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Effect of Organic Amendments on Aldicarb Sorption-Desorption and Soil-Bound Residue

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Abstract: Understanding the behaviour of pesticides in the environment is of great importance for their application and regulation. Therefore, this research was carried out to study the sorption-desorption isotherms of aldicarb and formation of its soil-bound residues in three common Egyptian soil types. Also, the effect of different organic amendments; litter compost, sludge compost, animal manure and chicken manure with different application rats; 5, 10 and 20 % on sorption-desorption processes for aldicarb was evaluated. The results of this study indicated that its adsorption isotherm forms on clay, litter compost and sludge compost were S-type, while that of calcareous soil, sandy soil, animal manure and chicken manure were C-type. Also, results indicated that the composting process has increased the sorption capacity of organic amendments. Adsorption of aldicarb was found to conform to Freundlich equation. In addition, the magnitude of adsorption was found to be in the order: clay soil > calcareous soil > sandy soil. This relation is consistent with the organic matter content of the different tested soils. According to the values of adsorbent organic carbon partition constant (K_{oc}), it could be suggested that the low amounts of organic amendment may greatly influence aldicarb sorption when added to the soil, specifically that is relatively poor in organic matter content. Our data revealed that the desorbed amounts of aldicarb from different tested soils were, in general, higher than the extracted ones. In contrast, the extracted aldicarb quantities from the tested organic amendments were higher than its desorbed amounts. Based on our results, the aldicarb soil-bound residues can be presented in the order: clay soil > calcareous soil > sandy soil. On the other hand, aldicarb bound residues on organic amendments can be arranged in the order; litter compost > sludge compost > animal manure > chicken manure. All organic amendments, proportionally with their concentration, have increased the soil-bound aldicarb residue particularly in calcareous and sandy soils. It is important to use the sorption-desorption kinetics, mechanism and capacity determined from soil and the effects of organic amendments on the sorption properties of pesticides applied onto soils for their fate and bioavailability predictions in the environment.

Keywords: Pesticides; Aldicarb, Soil, Sorption, Desorption, Bound residue, Amendment, Compost, Manure.

INTRODUCTION

The application of pesticides has both benefits and risks in the environment. With the proper management, benefits can be maximized while minimizing other risks. Pesticides are one of the major organic contaminants in the environment because of its heavy use in agriculture and industry. Soils play an important role in the environment by controlling the fate and availability of organic compounds because of their sorption capability[14,29]. Understanding the behaviour of pesticides in the environment is of great importance for their application and regulation. It is important to use the sorption and desorption mechanisms of pesticides applied onto soil for understanding and predicting their fate in the environment[31].

Ecologically and from the environmental prospective, it is important to understand the adsorption of soil-applied pesticides since it controls other processes such as leaching into groundwater, uptake by living organisms, transport into surface waters and the rate of volatilization of pesticides[43,35]. Sorption is chemical or physical. Anionic or cationic compounds are chemically sorbed, whereas nonionic compounds are physically sorbed. Hydrogen bonding is intermediate between physical and chemical sorption. The negative correlation between sorption and mobility of pesticides has been well established[44]. However, sorption is often considered a process that limits pesticide degradation[26]. Desorption of soil-associated pesticides has received considerable attention in the literature. The most common phenomenon reported is

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sorption-desorption hysteresis[12,42]. The formation of pesticide-soil organic matter (OM) complexes has been proposed as possible mechanisms responsible for hysteresis[56]. Recent work has shown that desorption rates of pesticides can be characterized by three types of processes; rapid desorption, rate-limited desorption, and a fraction that does not desorb over experimental time scales[41,48]. Many factors affect the sorption-desorption of pesticides such as pesticide type; soil properties, organic matter, clay content, soil pH and environmental conditions[2,25,21,28]. The importance of organic matter in the sorption process of pesticides by soils was emphasized in many studies[27,13].

Land application of sludge can have both beneficial and harmful aspects in the environment and for living organisms. As an excellent soil builder and conditioner, sewage sludge has shown improvements in both soil chemical and physical conditions[4,9]. However, some environmental problems may also occur because of its trace metal contamination[9]. Thus, the rates and frequency of the application of sludge is usually calculated, but these calculations do not take into account the effect of these amendments on pesticides behavior in soil. Utilization of animal manure can positively provide many chemical and physical factors necessary for the establishment of agronomic crops on sand and gravel soils[49]. Also, manure from livestock is an important source of plant nutrients for crop production in many areas in the world. However, the efficient management of manure is critical to improve its economic use and to minimize its negative impacts[55]. The use of organic manure might solve environmental pollution[32]. Furthermore, several studies demonstrated that the application of organic amendments onto soils improved their physical properties[38] and increased their organic matter content and thus may greatly affect their capacity for pesticide sorption-desorption processes[10].

Aldicarb is a broad-spectrum, systemic carbamate insecticide and nematicide used to control a variety of insects, mites and nematodes[23]. Aldicarb has high solubility and mobility in soil. Therefore, it was detected in the groundwater from leached soils. Leaching of pesticides is the most extensive phenomenon in sandy or sandy loam soils[16,53], as their adsorption to soil is a function of the organic matter content[37]. The kinetics and isotherms of adsorption/desorption of aldicarb by five different types of Egyptian soil was carried out by El-Aswad and Hedia[22]. It was found that the highest rate of adsorption of aldicarb on soil has been attributed to a higher OM content.

Adsorption of pesticides on soil is extensively studied. On contrary, limited data is available on desorption of pesticides, while very little information is available on the soil-bound pesticide residue. This study was therefore carried out to study the sorption/desorption isotherms of aldicarb and formation of the soil-bound residues in three common types of Egyptian soils. Also, the changes on the sorption, desorption, and bound residues that occur were monitored in soils amended with four different organic amendments (litter compost, sludge compost, animal manure and chicken manure) with different rates (5, 10 and 20%).

MATERIALS AND METHODS

Sorbents: Three soils representing the main soil types in Egypt were used as sorbents for aldicarb. Soil samples were collected from the top layers (0-20 cm) from Kafr El-Zyat region, Borg El-Arab region and Nubaria soil to represent Nile alluvium, calcareous deposits, and sandy desert soils, respectively. Air-dried soil samples, less than 2 mm particle size, were analyzed by standard methods according to Klute[33]. The pH was measured in a slurry 1:2.5 soil/aqueous calcium chloride (0.02 M). Organic matter content (OM) was determined by the Walkly-black method. All of these soil's characteristics are shown in Table (1).

