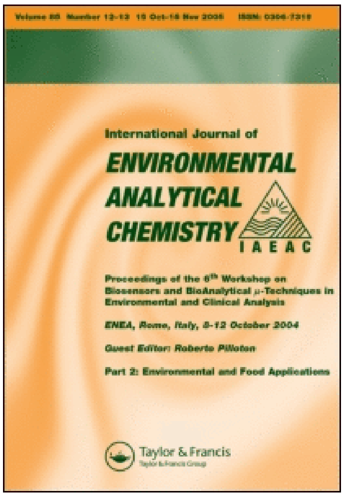

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A NEW ORGANOPHOSPHORUS INSECTICIDES REMOVAL PROCESS USING FLY ASH

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Fly ash and soil mixtures with a range of fly ash content from 1 to 100% were used to study adsorption and desorption of four organophosphorus insecticides, ethyl parathion, methyl parathion, fenitrothion and fenthion, in batch experiments. The object of the study was to develop a treatment process using fly ash as sorbent material to isolate/immobilize organic contaminants from aqueous solutions. The adsorption isotherms fit the Freundlich equation $x/m=K_dC^{1/n}$. The K_d values increase with the increase of the fly ash content. The isotherms seem to fit the S type, in mixtures of soil with a fly ash content from 0 to 10%, which implies that adsorption becomes easier as the concentration in the liquid phase increases. In mixtures of soil with a fly ash content from 25 to 50% the isotherms become L type and correspond to a decrease of site availability as the solution concentration increases. Finally in mixtures of soil with a fly ash content over 50%, C type adsorption was observed which correspond to a constant partition of the insecticides between the bulk solution and the adsorbent. Mass balance estimations show that the mean percent amounts of insecticides for a range of concentration 0.5–15 mg/l, removed by adsorption in the soil sample are 81.56 % for ethyl parathion, 48.97 % for methyl parathion, 67.06 % for fenitrothion and 86.65 % for fenthion. The adsorption increases as the fly ash content increased and reach the 100% in the "pure" fly ash. The adsorbed amounts of insecticides in mixtures of soils with >50% fly ash content, are up to 99%. In contrast, the amounts of desorption in water decrease as the fly ash content increase.

The results of this research demonstrate that the fly ash shows a significant capacity for adsorption of organophosphorus compounds from aqueous solution and can be used for pesticide removal process.

Keywords: Organophosphorus insecticides; adsorption- desorption; fly ash; soil mixtures

INTRODUCTION

Organophosphorus compounds are well known as powerful insecticides and have been widely used since the use of organochlorine pesticides was prohibited pesticides because of concerns over their persistence and bioaccumulation in the

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environment[1]. Parathion ethyl and parathion methyl two of the studied insecticides, are used at a rate of >1,100 tones per year in three Mediterranean countries, Italy, Greece and Spain[2]. Several oragnophopshorus insecticides as azinphos ethyl, azinphos methyl, diazinon, dimethoate, fenitrothion, fenthion, malathion, parathion ethyl and parathion methyl were detected in underground waters and surface waters in European countries[2–5]. In addition, in the surface organic microlayer of water bodies, pesticides can cause deleterious effects on fish embryos[6], and recent research has been carried out to bioassay the pesticides present in the surface organic microlayer[7]. Consequently, these compounds are of great environmental concern.

Most organophosphorus insecticides are regarded as being non-persistent, but several reports have indicated that residues of them are persisting for extent periods in organic soils[8–10] and surrounding drainage systems[11]. Hydrolysis, microbial degradation and photodegradation are the main transformation pathways. Study of interaction between soil clay minerals and pesticides is of great interest from two points of view: on one hand from the environmental aspect, since adsorption by soil colloids influences most processes determining the evolution of pesticides in the soil and on the other from the point of view of pest control, when pesticides are active in the ground, because effectiveness and frequency of application, apart from depending on the tendency of the pesticide to degrade, also depend on adsorption.

Coal fly ash, which is produced as a byproduct in power plants, has shown significant adsorption capacity for organic pollutants[12]. Fly ash has been used also to improve the physical and chemical characteristics of soils[13]. Apart from its use as a fertilizer in soil, fly ash has an increased capability in soil detoxification of methyl parathion residues[14]. Adsorption/ desorption of pesticides on organic and inorganic soil colloids represent a predominant process in controlling the fate of these chemicals in soil[15]. Results of leaching tests of metals from soil mixtures with fly ash have shown that as the fly ash content and pH values increase, the concentration of Mg, Mn and Fe decreases in the aqueous solutions by metal precipitation[16]. The concentration of Ni, Cu and Zn remains at low levels and the concentration of Cr increase due to the formation of more soluble metal species at high pH values. Fly ash use as fertilizer could be more safe, after prewashing o f easily released metals as Cr and Cu in alkaline conditions[16].

