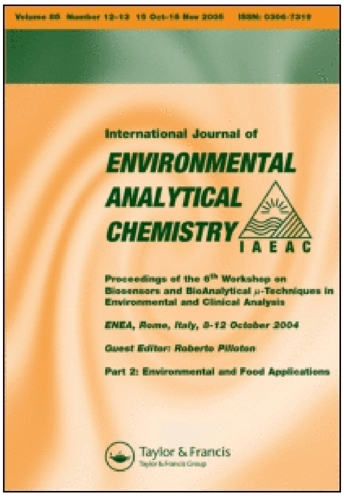

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Adsorption and desorption processes of the organophosphorus pesticides, dimethoate and fenthion, onto three Greek agricultural soils

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Adsorption and desorption processes of the organophosphorus pesticides, dimethoate and fenthion, onto three Greek agricultural soils

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Laboratory studies were conducted to determine the sorption and desorption behaviour of two commonly used organophosphorus pesticides dimethoate and fenthion, which are widely used in the studied area to treat the olivetrees. Three Greek soils from the region of Mytilene island (denoted M, KT and P) which differed with respect to pH (pH 5.45–6.90), clay content (6–26%), organic matter content (1.0–4.2%), cation exchange capacity (4.8–24.4 meq/100 g) and specific surface (10.79–109.22 $m^2 g^{-1}$) were selected for the experimental section that was conducted using the batch equilibrium technique. The sorption isotherms could be described by Freundlich and Langmuir equations for both compounds with correlation regression coefficients for fit of the isotherms to that models $R^2 \geq 0.9666$ and $R^2 \geq 0.8117$, respectively. Freundlich sorption coefficients K_f were normalised to soil organic matter content and K_{OM} estimated values for M, KT and P soils respectively were 60.19, 163.58 and 663.43 for dimethoate and 1365.84, 820.73 and 2902.52 for fenthion. Desorption studies revealed that dimethoate was adsorbed very weakly on soils tested and easily desorbed with water, while on the contrary fenthion was adsorbed very strongly on studied matrices with acetone extractable amounts.

Keywords: organophosphorus pesticide; adsorption; desorption; soils; partition coefficient; Langmuir isotherms; Freundlich isotherms

1. Introduction

Among the various processes that affect the fate of organic pesticides in soil environments, volatilisation, adsorption and desorption, chemical and biological degradation, and finally transport including leaching, preferential flow and run-off are considered as the most important ones. All of the above mentioned processes are more or less interdependent and several interactions exist between them [1,2]. Adsorption by soil is one of the major processes affecting the interactions among pesticides, soil water and the immobile and mobile solid phases of a soil [3,4]. Adsorption and desorption processes of chemicals have an effect on transport processes and on their bioavailability. In several environmental ecosystems adsorption in general reduces the concentration of the chemical in the

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aqueous phase. Factors governing pesticide sorption onto soil include organic matter and clay contents, soil pH, soil water content and soil temperature, but also the structure of the pesticide [5]. Structural factors such as the pesticide's molecular size, hydrophobicity, molecular charge, hydrogen bonding, arrangement and interactions of molecular fragments and its coordination are reported in the literature to influence the adsorption process [6]. The pesticide sorption process incorporates a wide range of different chemical mechanisms including ion exchange, cation-bridging, ion-dipole interactions, ligand exchange, charge transfer, hydrogen bonding and van der Waals' forces [7,8].

Organophosphorus compound is the general name for a large group of organic compounds containing phosphorus. A number of these compounds are used by industry and are known as non-pesticides, while other phosphorus-containing compounds are used as pesticides and are known as organophosphorus pesticides (OPPs). The available information on the production and use of both OPPs and non-pesticides is limited, fragmentary and in some cases unreliable [9]. On the basis of the limited information received from the Mediterranean countries the OPPs dimethoate, chlorpyrifos, malathion, methamidophos, phenthoate, dichlorvos, fenitrothion and parathion were the ones mostly used during 1980s and 1990s, whereas other important compounds used in the same period were methidathion, fenthion and azinphos methyl [9].

OPPs are widely used throughout the world as alternative insecticides to organochlorine pesticides, such as DDT, owing to their relatively rapid decomposition and lower bioconcentration potential in aquatic organisms [9,10]. The rapid growth in their usage has been encouraged by all these advantages and methyl parathion is second only to malathion in usage worldwide [11]. In general they are considered unstable in water and organisms due to mechanisms of hydrolysis and ester cleavage [9] but still many studies have been published referring that OPPs can be persistent in natural environments. Reported values of dimethoate's half-life varied from 18 h [12] to 423 d [13] in aqueous media showing that stability of the molecule and rate of degradation is dependent on the prevailing environmental conditions such as pH, temperature and nature of the pesticide [3,13]. The importance of biological factors has been demonstrated by the difference in the persistence of parathion in biotic and abiotic water [9,14]. Similar observations have been reported for fenthion as the half life of the substance is usually few days, but in ultrapure water half-life was increased to 189 d [13].

Organophosphorus compounds undergo chemical and metabolic transformations that can convert either an inactive compound to an active one, or the opposite consequence. Any metabolic transformation which brings the structure of the parent compound nearer to the structure of organophosphorus triesters, increases the ability to inhibit acetylcholinesterase (AChE) and converts a pro-insecticide to an active insecticide. A great number of toxicological surveys on OPPs have been performed and proved that many of them are highly toxic towards non-target organisms even at low concentrations, due to their cholinesterase inhibition effect [15–17].

Adsorption and desorption data of OPPs are necessary for the evaluation of their migratory tendency into air, water and soil or sediment compartments of the environment. These data are needed to estimate leaching of these molecules through the soil, volatility from water and soil, photodegradation in the adsorbed state on aerosol surfaces and concentration in water or run-off from land surfaces into natural waters. Although many works have been carried out on adsorption of organophosphorus insecticides on various types of soils, individually and under different conditions, only limited work has been carried out to understand the desorption characteristics of these compounds on

Mediterranean soils [18,19]. Moreover, adsorption studies were conducted under a variety of experimental conditions which make the comparison of adsorption behaviour difficult.

The aim of the present study was to evaluate the adsorption and desorption characteristics of two selected OPPs widely used in Mediterranean region for treating olive trees against *Dacus oleae*, dimethoate and fenthion, on three different Greek soils with different physical and chemical properties such as soil type, pH, clay content and organic matter content. The fact that Mediterranean soils are characterised by low organic matter content which is concerned as one of the major factors that influence adsorption capacity of organic molecules onto soil particles gives the present study an extra importance. Estimations of Langmuir (q_{max} and Freundlich adsorption coefficients (K_f and n) were performed and adsorption/desorption per cent balances were studied as an indication of the predominant forces and the reversibility of the binding forces.

2. Experimental

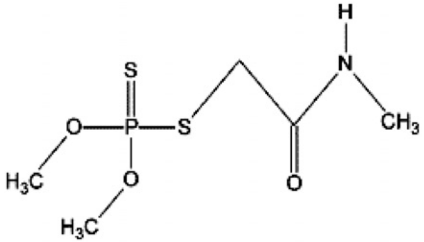
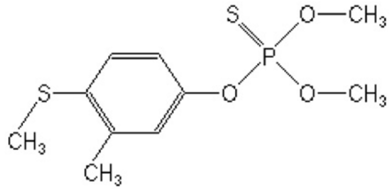
2.1 *Chemicals, reagents and standards*

The tested compounds dimethoate (*O*,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate) and fenthion *O*,*O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorothioate) were residue analysis grade (purity $>99.5\%$), obtained from Dr Ehrenstorfer-Schäfers (Augsburg, Germany) and used without further purification. The chemical structure and the main physicochemical properties of these OPPs are shown in Table 1 [20,21].

