important for organophosphates and several other pesticide families (Weber, 1972). In addition, it has been reported that carbamate and organophosphate insecticides were adsorbed by soil organic matter (Leenheer and Ahlrichs, 1971).

The objectives of this investigation were: (1) to determine the adsorption of eight new organic pesticides (six herbicides and two insecticides) in comparison to three well known herbicides by soil organic matter and an expanding-type clay mineral and (2) to gain information about their mechanisms of adsorption by desorbing with two desorbing solutions, deionized water and 1 N CaCl$_2$.

MATERIALS AND METHODS

Commercially formulated compounds were employed with sufficient ^{14}C-labeled material added to the emulsion or suspension to allow for liquid scintillation analysis. The mixture was equilibrated overnight. Common and chemical names and water solubilities of the compounds are given in Table I.

Calcium-saturated montmorillonite, a smectite layer silicate, was prepared from Wyoming Bentonite. The clay was boiled in hot H$_2$O$_2$ for removal of organic material. The fraction with particle size less than 2 μm was then removed according to the procedure of Day (1965) and saturated with Ca by washing three times with 1 N CaCl$_2$. The suspension was dialyzed until free of Cl and then freeze-dried and stored in sealed containers until used. That fraction with particle size greater than 2 μm was discarded.

Organic matter was prepared from a peaty muck (Histosol) soil. The material was sieved to a particle size less than 210 μm and washed with 1 N HF and 1 N HCl to remove any mineral material and to saturate with H according to the procedure of Broadbent (1965). It was then dialyzed until free of Cl, freeze-dried, and stored in sealed containers until used. The material was 94% combustible.

Adsorption by Ca-Montmorillonite. Isotherms for asulam, dicamba, norflurazon, fluometuron, prometryn, and methazole with montmorillonite as the adsorbent were determined in 50-ml polypropylene centrifuge tubes, while isotherms for butralin, oxadiazon, profluralin, leptophos, and TH 6040 were determined in glass serum bottles with ground glass stoppers. Temperature was held constant at 24 ± 1°.

During the course of the investigation, it was determined that butralin and profluralin were readily adsorbed by polypropylene, Teflon, parafilm, stopcock grease, and aluminum foil; however, the amounts adsorbed were not measured. The tendency for these low water-soluble molecules to escape aqueous suspensions and adhere to hydrophobic surfaces is very high.

Ten-milliliter aliquots of clay suspension, containing 4.0 mg of clay each, were added to each of the adsorption containers. To this were added 10-ml aliquots of pesticide standards to give a total of 20 ml of pesticide solution at concentrations of 10, 20, 30, 40, and 50 × 10^{-6} M for all compounds except butralin and profluralin, which had final concentrations of 2.5, 5, and 10 × 10^{-6} M. Low water solubilities of the latter two compounds prevented using them at higher concentrations.

The samples were placed onto a rotary shaker and allowed to equilibrate for 4 hr. Preliminary studies showed that there was no increase in adsorption after 4 hr. After equilibration, the samples were centrifuged at 20,000 rpm for 2 min. One milliliter of the supernatant was removed and placed into a 15-ml aliquot of scintillation cocktail, which consisted of a mixture of 5.0 g of 2,5-diphenyloxazole, 0.1 g of 1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene, 1000 ml of Triton X-100, and 1000 ml of toluene. The samples were counted for three 10-min periods in a

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Table I. Pesticides and Their Water Solubilities

