Adsorption−Desorption Studies of Selected Herbicides in Soil−Fly Ash Mixtures

I. K. Konstantinou and T. A. Albanis*

Chemistry Department, University of Ioannina, Ioannina 45110, Greece

Fly ash and soil mixtures with a range of fly ash content from 0 to 100% were used to study the adsorption and desorption of herbicides atrazine, propazine, prometryne, propanil, and molinate in batch experiments. The isotherms shapes according to Giles classification (Giles et al., 1960) were S, L, and H as the substrate changed from sandy clay loam (SCL) to fly ash, depending on the percent of fly ash in the mixture. The adsorption isotherms fit the Freundlich equation $x/m = K_f C^{1/n}$. The K_f values increase with the increase of the fly ash content. The mean percent amounts of herbicides, for a range of concentration 1−20 mg L^{-1}, adsorbed on the soil were 21.9% for atrazine, 50.7% for propazine, 29.04% for prometryne, 43.14% for molinate, 31.35% for propachlor, and 46.34% for propanil. Mass balance estimations show that the adsorbed amounts of the herbicides increase along with the fly ash content in the sorbent mixture and reach the 99% in the "pure" fly ash. In contrast, the amounts desorbed with water decrease as the fly ash content increases. The n values ranged from 0.82 to 3.05 indicating that the carbon content of fly ash plays a significant role during the sorption process and an increase of heterogenity of solid substrate. The increase of the amounts desorbed with acetone indicates that the sorption of organic compounds onto fly ash is believed to occur principally via the weak induction forces of London or dispersion forces which are characteristic of the physical adsorption process. The results of this research demonstrate that the fly ash shows a significant capacity for adsorption of organic compounds from aqueous solution.

Keywords: *Adsorption−desorption, herbicides, soil−fly ash mixtures*

INTRODUCTION

Herbicides are used in agriculture to remove weeds that would otherwise compete with the crop. Among the different chemical classes of herbicides, s-triazines, acetanilides, and carbamates represent the most used and monitored compounds. Three of the most common triazines used in Greece are atrazine (2-chloro-4-ethyl-amino-6-isopropylamine-s-triazine), propazine (2-chloro-4,6-bis isopropyl-amino-s-triazine), and prometryne (2-methylthio-4,6-bis isopropyl-amino-s-triazine). They all are used as pre- and post-emergence herbicides for the control of annual and perennial grasses and annual broad-leaved weeds. The potential for contamination of water and sediment is high owing to their physicochemical properties such as water solubility, adsorptivity (K_{oc}), and hydrolysis half-life (>25 weeks) (Durand and Barcelo, 1990).

Propachlor (2-chloro-N-isopropylacetanilide) and propanil (3,4-dichloropropioanilide) are structurally related chloroacetanilide herbicides that are used extensively in Greece for the control of some annual grasses and broadleaf weeds in several different crops. Molinate (S-ethyl-N-hexamethylenethiocarbamate) is widely used for the control of barnyard grass in paddy fields. It undergoes volatilization, adsorption, chemical and microbiological transformation in the environment. Soderquist et al., (1977) reported that molinate dissipation from a herbicide-treated field was attributable to soil adsorption (<10%), plant uptake and metabolism (<5%), aqueous microbial metabolism (<1%), hydrolysis (1%), photolysis (5−10%), and volatilization (75−85%).

Coal fly ash, which is produced as a byproduct in power plants, has shown significant adsorption capacity for organic pollutants (Kumar et al., 1987; Pollard et al., 1992). Fly ash has been used also to improve the physical and chemical characteristics of soils (El-Mogazi et al., 1988). Incorporation of fly ash increases the pH of acid soils to aid revegetation (Taylor and Schuman, 1988). The increase in soil pH as a result of fly ash application affects the availability of indigenous soil nutrients and of nutrients in applied fly ash. Apart from its use as a fertilizer in soil, fly ash has the ability to detoxify soil that contains methyl parathion residues (Albanis et al., 1985). Adsorption and desorption of herbicides on organic and inorganic soil colloids represent predominant processes in controlling the fate of these chemicals in soil. Interaction at interfaces between soil components and herbicides may affect herbicide movement, their bioavailability, and their transformation by abiotic or biotic agents (Kozak, 1996).

The objectives of this work were: 1) to study the influence of fly ash on adsorption and desorption of six selected herbicides, by its mixtur with soil and to measure, describe, and explain the equilibrium sorption characteristics, 2) to estimate the predominant forces and the reversibility of the binding process, and 3) to examine the sorptive capacity of fly ash in mixtures with soil as a possible technique for pesticide immobilization in environment.

* To whom all correspondence should be addressed. E-mail: talbanis@cc.uoi.gr.

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Table 1. Physicochemical Properties of Herbicides Used

compound	molecular weight	solubility in water (mg/L)[a]	soil sorption (K_{oc})[b]	pK_a
atrazine	215.7	35	160	1.68
propazine	230.0	8.6	160	1.85
prometryne	241.4	40	610	4.05
propachlor	211.7	700	80	-
propanil	218.1	500	150	-
molinate	187.3	856	415	-

[a] RSC–The Agrochmicals Handbook, 1987. [b] K_{oc}, sorption coefficient normalized to organic carbon content from Jury et al., 1987 and Wauchop et al., 1992.

Table 2. Characteristics and Composition of the Soil Sample

location and soil type	Mechanical analysis[a] (%)			CaCO₃ %	organic matter	pH[b]	specific surface (m²g⁻¹)
	clay	silt	sand				
sandy clay loam (SCL)	33.32	24.00	43.68	0.63	0.90	7.75	26.2

[a] Sand, 2.0–0.05 mm; silt, 0.05–0.002 mm; clay, below 0.002 mm. [b] pH was measured in 1:1, soil:water (w/v).

Table 3. Chemical Composition of Fly Ash

component	%	component	%
SiO_2	38.90	MgO	2.30
Fe_2O_3	5.18	SO_3	5.75
Al_2O_3	19.50	Na_2O	0.78
TiO_2	0.32	K_2O	1.13
CaO	26.60	% O.C.[a]	1.94

[a] O.C., organic carbon.

MATERIALS AND METHODS

Chemicals. The tested compounds in this study, atrazine, propazine, prometryne (s-triazines group) and propachlor, propanil (acetanilides) and molinate (thiocarbamate), were residue-analysis grade, purchased from Riedel-de Haen (Germany) and used without further purification. The physicochemical properties of the selected herbicides are shown in Table 1. Aqueous solutions of 0.01 M $CaCl_2$ were prepared at final concentrations of 1, 2.5, 5, 10, and 20 mg L⁻¹. The concentration level of 20 mg L⁻¹ was not used in the case of propazine because of solubility limitations. The 0.01 M $CaCl_2$ solution was spiked with 25 μL of methanolic standard solution of propazine in order to increase the solubility until 10 ppm. The low final methanol content (up to 0.25%) is not likely to affect the adsorption process (Singh et al., 1989).