Pesticide grade organic solvents such as hexane, methanol and dichloromethane were purchased from Pestiscan (Labscan Ltd, Dublin, Ireland). Organic free water was prepared with a Milli-Q/Milli-Ro system (Millipore Corp., Bedford, MA, USA). Other chemical reagents and solvents used were of HPLC grade and procured from Merck (Merck, Germany).

Stock standard solutions of each pesticide ($1000\,mg\,L^{-1}$) were prepared by dissolving the required amount in methanol and were stored under refrigeration. Dilutions were made with 0.01 M calcium chloride aqueous solution (0.01 M $CaCl_2$) to the desired final concentrations, according to the respective OECD Test Guideline 106 [22]. The use of an organic solvent (carrier) is recognised as being essential in studies dealing with the behaviour of organic molecules in aqueous systems [23]. Furthermore several authors in published literature propose the introduction of co-solvents in soil-water systems, because this way a significant increase in the solubility of substances can be achieved [24–26]. The use of an appropriate carrier solvent is advocated especially for the more hydrophobic compounds ($\log K_{ow} > 4$), because it greatly facilitates batch and column experimentation and minimises experimental artifacts. This approach has already been adopted by a great number of researchers for measuring the adsorption of several organic compounds by soils [27–29]. Sorption coefficients of hydrophobic substances on soils are generally measured in water and various water-miscible organic solvents, such as methanol, acetone, and acetonitrile. In any case, the proportion of the carrier solvent should be kept to a minimum so that the pesticide partitioning behaviour is not significantly altered [28,30]. Thus, in the present study, stock concentrations of target OPPs and volumes transferred were designed in order to maintain a methanol concentration of 2% by volume in the initial aqueous solutions of pesticides, a level at which methanol has no measurable effect on sorption [31].

Table 1. Chemical structure and main physicochemical properties of selected pesticides*.

	Dimethoate	Fenthion
Chemical structure		
IUPAC Name	*O*,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate	*O*,*O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorothioate
CAS No.	60-51-5	55-38-9
Molecular formula	$C_5H_{12}NO_3PS_2$	$C_{10}H_{15}O_3PS_2$
Phase	Crystalline solid	Liquid
Molecular weight (Da)	229.28	278.33
Solubility in water (mg L^{-1}, at 20°C and pH = 7)	23,800	55
Log K_{ow}	0.704	4.84
Vapour pressure (mPa, at 20–25°C)	0.29 (20°C)	1.4 (25°C)
Henrys law constant (Pa m^3 mol^{-1}, at 20°C)	$5 \cdot 10^{-2}$	$1.20 \cdot 10^{-6}$
Melting point (°C)	41–49	7

*Data taken from References [20,21].

2.2 *Experimental soils*

Three commonly found soils in Greece were used for the present study. Fresh and agricultural surface (0–20 cm) soil samples were collected from the region of Mytilene (Greece) and from fields which were previously not treated with the target compounds. The soils were chosen so as to correspond to intensively cultivated island areas in Greece and to have different clay and organic matter. Soil samples were identified and classified based on textural analysis as a loam (L type) soil, collected from Mandamados area (M), and as two sandy loam (SL type) soils taken from Kato Tritos (KT) and Parakila (P) areas respectively and according to United States Department of Agriculture (USDA) particle size classification (clay: $<2\,\mu$m; silt: 2–50 μm and sand: 50–2000 μm).

The soil pH was determined in 0.01 M $CaCl_2$ solution with a soil/liquid phase ratio of 1 : 2 w/v and was measured using a direct reading type pH-meter with glass electrode and a calomel reference electrode (Crison, Spain) [32]. Particle size distributions were performed using the hydrometer method [33]. The organic matter (OM) content of the soil was determined by Walkley and Black modified method and organic matter was calculated by multiplying organic carbon by 1.72 [32]. The cation exchange capacity (CEC) and specific surface area of soils were determined according the ammonium acetate pH 8.2 and ethylene glycol monoethyl ether (EGME) methods, respectively [34]. The characteristics of different soils employed in the present study are given in Table 2.

2.3 *Preparation of soil samples*

Soil samples after randomly collected from each sampling location and transported to the laboratory in plastic bags were all homogenised, air-dried at room temperature ($<40^\circ$C), passed through a 2-mm sieve and stored at room temperature in the dark, until the time of analysis.

2.4 *Batch adsorption experiments*

The experiments were performed according to the Organization for Economic Co-operation and Development Guideline 106 [22]. Pesticide dilutions were prepared in 0.01 M $CaCl_2$ aqueous solution in order to maintain constant ionic strength as it minimises cation exchange and improves centrifugation procedure as well. Seven concentrations ranged between 0.5 and 20 mg L^{-1} were used for all combinations of compounds and soils

Table 2. Particle size distribution and selected physicochemical properties of the soils studied.

Soil sample	Textural analysis (%) Clay[1]	Silt[2]	Sand[3]	Soil classification (USDA)	pH (soil/$CaCl_2$, 1 : 2 w/v)	CEC[6] (meq/100 g)	OM[7] (%)	$CaCO_3$ (%)	Specific surface area ($m^2\,g^{-1}$)
M	26	40	34	L[4]	5.45	24.4	2.7	1.7	109.22
KT	6	32	62	SL[5]	5.75	4.8	4.2	1.3	10.79
P	18	17	65	SL[5]	6.90	14.0	1.0	1.3	58.25

[1]Clay: $<2\,\mu$m; [2]Silt: 2–50 μm; [3]Sand: 50–2000 μm; [4]L: loam; [5]SL: sandy loam; [6]CEC: cation exchange capacity; [7]OM: organic matter.

(called as adsorption systems). Each mixture consisted of 1 g of soil mixed with 10 mL of the pesticide solution in 15 mL glass centrifuge tube and sealed with screw caps with Teflon lining. Preliminary kinetic experiments had demonstrated that adsorption equilibrium was reached within 24 h. The tubes were shaken on a horizontal shaker (Gesellschaft für Labortechnik, GFL, Germany), at constant room temperature of 23 ± 0.2°C and for 24 h to achieve equilibrium. After achieving equilibration the suspensions were centrifuged at 5000 rpm for 30 min (Heraeus, Germany). Quantity of the aqueous supernatant (5 mL) was recovered for the determination of pesticide equilibrium concentration, as described below in Section 2.7. The amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentration in solution. The adsorption equilibration process was performed in three replicates for each adsorption system tested. One blank (without pesticide) and one control (without soil) were included in each sample batch to assure the quality control of the experiments.

2.5 *Batch desorption experiments*

Desorption of pesticides at 23 ± 0.2°C was determined on triplicate soil samples by using aliquots of samples from the sorption experiments. After the initial equilibration of 1 g of the soil sample with 10 mL of pesticide solution the soil/water mixtures were centrifuged and the supernatant was poured off and replaced by the same volume of 0.01 M $CaCl_2$ aqueous solution. At each desorption step the soil in the tubes was resuspended in solution using a vortex mixer (Scientific Industries, USA) and then the tubes were mechanically shaken at 23 ± 0.2°C. According to preliminary kinetic studies of desorption equilibrium the tubes were shaken as previously described for 6 h in order to achieve desorption equilibration process and centrifuged (5000 rpm for 30 min). A second step of releasing the adsorbed pesticides was carried out using 10 mL of acetone and combination of shaking (vortex) and ultrasonication. In each case of pesticide recovery (desorption with water or extraction with organic solvent) the amount of pesticide remaining adsorbed by the soil was calculated as the difference between the initial adsorbed amount and the desorbed amount [22].