Common name	Chemical name	Formulation[a]	Purity[b]	Water solubility, ppm
Asulam	Methyl sulfanilylcarbamate	SS	40.3%	5000.0
Butralin	4-(1,1-Dimethylethyl)-N-(1-methylpropyl)-2,6-dinitro-benzenamine	EC	61.9%	<1.0
Dicamba	3,6-Dichloro-o-anisic acid	DS	49.5%	4500.0
Fluometuron	1,1-Dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea	WP	83.5%	85.0
Leptophos	O-(4-Bromo-2,5-dichlorophenyl) O-methyl phenylphosphonothioate	EC	0.321 g/ml	0.03
Methazole	2-(3,4-Dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione	WP	88.5%	1.5
Norflurazon	4-Chloro-5-(methylamino)-2-(α,α,α-trifluoro-m-tolyl)-3(2H)-pyridazinone	WP	88.5%	28.0
Oxadiazon	2-$tert$-Butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one	EC	0.223 g/ml	0.7
Profluralin	N-(Cyclopropylmethyl)-α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine	EC	0.375 g/ml	<1.0
Prometryn	2,4-Bis(isopropylamino)-6-(methylthio)-s-triazine	WP	80.4%	48.0
TH 6040	1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea	WP	25.9%	0.3

[a] WP, wettable powder; EC, emulsifiable concentrate; SS, sodium salt; DS, dimethylamine salt. [b] Determined spectrophotometrically.

Table II. Dinitroaniline Adsorption by Organic Matter and Montmorillonite

	Butralin				Profluralin			
Initial concn $\times 10^{-6} M$	Equil. concn $\times 10^{-6} M$	Amt adsorbed		Initial concn $\times 10^{-6} M$	Equil. concn $\times 10^{-6} M$	Amt adsorbed	
		μmol/g	%			μmol/g	%
(A) By Organic Matter							
2.5	0.59	1.53	77	2.5	0.64	1.49	74
5.0	0.91	3.27	82	5.0	1.72	2.62	66
10.0	2.24	6.21	78	10.0	3.35	5.32	66
LSD (0.05)		0.80		LSD (0.05)		0.39	
(B) By Montmorillonite							
2.5	1.98	2.60	21	2.5	2.26	1.20	9
5.0	4.37	3.15	13	5.0	4.51	2.45	10
10.0	9.09	4.56	9	10.0	9.01	4.94	10
LSD (0.05)		2.52		LSD (0.05)		2.21	

liquid scintillation spectrometer. Counting efficiencies ranged from 50 to 60%. The difference between the initial concentration and the equilibrium concentration was taken to be the amount of pesticide adsorbed.

Each treatment was replicated three times with the exception of the treatment with the highest initial concentration, which was replicated four times.

Adsorption by Organic Matter. The adsorption containers were the same as those described in the adsorption by Ca-montmorillonite studies. For all the compounds, 25 mg of organic matter was weighed into each of the appropriate containers, followed by a 20-ml aliquot of pesticide solution at concentrations of 10, 20, 30, 40, and 50 $\times$ 10^{-6} M, except for butralin and profluralin, which had final concentrations of 2.5, 5, and 10 $\times$ 10^{-6} M. The freeze-dried adsorbents hydrated readily in the aqueous suspensions. The samples were placed onto a rotary shaker and allowed to equilibrate for 4 hr. They were then removed from the shaker and allowed to stand for approximately 10 min to allow the organic matter to settle out. The sampling and analysis procedures were the same as those described in the adsorption by Ca-montmorillonite studies.

Each treatment was replicated three times with the exception of the treatment with the highest initial concen-

tration, which was replicated four times.

Desorption from Montmorillonite and Organic Matter. The 11 pesticides were desorbed from both adsorbents by the same procedure. Sixteen milliliters of the supernatant from the samples with the highest initial concentration was removed, analyzed, and then discarded. Sixteen-milliliter aliquots of desorbing solution were then added to each of the samples. They were then placed onto a rotary shaker and allowed to equilibrate for 4 hr. The samples were then either centrifuged or allowed to stand, depending upon the adsorbent. Another 16 ml was removed, analyzed, and discarded. This procedure was repeated for a total of three desorptions. It was previously mentioned that four replications of the highest initial concentration were utilized in determining adsorption. Two replications were used for desorption with deionized water and the remaining two were desorbed with 1 N CaCl$_2$.