The purpose of this work is: 1) to quantify sorption properties of selected organophosphorus insecticides on soil and fly ash mixtures under batch conditions and 2) to study the influence of fly ash on adsorption and desorption of insecticides by its mixtures with soil. The desorption study was carried out in water and acetone in order to estimate the reversibility of the binding process.

EXPERIMENTAL

Soil and fly ash

A sandy clay loam (SCL) soil sample was collected from a field with no previous history of persistent pesticide use from the region of Preveza (Greece). Mechanical analysis of the soil show that the containing amounts of clay, silt and sand were 33.3 %, 24.0 % and 43.7 % respectively. Soil pH was 7.0, organic matter 0.90 % the $CaCO_3$ 0.63% and the specific surface area of the soil was 26.2 m^2g^{-1}. The fly ash was from the Thermal Station (raw material lignite) of the Public Organization of Electricity at Ptolemaida (Greece). Its chemical composition was a variety of oxides such as: SiO_2 (38.9 %), Fe_2O_3 (5.18 %), Al_2O_3 (19.5 %), TiO_2 (0.32 %), CaO (26.6 %), MgO (2.30 %), SO_3 (5.75 %) Na_2O (0.78 %) and K_2O (1.13 %). Fly ash and soil were mixed in order to achieve final concentrations of fly ash in the range of 0–100%. The pH values of SCL soil and fly ash mixtures were measured in suspensions with distilled water in a ratio 1:10 (w/v). The pH value for the pure soil suspension was 7.75. The pH values for the soil suspensions with 5, 10, 25, 50 and 75% fly ash content were 9.36, 10.97, 11.39, 11.68 and 11.70 respectively. At last the pH value for the pure fly ash suspension reached 11.82.

Chemicals

The tested insecticides in this study, ethyl parathion, methyl parathion, fenitrothion and fenthion were purchased from Riedel-de Haën (Seelze-Hannover, Germany) and used without further purification. The physicochemical properties of these insecticides are shown in Table I. Aqueous solutions of each insecticide were prepared in 0.01M $CaCl_2$ and the final concentrations were 1, 2.5, 5, 10, 15 mg/l for ethyl parathion, 0.5, 1, 2.5, 5, 10 mg/l for fenthion, 1, 2, 4, 8, 10 mg/l for methyl parathion and fenitrothion.

TABLE I Physicochemical properties of selected insecticides

	ethyl parathion	*methyl parathion*	*fenitrothion*	*fenthion*
Molecular weight	291	263	277	278
Solubility in water at 20°C (mg/l)	24	50	30	55
Log Kow[a]	3.8	2.9	3.4	4.1
Log Koc[b]	4.0	3.7	4.1	3.9

a. Log Kow, data of partition coefficients n-octanol-water from Noble (1993)[17].

b. Log Koc, data of sorption coefficient normalized to organic carbon content from Jury at al.[18] and Wauchop et al.[19].

Experimental procedures

The batch sorption experiments were carried out in 15 ml polypropylene centrifuge tubes where 1g of fly ash mixtures with soil and 10 ml of the above insecticides solutions were added. The centrifuge tubes were capped and shaken in a wrist-action shaker for 24 h at 20°C. Preliminary kinetic experiments had demonstrated that adsorption equilibrium was reached within 24 h. At the end of the equilibrium period, samples were centrifuged at 6000 g for 15 min and 5ml of the supernatant recovered with a pipette for determination of insecticide equilibrium concentration and pH. 10ml of 0.01 M $CaCl_2$ were added to the remaining soil, the centrifuge tube was capped and shaken for a further 3 h. Preliminary kinetic experiments had demonstrated that desorption equilibrium was reached within 3 h. After centrifugation the supernatant was taken for determination of insecticide desorption equilibrium concentration. A second desorption step was carried out using 5 ml of acetone and shaking for 30 min.

All the aqueous phases extracted 2 times with 2.5 ml n-hexane for 1 min with a vortex and the n-hexane extracts were transferred into another test tube with a few crystals of anhydrous Na_2SO_4. The acetone extracts after drying with anhydrous Na_2SO_4 were ready for the chromatographic analysis. 1.5 μl of the n-hexane and acetone extracts was injected into a Shimadzu 14A gas chromatograph equipped with a flame thermionic detector. The column used was a SPB-5 capillary, 30m × 0.32mm id contained 5% diphenyl-95% dimethylsiloxan (Supelco) and was programmed from 190°C (2 min) to 210°C (10 min) at 5°C/min and to 270°C at 20°C/min. The injector temperature was 220°C and detector at 250°C. Helium was the carrier and make up gas. The detector gases were hydrogen and air, and their flow rates were regulated according to results given through the simplex optimization of the analytical variables, in this instance air and hydrogen flow rates in the detector. The ion source of FTD was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire. Triplicate samples were measured for each initial concentration.