2.6 *Extraction of pesticides from aqueous supernatants*

After centrifugation of mixtures containing soil and pesticide solution 5 mL of the supernatant aqueous phase was transferred and extracted twice with 5 mL of the appropriate organic solvent (hexane or dichloromethane), using vortex for 1 min. Two extracts were combined and a small amount of anhydrous Na_2SO_4 was added in order to eliminate the humidity. Only an aliquot of the organic extract (1 μL) was used for gas chromatographic analysis. Mean percentage recoveries ($n = 9$) for the two selected pesticides derived from the application of liquid–liquid extraction of aqueous phases with organic solvent at three spiking concentrations of 0.5; 1 and 2 mg L^{-1} were 95.2 ± 2.4% for dimethoate and 104.6 ± 2.1% for fenthion.

2.7 *Chromatographic analysis*

Analysis of OPPs residues extracted was performed on a Hewlett Packard Gas Chromatographic system (GC), Model HP-5890, Series II (Hewlett Packard, USA)

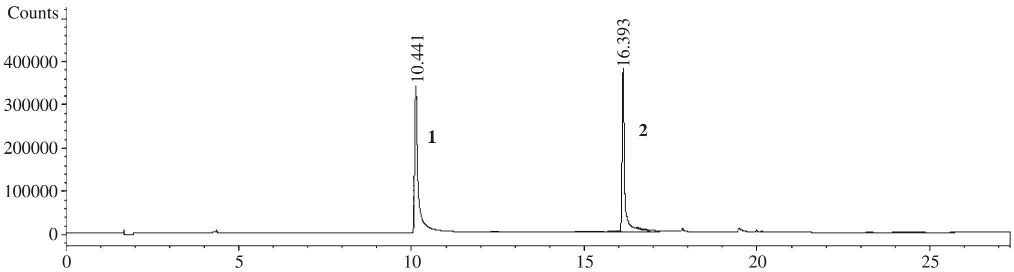


Figure 1. Representative GC-NPD chromatogram of a pesticides mixture of the two target compounds. Peaks identification: (1) dimethoate; (2) fenthion.

equipped with a Nitrogen Phosphorus Detector (NPD). The chromatographic conditions were: injection port 150°C; on column injection volume, 1 µL; MDN-5 fused silica capillary column (30 m × 0.32 mm i.d. and 0.25 µm film thickness) (Supelco, USA); column initial temperature, 150°C; oven temperature programme, at 150°C for 3 min, from 150°C to 170°C with rate 20°C min^{-1}, from 170°C to 190°C with rate 2°C min^{-1}, from 190°C to 250°C with rate 15°C min^{-1}, at 250°C for 15 min; carrier gas, nitrogen at 1.2 mL min^{-1} (constant flow on); make up gas, helium at 20 mL min^{-1}; detection temperature, 280°C; detector gasses, hydrogen at 3.5 mL min^{-1} and air at 110 mL min^{-1}.

A typical chromatogram of GC-NPD analysis of dimethoate and fenthion is shown in Figure 1. Retention times were 10.441 and 16.393 min for dimethoate and fenthion, respectively.

Quantification of the analytes was carried out by automatic integration of peak areas. Quantification or recovery of the pesticides in the fortified samples was performed by comparing the detector responses for each of the target compound in samples with those measured in calibration standards solutions, according to the equation of the appropriate calibration curve.

The limit of detection (LOD) and limit of quantification (LOQ) for the examined analytes were defined in aqueous and solid matrices in the range of 0.5–2 mg L^{-1} or 0.5–2 mg Kg^{-1} for the cases of water or soil samples, respectively. In any case studied three different concentrations prepared in triciplate, thus $n = 9$. Under the above-stated experimental conditions, the LOD was estimated as the analyte concentration resulted in signal (S)-to-noise (N) ratio equal to 3/1 (S/N = 3/1) and verified by the analysis of the pesticides mixture fortified at 0.5 mg L^{-1} as three times the standard deviation (SD) (LOD = 3 × SD) [35]. LOD values were: for dimethoate, 0.0050 µg L^{-1} for aqueous and 0.0033 µg L^{-1} for soil samples; for fenthion, 0.0025 µg L^{-1} for aqueous and 0.0017 µg L^{-1} for soil samples. The LOQ was defined as the analyte concentration resulting in S/N of 10/1 and verified by the aforementioned procedure applied for LOD [35]. LOQ for dimethoate was 0.0165 µg L^{-1} for aqueous and 0.0110 µg L^{-1} for soil samples, while for fenthion, it was 0.0083 µg L^{-1} for aqueous and 0.0055 µg L^{-1} for soil samples.

3. Results and discussion

3.1 *Adsorption isotherms*

Adsorption isotherm studies were conducted at 23°C for dimethoate and fenthion using three different soils. Isotherms obtained for each of the two selected OPPs and for all of

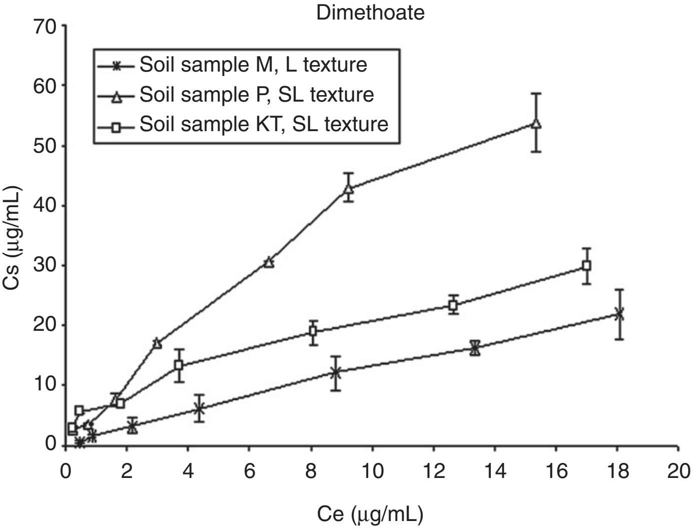


Figure 2. Adsorption isotherms of dimethoate on various soils of the study. (Error bars represent standard deviations of three replicates.)

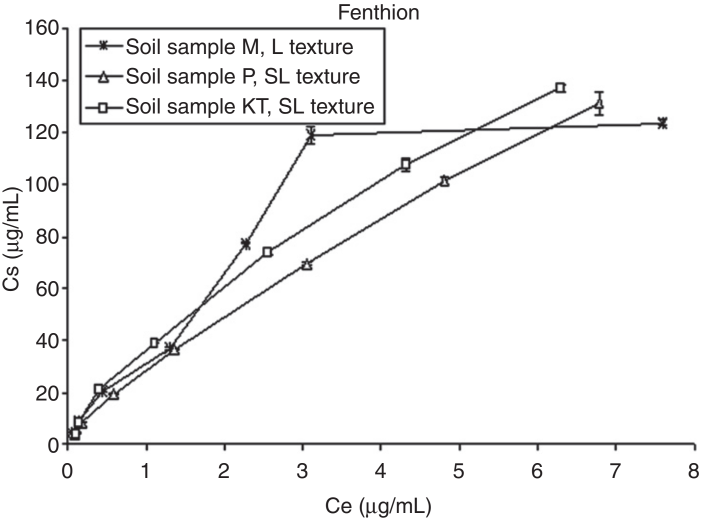


Figure 3. Adsorption isotherms of fenthion on various soils of the study. (Error bars represent standard deviations of three replicates.)

the adsorption systems investigated are presented in Figures 2 and 3 for the case of dimethoate and fenthion, respectively.