RESULTS AND DISCUSSION

Organic Matter Adsorption–Desorption. Except for dicamba, all of the compounds were adsorbed by organic matter. Amounts of butralin and profluralin adsorbed are given in Table II, part A. Adsorption isotherms of the re-
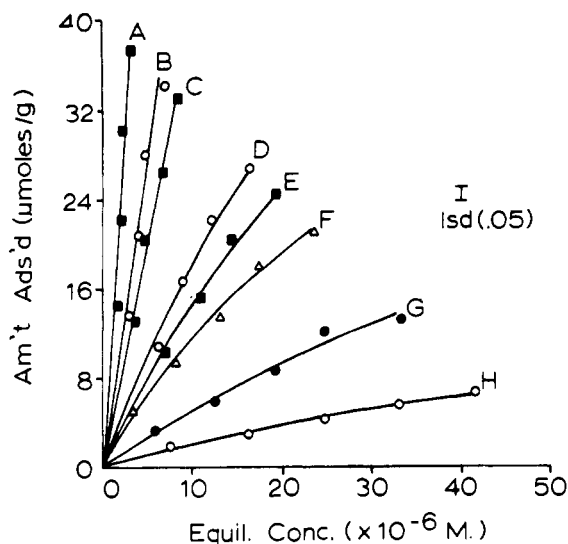
Figure 1. Adsorption by organic matter: (A) prometryn; (B) leptophos; (C) TH 6040; (D) oxadiazon; (E) methazole; (F) norflurazon; (G) fluometuron; (H) asulam.

maining compounds are shown in Figure 1. The compounds were divided into four groups according to chemical and physical properties—acidic herbicides, basic herbicides, miscellaneous nonionic pesticides, and dinitroaniline herbicides.

Acidic Herbicides. Asulam and dicamba are organic acids with pK_a values of 4.82 and 1.90, respectively. Dicamba did not show any detectable adsorption on organic matter, whereas asulam did adsorb slightly (Figure 1). Weber (1972) reported that dicamba was adsorbed by soil organic matter in small amounts through hydrogen bonding of molecular species to the colloid surface. Weber's studies were conducted at pH 4.0 using 100 mg of adsorbent. These factors may have contributed to this discrepancy.

The difference in adsorption between dicamba and asulam was probably due mostly to the difference in pK_a values. Although the suspension pH was approximately 5.5, the pH at the colloid surface was probably much lower due to hydrogen saturation. At the lower pH, a majority of asulam molecules in solution would be in their molecular form, while a majority of dicamba molecules would be in anionic form. Since organic matter has a net negative charge (Stevenson, 1972), dicamba anions would be repelled by the organic matter. However, asulam molecules would not be repelled, but would be adsorbed by weak physical forces or, as Weber (1972) suggested for dicamba, through hydrogen bonding of molecular species.

Desorption studies verified that adsorbed asulam was weakly bonded. More asulam was desorbed by deionized water than by 1 N CaCl$_2$ (Table III). This may have been due to a lower solubility of asulam in CaCl$_2$ than in water, although this was not determined.

Basic Herbicide. Prometryn, a basic *s*-triazine herbicide, was adsorbed in the greatest amounts relative to the other chemicals (Figure 1). Frissel and Bolt (1962) and Weber (1966) among others reported that *s*-triazines protonate in an acid environment. Weber et al. (1969) suggested that when *s*-triazines become protonated, they become positively charged species and are adsorbed in large amounts through a cation exchange mechanism. They also suggested that *s*-triazines become directly associated with hydrogen on the colloid surface and adsorb as cations. The latter probably occurred in this investigation, because the organic matter used was hydrogen saturated.

Desorption studies showed that much more prometryn was desorbed by 1 N CaCl$_2$ than by deionized water

(Table III). This verifies that the mechanism of adsorption was by cation exchange, since the excess Ca was very effective in displacing prometryn from the colloid surface.