Soil and Fly Ash. A sandy clay loam (SCL) soil sample was collected from a field with no previous history of persistent pesticide use. The sampling field was located in the region of Preveza (Greece). The sample was collected from the top 20-cm layer of the soil profile. Samples were air-dried, ground in a porcelain mill, and sieved through a 2-mm mesh. Organic carbon was determined by the Walkley-Black method and soil pH value was measured in slurry made at a soil/water ratio of 1:1. The soil characteristics are shown in Table 2. The fly ash was used as received from the thermal station (raw material lignite) of the public organization of electricity at Ptolemaida (Greece) and its chemical composition is shown in Table 3. The individual particle size of fly ash ranges from 1 to 100 μm. Fly ash and soil were mixed in order to achieve final concentrations in the range of 0–100%. The fly ash content of these mixtures and their pH values are shown in Table 4.

Experimental Procedures. The batch sorption experiments were carried out in 15 mL polypropylene centrifuge tubes where 1 g of fly ash–soil mixture and 10 mL of the above pesticide solution were added. To evaluate the absence of interferences in the soil, a test with $CaCl_2$ solution and without the tested herbicides was carried out as described below for

Table 4. pH Values[a] of SCL Soil and Fly Ash Mixtures

fly ash (%)	pH	fly ash (%)	pH
0	7.75	50	11.68
5	9.36	75	11.70
10	10.97	100	11.82
25	11.39		

[a] Measured with 1:1, solid:water (w/v).

adsorption test. Blank samples, i.e., no adsorbent added, indicated that losses due to adsorption onto polypropylene centrifuge tubes were negligible. The centrifuge tubes, prepared as above, were subsequently capped and shaken in a wrist action shaker for 24 h at constant room temperature (20 °C). Preliminary kinetic experiments had demonstrated that adsorption equilibrium was reached within 24 h. At the end of the apparent equilibration time, samples were centrifuged at 6000g for 10 min and the supernatant was recovered with a pipet for determination of herbicide equilibrium concentration and pH. A 10 mL portion of 0.01 M $CaCl_2$ solution was added to the remaining soil, the centrifuge tube was capped and shaken for a further 3 h (20 °C). Preliminary kinetic experiments demonstrated that desorption apparent equilibrium was reached within 3 h. After centrifugation, the supernatant was taken for determination of pesticide desorption equilibrium concentration. A second desorption step was carried out using 5 mL of acetone and shaking for 30 min (20 °C). Triplicate samples were measured for each initial concentration.

The calculation of percent balances of herbicides, adsorbed in 10 mL of aquatic suspensions and desorbed with 10 mL of water and 5 mL of acetone, for five different concentrations was based on the following equation:

[Initial amount] = [Free amount] + [Adsorbed amount]

The adsorbed amount could be analyzed as follows:

[Adsorbed amount] = [Desorbed amount with water] +
[Desorbed amount with acetone] +
[Decomposed or bound residues]

The decomposed or bound residues amount is calculated from the difference between adsorbed amount and the sum of the desorbed with water and acetone amounts. Bound residues could be also expressed as permanent adsorbed (remained) or non extractable residues.

Five mL of the aqueous phase was extracted twice with 2.5 mL of *n*-hexane using a vortex for 1 min. Into the combined extracts was added a small amount of anhydrous Na_2SO_4 in order to eliminate the humidity. The acetone desorption phase was dried with a small amount of anhydrous Na_2SO_4. An aliquot of 1.5 μL of the *n*-hexane and acetone extract was injected into a Shimadzu gas chromatograph equipped with a flame thermionic detector (FTD). The column used was a DB-1 (30m × 0.32 mm i.d.). The temperature program was 150 °C for 2 min, from 150 to 210 °C with a rate of 5 °C/min, at 210 °C for 10 min, from 210 to 270 °C with a rate of 10 °C/min, and at 270 °C for 3min. The temperatures were set at 250 °C for the injector and 300 °C for the detector.

RESULTS AND DISCUSSION

Adsorption Isotherms. The adsorption isotherms of herbicides for the soil mixtures with fly ash are shown in Figures 1(a–c) and 2(a–c). The Freundlich adsorption isotherm model could describe sorption equilibria

$$x/m = K_f \, C^{1/n} \qquad (1)$$

where x/m is the adsorbed amount (μg g⁻¹), C is equilibrium concentration (mg L⁻¹) and K_f is the adsorption constant that represents the degree or strength