In adsorption surveys the shape of the adsorption isotherm line is an important characteristic because it provides information about the adsorption mechanism [36,37], but in any case it only suggests and does not give confirmations about the adsorbate-adsorbent interaction [38]. Giles *et al.* have proposed a classification of isotherms into four categories, S-, L-, H- and C-shape, based on the initial slope $d(x/m)/dC_e$, which is important as it depends on the rate of change of adsorption site availability [36].

Adsorption isotherms obtained for dimethoate and fenthion on loam and sandy loam soils of the study were of S- and L-shape, while the L-shaped isotherms (Langmuir) were the mostly observed ones. S-shape is a common feature for the adsorption of organic chemicals on soils with low organic matter or clay contents [39] and is attributed to a slight concavity in the initial stage of adsorption. This isotherm type indicates a low pesticide-soil affinity at low concentrations, with strong competition with aqueous phase, and adsorption becomes easier as pesticides concentration in the aqueous phase increases [37]. S-type isotherm suggests cooperative adsorption that operates if adsorbate-adsorbate interaction is stronger than adsorbate-adsorbent interaction. This condition favours the clustering of adsorbate molecules at the surface because they bond more strongly with one another than with the surface [38]. Only the isotherm of dimethoate on P-soil sample resembles S-type isotherm, as it was expected, because this soil matrix has the lowest organic carbon content of all soils examined (1.0%OM). Isotherms of dimethoate are transformed to L-shape as the organic matter in soils increases (L soil from Mandamados with 2.7%OM and SL soil from Kato Tritos with 4.2%OM). Fenthion gave L-shaped isotherms in all of the three soils studied and this reflected a relatively high affinity between the three soils examined and this organophosphorus compound. L-shape generally corresponds to a constant partition of the solute between bulk solution and the adsorbent [37,40] and is observed when the adsorbent surface possesses a high affinity for the adsorbent solute. L-type adsorption isotherms of OPPs of the present study were the dominant ones and indicated that dimethoate and fenthion were most likely to be absorbed rapidly in a flat position on three Greek soils tested and they did not suffer strong competition from water molecules. Furthermore, as the solution concentration increased, the adsorption of the pesticides decreased. Similar types of results have been reported by a large number of researchers [18,40,41]. Krishna *et al.*, while studying the adsorption behaviour of methyl parathion on Indian soils, reported S- and L-shape isotherms [41]. Patacioutas *et al.* observed isotherms L-shaped type for the adsorption of primiphos methyl on all of the four Greek soils studied [18]. In general, the differences observed in the shape of the isotherms of present survey showed a variation of adsorption mechanisms as the physicochemical properties of the soil and the pesticide change.

3.2 *Adsorption isotherm models and coefficients*

Langmuir and Freundlich isotherm models, described by Equations (1) and (2), were used to calculate the isotherm constants and maximum adsorption capacity of different pesticides on various soils employed in the study:

$$q = \frac{q_{max} b C_e}{1 + b C_e} \tag{1}$$

$$x/m = C_s = K_f C_e^{1/n} \tag{2}$$

where $x/m = q = C_S$ (mg Kg^{-1} or μg g^{-1}) is the amount of pesticide adsorbed by soil per unit mass of soil; C_e (mg L^{-1} or μg mL^{-1}) is the pesticide concentration in equilibrium solution; K_f is the Freundlich empirical adsorption constant that represents the degree or strength of adsorption; n represents energy distribution of sorption sites; $(x/m)_{max} = q_{max}$ (mg Kg^{-1} or μg g^{-1}) is the maximum adsorption capacity of the adsorbent which in the present study is soil; and finally b is Langmuir constant.

Table 3. The adsorption isotherm constants of selected pesticides OPPs on different soils by Langmuir and Freundlich models (n = 3).

	Langmuir isotherm model			Freundlich isotherm model		
Soil sample	q_{max} ($\mu g\,g^{-1}$)	b	R^2	K_f ($mL\,g^{-1}$)	n	R^2
			Dimethoate			
M	11.87 ± 2.05	0.17 ± 0.09	0.9636	1.62 ± 0.20	1.10 ± 0.14	0.9953
KT	25.51 ± 5.50	1.01 ± 0.37	0.9382	6.87 ± 0.17	2.06 ± 0.26	0.9679
P	18.45 ± 2.70	0.53 ± 0.23	0.8117	6.63 ± 0.20	1.29 ± 0.08	0.9666
			Fenthion			
M	93.30 ± 25.25	0.93 ± 0.50	0.9928	36.88 ± 1.45	1.36 ± 0.05	0.9753
KT	170.87 ± 15.01	0.28 ± 0.12	0.9697	34.47 ± 0.52	1.25 ± 0.07	0.9830
P	150.35 ± 18.44	0.39 ± 0.25	0.9964	29.03 ± 0.36	1.26 ± 0.04	0.9980

Both isotherm models used fitted the experimental data reasonably well and the results are summarised in Table 3. However the correlation coefficient values (R^2) show that the data fitted better with Freundlich isotherm model ($R^2 \geq 0.9666$) than Langmuir model ($R^2 \geq 0.8117$).

The maximum adsorption capacity of dimethoate and fenthion was estimated by Langmuir isotherm model for the soils of the study. Dimethoate showed the least adsorption for all three soils examined ($q_{max} \leq 25.51\,\mu g\,g^{-1}$), while fenthion exhibited much higher adsorption capacity in all cases ($q_{max} \geq 93.30\,\mu g\,g^{-1}$). Among the two pesticides studied, maximum adsorption occurred for fenthion on KT soil sample with SL type texture ($170.87\,\mu g\,g^{-1}$).

In Table 3 values of constants K_f and n of Freundlich isotherm model (Equation (2)) are listed. The K_f values obtained are different for each adsorption system of pesticide and soil. In all three cases of soils samples tested K_f values are in the order: dimethoate < fenthion (Table 3), while solubility of the target OPPs in water at 20°C is in the order: fenthion < dimethoate (Table 1). Thus, it can be noted that the less water-soluble the pesticide is, the more soil-partitioned it is, assuming that order factors remain constant. Moreover the obtained experimental data indicate that the lipophilic or the hydrophilic character of the OPPs molecule is the most important parameter for the adsorption of the studied pesticides on soils. Thus, many leaching predicting models in published data are based onto these properties for assessing the mobility of an organic compound in soil [42].

The exponent 1/n takes into account non-linearity in the adsorption isotherm. When Freundlich constant n is close to 1, adsorption would be linearly proportional to equilibrium solution concentration and this value would be used as distribution coefficient K_f. In the present study, it was observed that the n values varied from 1.10 to 2.06 for various soils. Calvet observed that low values of n are frequently associated with high soil organic matter content [37] and similar trend was observed in the present study also, with the exception of dimethoate on KT soil.

3.3 *Effect of soil organic matter content on adsorption process*

Pesticides have a strong affinity for soil organic matter. Soil organic matter has an important effect on the bioactivity, persistence, biodegradability, leachability and volatility of pesticides. In fact organic matter is considered to be as the soil component most important in organic pesticide retention [43]. Soil organic matter consists of non-humic and humic substances. Humic substances can be defined as 'a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterised as being yellow to black in colour, of high molecular weight and refractory'. They are amorphous, partly aromatic, polyeletrolyte materials that no longer have specific chemical and physical characteristics associated with well-defined organic compounds. Humic substances can be subdivided into humic acids, fulvic acids and humic, based on their solubility in acid or base [43].