Table 1: Physical and chemical properties of tested soils

Characteristics	Soil type		
	Clay	Calcareous	Sandy
Sand (%)	22	52	89
Silt (%)	38	23	3.5
Clay (%)	40	25	7.5
Texture	Clay loam	Sandy clay loam	Sandy
$CaCO_3$ (%)	3	34	9.6
OM (%)	1.37	0.47	0.14
pH	7.6	7.9	8.4
EC m mhos/cm	8.2	3.2	1.01
Region	Kafer El-Zayat	Borg El-Arab	El-Nobaria

Organic Amendments: The sewage sludge compost used in this experiment was obtained from the General Organization Sanitary of Alexandria city (at station No.9, 45 km south west the city of Alexandria, Egypt). Litter compost was obtained from the municipal litter plant of Abis, Alexandria, Egypt. Both animal manure and chicken manure were collected from the experimental station, Abis, Alexandria. Samples were air-dried and sieved through 2 mm screen. Organic matter content (OM) was determined by the Walkly-black method. The percentages of OM content were 17.84, 22.99, 20.59 and 23.68% for litter compost, sludge compost, animal manure and chicken manure, respectively.

Sorbate: The analytical standard for aldicarb [2-methyl-2-(methylthio) propionaldehyde-o-(methylcarbamoyl)-oxime] with 98.5% purity, was obtained from the Agrochem Company.

Determination of Aldicarb: Aldicarb was determined after hydrolysis in alkaline solution by colorimetric analysis at 530 nm by Sequoia-Turner Corp. Model 390 Spectrophotometer. This method was described by Meagher *et al.,*[39] and was slightly modified by Aly[1] to increase its sensitivity.

Adsorption Studies: Adsorption of aldicarb was studied using a batch equilibration procedure. Triplicate of 1.0 g samples of soils (clay, calcareous and sandy) or organic matter-amended soils (5, 10 and 20% of litter compost, sludge compost, animal manure and chicken manure in soil) were treated with 10 ml of aldicarb solutions of concentration (C_o) ranging from 5 to 60 mg/L. $CaCl_2$ (0.01 M) was used as a background electrolyte to minimize the changes in ionic strength of solutions and to promote flocculation[17]. Suspensions were shaken at 20 ± 2 ºC for 1 h in 50 ml centrifuge tubes and then centrifuged at 5000 xg at the same temperature for 15 min. Equilibrium concentration (C_e) was determined in the supernatant. Previously, it was checked that equilibrium was reached at 1 h and that no apparent degradation occurred during this period. Differences between C_o and C_e were assumed to be due to adsorption. Blanks containing no aldicarb were used and blanks with no soil indicated that adsorption of aldicarb to reaction vessel was insignificant.

Desorption Studies: Samples, which were previously equilibrated with a solution of aldicarb in the adsorption experiment, were used for this study. 10 ml of 0.01 M $CaCl_2$ aliquot was added to the centrifugation tubes containing samples. To establish new equilibrium, these samples were resuspended and shaken again followed by centrifugation. Supernatant was used for the determination of the new equilibrium concentration. Pellets were exposed to another centrifugation cycles but using acetone as a nonpolar solvent to assess the soil-bound residues and the extracted aldicarb was determined. For mass balance, the quantity of desorbed aldicarb by $CaCl_2$ solution and extracted aldicarb by acetone were corrected for the amount in the solution left with the soil in the centrifuge sediment, taking into account the final concentration of the solution and the weight of retained solution.

RESULTS AND DISCUSSIONS

As described above, a batch experiment was conducted to determine the equilibrium time of aldicarb adsorption on soils. Data showed that the obtained equilibrium times have varied slightly among soils as sorbents but they were within the first 1 h of reaction. Thereafter, the concentration of the adsorbed chemical was almost constant up to 24 h of shaking.

Similar result was achieved by El-Aswad and Hedia[22]. They found that the adsorption equilibrium times of aldicarb in different soil types were within the first 1 h. The time required for a pesticide-soil system to reach adsorption equilibrium depends on type of pesticide and soil characteristics[40]. Based on this result, an equilibrium time of 1 h was used in the subsequent adsorption and desorption experiments.

Sorption Study: The adsorption isotherms of aldicarb by soils and organic amendments showed different forms according to adsorbent characteristics (Fig. 1). Those for soil with the highest OM and clay content were S-type (initial convex curvature) according to the classification of Sposito[51]. Although the initial concave and convex curvatures of the isotherms obtained in this work were smooth (all of them approached type C), their shapes showed that the affinity of soils for aldicarb was related to their organic matter content. This finding is supported by the results obtained by Nkedi-Kizza and Brown[40]. Both calcareous and sandy soils represented typical C-type isotherms. However, calcareous soil showed higher affinity to aldicarb compared to sandy soil. Aldicarb adsorption isotherm forms for organic amendments indicated that the isotherms of sludge compost and litter compost were S-type, while the isotherms of animal manure and chicken manure were C-type. Although the organic matter content of different organic amendments was found to decrease in the order: chicken manure, 23.7% > sludge compost, 23.0% > animal manure, 20.6% > litter compost, 17.8%, the affinity of organic amendments for aldicarb was found to decrease in the order: sludge compost > litter compost > animal manure >chicken manure. Therefore, it was suggested that the affinity of an organic amendment for aldicarb is not related only to its organic matter content but also related to the characteristics of organic amendment as well as the type, composition and configuration of its organic matter. Pusino *et al.,*[46] concluded that the reactivity of the organic matter as altered by specific interactions with the inorganic components may be the main factor regulating metolachlor adsorption. Also, Celis *et al.,*[11] discussed the effects of the molecular weight of organic matter in liquid sewage sludge. In addition, various intrinsic factors of adsorbent and adsorbate, which influence adsorption of insecticides, are summarized by Bailey and White[5]. It has been reported that for diagnostically old organic matter, condensed domains are enriched in aromatic carbons while for relatively young organic matter, condensed domains can be enriched in aliphatic carbons. Therefore, both aromatic and aliphatic components of organic matter can contribute to high sorption capacity[18]. Furthermore, interaction between minerals and organic matter may render the structural configuration of organic matter to a more condensed state. Additionally, sorption processes may be strongly affected by physical conformation[29]. It is interesting to state that the composting process has improved the characteristics of organic amendments.

Adsorption isotherm: Adsorption isotherms for the tested soils and organic amendments are illustrated in Fig. (2). Data were found to conform to the principal isothermal Freundlich relationship written as: $x/m = KC^{1/n}$.