RESULTS AND DISCUSSION

Adsorption isotherms

The adsorption isotherms of insecticides, ethyl parathion, methyl parathion, fenitrothion and fenthion for the soil mixtures with fly ash are shown in Figures 1–4. The equilibrium adsorption data could be described by the Freundlich sorption isotherm:

$$x/m = K_f C_e^{1/n}$$

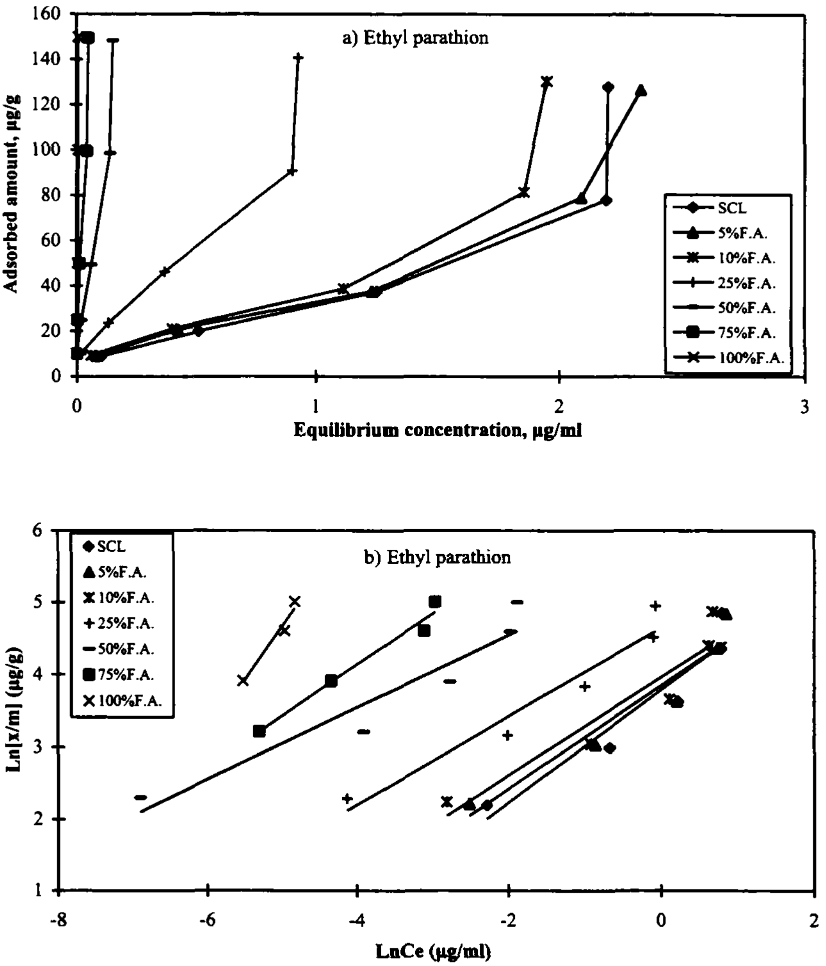

FIGURE 1 Adsorption of ethyl parathion on mixtures of fly ash with soil

where x/m is the adsorbed amount (µg g^{-1}), $C_e$is equilibrium concentration (mg l^{-1}) and K_f is the adsorption constant that represents the degree or strength of adsorption. The high correlation coefficient ($R^2 > 0.9$) show that the Freundlich isotherm model fits the experimental data reasonably well (Table II). The exponent 1/n takes in account non linearity in the adsorption isotherm. When n ranged near unit, adsorption would be linearly proportional to the equilibrium solution concentration and thus, a distribution coefficient (K_d) would more appropriate to use[20]. In Table II 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.

TABLE II Freündlich constants K_l (ml/g), n values and relative correlation coefficients for the adsorption of organophosphorus insecticides in mixtures of soil with fly ash

Fly ash (%)	*ethyl parathion*			*methyl parathion*		
	K_l	n	R^2	K_l	n	R^2
0	44.0	1.29	0.90	8.6	0.85	0.88
5	46.7	1.41	0.92	19.8	1.11	0.97
10	52.5	1.48	0.89	31.2	0.94	0.99
25	103	1.64	0.94	256	1.00	0.95
50	253	2.01	0.91	1939	1.32	0.99
75	1072	1.41	0.98	180954	0.74	0.96
100	176310	0.67	0.96	n.c	n.c	n.c

Fly ash (%)	*fenitrothion*			*fenthion*		
	K_l	n	R^2	K_l	n	R^2
0	21.5	1.30	0.91	88.7	0.81	0.97
5	29.6	1.43	0.84	93.0	0.97	0.95
10	42.3	1.16	0.99	139	0.81	0.97
25	103	1.68	0.93	299	1.10	0.95
50	1329	1.32	0.88	485	1.49	0.99
75	8903	1.18	0.74	20698	0.76	0.99
100	n.c	n.c	n.c	n.c	n.c	n.c

n.c.= no calculated due to the total adsorption of insecticides on adsorbent material.