Factors that affect the retention of pesticides by soil organic matter are number, type and accessibility of its functional groups, nature of the pesticides, properties of the soil including types and quantities of clay minerals and other soils components, pH, exchangeable cations, moisture and temperature [5,44]. Although the mechanisms by which pesticides are retained by soil organic matter are not clearly understood, agrochemicals may be strongly retained in the internal voids of humus molecules that are sieve-like [43]. According to Koskinen and Harper, adsorption of pesticides on humic substances occurs via ion exchange and protonation, H bonding, van der Waals forces, ligand exchange (an organic functional group such as carboxyl or hydroxyl replaces an inorganic hydroxyl or water molecule of a metal oxide, resulting in an inner-sphere complex) and cation and water bridging. Humic substances can also combine with non polar organic compounds via a partitioning mechanism [45]. This partitioning of hydrophobic soil organic matter surfaces results from a weak solute-solvent interaction or the low solubility of hydrophobic nature of the solute. Important hydrophobic sites on humic substances include fats, waxes and resins and aliphatic chains. Since humus has an aromatic framework and contains polar groups it may have both hydrophobic and hydrophilic sites. Soluble humic substances can enhance the transport of pesticides in soils and into groundwater. Fulvic acids, which have low molecular weight and high acidities, are more soluble than humic acids, can transport pesticides and other organic materials quite effectively [43].

On the basis of the great importance of the soil organic matter in controlling adsorption of organic compounds of limited water solubility Freundlich sorption coefficients K_f were normalised to soil organic matter content. Organic matter adsorption constants (K_{OM}) values were estimated from Equation (3):

$$K_{OM} = K_f/f_{OM} \tag{3}$$

where f_{OM} is the percentage of organic matter in the soil. This simplifies the comparison between K_f values from the different adsorption systems examined. Moreover, K_{OM} values usually illustrate the hydrophobicity of pesticides and may be used to estimate or predict the migration and behaviour of an organic compound in the environment [46].

Mean values of K_{OM} and $\log K_{OM}$ obtained in present study with their standard deviations ($n = 3$) are summarised in Table 4.

Estimated values of the present study proved that according to the McCall classification for the mobility of pesticides [47] dimethoate is a mobile compound with respect to leaching, as its sorption was generally weak in studied soils (especially in M soil, 2.7% organic matter, CEC 24.4 meq/100 g) and therefore this compound has the potential to contaminate the groundwater. On the contrary fenthion can be classified as immobile and therefore it can be concluded that this compound is not susceptible to

Table 4. Values of K_{OM}, and $\log K_{OM}$ for the adsorption of dimethoate and fenthion on various Greek soils with different organic matter content (n = 3).

Pesticide	Soil sample	OM content (%)	K_{OM}	$\log K_{OM}$
Dimethoate	M	2.7	60.19 ± 7.57	1.78 ± 0.06
	KT	4.2	163.58 ± 4.01	2.21 ± 0.01
	P	1.0	663.43 ± 20.53	2.82 ± 0.01
Fenthion	M	2.7	1365.84 ± 54.33	3.14 ± 0.02
	KT	4.2	820.73 ± 12.35	2.914 ± 0.006
	P	1.0	2902.52 ± 36.45	3.463 ± 0.005

leaching losses from the zone of application, and tends to remain on the surface or in the upper soil layers.

Furthermore experimental results of dimethoate's adsorption indicated that adsorption process of this OPP was not increased or even diminished with the increasing of soil organic matter content, which pointed the small role that OM played in dimethoate's retention, similar to other highly polar or ionisable pesticides [11,48,49]. These results and observations correspond with those of other researchers [11,49] who have reported that when organic carbon is low, there may be no relationship between adsorption of pesticides and organic matter, but other factors in the soil may play an important role, such as the inorganic matter [50–52], calcium concentration [53], and cation exchange capacity [53,54] and several other characteristics. Fenthion, which is a non-polar member of organophosphorus pesticides, followed the same pattern of adsorption onto the soils examined with dimethoate. No enhancement of the adsorption capacity of the soils occurred when the %OM of the soil matrices was increased, and instead reduction of adsorption affinity was observed. This phenomenon can be attributed either to the different nature of the OM components of the soils [48,55,56], or to the fact that other physicochemical factors of the soil, such as clay content, CEC and specific area were more significant for the process.

According to the average values shown in Tables 2 and 4, where physicochemical properties of the soils and K_{OM} adsorption constants are listed respectively, f_{OM} soil content was correlated with the observed K_{OM} values of the two pesticides retained onto the three soils tested. OPPs adsorption was correlated positively with the decrease in f_{OM} of soils. The relationships are given by the following linear Equations (4) and (5) for the case of dimethoate and fenthion, respectively:

$$K_{OM} = -160.46 \cdot f_{OM} + 718.08 \quad \text{with } R^2 = 0.6349 \tag{4}$$

$$K_{OM} = -656.32 \cdot f_{OM} + 3424.85 \quad \text{with } R^2 = 0.9470 \tag{5}$$

In general, the values of K_{OM} of present study are in agreement with previously reported results in the literature. Hernández-Soriano *et al.* reported that the value of $\log K_{OM}$ for dimethoate has been estimated to be 1.7 [48], and according to Tomlin organic matter adsorption constants for the same analyte retained on a number of different soils varied within the range of 1.2–1.7 [20]. Finally the Food and Agriculture Organization (FAO) of the United Nations in a reference manual assessing soil contamination due to organic agrochemicals reports that $\log K_{OM}$ for the molecule of fenthion is equal to 3.1 [49].

3.4 *Free energy change of adsorption ($\Delta G°$)*

Weber *et al.* summarised the possible interactions between solute and sorbent included into three loosely defined categories of adsorption: physical, chemical and electrostatic. The physical adsorption processes involve interactions between dipole (permanent or induced) moments of sorbate and sorbent molecules. The relatively weak bonding forces associated with physical adsorption are often amplified in the case of hydrophobic molecules by substantial thermodynamic gradients for repulsion from the solution in which they are dissolved. Chemical interactions involve covalent bond and hydrogen bond, while electrostatic interactions involve ion-ion and ion-dipole forces [57]. The type of interactions and the approximate values of energy associated are: van der Waals interactions (4–8 $\mathrm{kJ\,mol^{-1}}$), hydrophobic bonding (4 $\mathrm{kJ\,mol^{-1}}$), hydrogen bonding (2–40 $\mathrm{kJ\,mol^{-1}}$), change transfer, ligand-exchange and ion bonding (40 $\mathrm{kJ\,mol^{-1}}$), direct and induced ion-dipole and dipole-dipole interactions (2–29 $\mathrm{kJ\,mol^{-1}}$), and chemical adsorption (covalent bond) (60–80 $\mathrm{kJ\,mol^{-1}}$) [37,58].

The change in the partial molar free energy, ΔG°, as a result of the adsorption process, assuming that the target analytes were adsorbed mainly by the organic matter, was calculated from the thermodynamic relationship described by Equation (6):

$$\Delta G^\circ = -RT \ln K_{OM} \tag{6}$$

where ΔG° is the free energy change ($\mathrm{cal\,mol^{-1}}$), R is the gas constant (1.986 cal $\mathrm{K^{-1}\,mol^{-1}}$) and T is the absolute temperature. The value of ΔG° was used as a measure of the extent of the driving force of the adsorption process. The greater the absolute magnitude of ΔG° value, the greater is the extent to which the adsorption reaction may take place. The small negative value of free energy change indicates the exothermic nature of the phenomenon. In such cases, it can be inferred that adsorption is physical in nature involving weak forces of attraction. Furthermore, the negative ΔG° values indicate spontaneous process.