Where x/m is the amount of aldicarb (x) adsorbed by a given amount of adsorbent (m). The constants K and n embrace all factors affecting adsorption from solution namely, properties of the adsorbate, adsorbent, and solvent, and the equilibria between the adsorbate-adsorbent, adsorbate-solvent and solvent-adsorbent[6]; while C is the equilibrium concentration of the adsorbate in solution. Conformity to the Freundlich equation existed for all systems with a correlation coefficient $r > 91$. The calculated values of K and 1/n, the reciprocal of the slope of the isotherm, are listed in Table (2). Using 1/n to indicate the extent of adsorption, clay soil showed greater affinity for aldicarb than both calcareous and sandy soils. The high value of K for calcareous soil (K = 1.545) indicates a strong initial adsorption, which is probably due to the presence of a large amount of $CaCO_3$[3]. Adsorption of aldicarb per gram adsorbent was found to be in the order: clay soil > calcareous soil > sandy soil. This relation is consistent with the organic matter content of these different soils. This result is in agreement with that obtained by El-Aswad and Hedia[22] as they found that the greater the adsorption of aldicarb by soil, located at Abis, Alexandria, has been attributed to the higher organic matter content. Also, Aly *et al.,*[3] found that the Nile alluvial soil exhibited the highest degree of adsorption followed by calcareous soil. Regarding to the parameters of Freundlich isotherm of aldicarb by different organic amendments, 1/n values indicate that its highest adsorption took place by litter compost, while its lowest adsorption took place by animal manure. Moreover, the strongest initial adsorption was observed by sludge compost which has the highest K value (K = 34.4).

In addition, the distribution coefficient, K_d, that represents adsorption at equilibrium concentrations higher than K value, was calculated. K_d is defined as the ratio between the pesticide concentration in the adsorbent and that in the equilibrium solution at a given equilibrium concentration. There is a general consensus that the magnitude of K_d values usually indicates the affinity of the chemical to the adsorbent matrix[15]. Our results showed that the K_d value of aldicarb was high for clay soil compared to that of sandy soil. This indicates that aldicarb was strongly bound to clay soil matrix and hence, its mobility in this soil is expected to be low. In contrast, the mobility of aldicarb is expected to be high in sandy soil. This finding is in agreement with similar results obtained by Sundaram *et al.,*[52].

Regarding aldicarb interaction on organic amendments, our results indicated that aldicarb sorption on compost of sludge and litter as characterized by K_d value is about 1.5-fold higher than its sorption on animal and chicken manures. These results are in agreement with those obtained by Barriuso *et al.,*[7]. The K_d value is related to adsorbent OM and organic carbon (OC) by the following equation:

$K_{om} = (K_d/\%OM) \times 100$ and $K_{oc} = (K_d/\%OC) \times 100$, where K_{om} is the adsorbent OM partition constant and K_{oc} is the adsorbent OC partition constant[36,42]. Results of this study showed that K_{om} value, which is very frequently used as a measure of the pesticide adsorption capacity, was ranged from 580 to 3800 of tested soils and from 25 to 45 of tested organic amendments. The effectiveness of the organic carbon of soil and organic amendments in sorbing aldicarb can be compared by normalizing the Freundlich sorption coefficient to the respective organic carbon contents, K_{oc}. As shown in Table (2), K_{oc} values of the different studied soils were about 15 fold higher than that of the tested organic amendments. Furthermore, K_{oc} value of sandy soil was higher than that of calcareous soil followed by clay soil. Among organic amendments, sludge compost showed the highest value of K_{oc}, while the lowest K_{oc} was for chicken manure. In general, the K_{oc} coefficient represents the sorption on a unit carbon basis and allows a comparison of sorption on compounds with different organic matter content[7,19]. Accordingly, it could be suggested that the adsorption efficiency of organic matter increased with OM content decrease.

Effect of Soil Organic Amendments on the Aldicarb Adsorption: In this study, the adsorption characteristics of aldicarb by soils in the presence of four organic amendments; litter compost, sludge compost, animal manure and chicken manure at three concentrations; 5, 10 and 20% were evaluated. Experimental results are shown in Fig. (3), where the amount of aldicarb adsorbed per unit mass of soil has been plotted against the amendment concentration in a dimension and aldicarb concentration in another dimension. The data show that the adsorbed quantities of aldicarb in all cases; tested soils, organic amendment types and organic amendment concentrations were increased proportionally with the initial concentration of aldicarb. Addition of litter compost slightly increased aldicarb sorption by clay soil (A1), while significantly increased its sorption by calcareous soil. The adsorption of

Table 2: Freundlich adsorption isotherm parameters of aldicarb in soils and organic amendments

Adsorbents	K_{ads}	1/n	r	K_d	K_{om}	K_{oc}
Clay soil	1.276	3.680	0.955	7.94	580	995
Calcareous soil	1.545	2.355	0.930	6.17	1122	1934
Sandy soil	0.572	2.171	0.980	5.20	3796	6500
Litter compost	6.625	2.150	0.910	8.00	44.8	77.1
Sludge compost	34.408	1.627	0.935	8.71	37.9	65.1
Animal manure	8.421	1.231	0.919	5.50	26.7	45.9
Chicken manure	4.693	1.767	0.917	5.98	25.3	43.4

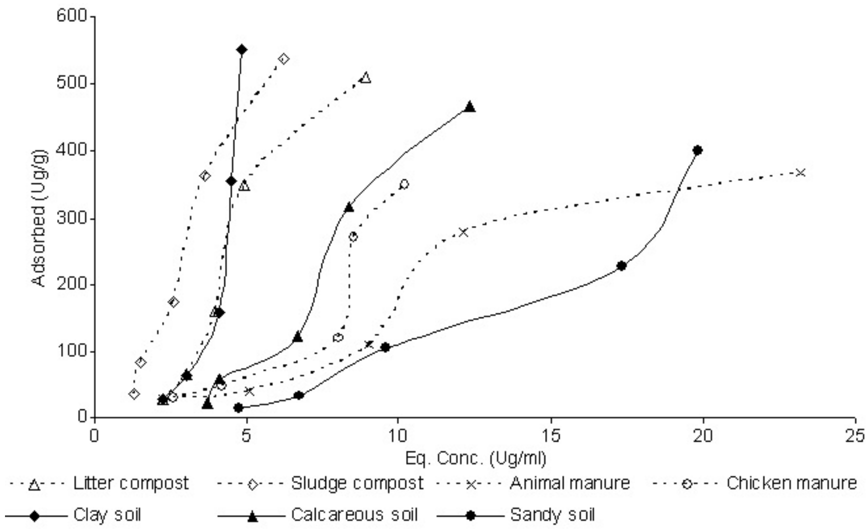

Fig. 1: Adsorption isotherm of aldicarb by soil and organic amendments.