The adsorption of organophosphorus insecticides described by S, L and C shaped isotherms. In SCL soil and until 10% content of fly ash S shaped isotherms are observed, that means adsorption becomes easier 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 as the SCL[21–23]. S curves are transformed to L curves for the soil mixtures with 25–50 % fly ash content and C curves for the fly

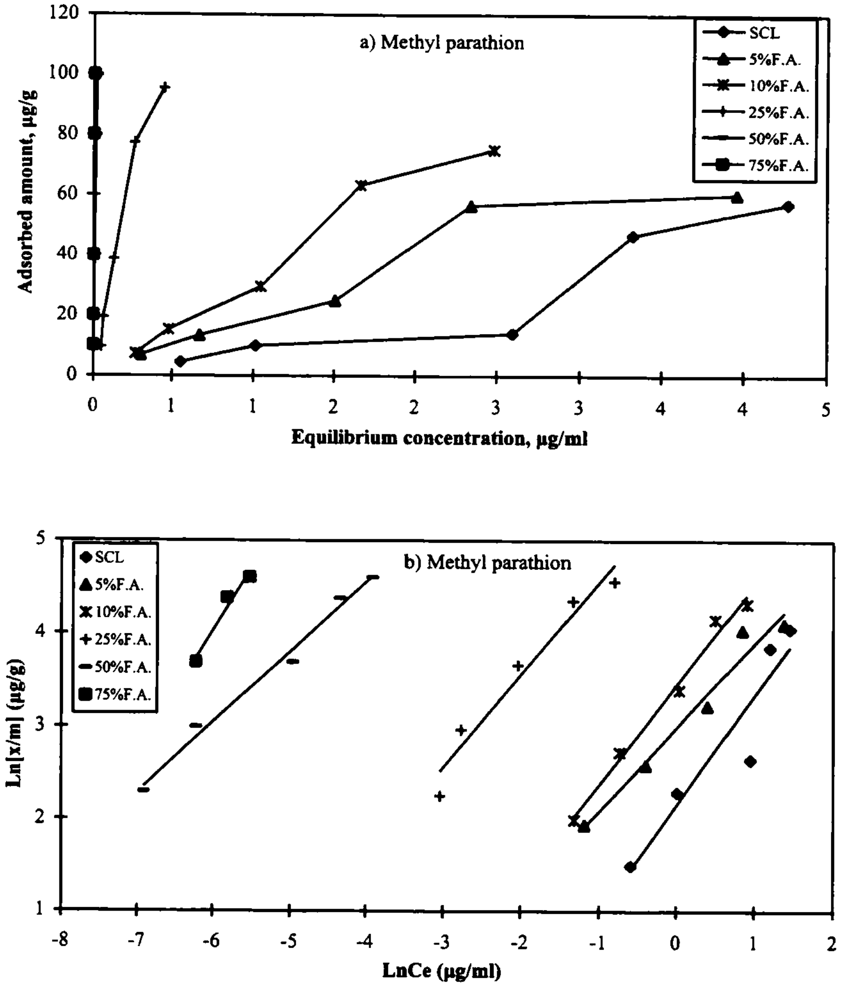

FIGURE 2 Adsorption of methyl parathion on mixtures of fly ash with soil

ash content over 50 %, 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 non-polar compounds[24,25]. 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[26]. Except for organic carbon and silica or alumina, the other major chemical constituents of fly ash did not correrate clearly with the adsorption capacity[27].