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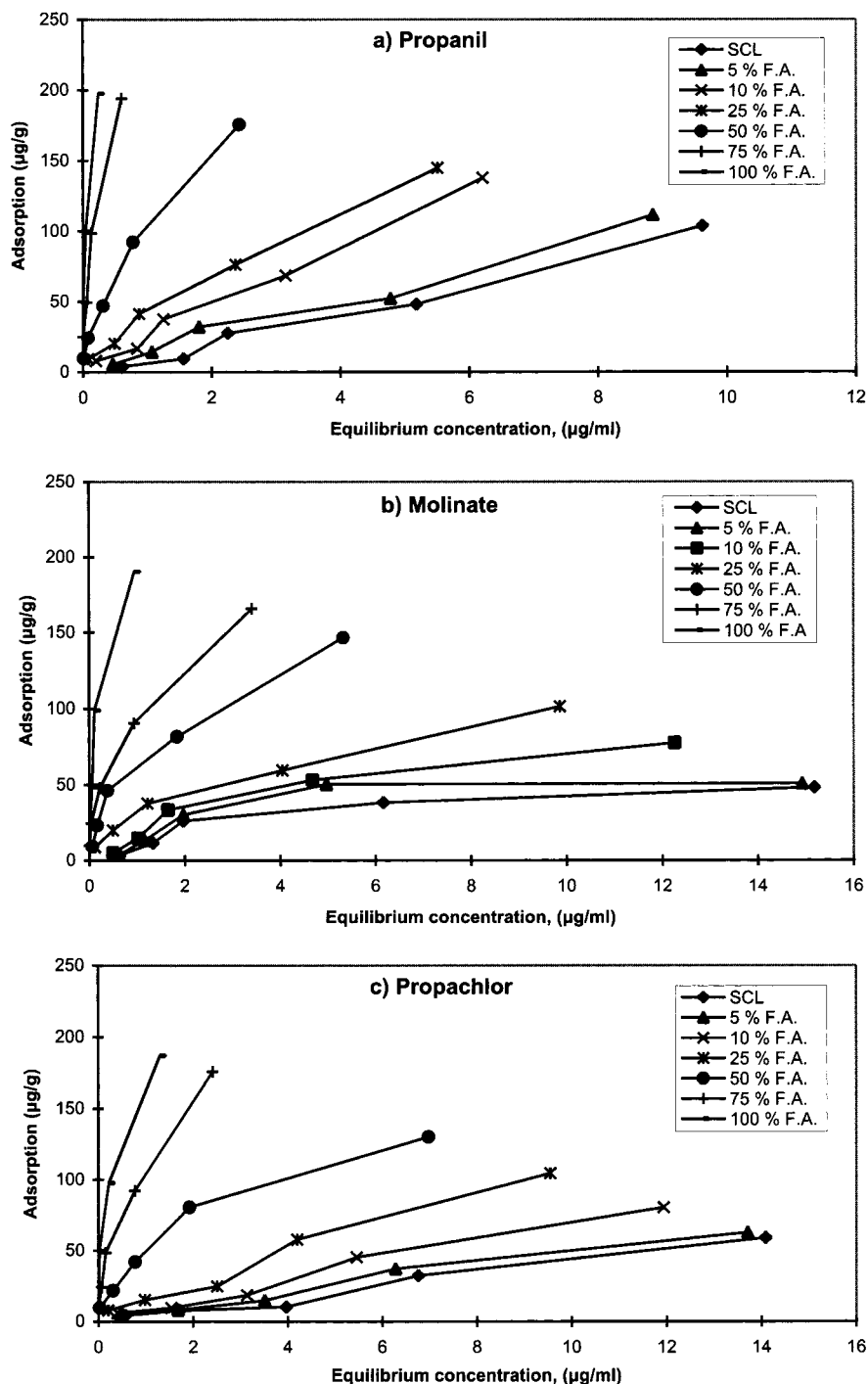
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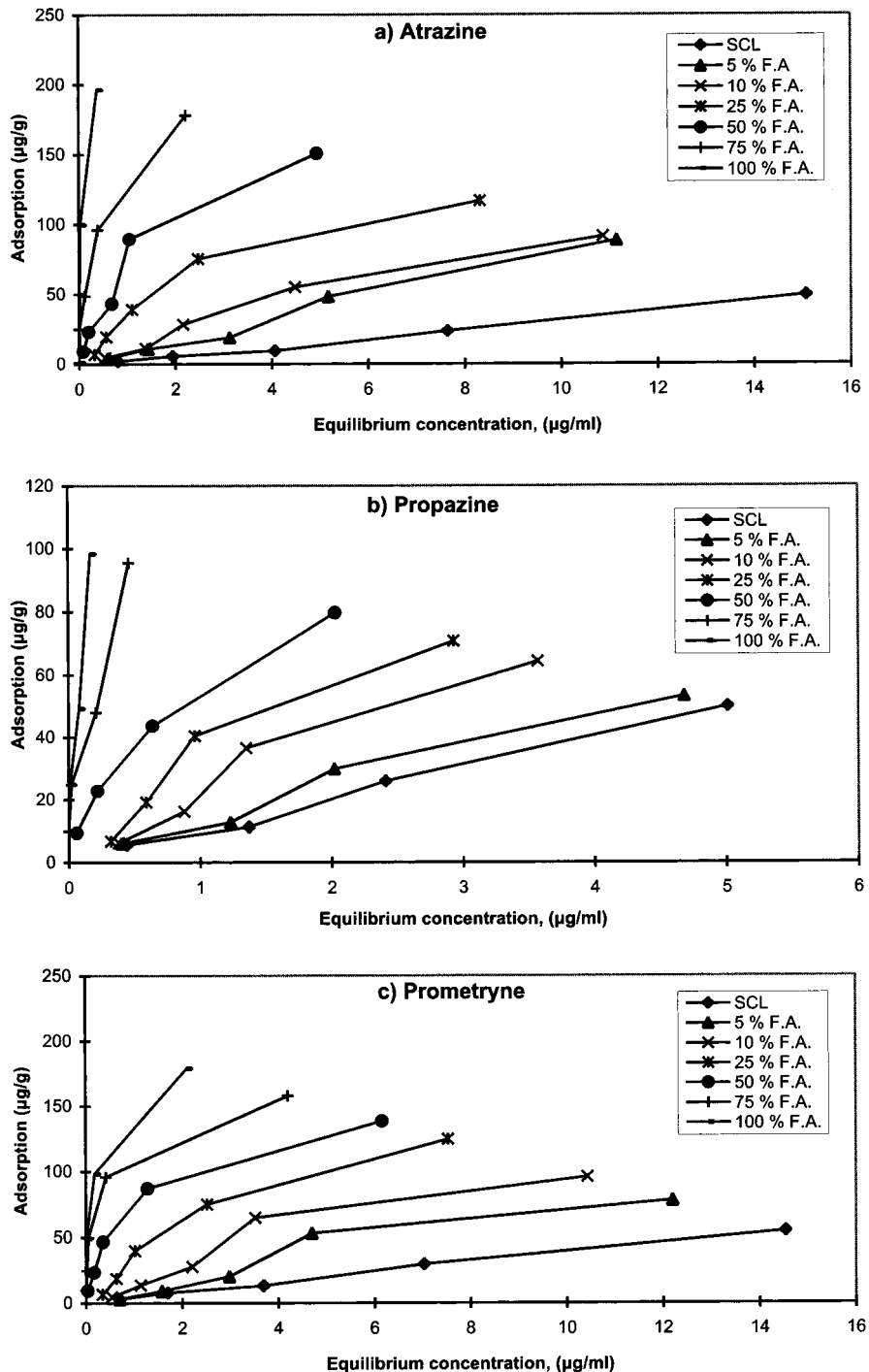
Figure 1. (a–c) Adsorption of s-triazine herbicides on mixtures of fly ash with SCL soil at 20 °C (*a*, atrazine; *b*, propazine; *c*, prometryne).

of adsorption. The high correlation coefficient ($R^2 > 0.91$) shows that the Freundlich isotherm model fits the experimental data reasonably well. The exponent $1/n$ takes into account the nonlinearity of the adsorption isotherm. When *n* ranged near unit, adsorption would be linearly proportional to the equilibrium solution concentration and thus, a partition coefficient (K_p) would be more appropriate to use (Seybold and Mersie, 1996). In Table 5 are presented the constants (K_f and *n*) along with correlation coefficients from the logarithmic form of the Freundlich equation, for fit of the isotherms to the adsorption data.