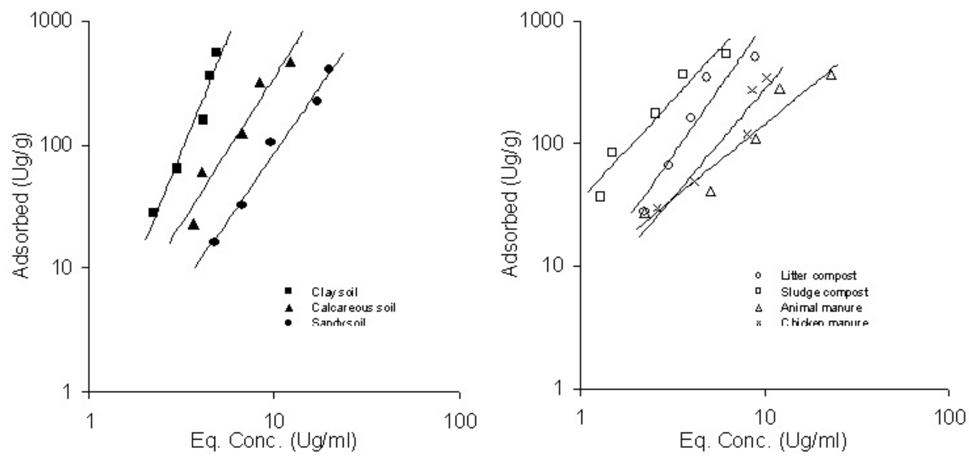

Fig. 2: Adsorption isotherm of aldicarb by soils and organic amendments fitted with Freundlich equation.

aldicarb was reduced in calcareous soil when amended with 20% of litter compost, sludge compost or animal manure compared to that in the same soil when it was amended with 5 or 10% of the three organic amendments (B1, B2, B3). Regardless its concentration, chicken manure showed no significant effect on aldicarb adsorption on clay soil, while it was promising in the case of calcareous soil (A4, B4). The pronounced increase of aldicarb adsorption was obtained by the sandy soil amended with 5% of the four organic amendments compared to same soil with no amendments. This effect did not increase

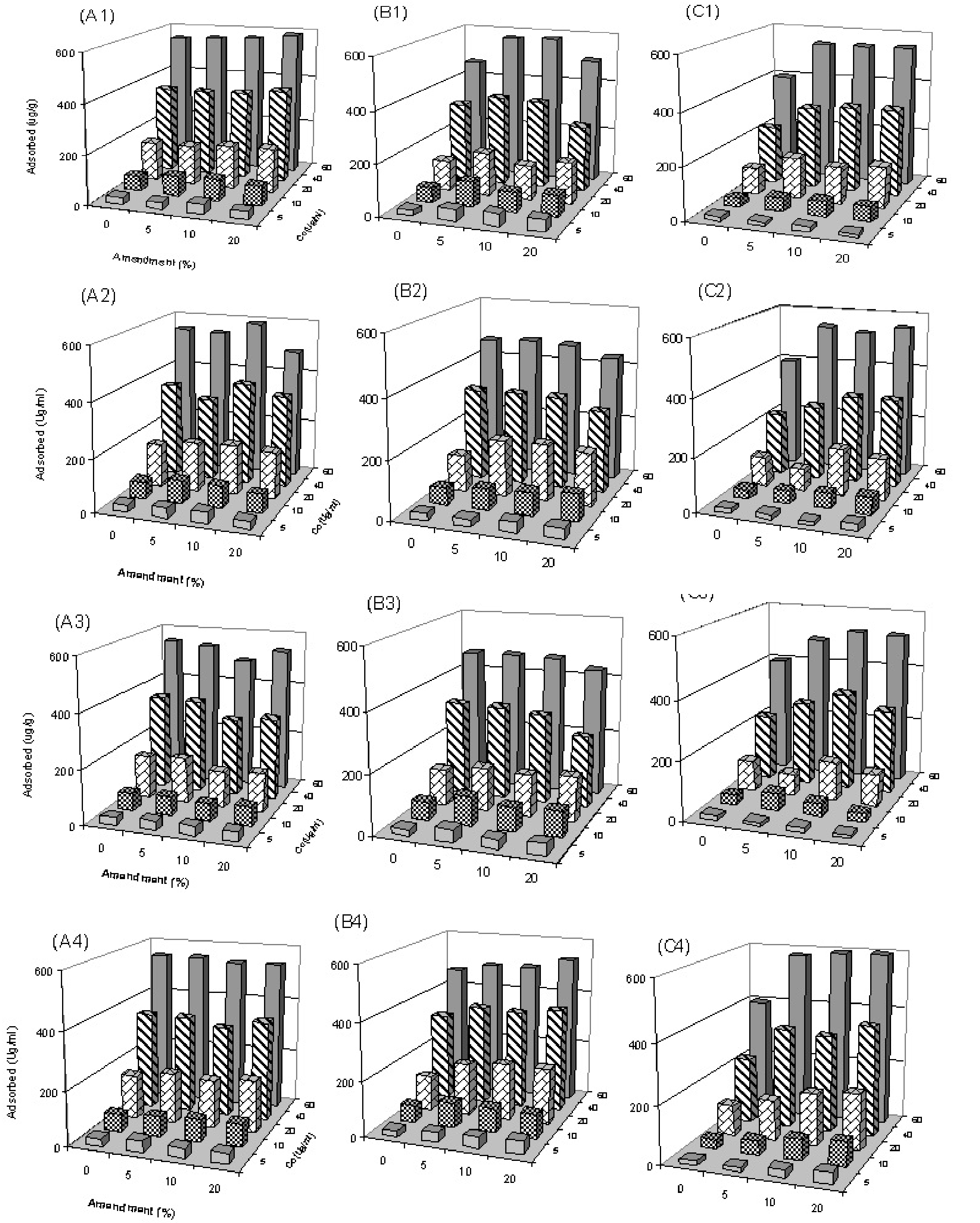

Fig. 3: Adsorption of aldicarb by soils amendment with organic amendments
(A: Clay soil, B: Calcareous soil, C: Sandy soil, 1: Litter compost 2: Sludge compost, 3: Animal manure, 4: Chicken manure)

with increasing the amounts of organic amendments into 10% or even 20% (C1, C2, C3, C4). This suggests that little amounts of an organic amendment may greatly influence aldicarb sorption, especially when added to soils relatively poor in organic matter.