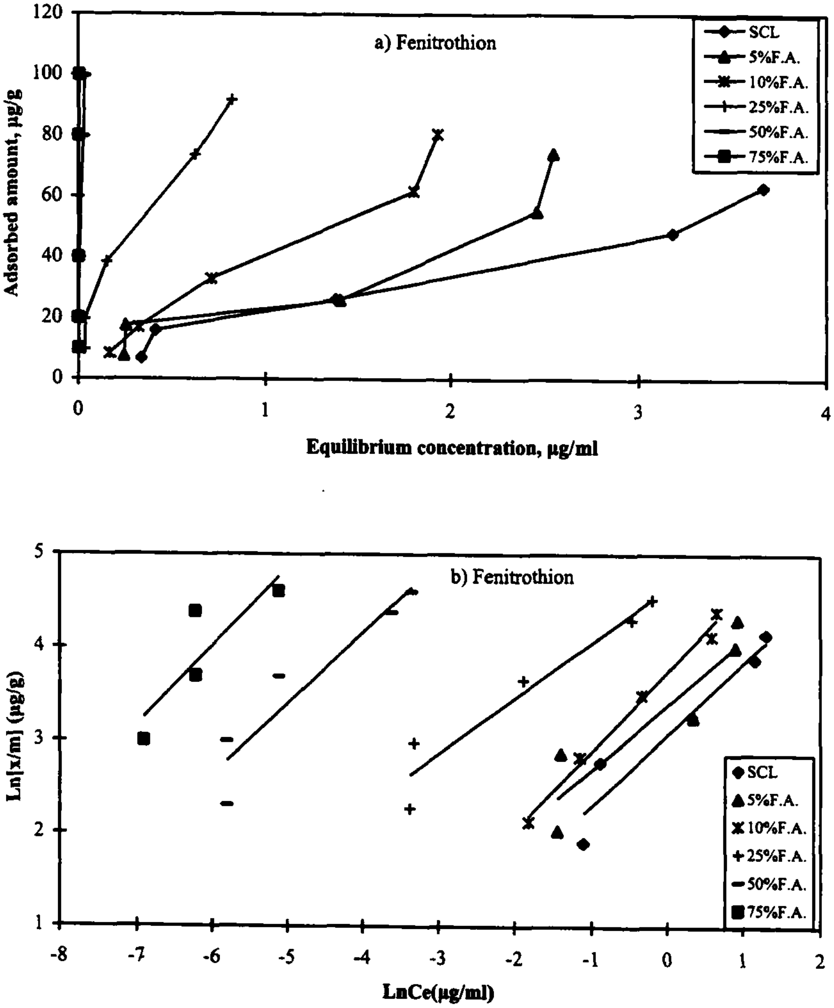

FIGURE 3 Adsorption of fenitrothion on mixtures of fly ash with soil

The mechanism of sorption of insecticides, for a fly ash mixture with soil from 0 to 10%, behaved in a manner that is consistent with concept of solute partitioning which is presumed to be analogous to the partitioning between octanol and water. The K_{ow} values (Table I) of the insecticides indicate that the amount adsorbed from water for a given equilibrium concentration should increase in the order methyl parathion < fenitrothion < ethyl parathion < fenthion. The pH values of soils mixture suspensions were between 7.75 and 11.82. The hydrolysis rate of organophosphorus insecticides increase with pH values[28–30]. The hydrolysis constant rates (k) increase from 0.0095 to 0.0252 for ethyl parathion, from 0.0139 to 0.0565 for methyl parathion, from 0.0147 to 0.0588 for fenthion and from 0.0176 to 0.0646 for fenitrothion as the pH values increase from 6.95 to 10[31]. The percentage amount of insecticides hydrolyzed at sorption experimental conditions for 24 hours was 4 and 5 % for ethyl parathion, 3 and 4 % for methyl parathion, 8 and 10 % for fenitrothion and 8 and 14% for fenthion at pH value 6.95 and 10 respectively[31].

A strong dependency of K_d on the fly ash content was found for all sorbed mixtures as elsewhere[16]. The relationship between K_d values for organophosphorus insecticides and fly ash content in mixtures with soil is exponential, with high correlation coefficients. The corresponding equations for each insecticide along with correlation coefficients are represented in Table III. The K_d values increase with the increase of fly ash content.

TABLE III Partition coefficient K_d dependency of fly ash content (%F.A)

ethyl parathion	$K_d = 22.25\ e^{0.072(\%F.A)}$	R^2=0.86
methyl parathion	$K_d = 8.84\ e^{0.126(\%F.A)}$	R^2=0.98
fenitrothion	$K_d = 18.75\ e^{0.082(\%F.A)}$	R^2=0.99
fenthion	$K_d = 63.73\ e^{0.066(\%F.A)}$	R^2=0.88

where (%F.A) = Percentage of fly ash content in mixtures with soil.

Percent balances of adsorption and desorption

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

$$[\text{Initial amount}] = [\text{Free amount}] + [\text{Adsorbed amount}].$$

The adsorbed amount could be analyzed as follows:

$$[\text{Adsorbed amount}] = [\text{Desorbed amount with water}] + [\text{Desorbed amount with acetone}] + [\text{Decomposed or bound residues}].$$

The decomposed or the bound residues amount is calculated from the difference between adsorbed amount and the sum of the desorbed with water and acetone amounts. The hydrolyzed amount of insecticides is smaller and included in decomposed and/or bound residues of studied compounds. The mean percent balances for the adsorbed and desorbed amounts of insecticides, for five different concentrations at the range of 0.5–15 mg/l, from the soils with different fly ash