The adsorption of s-triazines herbicides is described by L or H shaped isotherms (Figure 1a-c), according to

Giles isotherm classification (Giles et al., 1960), as the substrate changes from SCL to fly ash, depending on the percent of fly ash in the mixture.Weber et al. (1969) and Calvet (1989) proposed also an L shaped isotherm for the adsorption of triazines in different soils. Generally, L shaped isotherms are observed when the molecules are adsorbed in a flat position, not suffering a strong competition from the solvent molecules, which explains the high affinity of sorbent for solute at low concentrations (Giles et al., 1960). As it is known, s-triazines could be adsorbed in the above way on the soil humic substances matrix. The adsorption on SCL soil could be described also by C shaped isotherm, which means a partition of the triazines between the bulk

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Figure 2. (a–c) Adsorption of herbicides on mixtures of fly ash with SCL soil at 20 °C (*a*, propanil; *b*, molinate; *c*, propachlor).

solution and the soil, especially the organic matter fraction. It happens frequently that adsorption isotherms are strictly L curves, but they are very close to C curves which can be taken as approximate descriptions (Calvet, 1989). Finally, H-type curves were observed in the 75% mixture and in fly ash, showing a high affinity of the adsorbent surface for the adsorbed solute. The shape of adsorption isotherms is an important characteristic because it provides information about adsorption mechanisms. The above mentioned classification is based on the initial slope, which is important because it depends on the rate of change of site availability (Calvet, 1989). The different adsorption mechanisms that operated for the selected herbicides on soil and fly ash may include ionic bonds, H-bonding,

van der Waals forces, and charge-transfer complexes, depending on the polarity of the solute and the sorbent (Torrents et al., 1997) and resulting in these alterations to the isotherm's form. Charge transfer (π) or van der Waals bonds could be formed between the aromatic nuclei of the herbicide and the aromatic rings of the organic matter surface. H–bonding could also be formed between the carbonyl oxygen in the amide group of anilide herbicides or the hydrogen in the amino group of triazines and the carboxyl or hydroxy groups presented in organic matter surface.

The adsorption of substituted anilides was described by S, L or H shaped isotherms (Figure 2a-b). In SCL soil and up to 25% content of fly ash, s-shaped isotherms are observed, meaning that adsorption becomes easier

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Table 5. Freundlich Constants K_f (mL g^{-1}) and n Values and Relative Correlation Coefficients of the Adsorption Isotherms

fly ash (%)	K_f	n	R^2	K_f	n	R^2	K_f	n	R^2
	atrazine			propazine			prometryne		
0	2.51	0.93	0.99	10.72	1.09	0.97	4.34	1.05	0.99
5	7.03	0.94	0.99	13.10	1.09	0.97	5.36	0.84	0.95
10	9.57	0.96	0.96	19.40	0.94	0.96	11.20	0.95	0.94
25	26.86	1.19	0.91	29.05	0.97	0.91	26.25	1.09	0.92
50	60.86	1.43	0.95	54.51	1.64	0.99	63.73	1.85	0.97
75	130.8	2.29	0.98	110.2	2.53	0.92	110.3	3.05	0.94
100	292.4	2.80	0.95	188.4	2.22	0.93	149.1	4.13	0.99
	propachlor			propanil			molinate		
0	5.49	1.21	0.91	7.14	0.84	0.97	7.77	0.88	0.94
5	7.54	1.31	0.93	13.26	1.02	0.97	9.25	0.82	0.91
10	9.60	1.25	0.93	26.99	1.19	0.97	13.48	0.96	0.92
25	18.71	1.46	0.94	42.85	1.51	0.98	29.59	1.83	0.99
50	49.57	2.01	0.98	100.48	1.90	0.99	60.62	1.71	0.97
75	110.9	1.90	0.98	273.3	1.75	0.96	95.09	2.33	0.99
100	166.9	3.21	0.99	323.7	2.8	0.99	209.9	2.18	0.96

as the concentration in the liquid phase increases. Otherwise, S type isotherms signify that the solid has a higher affinity for the solvent than for the solute at low concentrations. Literature shows that S-isotherms are often observed with clays and generally soils with low organic matter content, such as the SCL (Kozak et al., 1983; Crisanto et al., 1995; Weber and Peter, 1982). S curves are transformed to L curves for the 50% fly ash and H-curves for the 75% and 100% fly ash, showing a variation of adsorption mechanism from soil to fly ash. The −Si−O−Si-bonds of the clay minerals in soil and fly ash are hydrophobic in nature and thus, potential sites for the sorption of nonpolar compounds (Francioso et al., 1992; Chen, 1976). The variation of the adsorption isotherm for the mixtures up to 50% of fly ash content is probably due to the residual carbon content of fly ash which plays a significant role during the adsorption process as it is reported elsewhere (Mott and Weber, 1992). Except for organic carbon and silica or alumina, the other major chemical constituents of fly ash probably do not correlate clearly with the adsorption capacity (Banerjee et al., 1995).

Molinate presents the same behavior except in the case of the soil mixture with 25% fly ash content which gave an L type curve (Figure 2b). Analogous results for thiocarbamate herbicides were reported elsewhere (Singh et al., 1990). It is observed that the adsorption capacity of SCL and 5% and 10% of fly ash for molinate remain almost constant for initial solution concentrations over 10 ppm, probably owing to the lack of functional groups in the molecule that can interact mainly with the humic matrix and second with the fly ash particles. In Figure 3 is presented the relationship between K_f constants and the percent of fly ash content in the soil for each herbicide. A strong dependency of K_f on the fly ash content was found for all sorbed mixtures as elsewhere (Albanis et al., 1998). The relationship between K_f and fly ash content is exponential, except for prometryne,
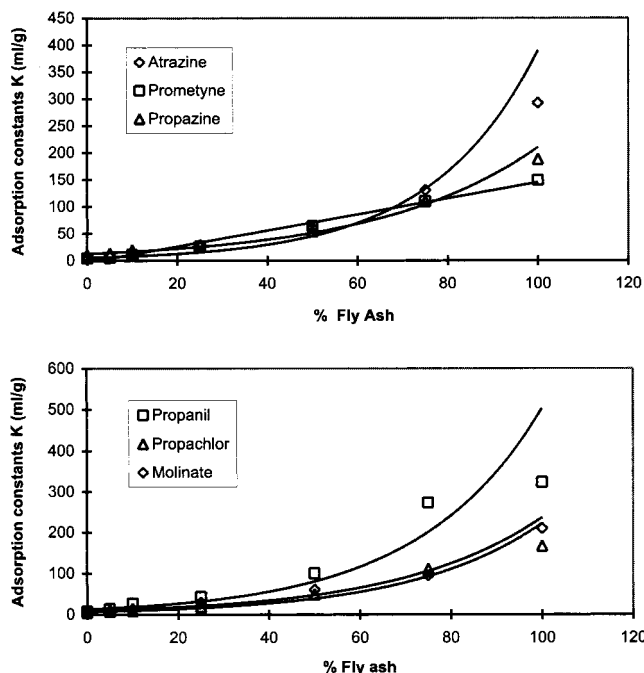
Figure 3. Relation between the adsorption constant K_f of selected herbicides on mixtures of fly ash with SCL soil.