The proportional relation between concentrations of the four organic amendments and the K values (Table 3) was observed. The highest values of K were obtained in calcareous soil when amended with different concentrations of all four amendments. The greater values of 1/n were detected in the case of sandy soil. This may indicate that the effect of organic amendment on the aldicarb adsorption is more dependent on the type of soil rather than the type or the concentration of that organic amendment. It is generally accepted that the effect of tested organic amendments on the adsorption of aldicarb by clay soil is not significant. This may be due to the adsorption of aldicarb in clay soil is already high and the sorptive

Table 3: Freundlich isotherm parameters of aldicarb in soils amended with different organic amendments

Organic amendment (%)		Clay soil			Calcareous soil			Sandy soil		
		K_{ads}	1/n	r	K_{ads}	1/n	r	K_{ads}	1/n	r
Litter compost	5	1.423	3.141	0.830	28.805	1.068	0.938	0.264	2.783	0.916
	10	3.615	2.120	0.974	30.710	0.905	0.814	0.437	2.595	0.985
	20	6.846	1.872	0.981	38.070	0.749	0.940	0.681	2.254	0.876
Sludge compost	5	8.168	1.533	0.919	4.062	1.850	0.791	1.343	1.738	0.885
	10	10.324	1.700	0.995	20.708	1.035	0.868	1.789	1.926	0.915
	20	14.090	1.241	0.935	30.208	0.838	0.904	2.279	1.952	0.972
Organic manure	5	6.531	1.610	0.980	12.674	2.136	0.917	0.259	2.662	0.902
	10	10.002	1.199	0.955	14.362	0.967	0.993	0.266	2.651	0.963
	20	14.223	1.166	0.935	27.266	0.817	0.871	0.295	2.432	0.985
Chicken manure	5	11.834	1.424	0.966	14.272	1.340	0.922	0.028	3.857	0.954
	10	12.588	1.337	0.977	26.827	0.901	0.985	3.508	1.878	0.925
	20	17.670	1.303	0.962	38.547	0.982	0.928	8.892	1.882	0.975

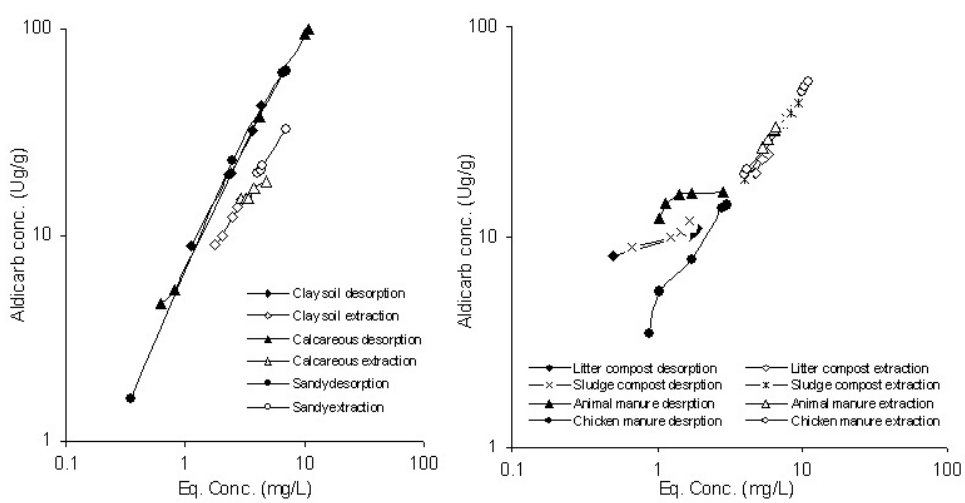

Fig. 4: Desorption and extraction isotherms of aldicarb from soils and organic amendments.

sites was saturated. Also, results showed that the adsorption of aldicarb was significantly increased by calcareous soil amended with 5% and 10% of all tested organic amendments except the chicken manure, while was decreased by 20% addition. It could be that the addition of 10% of organic amendment has caused the sorption sites to reach the saturation level. This can be explained by the interaction between the soil and the organic matter that could result in some blockage of sorption sites for aldicarb on both soil and organic amendment. Similar results were obtained from studying the effect of organic amendment addition to soil on the adsorption of dimefuron and carbetamide[8], napropamide[34] and of atrazine[11]. Aldicarb adsorption by sandy soil has clearly increased with 5% addition of any tested organic amendment. The increase in pesticide sorption by organic amendments addition to soil has been previously reported by several authors and attributed to the high sorption capacity of the organic matter added to soil[30,10].

Desorption and Extraction Study: Fig. (4) exhibits desorption and extraction isotherms of aldicarb from both soils and organic amendments. Aldicarb concentrations at desorption equilibrium in all tested organic amendments were low compared to the extraction equilibrium. Furthermore, desorption of aldicarb from clay soil reached to the equilibrium at a lower concentration compared to that of calcareous and sandy soils. Also, the extraction of aldicarb from presorbed litter compost and animal manure reached to the equilibrium in concentrations lower than that of sludge compost and chicken manure. This observation could be due to the organic matter content, which is lower in litter compost and animal manure than that in sludge compost and chicken manure.

Aldicarb adsorption, desorption and extraction in clay, calcareous and sandy soil and different organic amendments; sludge compost, litter compost, animal manure and chicken manure are shown in Fig. (5). Results indicated that the aldicarb desorbed from clay, calcareous and sandy soil, was about 10, 24 and 27%, while the extracted aldicarb was about 5, 8 and 16% of the adsorbed quantity, respectively (A1 & A2 & A3).

This indicates that tested soils retained most of the adsorbed aldicarb and that the adsorption is an irreversible process. These results are in agreement with those obtained by El-Aswad and Hedia[22]. Moreover, many authors reported that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed[54-50].

Regarding the four organic amendments; sludge compost, litter compost, animal manure and chicken manure, desorption of aldicarb from all these adsorbents ranged from 5 to 10%. On the other hand, the extracted fraction of aldicarb ranged from 10 to 20% from the adsorbed concentration (B2 & B3). This finding indicates a high affinity between aldicarb molecules and each organic amendment. Clearly, the desorbed amounts of aldicarb from different tested soils were higher than extracted ones. In contrast, the extracted aldicarb quantities from tested organic amendments were higher than desorbed amounts. Thus, the values of 1/n (des) for soils ranged from 1.13 to 1.23 whereas 1/n (ext) ranged from 0.43 to 1.0. In contrast, 1/n (des) for organic amendments ranged from 0.16 to 0.28 while, 1/n (ext) ranged from 0.74 to 1.0 (Table 4).