Miscellaneous Nonionic Pesticides. The order of adsorption of the nonionic pesticides other than the dinitroanilines (greatest to least amounts of adsorption) was: leptophos > TH 6040 > oxadiazon > methazole > norflurazon > fluometuron (Figure 1). Isotherms for leptophos and TH 6040 were linear, while those for the other compounds appeared to be curvilinear. Adsorption appeared to be inversely related to the water solubilities of the chemicals; compounds of lowest water solubilities adsorbed in the greatest amounts. Weber (1972) also found an inverse relationship between water solubility and adsorption and desorption on ethyl cellulose and an anion-exchange resin of a series of phenylureas, including fluometuron. Savage and Wauchope (1974) observed high correlation between fluometuron adsorption in eight soils and organic matter content. The chemical was desorbed with water suggesting that a physical adsorption mechanism was involved.

The relationship between water solubility and amount of adsorption is shown in Figure 2. The average amount adsorbed or desorbed for each chemical is the mean of the five concentrations employed as shown in Figure 1. The log water solubility values are the logs of the water solubility given in parts per million in Table I. This relationship suggests that the adsorption mechanism of these compounds may be due primarily to hydrophobic association of the organic molecules with the soil organic matter surface. Organic matter contains saturated and unsaturated cyclic and heterocyclic ring structures, alcohols, proteins, carboxyls, and carbohydrate residues. Polymerization of these constituents yields molecular weights as high as 300,000 (Stevenson, 1972). Certain portions of these polymers are hydrophobic. Compounds of low water solubility are preferentially adsorbed to these hydrophobic areas and are removed from solution. The lower the water solubility of the compound, the greater its hydrophobic nature, and, therefore, the greater its adsorption by organic matter. In Weber's (1972) studies with phenylureas, the compounds were higher in water solubility and hydrophobic bonding was not suggested.

Desorption studies add further evidence that hydrophobic bonding may be involved in adsorption of nonionic chemicals since the less soluble compounds were also less easily desorbed from the organic matter surface (Figure 2). Adsorption was due to physical adsorbate-adsorbent attractions, and was not due to cation exchange mechanisms, since there was very little difference between desorption with water and 1 N CaCl$_2$, with the exception of oxadiazon (Table III). More oxadiazon was desorbed by deionized water than by CaCl$_2$.

Dinitroaniline Herbicides. Butralin and profluralin were strongly adsorbed by organic matter (Table II, part A). Weber (1972) also found very high adsorption of a related dinitroaniline, trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine), by soil organic matter. Weber and Monaco (1972) suggested that the dinitroaniline herbicides probably associated with hydrophobic sites on soil organic matter.

Desorption studies showed very little desorption by either water or 1 N CaCl$_2$ solution (Table III), indicating a very strong adsorbate-adsorbent association. In agreement with Weber and Monaco (1972), this association was considered to be a physical attraction between two hydrophobic entities, since there were no differences in desorption between the two desorbing soluions.

Montmorillonite Adsorption-Desorption. Of the pesticides studied, only prometryn, dicamba, methazole, butralin, and profluralin were adsorbed by montmorillonite. Amounts of adsorption of butralin and profluralin are given in Table II, part B, while isotherms for prometryn, dicamba, and methazole are shown in Figure 3.

Table III. Desorption of Adsorbed Pesticides from Organic Matter

| Compound | Amt adsorbed,[a] μmol/g | Desorption with water[b] | | | | | Desorption with $CaCl_2$[c] | | | | |
| | | μmol/g | | | | | μmol/g | | | | |
		1st	2nd	3rd	Total	%	1st	2nd	3rd	Total	%
Basic											
Prometryn	37.55	2.89	1.40	1.60	5.89	15.7	16.55	5.80	3.70	26.05	69.4
Acidic											
Asulam	6.80	4.06	0.98	0.70	5.74	84.4	1.74	1.18	1.06	3.98	58.5
Dicamba	0.00	0.00	0.00	0.00	0.00	00.0	0.00	0.00	0.00	0.00	00.0
Misc. nonionic											
Leptophos	34.10	2.96	0.62	0.06	3.64	10.8	3.81	0.82	0.00	4.63	13.6
TH 6040	33.27	4.64	1.47	0.05	6.16	18.5	5.28	1.28	0.22	6.78	20.4
Oxadiazon	26.90	11.15	5.32	1.24	17.71	65.8	6.79	4.29	0.83	11.91	44.3
Methazole	24.22	3.40	2.84	2.67	8.55	35.3	3.49	3.02	3.24	9.75	40.3
Norflurazon	21.36	4.93	5.41	2.50	12.84	60.1	6.34	5.04	2.73	14.11	66.1
Fluometuron	13.19	7.29	2.50	1.60	11.39	86.4	7.09	2.20	1.40	10.69	81.0
Dinitroanilines											
Butralin	6.21	0.23	0.30	0.30	0.83	13.2	0.16	0.26	0.27	0.69	11.1
Profluralin	5.32	0.03	0.41	0.24	0.68	12.8	0.00	0.42	0.21	0.63	11.8