Table 6. Partition Coefficient K_f Dependency of Fly Ash Content (% FA)[a]

herbicide	K_f	R^2
atrazine	$5.32\,e^{0.0429\,(\% FA)}$	0.939
propazine	$12.66\,e^{0.0281\,(\% FA)}$	0.987
prometryne	$1.49(\% FA) - 3.38$	0.990
propachlor	$6.77\,e^{0.0349\,(\% FA)}$	0.978
propanil	$12.88\,e^{0.0367(\% FA)}$	0.927
molinate	$9.48\,e^{0.0322\,(\% FA)}$	0.971

[a] (% FA), percentage of fly ash content in mixtures with soil.

for which a linear relation fits better. The corresponding partition coefficient equations for each herbicide, along with their correlation coefficients, are given in Table 6. At levels above the 25% mixture for s-triazines, and the 10% mixture for anilides and molinate, a bigger increase of K_f is observed. The n values ranged from 0.8 to 3.21. Similar K_f and n values were observed for other organic adsorbents with high specific surfaces such as activated carbon, peat, etc (Grover, 1974).
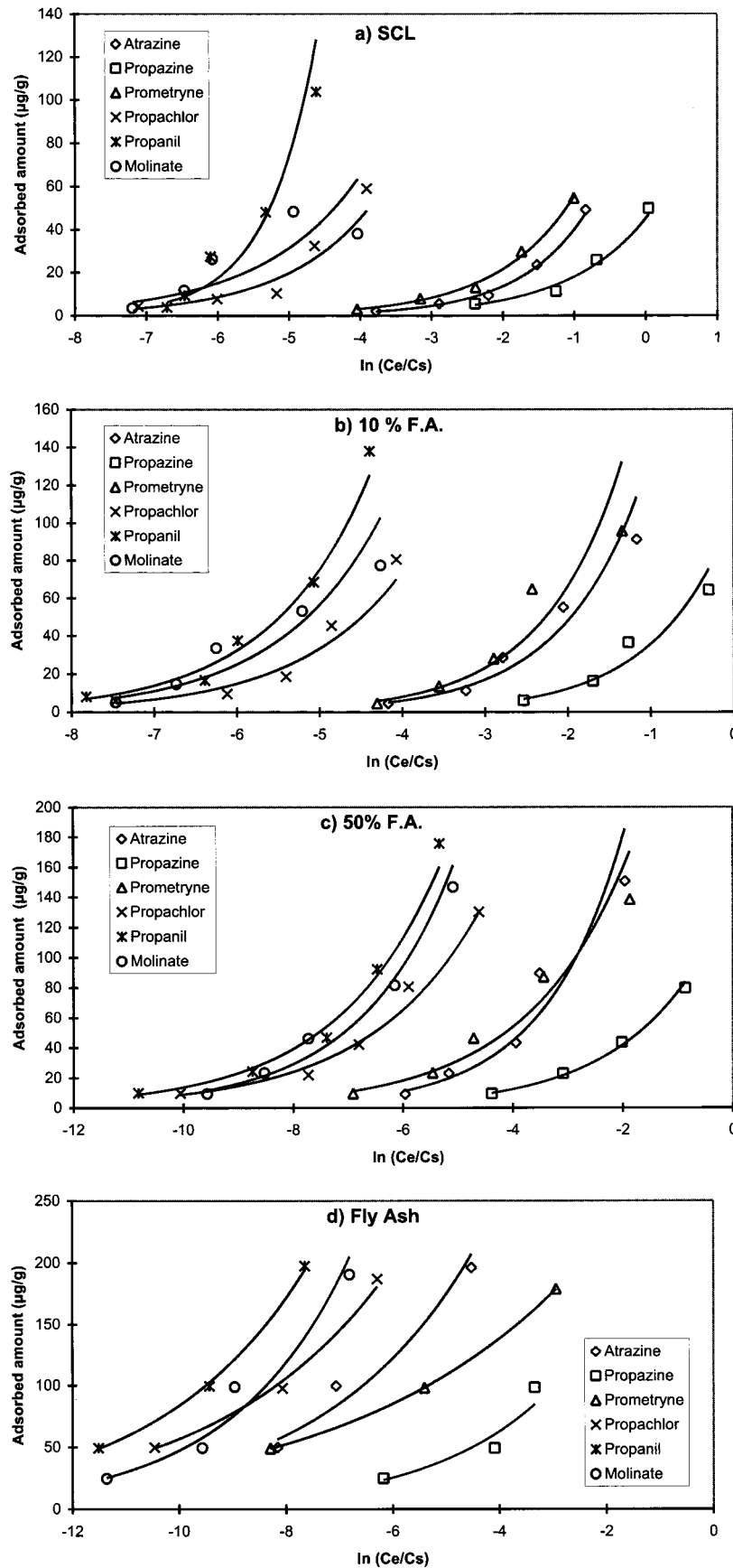
The relation describing the desorption of a given molecule can be properly illustrated in a different manner by normalizing the partition coefficient K_f constant to a 1 g fly ash basis, according to the equation

$$K_{FA} = \frac{K_F}{\%FA} \times 100 \qquad (2)$$

The normalized sorption coefficients appear to be less variable. In Table 7 are listed the values of the normal-

Table 7. Values of K_{FA} Coefficient for the Adsorption of Selected Hebicides in Soil− Fly Ash Mixtures

fly ash (%)	K_{FA}					
	atrazine	propazine	prometryne	propachlor	propanil	molinate
5	140.6	262.0	107.2	150.8	265.2	185.0
10	95.7	194.0	112.0	96.0	269.9	134.8
25	107.4	116.2	105.0	74.8	171.4	118.4
50	121.7	109.0	127.5	99.1	201.0	121.2
75	174.5	146.9	147.1	148.0	364.5	126.8
100	292.4	188.4	149.1	167.0	323.7	210.0
average value	155.4	169.4	124.6	122.6	265.9	149.4

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Figure 4. Panels a to c: Affinity of the selected herbicides for the fly ash mixtures with SCL soil.

ized sorption coefficient for the adsorption of the tested herbicides in soils with differing fly ash content.