Distribution of Aldicarb among Desorbed, Extracted and Soil-bound Residue: Data presented in Fig (6) show the distribution of aldicarb among desorbed, extracted and soil-bound residue. It can be generally recorded that the amount of desorbed aldicarb from each tested soil is greater than the extracted. The amounts of desorbed and extracted aldicarb from clay

Table 4: Freundlich desorption and extraction isotherm parameters of aldicarb in soils and organic amendments

Adsorbents	Desorption			Extraction		
	K_{des}	1/n	r	K_{ext}	1/n	r
Clay soil	0.008	1.128	0.996	0.005	1.002	0.999
Calcareous soil	0.007	1.111	0.999	0.009	0.430	0.854
Sandy soil	0.006	1.225	0.996	0.006	0.915	0.998
Litter compost	0.009	0.204	0.977	0.007	0.739	0.912
Sludge compost	0.010	0.283	0.853	0.005	0.990	1.000
Animal manure	0.014	0.241	0.810	0.005	0.983	0.997
Chicken manure	0.005	0.163	0.969	0.005	0.999	1.000

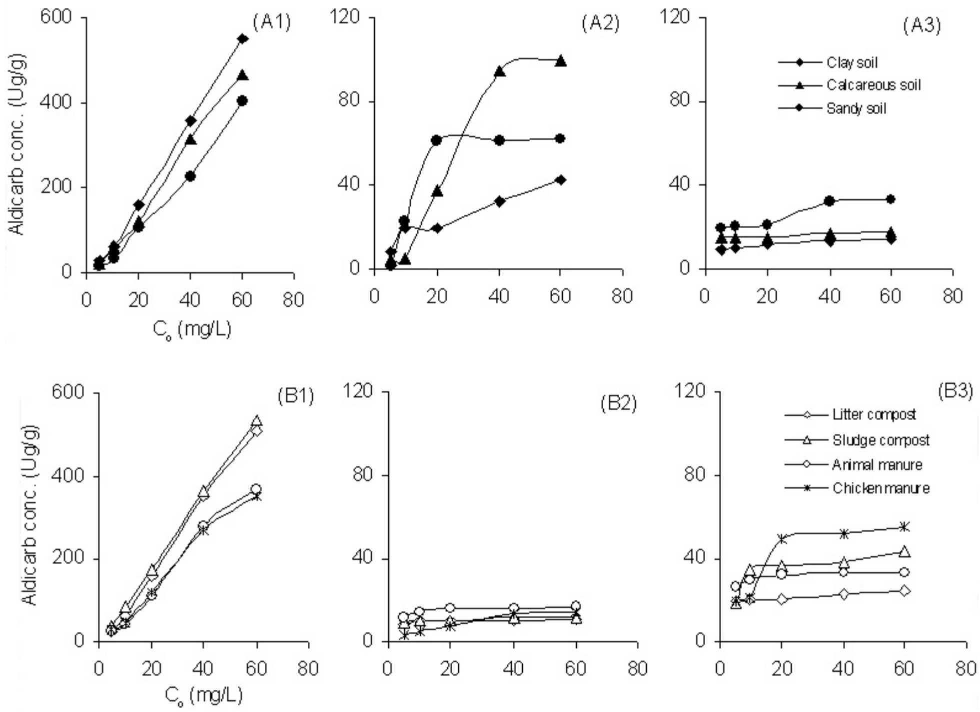

Fig. 5: Adsorption, desorption and extraction of aldicarb in soils and organic amendments. A: soils, B: organic amendments, 1: adsorption, 2: desorption, 3: extraction.

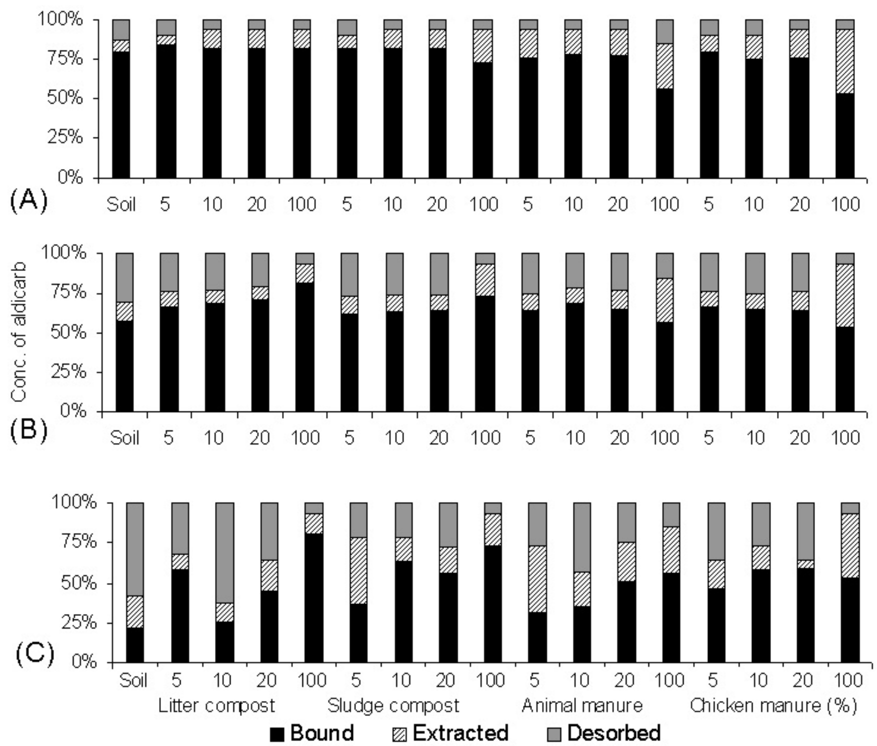

Fig. 6: Distribution of aldicarb among desorption, extraction and bound residue,

A: Clay soil, B: Calcareous soil, C: Sandy soil.

soil (A) are less than that of calcareous soil (B) followed by sandy soil (C). While, the amounts of extracted quantity and non-extracted (bound residue) of aldicarb from sandy soil are almost the same. Consequently, the soil aldicarb-bound residues can be presented in the order: clay soil > calcareous soil > sandy soil. Concerning the organic amendments, the amounts of desorbed aldicarb from litter compost, sludge compost and chicken manure were not significantly different, but were lower than that from animal manure. According to the amount of extracted aldicarb, organic amendments can be arranged in the order: litter compost < sludge compost < animal manure < chicken manure. In contrast, according to the amounts of bound-aldicarb residue, the previous sequence of these organic amendments is reversed. Addition of litter compost decreased aldicarb desorbed amounts of all tested soils, while adding animal manure increased its extracted amount. Addition of organic amendments, particularly animal manure and chicken manure decreased the formation of clay soil aldicarb-bound residues. Barriuso *et al.,*[7] recorded that addition of compost decreased the formation of many herbicide bound residues in soil. All organic amendments magnified, proportionally with their concentration, the soil bound aldicarb residue in calcareous and sandy soil. The increase of soil bound residue after the amendment of organic matter has also been reported for pentachloronitrobenzene[20], 2,4-D[47] and for atrazine[31]. Moreover, the addition of organic amendments promoted the formation of soil-bound residue[24,45, 21].