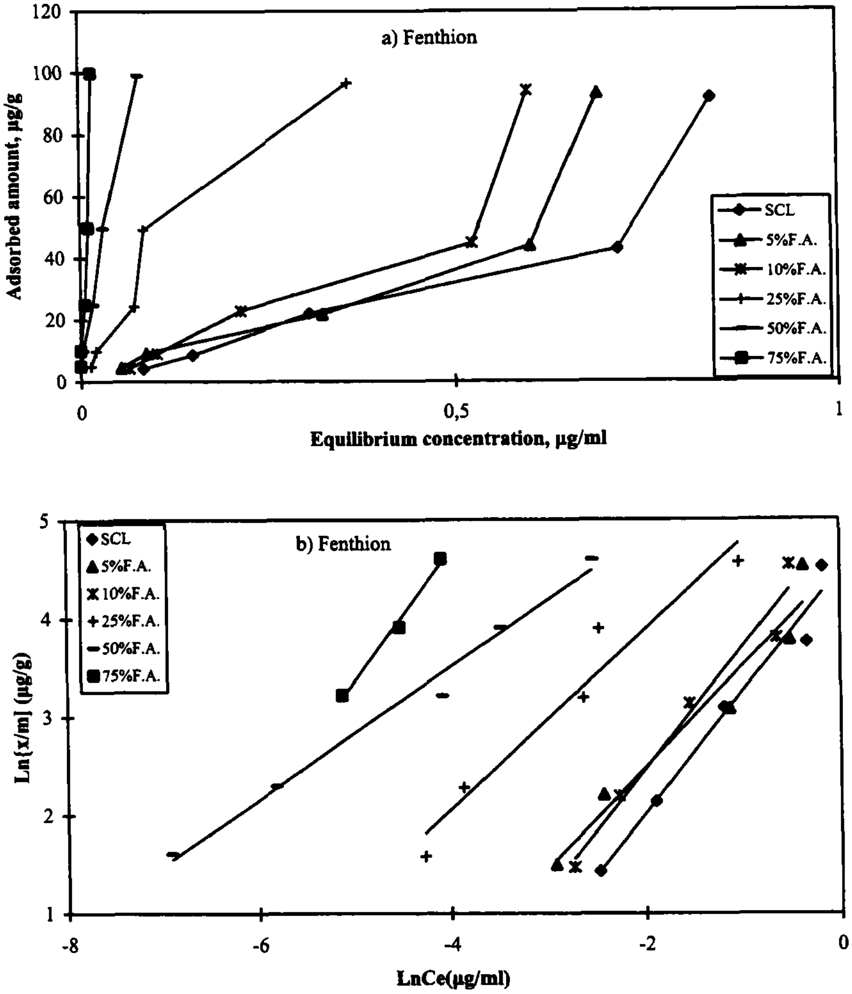

FIGURE 4 Adsorption of fenthion on mixtures of fly ash with soil

content are summarized in Table IV. In this table, out of the parentheses, are listed the amounts in regard to the initial concentration, and inside the parentheses are listed the amounts in regard to the adsorbed amount. As we have already concluded from the partition coefficient K_d, the adsorption increases as the fly ash content increase. The mean percent amounts of insecticides for a range of concentration 0.5–15 mg/l, removed by adsorption in the soil sample are 81.6 % for ethyl parathion, 49.0 % for methyl parathion, 67.1 % for fenitrothion and 86.6 % for fenthion. The adsorption increases as the fly ash content increased and reach the 100% in the "pure" fly ash. The desorbed amounts with 10 ml water for all the tested insecticides decreased, as the fly ash content increase. The percent amounts in soil ranged from 11.0 % for ethyl parathion, 13.2 % for methyl parathion, 11.2 % for fenitrothion and 10.9 % for fenthion to 0.03 %, 0.02 %, 0.00 % and 0.01 % in fly ash respectively. The desorption with 5 ml acetone increase in general with the increase of fly ash content until a value which reaches a plateau and no more desorption can exist. The analogous percentages of insecticides vary in order, fenitrothion<methyl parathion<ethyl parathion<fenthion, from 16.7%, 18.7 %, 23.7 % and 30.2 % to 49.3 %, 40.2 %, 52.7 % and 54.7 % respectively. Finally, the insecticide amounts defined as decomposed or permanent adsorbed were in relative high levels for all tested compounds, 59.8 % for methyl parathion, 50.7 % for fenitrothion, 47.2 % for ethyl parathion and 45.3 % for fenthion, in the sample of "pure" fly ash (Table IV).