To compare the intrinsic affinity of the adsorbent toward the adsorbate, one needs to replot the isotherms with regard to the degree of adsorption under saturation conditions, i.e., $\ln(Ce/Cs)$ (Michot and Pinnavaia, 1991; Cases, 1979), where Ce is the equilibrium concentration and Cs is the solubility limit of the adsorbate. Figure

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Table 8. Adsorbed, Desorbed with Water or Acetone, and Decomposed or Permanently Adsorbed Amounts (%) of Herbicides from Aqueous Solutions by Soil Mixtures with Fly Ash[a]

fly ash (%)	adsorbed (%)	desorbed in water (%)	desorbed in acetone (%)	decomposed or bound residues (%)
		Atrazine		
SCL (0)	21.89	10.70 (48.55)	2.14 (10.00)	9.05 (41.45)
5	42.79	10.21 (23.96)	4.99 (11.77)	27.59 (64.28)
10	49.69	10.40 (21.97)	9.47 (19.69)	29.82 (58.34)
25	71.46	9.59 (14.06)	28.70 (39.98)	33.17 (45.95)
50	86.84	5.58 (6.69)	63.94 (73.53)	17.32 (19.78)
75	96.52	1.81 (1.92)	85.06 (88.11)	9.65 (9.97)
100	99.52	0.29 (0.29)	93.70 (94.16)	5.53 (5.55)
		Propazine		
SCL (0)	50.73	13.05 (26.03)	8.70 (17.90)	28.98 (56.07)
5	55.90	11.17 (20.40)	11.93 (21.81)	32.80 (57.79)
10	66.03	10.38 (16.39)	17.15 (26.65)	38.50 (58.16)
25	73.98	9.28 (12.51)	33.63 (45.58)	31.08 (41.91)
50	88.03	5.28 (6.10)	59.00 (66.51)	23.75 (27.39)
75	97.60	2.53 (2.62)	79.33 (81.05)	15.75 (16.33)
100	99.08	0.43 (0.43)	89.65 (90.44)	9.00 (9.13)
		Prometryne		
SCL (0)	29.04	7.27 (24.85)	4.01 (13.86)	17.76 (61.30)
5	39.84	6.08 (16.78)	4.72 (12.33)	29.04 (70.89)
10	53.77	5.02 (9.89)	8.91 (17.05)	39.84 (73.06)
25	71.50	5.16 (7.47)	19.56 (27.15)	46.78 (65.38)
50	87.65	1.61 (2.05)	40.27 (45.87)	45.77 (52.08)
75	94.59	0.71 (0.82)	53.05 (56.01)	40.83 (43.17)
100	97.49	0.34 (0.38)	56.54 (57.89)	40.61 (41.73)
		Molinate		
SCL (0)	41.14	11.12 (28.04)	6.68 (16.79)	23.34 (55.16)
5	45.66	12.00 (29.49)	10.15 (23.09)	23.51 (47.42)
10	53.82	12.68 (24.2)	15.19 (29.02)	25.95 (47.59)
25	70.84	10.78 (15.46)	37.06 (51.79)	23.00 (32.75)
50	86.91	7.12 (8.29)	62.97 (71.67)	16.82 (20.04)
75	92.91	3.77 (4.19)	76.11 (81.25)	13.03 (14.56)
100	98.51	1.23 (1.26)	88.38 (89.59)	8.90 (9.15)
		Propachlor		
SCL (0)	31.35	7.32 (24.24)	2.09 (6.95)	21.94 (68.82)
5	37.05	6.67 (18.88)	5.05 (13.54)	25.33 (67.58)
10	44.26	6.80 (15.81)	8.75 (21.11)	28.71 (63.09)
25	59.97	6.08 (10.42)	16.61 (28.97)	37.28 (60.61)
50	82.96	4.45 (5.72)	49.79 (59.11)	28.72 (35.17)
75	94.88	2.75 (2.98)	61.43 (64.24)	30.70 (32.78)
100	98.02	1.12 (1.17)	65.35 (66.29)	31.55 (32.53)
		Propanil		
SCL (0)	46.34	11.56 (25.99)	12.83 (29.04)	21.95 (44.97)
5	56.63	10.38 (18.40)	24.37 (43.21)	21.88 (38.39)
10	71.77	9.88 (13.82)	36.80 (51.26)	25.09 (34.92)
25	80.75	7.58 (9.82)	59.13 (72.03)	14.04 (18.14)
50	93.93	2.17 (2.40)	73.23 (77.39)	18.53 (20.21)
75	98.90	0.77 (0.78)	88.15 (89.11)	9.98 (10.11)
100	99.66	0.15 (0.15)	94.03 (94.36)	5.48 (5.50)

[a] First entry (no parentheses) is the amount in regard to the initial concentration. Second entry (inside the parentheses) is the amount in regard to the adsorbed amount.
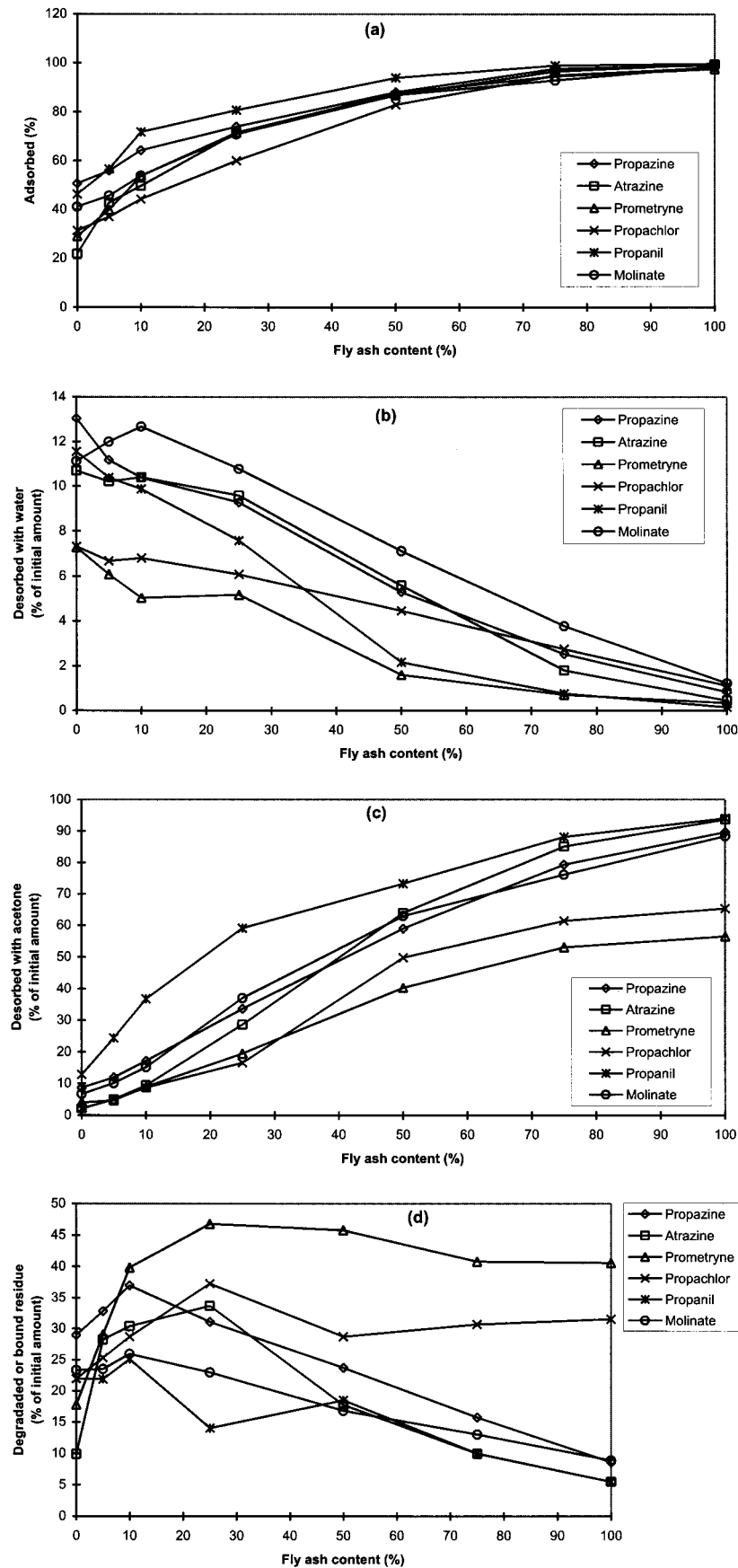
4(a−d) presents the results of such a treatment for SCL soil, fly ash, and the mixtures with 10% and 50% of fly ash. The affinity of the mixtures toward the pollutants increases in the order propazine > atrazine >prometryne and propachlor> molinate >propanil as the isotherms shift toward lower $\ln(Ce/Cs)$ values in that order. It is interesting to note that the isotherms are similar in shape with a small change in the case of molinate adsorption on soil. This suggests that the mechanism of adsorption is the same for all the herbicides (Michot and Pinnavaia, 1991).