Conclusion: From the results of this study, it can be concluded that the organic amendments increased soil OM content and thus greatly affected aldicarb sorption-desorption processes. The adsorption isotherm forms of clay, litter compost and sludge compost were S-type, while that of calcareous soil, sandy soil, animal manure and chicken manure were C-type. The composting process improved the characteristics of organic amendments and increased their sorption capacity for aldicarb. Adsorption of aldicarb was found to conform to Freundlich equation. In addition, the magnitude of adsorption was found to be in the order: clay soil > calcareous soil > sandy soil. This relation is consistent with the organic matter content of the different soils. As characterized by K_d values, sorption of aldicarb on compost of sludge and litter was about 1.5-fold higher than that on manure of animal and chicken. According to K_{oc} values, it could be suggested that adding slight amounts of organic amendments may greatly influence aldicarb sorption when added to soils relatively poor in organic matter. The desorbed amounts of aldicarb from different tested soils were higher than extracted ones.

In contrast, the extracted quantities of aldicarb from organic amendments were higher than desorbed amounts. For examined soils, the aldicarb bound residues can be presented in the order: clay soil > calcareous soil > sandy soil. On the other hand, for the examined organic amendments, the aldicarb bound residues can be presented in the order: litter compost > sludge compost > animal manure > chicken manure. All organic amendments, proportionally with their concentration, increased soil bound aldicarb residue particularly in calcareous and sandy soils. It is suggested that the risk of groundwater contamination by aldicarb desorption is potentially high especially in calcareous and sandy soils but can be progressively reduced as the soil becomes incorporated with organic amendments. Thus, it is important to use the sorption-desorption kinetics, mechanism and capacity determined from various soils and the effect of organic amendments on the sorption properties of pesticides for predicting their fate and bioavailability in the environment.

REFERENCES

1. Aly, M.I., 1977. Interaction between pesticides and soil. Ph.D. Thesis. Faculty of Agric., Alex. Univ.
2. Aly, M.I. and N.M. Bakry, 1986. The influence of saturating ions and moisture on aldicarb persistence on kaolinite. Alex. J. Agric. Res., 31: 407-417.
3. Aly, M.I., N.M. Bakry, F. Kishk and A.H. El-Sebae, 1980. Carbaryl adsorption on calcium-bentonite and soils. Soil Sci. Soc. Am. J., 44: 1213-1215.
4. Baham, J. and G. Sposito, 1994. Adsorption of dissolved organic carbon extracted from sewage sludge on montmorillonite and kaolinite in the presence of metal ions. J. Environ. Qual., 23: 147-153.
5. Bailey, G.W. and J.L. White, 1970. Factors influencing the adsorption, desorption and movement of pesticides in soils. Residue Reviews, 32: 29-92.
6. Bailey, G.W., J.L.White and T. Rothberg, 1968. Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. Soil Sci. Soc. Am. Proc., 32: 222.
7. Barriuso, E., S. Houot and C. Serra-Wittling, 1997. Influence of compost addition to soil on the behaviour of herbicides. Pestic. Sci., 49: 65-75.
8. Barriuso, E., U. Baer and R. Calvet, 1992. Dissolved organic matter and adsorption-desorption

of dimefuron, atrazine and carbetamide by soils. J. Environ. Qual., 21: 359-367.
9. Brown, S., R. Chaney and J.S. Angle, 1997. Subsurface liming and metal movement in soils amended with lime-stabilized biosolids. J. Environ. Qual, 26: 724-732.
10. Businelly, D., 1997. Pig slurry amendment and herbicide coapplication effects on s-triazine mobility in soil: an adsorption-desorption study. J. Environ. Qual., 26: 102-108.
11. Celis, R., E. Barriuso and S. Hout, 1998. Effect of liquid sewage sludge addition on atrazine sorption and desorption by soil. Chemosphere, 37(6): 1091-1107.
12. Chen, W., A.T. Kan, C.J. Newell, E. Moore and M.B. Tomson, 2002. More realistic soil cleanup standards with dual-equilibrium desorption. Ground Water, 40: 153-164.
13. Chiou, C.T., 2002. Partition and Adsorption of Organic Contaminants in Environmental Systems. Wiley, Hoboken NJ, USA.
14. Chiou, C.T., S.E. McGroddy and D.E. Kile, 1998. Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environ. Sci. Technol, 32: 264-269.
15. Cleveland, C.B., 1996. Mobility assessment of agrochemicals: Current laboratory methodology and suggestions for future directions. Weed Technology, 10: 157-168.
16. Cohen, S.Z., S.M. Creeger, R.F. Carsel and C.G. Enfield, 1984. Potential pesticide contamination of groundwater from agricultural uses. *In:* Treatment and Disposal of Pesticide Wastes. R. F. Krueger and J. N. Seiber (eds.). ACS Symp. Ser. No. 259, Am. Chem. Soc., Washington, DC. pp: 297.
17. Cox, L., M.C. Mermosin and J. Cornejo, 1995. Adsorption mechanisms of thiazafluron in mineral soil clay components. European J. Soil Sci., 46: 431-438.
18. Cuypers, C., T. Grotenhuis, K.G.J. Nierop, E.M. Franco, A. de Jagar and W. Rulkens, 2002. Amorphous and condensed organic matter domains: The effect of persulfate oxidation on the composition of soil/ sediment organic matter. Chemosphere, 48: 919-931.
19. Deer, H., 2004. Pesticide adsorption and half-life. Report I, Cooperative Extension Service, Utah State Univ., Logan, Utah.
20. Doyle, R.C., D.D. Kaufman and G.W. Burt, 1978. Effect of dairy manure and sewage on ^{14}C-pesticide degradation in soil. Journal of Agricultural and Food Chemistry, 26: 987-989.
21. El-Aswad, A.F., 1998. Behaviour of pesticides in soil: Environmental behaviour of herbicides alachlor and picloram (Laboratory studies) and pollutantsPAHs and PCBs (Lysimeter studies). Ph.D. Thesis, Faculty of Agric., Alex. Univ.
22. El-Aswad, A.F. and R.M. Hedia, 2002. Fate and behaviour of aldicarb under Egyptian soil conditions. I. Sorption/desorption kinetics and soil-bound residues. National Symposium on Problems of Land Degradation in Egypt and Africa: Causes, Environments Hazards and Conservation Methods. Institute of Africa Research & Studies. Department of Natural Resources, Cairo Univ., March, 23-24, pp: 57-68.
23. EPA, 1999. Summary of Pesticide Use Report Data. Department of Pesticide Regulation, California.
24. Fuehr, F., 1987. Non-extractable pesticide residues in soil. In: R. Greenhalgh and T. R. Robert (ed.). Pesticide Science and Technology 6th IUPAC Congress Pest. Chem. Proc., Blackwell, London, pp: 381-389.
25. Gaber, H.M., S.D. Comfort, W.P. Inskeep and H.A. El-Attar, 1992. A test of the local equilibrium assumption for adsorption and transport of picloram. Soil Sci. Soc. Am. J., 56: 1392-1400.
26. Gamerdinger, A.P., R.S. Achin and R.W. Traxler, 1997. Approximating the impact of sorption on biodegradation kinetics in soil–water systems. Soil Sci. Soc. Am. J., 61: 1618-1626.
27. Ghosh, U., J.W. Talley and R.G. Luthy, 2001. Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. Environ. Sci. Technol., 35: 3468-3475.
28. Gonzalez-Pradas, E., M. Fernandez-Perez, M. Villafranca-Sanchez and F. Flores-Cespedes, 1999. Mobility of imidacloprid from alginate-bentonite controlled-release formulations in greenhouse soils. Pestic. Sci., 55: 1109-1115.
29. Gunasekara, A.S. and B. Xing, 2003. Sorption and desorption of naphthalene by soil organic matter: Importance of aromatic and aliphatic components. J. Environ. Qual., 32: 240-246.
30. Guo, L., T.J. Bicki, A.S. Felsot and T.D. Hinesly, 1993. Sorption and movement of alachlor in soil modified by carbon-rich wastes. J. Environ. Qual., 22: 186-194.
31. Hafez, H.F. and A.F. El-Aswad, 2005. Sorption-desorption of atrazine in soil. Alex. Sci. Exch., 26(1): 41-53.
32. Kaloosh, A.A. and E.A. Koreish, 1995. Nitrobin, ammonium nitrate and chicken manure effects on wheat growth, soil nitrate, soil microbial biomass and carbon dioxide evolution. J. Agric. Sci. Mansura Univ., 20(8): 3943-3949.
33. Klute, A., 1986. Methods of Soil Analysis. Agron. Ser. 9 and 10. Madison, WI.