[a] Initial concentrations were 50×10^{-6} M for all chemicals except for the dinitroanilines, which were 10×10^{-6} M. [b] LSD (0.05) = 10.36 for percent desorption with water for all compounds. [c] LSD (0.05) = 9.75 for percent desorption with $CaCl_2$ for all compounds.

Table IV. Desorption of Adsorbed Pesticides from Montmorillonite

| Compound | Amt adsorbed,[a] μmol/g | Desorption with water[b] | | | | | Desorption with $CaCl_2$[c] | | | | |
| | | μmol/g | | | | | μmol/g | | | | |
		1st	2nd	3rd	Total	%	1st	2nd	3rd	Total	%
Prometryn	67.93	13.05	15.12	8.80	36.97	54.4	52.63	13.45	1.85	67.93	100.0
Dicamba	29.11	7.74	0.96	0.84	9.54	32.8	10.67	0.70	0.74	12.11	41.6
Methazole	23.15	23.15	0.00	0.00	23.15	100.0	23.15	0.00	0.00	23.15	100.0
Butralin	4.56	0.00	2.41	1.77	4.18	91.7	0.00	2.02	1.10	3.12	68.4
Profluralin	4.94	0.00	2.68	1.93	4.61	93.3	0.00	2.23	1.18	3.41	69.0

[a] Initial concentrations were 50×10^{-6} M for all chemicals except the dinitroanilines, which were 10×10^{-6} M. [b] LSD (0.05) = 14.54 for percent desorption with water for all compounds. [c] LSD (0.05) = 18.75 for percent desorption with $CaCl_2$ for all compounds.
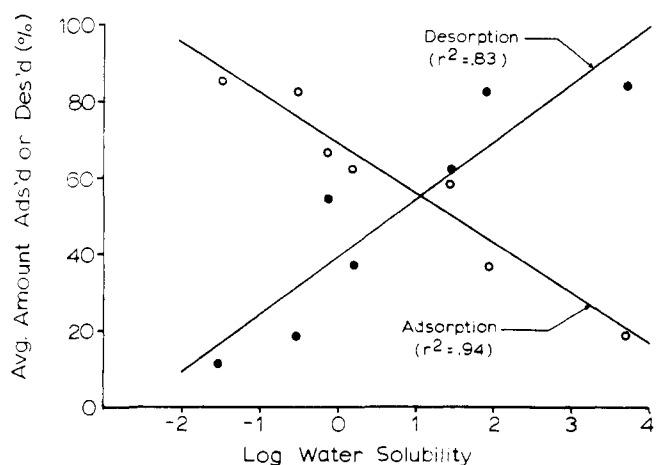

Figure 2. Adsorption and desorption (with water) of asulam, fluometuron, norflurazon, methazole, oxadiazon, TH 6040, and leptophos by organic matter as related to log water solubilities.

Figure 3. Adsorption by montmorillonite: (A) prometryn; (B) dicamba; (C) methazole.