TABLE IV Adsorbed, desorbed with water and acetone and decomposed or permanently adsorbed amounts of insecticides, from aqueous solutions, by soil mixtures with fly ash

Fly ash (%)	*% Adsorbed*	*% Desorbed in water*	*% Desorbed in acetone*	*% Decomposed or bound residues*
		Ethyl parathion		
0	81.6	11.0 (13.8)	23.7 (29.7)	46.8 (56.4)
5	82.8	9.07 (11.3)	33.8 (41.1)	39.9 (47.6)
10	84.8	7.49 (9.07)	39.5 (46.7)	37.8 (44.2)
25	94.1	2.19 (2.36)	50.7 (53.8)	41.2 (43.8)
50	99.1	0.70 (0.71)	55.2 (55.7)	43.2 (43.6)
75	99.6	0.23 (0.23)	53.7 (53.8)	45.8 (45.9)
100	100.0	0.03 (0.03)	52.7 (52.7)	47.2 (47.2)
		Methyl parathion		
0	49.0	13.2 (27.6)	18.7 (40.6)	17.1 (31.8)
5	65.9	11.2 (16.9)	30.4 (46.7)	24.2 (36.4)
10	75.5	7.56 (10.0)	36.0 (48.0)	31.9 (41.9)
25	96.2	1.54 (1.60)	47.6 (49.5)	47.1 (48.9)
50	99.8	0.17 (0.17)	41.6 (41.7)	58.1 (58.2)
75	100.0	0.08 (0.08)	39.9 (39.9)	60.0 (60.0)
100	100.0	0.02 (0.02)	40.2 (40.2)	59.8 (59.8)

Fly ash (%)	*% Adsorbed*	*% Desorbed in water*	*% Desorbed in acetone*	*% Decomposed or bound residues*
		Fenitrothion		
0	67.1	11.2 (17.1)	16.7 (25.4)	39.2 (57.5)
5	74.5	10.2 (14.1)	29.0 (38.8)	35.3 (47.1)
10	81.6	6.49 (8.00)	52.1 (63.7)	23.0 (28.3)
25	95.0	1.29 (1.38)	45.4 (47.9)	48.3 (50.8)
50	99.7	0.21 (0.21)	54.4 (50.8)	45.1 (37.1)
75	100.0	0.02 (0.02)	49.6 (49.6)	50.3 (50.4)
100	100.0	0.00 (0.00)	49.3 (49.3)	50.7 (50.7)
		Fenthion		
0	86.6	10.9 (12.6)	30.2 (35.0)	45.5 (52.3)
5	89.7	7.05 (7.94)	42.6 (47.8)	40.1 (44.3)
10	90.3	5.19 (5.73)	39.7 (44.1)	45.5 (50.2)
25	97.4	1.77 (1.82)	55.0 (56.5)	40.6 (41.7)
50	99.5	0.49 (0.50)	49.3 (48.7)	50.6 (50.8)
75	99.9	0.13 (0.13)	47.3 (47.3)	52.5 (52.6)
100	100.0	0.01 (0.01)	54.7 (54.7)	45.3 (45.3)

*Out of the parentheses are the amounts in regard to the initial concentration and inside the parentheses are the amounts in regard to the adsorbed amount.

As it is already stated the desorption with water decreases with the fly ash content. Contrary, the desorption with acetone increase with the fly ash showing a most reversible way of binding. Organic solvents such as methanol, acetone and acetonitrile have been used to break bonds that water may not break[32]. Acetone-desorbable insecticide may be desorbable with water, however, only after a much longer time period.

These results show that fly ash could be used for organophorphorus insecticides adsorption as additative in acidic agricultural soils in order to decrease their leaching and persistence to surface and underground waters. According to the above conclusions, in the natural environment, soils with high fly ash content are expected to immobilize the insecticides, preventing their movement to water table. In contrast, in soils with very low fly ash content, insecticides are likely to be detected in deeper soil layers. Fly ash use as fertilizer could be more safe, after prewashing of easily realeased metals as Cr and Cu in alkaline conditions[16].

CONCLUSIONS

Fly ash, a raw material from thermal stations influence strongly the adsorption of the studied organophosphorus insecticides in mixtures with soil systems. The results of the present batch experiments show that the soil mixtures with fly ash from 25 to 100 % by weight, gave an adsorption capacity which allows the total removal of insecticides from aqueous solutions. The alterations of isotherms as the fly ash content increases may be due to the high initial concentrations of the insecticides used. Mass balance estimations show that the adsorbed amounts of insecticides by soil mixtures with 100 % fly ash content, reach almost 100 % for all the tested compounds. The adsorption coefficient K_d 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 high fly ash content are expected to immobilize these insecticides, preventing their movement to the water table. In contrast, in soils with very low fly ash content the insecticides are likely to be detected in deeper soil layers. Finally, the results demonstrate that fly ash could be used as sorbent material to isolate/immobilise organic contaminants.