34. Lee, D.Y., W.J. Farmer and Y. Aochi, 1990. Sorption of napropamide on clay and soil in the presence of dissolved organic matter. J. Environ. Qual., 19: 567-573.
35. Lesan, H.M. and A. Bhandari, 2003. Atrazine sorption on surface soils: time-dependent phase distribution and apparent desorption hysteresis. Water Research, 37: 1644-1654.
36. Li, H., G. Sheng, B.J. Teppen, C.T. Johnston and S.A. Boyd, 2003. Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. Soil Sci. Soc. Am. J., 67: 122-131.
37. Lorber, M.N., S.Z. Cohen, S.E. Noren and G.D. Buchananne, 1989. A national evaluation of leaching potential of aldicarb. Part I: An integrated assessment methodology. Groundwater Monit. Rev., 9(4): 109.
38. Mamo, M., C.J. Rosen and T.R. Halbach, 1999. Nitrogen availability and leaching from soil amended with municipal solid waste compost. J. Environ. Qual., 28: 1074-1082.
39. Meagher, W.R., R. Hendrickson and B.G. Shively, 1967. Spectrophotometric determination of temik residues in citrus. J. Ass. Offic. Analyt. Chem., 50: 1242.
40. Nkedi-Kizza, P. and K.D. Brown, 1998. Sorption, degradation and mineralization of carbaryl in soils, for single pesticide and multiple-pesticide systems. J. Environ. Qual., 27: 1318-1324.
41. Park, J.H., X. Zhao and T.C. Voice, 2002. Development of a kinetic basis for bioavailability of naphthalene in soil slurries. Water Res., 36: 1620-1628.
42. Park, J., Y. Feng, S.Y. Cho, T.C. Voice and S.A. Boyd, 2004. Sorbed atrazine shifts into non-desorbable sites of soil organic matter during aging. Water Research, 38: 3881-3892.
43. Pignatello, J.J. and B. Xing, 1996. Mechanisms of slow sorption of organic chemicals to natural particles. Environ. Sci. and Technol., 30: 1-11.
44. Pignatello, J.J., F.J. Ferrandino and L.Q. Huang, 1993. Elution of aged and freshly added herbicides from a soil. Environ. Sci. Technol., 27: 1563-1571.
45. Printz, H., P. Burauel and F. Fuehr, 1995. Effect of organic amendment on degradation and formation of bound residues of methabenzthiazuron in soil under constant climatic conditions. J. Environ. Sci. Health, B30(4): 435-456.
46. Pusino, A, W. Liu and C. Gessa, 1992. Influence of organic matter and its clay complexes on metolachlor adsorption on soil. Pestic. Sci., 36: 283-286.
47. Seibert, K., F. Fuehr and W. Mittelstaedt, 1982. Experiments on the influence of roots and soils on 2,4-D degradation. Landwirtschaftliche Forschung, 35: 5-13.
48. Sharer, M., J.H. Park, T.C. Voice and S.A. Boyd, 2003. Aging effects on the sorption/desorption characteristics of anthropogenic organic compounds in soil. J. Environ. Qual., 32: 1385-1392.
49. Sharpley, A.N., B.J. Carter, B.J. Wagner, S.J. Smith, E.L. Cole and G.A. Sample, 1991. Impact of long-term swine and poultry manure application on soil and water resources in eastern Oklahoma. Tech. Bull. T-169. Oklahoma Agric. Exp. Stn., Stillwater, OK.
50. Sparks, D.L., 1995. Environmental Soil Chemistry. Academic Press, New York.
51. Sposito, G., 1984. The Surface Chemistry of Soils. Oxford Univ. Press, New York.
52. Sundaram, K.M.S., L. Sloane and R. Nott, 1997. Adsorption and desorption kinetics of diflubenzuron and fenitrothion in two different boreal forest soils. J. Environ. Sci. Health, B32(1): 1-24.
53. US-EPA, 1988. EPA notice of preliminary determination regarding continued registrations of products containing aldicarb. Fed. Regist., 53: 24630.
54. Verburg, K. and P. Baveye, 1994. Hysteresis in the binary exchange of cations on 2:1 clay : minerals: A critical review. Clays Clay Miner., 42: 207-220.
55. Williams, E.J., 1992. Nitrogen fertilizer and dairy manure effects on corn yield and soil nitrate. Soil Sci. Soc. Am. J., 56: 148-154.
56. Xie, H., T.F. Guetzloff and J.A. Rice, 1997. Fractionation of pesticide residues bound to humin. Soil Sci., 162: 421-429.