The ΔG° values obtained in the present study are exhibited in Table 5 and were all negative, which indicated that the process was exothermic and spontaneous. Therefore an increase in temperature would result in a decreased sorption and in an increased desorption process. Furthermore negative ΔG° values of this study indicated that physical adsorption was carried out by involving weak forces of attraction between pesticides' molecules and soil surfaces. Finally ΔG° values showed that the adsorption capacity of the selected soils would be in the order of P (SL type) > KT (SL type) > M (L type) in the case of dimethoate and P (SL type) > M (L type) > KT (SL type) in the case of fenthion. This order was in agreement with the maximum adsorption capacities of the studied soils that were calculated by Langmuir isotherm model (Table 3).

3.5 *Affinity of the pesticides towards the soil surfaces*

As already stated, in soil a pesticide can either degrade *in situ* by microbial or chemical processes, volatilise or photodegrade, but as long as pesticide residues remain at the surface they are vulnerable to loss in run-off. The affinity of individual pesticides for soil constituents will determine the extent to which this occurs. The longer pesticides remain in soil or on plant debris, the less likely that they will desorb, because they transfer to restricted sites during the more gradual phase of sorption.

Table 5. Free energy change values for the adsorption of dimethoate and fenthion on various Greek soils with different organic matter content ($n = 3$).

Pesticide	Soil sample	Organic matter content (%)	ΔG° ($\mathrm{cal\,mol^{-1}}$)
Dimethoate	M	2.7	-2408.79 ± 74.49
	KT	4.2	-2996.47 ± 14.53
	P	1.0	-3819.55 ± 16.93
Fenthion	M	2.7	-4244.04 ± 23.26
	KT	4.2	-3944.63 ± 8.87
	P	1.0	-4687.17 ± 7.38

Some soil constituents have a greater affinity for pesticides than do others. Clays and organic matter contain numerous sites that react with pesticide functional groups. In order to evaluate the intrinsic affinity of the organophosphorus insecticides dimethoate and fenthion towards the three Greek agricultural soils tested in the present study, the original isotherms were replotted with regard to the degree of adsorption under saturation conditions. Figures 4 to 6 present the plots of $\ln(x/m)$ as a function of $\ln(C_e/C_s)$, where C_e is the solute concentration in the aqueous phase at equilibrium and C_s the water solubility of the target compounds acting as adsorbates.

It is obvious that the affinity of the studied organophosphorus pesticides towards the three soil types examined decreases in the order fenthion > dimethoate as the isotherms shift towards lower values of $\ln(C_e/C_s)$ in that sequence for all of the soils tested, regardless their different physicochemical characteristics.

3.6 *Adsorption and desorption per cent balances*

Mass balance tests were performed by determining in addition to the concentrations in the solutions, the concentration of the substances in the soils. These additional measurements were accomplished after reaching the equilibration plateau and for seven different fortification levels of the soil, in the range of 5–200 $\mu g\,g^{-1}$ for each target compound. The adsorbed organophosphorus chemicals remaining onto soil particles were removed so that a mass balance could be attempted. The extraction mediums used were water (0.01 M $CaCl_2$) and the organic solvent of acetone in which the tested pesticides are very soluble. A volume of each medium equal to the volume of aqueous solution originally used to attain adsorption equilibrium (10 mL) was added to the soil and shaken vigorously to achieve desorption or extraction of adsorbed amounts of pesticides.

As already stated, the amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentration in solution. The combined concentrations of the studied chemicals in the aqueous and acetone extracts were subtracted from the initial adsorbed amounts and are reported as the amounts of pesticide that were decomposed or remained permanently adsorbed by the soil. The mean percentage balances for the adsorbed, desorbed with 10 mL water, extracted with 10 mL acetone and decomposed or permanently adsorbed amounts of studied pesticides are presented in Tables 6 and 7 for the batch

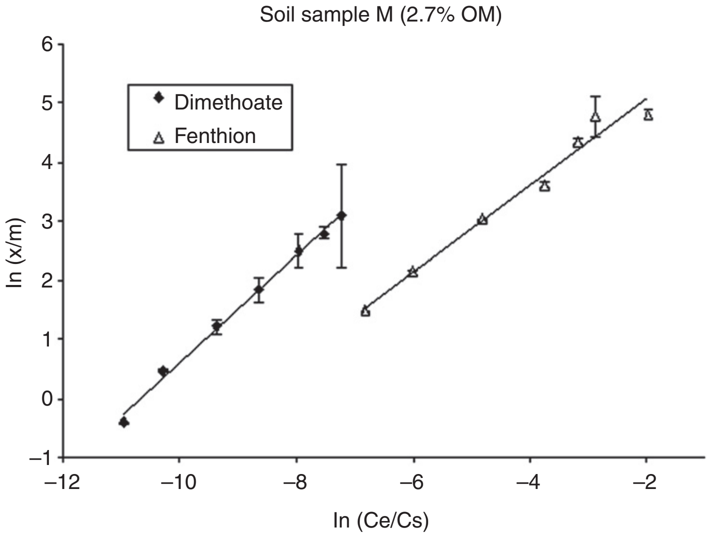


Figure 4. Affinity of dimethoate and fenthion towards the soil sample M, L texture. (Error bars represent standard deviations of three replicates.)

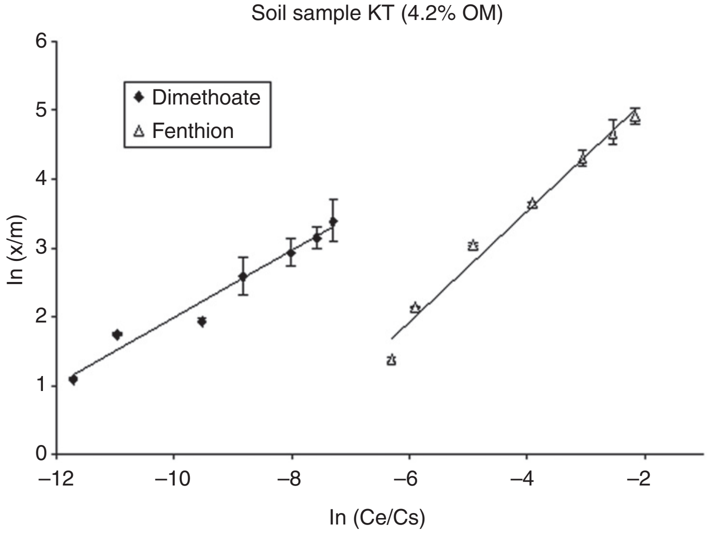


Figure 5. Affinity of dimethoate and fenthion towards the soil sample KT, SL texture. (Error bars represent standard deviations of three replicates.)

adsorption/desorption experiments of dimethoate and fenthion, respectively. The experimental procedure for the acquisition of mass balances was performed in three replicates. Thus, values shown in previously mentioned tables are mean values of triplicates with their standard deviations (mean value ± SD). Percentage amounts of pesticide for desorbed with water washings quantity, for extracted with acetone quantity and of decomposed or permanently adsorbed quantity are calculated in two

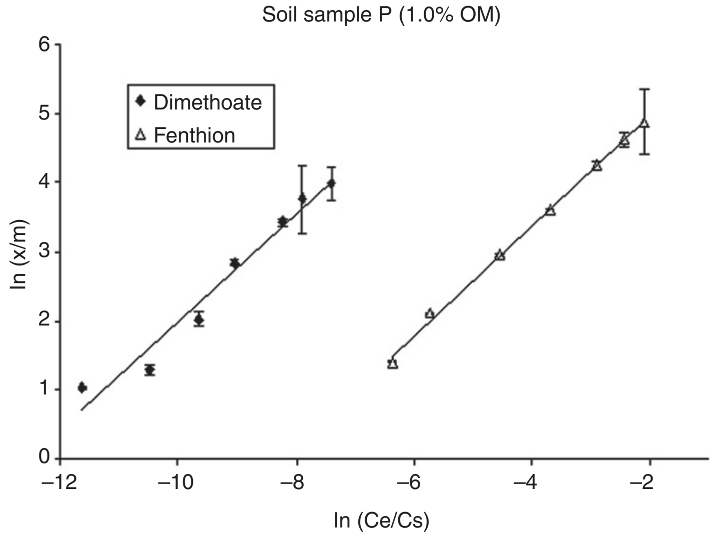


Figure 6. Affinity of dimethoate and fenthion towards the soil sample P, SL texture. (Error bars represent standard deviations of three replicates.)

ways, which are in regard in the initial pesticide concentration and in regard in the adsorbed pesticide concentration.