Basic Herbicide. Of the compounds adsorbed by montmorillonite, prometryn was adsorbed in the largest amount (Figure 3). The isotherm for prometryn was determined at pH approximately 6.0; the compound has a pK_a
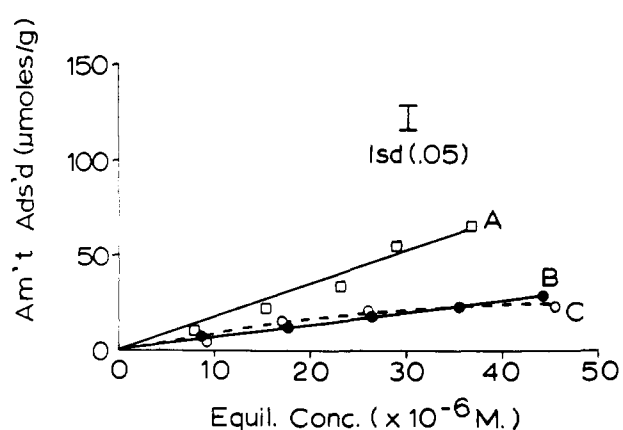
of 4.05 (Weber, 1966) and, therefore, the amount adsorbed was not the maximum possible, because maximum adsorption of s-triazines occurs in the vicinity of their pK_a values (Weber, 1966, 1970). Much more prometryn was desorbed with 1 N $CaCl_2$ than with deionized water (Table IV), indicating that prometryn cations were proba-

bly being displaced by excess Ca ions. This is in agreement with the results of Frissel and Bolt (1962) and Weber (1970), who found that s-triazines were strongly adsorbed by montmorillonite and suggested a cation exchange mechanism.

Acidic Herbicides. It was shown previously that asulam was adsorbed by organic matter and dicamba was not; the reverse was true for their adsorption by montmorillonite. The isotherm for dicamba is shown in Figure 3. Burnside and Lavy (1966) reported that dicamba was adsorbed by kaolinite but not by montmorillonite; however, they did not mention the saturation ion nor the degree of saturation for either of the clay minerals. These are important factors with respect to adsorption and may have contributed to this discrepancy.

Since the pH of the clay suspension was approximately 6.0, both asulam and dicamba were almost 100% ionized. Therefore, differences in pK_a values cannot explain differences in adsorption. One possible explanation is that the negatively charged dicamba ion complexes with the Ca ion on the clay surface. The asulam ion, however, may not have been able to form such a complex due to some type of steric interference between the Ca ion and the negative charge on the asulam ion. This is possible because the negative charge on asulam is localized at a nitrogen centered between a carbonyl group and a sulfonyl group, whereas on dicamba it is localized at an ionized carboxyl group.

Desorption studies showed that after one desorption very little dicamba was desorbed by the two desorbing solutions (Table IV). This suggests that small amounts were adsorbed very strongly.

Remaining Pesticides. Methazole (Figure 3) and butralin and profluralin (Table II, part B) were adsorbed in small amounts by montmorillonite. Desorption studies showed that adsorption of these chemicals was by very weak physical adsorption, because most of the pesticide was desorbed after three desorptions (Table IV). More butralin and profluralin were desorbed with deionized water than with 1 N CaCl$_2$. This was probably due to possible lower solubility of the compounds in salt solution than in water. Hollist and Foy (1971) and Weber et al. (1974) reported that the phytotoxicity of trifluralin was not reduced by the addition of montmorillonite to soil systems. This agrees with the low adsorption of dinitroaniline herbicides by montmorillonite clay minerals. It is reasonable that these hydrophobic organic molecules do not adhere to the highly hydrated surfaces of the clay.

The results of these studies might be projected to natural soil systems. Organic matter content of a soil would be the most important factor in determining adsorption and inactivation for all the compounds except dicamba and prometryn. Prometryn would probably be affected by clay and organic matter equally, while dicamba would probably be affected by clay to a greater extent than by organic matter in the soil. Clay content would be expected to have a significant effect on adsorption and inactivation of methazole, but only a slight effect on butralin and profluralin. Other factors such as the saturating cations on the organic and clay surfaces and the presence of surfactants and other ingredients of these formulated materials may also influence the relative adsorption of these compounds in soil systems. Inactivation in soil of the nonionic pesticides might be inversely related to their water solubilities as it was in these adsorption–desorption studies. This inactivation will influence the bioactivity, mobility, and persistence of these pesticides in the soil environment.

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