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References

[1] S.C. Schimmel, R.L. Garnas, J.M. Patrick Jr., and J.C. Moore, *J. Agric. Food Chem.* **31**, 104–113 (1983).

[2] M. Fielding, D. Barcelo, A.,Helweg, S. Galassi, L. Torstensson, P. Van Zoonen, R. Wolter and G. Angeletti *in Pesticides in ground and drinking water, Water Pollution Research Report 27*, Commission of the European Communities, 1991.

[3] T.A. Albanis, P.J. Pomonis and A.T. Sdoukos, *Chemosphere* **8**, 1023–1034 (1986).

[4] T. Albanis, T. Danis, D. Voutsa and T. Kouimtzis, *J. Environ. Sci. Health* **30**, 1945–1956 (1995).

[5] T.A. Albanis, D.G. Hela, T.M. Sakellarides and I.K. Konstantinou, *J. Chromatogr.* **823**, 59–71 (1998).

[6] H. Von Westernhagen, M. Landolt, R. Kocan, G. Fuerstenberg, D. Jansen and K. Kremling, *Mar. Environ. Res.* **23**, 273–290 (1987).

[7] P.D. Premdas and B.A. Kendrick, *Environ. Monit. Assess.* **22**, 169–180 (1992).

[8] S. Saltzman, B. Yaron, and U. Mingelgrin, *Soil Sci. Soc. Amer. Proc.* **38**, 231–234 (1974).

[9] C.R. Harris and J.R.W. Miles, *Residue Rev.* **57**, 27–79 (1975).

[10] J.R.W. Miles, C.R. Harris and P. Moy, *J. Econ. Entomol.* **71**, 97–101 (1978).

[11] J.R.W. Miles and C.R. Harris, *J. Econ. Entomol.* **71**, 125–131 (1978).

[12] S. Kumar, S.N. Upadhay and Y.D. Upadhya, *J. Chem. Tech. Biotechnol.* **37**, 281–290 (1987).

[13] D. El-Mogazi, D.J. Lisk and L.H.A. Weinstein, *Sci. Total Environ.*, **74**, 1–37 (1988).

[14] T.A. Albanis, P.J. Pomonis and A.T. Sdoukos, *J. Toxicol. Environ. Chem.* **17**, 351–362 (1985).

[15] J. Kozak, In: *Humic Substances in Terrestrial Ecosystems* A. Piccolo (ed.) Elsevier, pp. 625–664, Amsterdam, 1996.

[16] T.A. Albanis, T.G. Danis and M.G. Kourgia, *Environm. Technol.* **19**, 25–34 (1998).

[17] A. Noble, *J. Chromatogr.* **642**, 3–14 (1993).

[18] W.A. Jury, D.D. Focht and W.J. Farmer, *J. Environ. Qual.*, **16**, 422–428 (1987).

[19] R.D. Wauchope, T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers and J.P. Burt, *Rev. Environ. Cont. Toxicol.* **123**, 1–164 (1992).

[20] C.A. Seybold and W. Mersie, *J. Environ. Qual.* **25**, 1179–1185 (1996).

[21] K.S. Reddy, R.P. Gambrell, *Agric. Ecosyst. Enviorn.* **18**, 231–241 (1987).

[22] T. Crisanto, M. Sanchez-Camazano, M. Arienzo, M.J. Sanchez-Martin, *Sci. Total Environ.* **166**, 69–76 (1995).

[23] B.M. Gawlik, E.A. Feicht, W. Karcher, A. Kettrup, H. Muntau, *Chemosphere* **36**, 2903–2919 (1998).

[24] O. Francioso, E. Bak, N. Rossi and P. Sequi, *Sci. Total Environ.* **123/124**, 503–512 (1992).

[25] N.Y. Chen, *J. Phys. Chem.* **80**, 60–64 (1976).

[26] H.V. Mott and J.W. Weber, *Environ. Sci. Technol.* **26**, 1234–1242 (1992).

[27] K. Banerjee, P.N. Cheremisinoff and S.L. Cheng, *Environ. Sci. Technol.* **29**, 2243–2251 (1995).

[28] T. Wang, T. Kadlac and R. Lenahan, *Bull. Environ. Contam. Toxicol.* **42**, 389–394 (1989).

[29] S. Lacorte and D. Barcelo, *Environ. Sci. Technol.* **28**, 1159–1163 (1994).

[30] R. Garcia-Repetto, D. Martinez and M. Repetto, *Vet. Human Toxicol.* **36**, 202–204 (1994).

[31] T.M. Sakellarides, Ph.D. Thesis, University of Ioannina, Ioannina (2000).

[32] S.A. Clay and W.C. Koskinen, *Weed Science* **38**, 74–80 (1990).