The extent of recovery or release of adsorbed OPPs varied among soils and applied pesticides. The desorbed amounts with water ranged from 1.68 to 6.38% for dimethoate and from 4.58 to 14.27% for fenthion. The analogous percentage amounts for the extraction of bounded residues with acetone ranged from 0 to 0.07% for dimethoate and from 4.25 to 47.93% for fenthion. Finally, the pesticides amounts defined as decomposed or permanently adsorbed were found to be from 7.31 to 57.20% for dimethoate and from 6.29 to 69.58% for fenthion.

The per cent mass balances of Table 6 indicated that dimethoate remained mostly free or not adsorbed. It is worth noticing that the free or not adsorbed amounts of this analyte varied from 84.02 to 89.16% for M-soil, from 40.75 to 85.03% for KT-soil and from 44.31 to 71.73% for P-soil. From these values it is obvious that the mass balances for the free amounts which were observed on M-soil sample were significantly higher compared to the other two soils examined, especially for the low concentration levels tested (from 5 to $50\,\mu g\,L^{-1}$) and this phenomenon can be attributed to particular properties of the soil sample and the compound. As it can be seen from data of Table 2, M-soil has the highest clay content of all three examined soils that is 26%. It is also well known that the –Si–O–Si– bonds of the clay minerals in soil are hydrophobic in nature and are thus potential sites for the adsorption of lipophilic compounds, whereas dimethoate is a quite hydrophilic substance according to the values of its water solubility and $\log K_{ow}$ (Table 1). Results of desorption studies showed that the only desorbed amounts of dimethoate are due to water washings, while on the contrary extraction of the bonded molecules with acetone was negligible.

On the other hand, experimental data of fenthion presented in Table 7 indicated that this pollutant has the tendency to be strongly adsorbed onto soil, as the free or not

Table 6. Mean per cent balances for the adsorbed, desorbed with water, extracted with acetone and decomposed or permanently adsorbed amounts of dimethoate from soils studied (n = 3).

				Desorbed with water (%)		Extracted with acetone (%)		Decomposed or permanently adsorbed (%)	
Soil sample	Fortification level (μg g^{-1})	Adsorbed (%)	Free or not adsorbed (%)	In regard in the initial pesticide concentration	In regard in the adsorbed pesticide concentration	In regard in the initial pesticide concentration	In regard in the adsorbed pesticide concentration	In regard in the initial pesticide concentration	In regard in the adsorbed pesticide concentration
M	5	13.18 ± 3.88	86.82 ± 3.88	2.60 ± 0.82	22.27 ± 3.20	0.00 ± 0.00	0.00 ± 0.00	10.58 ± 1.55	77.73 ± 3.20
	10	15.98 ± 3.39	84.02 ± 3.39	2.01 ± 0.13	13.06 ± 3.67	0.07 ± 0.00	0.46 ± 0.10	13.90 ± 1.51	86.48 ± 3.77
	25	13.54 ± 5.20	86.46 ± 5.20	2.64 ± 1.50	23.44 ± 1.92	0.02 ± 0.00	0.16 ± 0.05	10.89 ± 1.39	76.40 ± 8.27
	50	12.61 ± 4.33	87.39 ± 4.33	2.52 ± 0.47	20.88 ± 4.02	0.01 ± 0.00	0.12 ± 0.05	10.08 ± 2.89	79.00 ± 4.07
	100	12.11 ± 2.78	87.89 ± 2.78	2.98 ± 0.53	26.20 ± 1.40	0.05 ± 0.00	0.39 ± 0.08	9.08 ± 2.31	73.41 ± 8.48
	150	10.84 ± 0.66	89.16 ± 0.66	2.66 ± 0.34	24.51 ± 2.07	0.05 ± 0.00	0.45 ± 0.05	8.13 ± 0.44	75.04 ± 2.03
	200	10.92 ± 2.11	89.08 ± 2.11	3.54 ± 0.92	32.53 ± 1.69	0.07 ± 0.01	0.64 ± 0.02	7.31 ± 1.64	66.83 ± 5.70
KT	5	59.25 ± 6.70	40.75 ± 3.70	2.05 ± 0.58	3.61 ± 0.57	0.00 ± 0.00	0.00 ± 0.00	57.20 ± 2.98	96.39 ± 2.57
	10	56.79 ± 4.37	43.21 ± 4.37	1.68 ± 0.18	2.95 ± 0.10	0.00 ± 0.00	0.00 ± 0.00	55.11 ± 4.19	97.05 ± 0.10
	25	27.96 ± 1.75	72.04 ± 1.75	2.52 ± 0.15	9.06 ± 1.12	0.00 ± 0.00	0.00 ± 0.00	25.44 ± 1.91	90.94 ± 1.12
	50	26.61 ± 1.59	73.39 ± 7.59	2.93 ± 0.90	10.99 ± 0.25	0.00 ± 0.00	0.00 ± 0.00	23.67 ± 1.69	89.01 ± 0.25
	100	18.96 ± 2.83	81.04 ± 2.83	5.34 ± 0.12	28.46 ± 3.63	0.00 ± 0.00	0.00 ± 0.00	13.61 ± 2.71	71.54 ± 3.63
	150	15.64 ± 1.42	84.36 ± 1.42	5.07 ± 0.53	32.69 ± 3.37	0.00 ± 0.00	0.00 ± 0.00	10.57 ± 1.95	67.31 ± 6.37
	200	14.97 ± 2.12	85.03 ± 2.12	5.89 ± 1.02	40.24 ± 2.49	0.00 ± 0.00	0.00 ± 0.00	9.08 ± 3.14	59.76 ± 4.49
P	5	55.69 ± 6.56	44.31 ± 6.56	1.72 ± 0.91	3.20 ± 1.01	0.00 ± 0.00	0.00 ± 0.00	53.97 ± 7.47	96.80 ± 2.01
	10	38.27 ± 0.87	61.73 ± 0.87	2.13 ± 0.44	5.59 ± 1.28	0.00 ± 0.00	0.00 ± 0.00	36.14 ± 1.32	94.41 ± 1.28
	25	34.65 ± 5.58	65.35 ± 5.58	1.96 ± 0.53	5.59 ± 0.62	0.00 ± 0.00	0.00 ± 0.00	32.69 ± 5.05	94.41 ± 0.62
	50	40.58 ± 0.74	59.42 ± 0.74	1.84 ± 1.04	4.55 ± 1.66	0.00 ± 0.00	0.00 ± 0.00	38.74 ± 1.78	95.45 ± 2.66
	100	34.15 ± 0.02	65.85 ± 0.02	5.53 ± 1.72	16.20 ± 5.06	0.00 ± 0.00	0.00 ± 0.00	28.62 ± 1.74	83.80 ± 5.06
	150	30.56 ± 2.19	69.44 ± 2.19	6.38 ± 1.03	20.82 ± 1.89	0.00 ± 0.00	0.00 ± 0.00	24.17 ± 1.15	79.18 ± 1.89
	200	28.27 ± 3.45	71.73 ± 3.45	6.26 ± 0.46	22.41 ± 1.35	0.00 ± 0.00	0.00 ± 0.00	22.01 ± 3.91	77.59 ± 4.35

Table 7. Mean per cent balances for the adsorbed, desorbed with water, extracted with acetone and decomposed or permanently adsorbed amounts of fenthion from soils studied (n = 3).