The adsorption of herbicides is correlated with K_{oc} (see Table 1) values only in the case of SCL, showing that the adsorbed amount from water for a given equilibrium concentration is higher for the molecules that have bigger K_{oc} values. This suggests a partition of herbicides in the organic matter content of soil. The pH values of

soil mixture suspensions were between 7.75 and 11.82, and exceeded by more than one log unit the pK_a values for s-triazines. Thus, under pH conditions of soil and fly ash mixture suspensions these triazines will all be present mostly with the neutral form. This fact explains the similar behavior of different herbicides such as triazines and anilides that are not ionic herbicides.

Adsorption and Desorption Percent Balances. The mean percent balances for the adsorbed and desorbed amounts of herbicides, for five different concentrations in the range of 1−20 mg l^{-1} from the soils with different fly ash content are summarized in Table 8 and Figure 5(a−d).

The mean percent amounts of herbicides, for a range of concentration 1−20 mg L^{-1}, removed by adsorption in the soil were 21.9% for atrazine, 50.7% for propazine, 29.04% for prometryne, 43.14% for molinate, 31.35% for

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Figure 5. Percentage of herbicide adsorbed on mixtures of fly ash with SCL soil (panel a) and desorbed with water (panel b). Percentage of herbicide desorbed with acetone (panel c) and decomposed or bonded residues on mixtures of fly ash with SCL soil (panel d).

propachlor, and 46.34% for propanil. The adsorption increases as the fly ash content increases and reaches

the 99% in the "pure" fly ash. The desorbed amounts with 10 mL of water for all the tested herbicides

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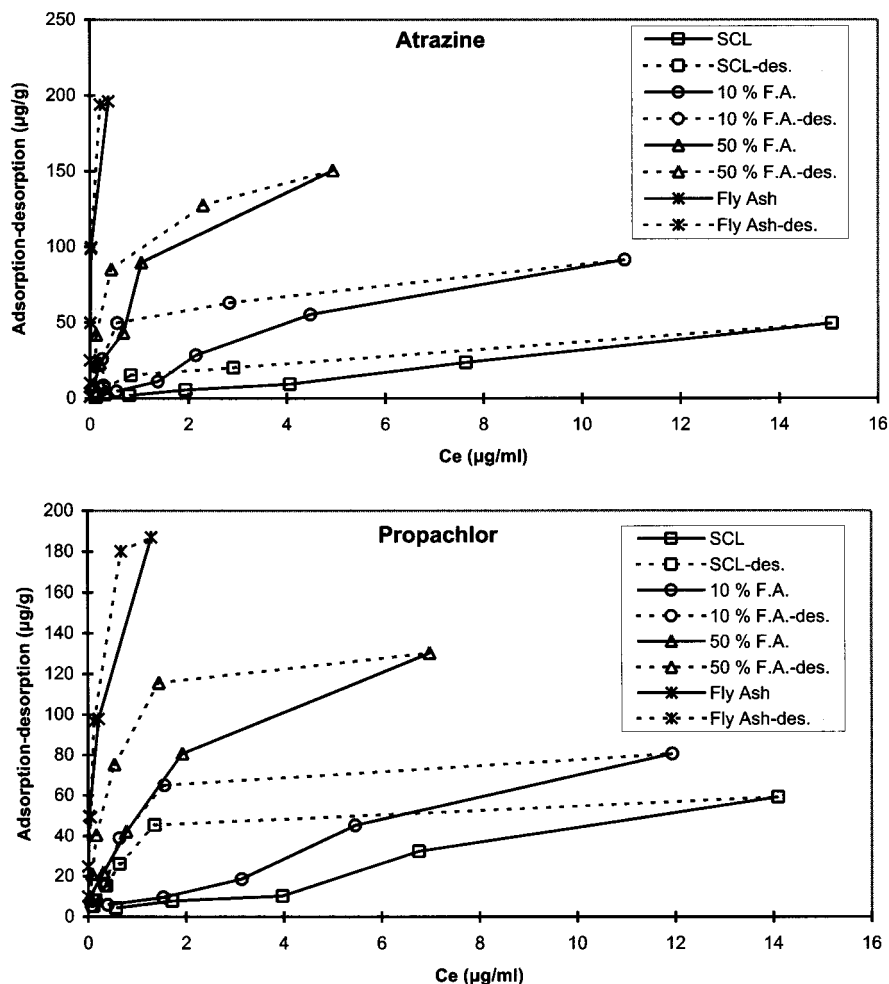
Figure 6. Desorption hysteresis of Atrazine and Propachlor from mixtures of fly ash with SCL soil.