				Desorbed with water (%)		Extracted with acetone (%)		Decomposed or permanently adsorbed (%)	
Soil sample	Fortification level ($\mu g\,g^{-1}$)	Adsorbed (%)	Free or not adsorbed (%)	In regard in the initial pesticide concentration	In regard in the adsorbed pesticide concentration	In regard in the initial pesticide concentration	In regard in the adsorbed pesticide concentration	In regard in the initial pesticide concentration	In regard in the adsorbed pesticide concentration
M	5	87.90 ± 2.25	12.10 ± 2.25	8.54 ± 1.18	9.73 ± 1.50	9.79 ± 2.32	11.12 ± 2.57	69.58 ± 2.50	79.15 ± 1.51
	10	86.39 ± 0.86	13.61 ± 0.86	4.58 ± 1.48	5.31 ± 1.76	18.16 ± 1.05	21.03 ± 1.40	63.65 ± 3.28	73.66 ± 3.16
	25	82.37 ± 0.09	17.63 ± 0.09	5.16 ± 0.14	6.27 ± 0.18	25.41 ± 2.71	30.85 ± 3.25	51.80 ± 2.59	62.88 ± 3.21
	50	73.93 ± 0.93	26.07 ± 0.93	6.90 ± 0.36	9.33 ± 0.57	45.50 ± 6.13	61.49 ± 7.53	21.53 ± 4.95	29.18 ± 6.98
	100	77.23 ± 0.33	22.77 ± 0.33	5.37 ± 2.35	6.95 ± 3.06	47.93 ± 10.11	62.08 ± 13.24	23.93 ± 12.62	30.96 ± 16.29
	150	79.27 ± 2.35	20.73 ± 2.35	9.53 ± 0.70	12.04 ± 1.12	45.52 ± 23.15	57.55 ± 29.38	24.21 ± 8.42	30.41 ± 8.63
	200	61.95 ± 0.46	38.05 ± 0.46	14.27 ± 1.76	23.04 ± 2.95	41.39 ± 1.37	66.81 ± 2.03	6.29 ± 2.78	10.15 ± 4.48
KT	5	79.56 ± 7.37	20.44 ± 1.40	6.06 ± 1.53	7.73 ± 2.64	10.96 ± 1.96	13.95 ± 3.76	62.55 ± 5.90	78.32 ± 6.40
	10	85.00 ± 1.30	15.00 ± 1.30	4.97 ± 0.67	5.85 ± 0.88	10.99 ± 3.71	12.97 ± 4.57	69.04 ± 5.69	81.18 ± 5.45
	25	84.01 ± 1.80	15.99 ± 1.80	7.25 ± 0.12	8.63 ± 0.32	18.37 ± 0.15	21.88 ± 0.65	58.38 ± 2.07	69.49 ± 0.97
	50	77.81 ± 0.10	22.19 ± 0.10	8.44 ± 0.33	10.84 ± 0.44	22.18 ± 4.38	28.51 ± 5.66	47.19 ± 4.80	60.65 ± 6.10
	100	74.09 ± 1.64	25.91 ± 1.64	9.13 ± 0.31	12.32 ± 0.14	23.10 ± 1.37	31.16 ± 1.15	41.86 ± 0.03	56.52 ± 1.29
	150	71.21 ± 1.73	28.79 ± 1.73	8.76 ± 0.33	12.30 ± 0.16	24.86 ± 1.89	34.95 ± 3.51	37.59 ± 3.29	52.75 ± 3.34
	200	68.38 ± 0.87	31.62 ± 0.87	9.01 ± 0.18	13.17 ± 0.09	22.85 ± 1.02	33.43 ± 1.92	36.51 ± 1.71	53.39 ± 1.83
P	5	81.00 ± 4.51	19.00 ± 4.51	8.36 ± 2.67	10.43 ± 3.87	4.25 ± 0.39	5.27 ± 0.78	68.39 ± 7.57	84.30 ± 4.65
	10	82.14 ± 2.20	17.86 ± 2.20	7.84 ± 0.09	9.55 ± 0.37	8.24 ± 1.58	10.06 ± 2.19	66.06 ± 3.87	80.39 ± 2.56
	25	76.52 ± 1.70	23.48 ± 1.70	8.65 ± 0.48	11.30 ± 0.37	13.30 ± 0.09	17.39 ± 0.27	54.57 ± 1.14	71.31 ± 0.10
	50	72.91 ± 0.75	27.09 ± 0.75	10.45 ± 0.09	14.34 ± 0.03	12.09 ± 0.79	16.57 ± 0.91	50.37 ± 0.13	69.09 ± 0.88
	100	69.39 ± 0.95	30.61 ± 0.95	10.97 ± 0.38	15.81 ± 0.33	12.83 ± 1.36	18.48 ± 1.70	45.59 ± 0.79	65.71 ± 2.04
	150	67.80 ± 1.11	32.20 ± 1.11	11.26 ± 0.53	16.61 ± 0.51	17.08 ± 1.01	25.18 ± 1.08	39.46 ± 0.43	58.21 ± 1.59
	200	65.70 ± 3.24	34.30 ± 3.24	12.41 ± 1.22	18.96 ± 2.80	19.41 ± 1.43	29.53 ± 0.73	33.87 ± 3.03	51.50 ± 2.07

adsorbed percentage amounts were lower compared to those of dimethoate and varied from 12.10 to 38.05% for all soils tested. The higher adsorption ability of fenthion is due to its low water solubility and high lipophilic character (Table 1). The bonds through which adsorption process took place cannot be broken easily by water. Significant higher desorption of bonded molecules occurred when soils were extracted with organic solvent of acetone. These results are in agreement with other published data [18,59].

Furthermore experimental results depicted hysteresis because pesticides' desorption isotherms did not coincide with adsorption isotherms, and discrepancies were observed. Phenomenon of hysteresis occurs often in adsorption-desorption studies of pesticides and soils, implying that a portion of the applied pesticide is very strongly or irreversibly bound to soil or may have degraded [37]. In any case hysteresis is dependent on the adsorption mechanism and on the chemical bonds and forces between the molecules of the adsorbate and the surface of the adsorbent [39]. According to the results contained in Tables 6 and 7, hysteresis was observed to be more evident for the soils with higher organic matter content, indicating that organic matter of the soil is the reason of hysteresis and this is in agreement with other published data [18,53]. Less obvious hysteresis occurred in the case of soils with low organic matter content implying that physical adsorption of pesticides proceed via weak interaction forces (such as London or dispersion forces) [18,54].

4. Conclusions

The adsorption/desorption characteristics of dimethoate and fenthion on three Greek soils were studied. Batch equilibrium experiments were carried out to asses adsorption coefficients obtained from Freundlich and Langmuir isotherm models (K_f and n; q_{max} and b, respectively), change in the partial molar free energy (ΔG°) and per cent balances for the adsorbed, desorbed with water, extracted with acetone and decomposed or permanently adsorbed amounts of selected OPPs, for seven different fortification levels of the soil. Freundlich isotherm fitted the adsorption experimental data better ($R^2 \geq 0.9666$) than the Langmuir isotherm ($R^2 \leq 0.8117$). Furthermore it was found that dimethoate was weakly adsorbed on three different studied soils and thus suspected for leaching, while on the contrary fenthion was strongly bonded onto soil and therefore it can be characterised as an immobile member of OPPs category.

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