Table 9. Free-Enthalpy Values for the Adsorption of the Selected Herbicides in Soil−Fly Ash Mixtures

mixture (% fly ash)	$\Delta G°$ (kcal mol^{-1}) ($T = 20$ °C)					
	atrazine	propazine	prometryne	propachlor	propanil	molinate
5	−2.93	−3.30	−2.77	−2.97	−3.30	−3.09
10	−2.70	−3.12	−2.79	−2.70	−3.31	−2.90
25	−2.77	−3.81	−2.75	−2.55	−3.04	−2.82
50	−2.84	−2.78	−2.87	−2.72	−3.14	−2.84
75	−3.06	−2.95	−2.95	−2.96	−3.49	−2.87
100	−3.36	−3.10	−2.96	−3.03	−3.42	−3.16

decreased as the fly ash content increase. The desorbed amounts in soil ranged from 10.7% for atrazine, 13.05% for popazine, and 7.27% for prometryne in soil, to 0.29%, 0.43%, and 0.34% in fly ash, respectively. The analogous percentages for the propachlor, propanil, and molinate ranged from 7.32%, 11.56%, and 11.12% to 1.12%, 0.15%, and 1.23% respectively. The desorption of 5 mL of acetone increases with increasing fly ash content. The percent amounts ranged from 2.14%, 8.7%, and 4.01% in soil to 93.7%, 89.65%, and 56.54% in fly ash for atrazine, propazine and prometryne, respectively. For propachlor, propanil, and molinate results were from 2.09%, 12.83%, and 6.68% in soil to 65.35%, 94.03%, and 88.38% in fly ash. In contrast, the amounts defined as decomposed or permanently adsorbed increased until the 10% mixture for anilides and molinate and until 25% mixture for s-triazines, decreasing for the rest of the mixtures. The above result is probably due to the complexation of herbicides with the humic substances and the contribution of fly ash, and it is mainly

expressed as bound residues and not as decomposed. The decrease of this percent for the mixtures up to 25% is due to the decrease of the soil contribution to the adsorption. For high percents of fly ash (over 50%) the high pH values may promote the hydrolysis of the herbicides (Albanis et al., 1985) but in very low levels the stability of s-triazines herbicides and anilide related herbicides may act against hydrolysis (Noblet et al., 1996; Kochany and Maguire, 1994).

As already stated, the desorption with water decreases with the fly ash content. Contrarily, the desorption with acetone increases with the fly ash content, showing a very reversible way of binding. Organic solvents such as methanol, acetone, and acetonitrile have been used to break bonds that water may not break (Clay and Koskinen, 1990; Singh et al., 1989). Acetone-desorbable herbicides may be desorbable with water, however, only after a much longer period of time (Clay and Koskinen, 1990; Smith, 1981).

The experimental results show that herbicide desorp-

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tion isotherms did not coincide with adsorption isotherms, indicating hysteresis. Hysteresis is often observed in pesticide adsorption–desorption studies with soils and with various adsorbents (Calvet, 1989). Measurement and interpretation of desorption data for solid–liquid systems are not well understood (Roy and Krapac, 1994; Clay and Koskinen, 1990). Hysteresis implies that a portion of the applied herbicide is very strongly or irreversibly bound to soil or may be degraded (Calvet, 1989). Hysteresis is strongly dependent on the adsorption mechanism. Once adsorbed, some adsorbates may react further with the surface with several interaction mechanisms according to their properties and the number of heterogeneous adsorbing sites on the soil with different adsorption energies (Raman et al., 1988).

In addition to this, the modifications that take place in the soil itself during the adsorption–desorption process (Calvet, 1989) and the changes in solution composition during desorption could contribute to the hysteresis. Soluble soil organic carbon decreases when 0.01 M $CaCl_2$ was used for the desorption replacement solution (Laird et al., 1994). However, experimental factors that can contribute to a hysteresis effect include nonattainment of equilibrium during the adsorption or desorption processes, formation of herbicide precipitates, and loss of herbicide due to chemical degradation or experimental error (Clay and Koskinen, 1990).

Hysteresis was more pronounced for the mixtures with a higher percent of soil than of fly ash. The corresponding curves are shown in Figure 6. The above observation provides evidence that the organic matter fraction of the soil is responsible for the presence of hysteresis. Other workers have similarly concluded that desorption hysteresis is associated with the organic matter percent (Singh et al., 1989; Peck et al., 1980; Torrents and Jayasundera, 1997). The lower hysteresis in fly ash implies that the sorption of herbicides is believed to occur principally via the weak induction forces of London or dispersion forces, which are characteristic of the physical adsorption process (Banerjee et al., 1995). The percentage of fly ash would probably affect the degradative capacity also. Assuming the adsorption of herbicides by fly ash, the change of free enthalpy ($\Delta G°$, 20 °C) of adsorption was calculated by using the value of K_{FA} in the following equation (Calvet, 1989).

$$\Delta G° = -RT \ln K_{FA} \qquad (3)$$

where ΔG is the free energy change (Kcal mol^{-1}), R is the gas constant (1.986 cal K^{-1}mol^{-1}), and T is absolute temperature. The free enthalpy values of herbicide adsorption by fly ash for the different percentages of fly ash are summarized in Table 9. These values of $\Delta G°$ vary between −2.70 and −3.81 for triazines and between −2.70 and −3.49 for anilides and molinate, are not significantly different from what was expected and are within the expected range for physical adsorption, providing evidence that sorption of herbicides on fly ash occurs through physical processes.

Environmental Relevance. The application of fly ash in agriculture as a fertilizer in order to improve the physical and chemical properties of soil is reported elsewhere (El-Mogazi et al., 1988). The increase of corn growth and yield was reported for soil amendments with fly ash compost in the 2–25% range (Ghuman et al., 1994). The uptake of K, Mn, and Cu was found to increase with increasing percentages of fly ash compost

in the same study. Fly ash applied in rates of 0–10% was found to increase plant-available soil boron (Kukler et al., 1994). Moreover, the utility of fly ash in soils at the rates of 0.2–30% was reported for the soil detoxification from 2,4-D, methyl parathion, alachlor, and metolachlor residues (Albanis et al., 1985; Albanis et al., 1992; Albanis et al., 1998).

In this study higher percentages of fly ash amendments and pure fly ash were tested for their adsorption–desorption behavior apart from the percentages commonly applied in agricultural practices, to describe the adsorption properties of fly ash. The results show that fly ash could be used for pesticide adsorption as an additive in acidic agricultural soils in order to decrease the leaching and persistence of organic chemicals to surface water and groundwater. Fly ash use as fertilizer could be safer, after pre-washing of easily released metals as Cr and Cu in alkaline conditions as it is reported in a previous study (Albanis et al., 1998).

CONCLUSIONS

Fly ash, raw material from thermal stations, influences strongly the adsorption of the studied herbicides in mixtures with soil systems. The results of the present batch experiments show that adsorption of the six studied herbicides is quite satisfactory in the case of soil mixtures with fly ash content up to 25% and exceeds 85% of the initial amount for the mixtures with 50–100% fly ash. The adsorption coefficient K_f show an exponential relation to the fly ash percent with sufficient correlation coefficients (R^2) that indicates the diversity of the mixtures substrate and the different adsorption mechanisms According to the above results, in the natural environment, soils with significant fly ash content are expected to immobilize these herbicides, preventing their movement to the water table. Finally, the results of this study demonstrate that fly ash has a significant capacity for adsorption of herbicides from aqueous solutions and possibly could be applied in organic waste immobilization.

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