



Sorption of alpha and beta hydrophobic endosulfan in a Vertisol from southeast region of Turkey

Ayşe Dilek Atasoy^{a,*}, Ahmet Ruhi Mermut^b, Halil Kumbur^c, Faruk İnce^b, Hüdaverdi Arslan^c, Emel Deniz Avcı^c

^a Department of Environmental Engineering, Harran University, Osmanbey Campus, 63100 Sanliurfa, Turkey

^b Department of Soil Science, Harran University, Eyyubiye Campus, 63100 Sanliurfa, Turkey

^c Department of Environmental Engineering, Mersin University, Ciftlikkoy, 33343 Mersin, Turkey

ARTICLE INFO

Article history:

Received 19 September 2008

Accepted 3 December 2008

Available online 20 January 2009

Keywords:

Pesticide

Endosulfan

Adsorption

Desorption

Contamination

Vertisol

ABSTRACT

Endosulfan has been applied to control numerous insects in a variety of food and non-food crops. Limited information is available on dynamics of this pesticide in the soil. The objective of this research was to determine the adsorption–desorption behavior of the alpha (α) and beta (β) endosulfan in a Vertisol from the southeast region of Turkey, where cotton is the main crop in the large irrigated lowlands. The α and β endosulfan were adsorbed considerably and Freundlich adsorption–desorption isotherms fitted the α and β endosulfan data ($R^2 > 0.98$). Freundlich adsorption coefficients (K_f) for the α endosulfan ranged between 21.63 and 16.33 while for the β endosulfan they were between 14.01 and 17.98 for the Ap and Bw2 horizons. The difference of K_f values of α and β endosulfan for two horizons were explained with the slight difference in the amount of organic matter and clay, but considerable difference in Fe contents of the two horizons. Alpha and β endosulfan K_{fd} values were 118.03 and 45.81 for the Ap and 48.08 and 68.71 for the Bw2 horizons. Higher adsorption and desorption behavior of the endosulfan isomers for the same horizon was attributed to poor physical bonding between the endosulfan molecule and the surfaces of fundamental soil particles. This fact is thought to increase the effective use of endosulfan in agriculture with a possibility of its movement to the surface and groundwater in the Vertisol studied.

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1. Introduction

Identifying and understanding the mechanisms controlling the fate of pesticides which are a threat for non-target organisms and one of a possible sources of contamination of water resources are still remaining to be a great public concern (Soulas and Lagacherie, 2001). The study of pesticide fate is, therefore, vital for both maintaining environmental quality and optimizing sustainable agricultural practices (Cupples et al., 2000).

Endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzodioxathiepin-3-oxide) is a chlorinated pesticide ($C_9H_6Cl_6O_3S$) of the cyclodiene group (Fig. 1). It is composed of two stereoisomers of alpha (α) and beta (β) endosulfan in approximate ratio of 70:30 (Mersie et al., 2003). It is being used extensively throughout the world for the control of numerous insects in many of food and non-food crops (Lopez-Blanco et al., 2002; Kumar and Philip, 2006).

Because of its persistence and toxicity, endosulfan contamination poses a significant environmental concern (Kullman and

Matsumura, 1996). Extensive use of this pesticide more than a decade for cotton plantation in the Harran plain, southeast of Turkey is great concern regarding the potential transport in the environment.

Sorption is one of the key processes affecting the fate of agrochemicals in the sediment–water–soil environments (Thorstensen et al., 2001). A complete understanding of the adsorption and desorption of endosulfan is needed for better understanding mechanisms and the prediction of pesticide movement in soils and aquifers (Clausen et al., 2001). Sorption of pesticides by inorganic clay particles and organic matter may take place by one or more of the following interactions: Van der Waals forces, H bonding, dipole–dipole interaction, ion exchange, covalent bonding, protonation, ligand exchange, cation bridging, water bridging, and/or hydrophobic partitioning. Sorption can also affect the persistence, biodegradability, leachability, and volatility of pesticides. Surrounding ecosystems can be impacted if conditions are conducive to pesticide drift, leaching, or surface runoff (Pierzynski et al., 1994).

As it is known in the literature, co-solvent content is recognized to be one important factor influencing adsorption. Ying and Kookana (2002) indicated that methanol had less effect on adsorption than did acetonitrile. Ravanel et al. (1999) found that the use

* Corresponding author. Tel.: +90 414 3440020/1116; fax: +90 414 3440031.
E-mail addresses: adilek@harran.edu.tr, adilekatasoy@hotmail.com (A.D. Atasoy).

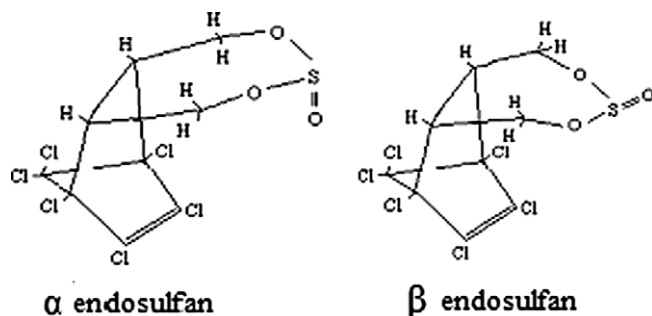


Fig. 1. The molecular structure of α and β endosulfan.

of methanol reduced the adsorption and caused a large increase in pesticide mobility. Since the methanol fraction increases the solubility of fipronil, a concomitant decrease in its adsorption is very likely. Several complementary hypotheses also have been proposed to explain the direct competition between the pesticide and solvent for adsorption sites, pesticide-co-solvent interactions via hydrophobic character and interactions of methanol with organic matter (OM), resulting in shrinking or swelling of the OM, which affects pesticide adsorption (Bobé et al., 1997).

The tendency of pesticides to leach from the soil is closely related to their solubility and their potential for adsorption. Strongly adsorbed molecules are not likely to move down the profile (Cox et al., 1998). Likewise, conditions that encourage adsorption will discourage leaching. Leaching is apt to be favored by water movement, taking place most readily in sandy soils that are low in clay and organic matter content but more permeable to water movement.

The use of uncontrolled and large amount of pesticides may deteriorate the soil and groundwater quality. The fate of the endosulfan as an insecticide has not been examined yet thoroughly in Turkey and specifically in the Harran Plain where the country's cotton production is concentrated. The hypothesis to be tested was that endosulfan isomers are likely adsorbed substantially by the Vertisol which is dominated by smectite silicate clay mineral causing an increase in the use of endosulfan applied in agriculture. The objectives of the research were to: (i) investigate the adsorption and desorption behavior of α and β endosulfan in the selected Vertisol under cotton and; (ii) explain the adsorption–desorption mechanisms of this pesticide in the Ap and Bw2 horizons of this soil.

2. Materials and methods

2.1. Study area and soil samples

Soil samples were taken from a Vertisol profile in the Harran plain, Şanlıurfa, Turkey (Fig. 2). This plain is intensely (>90%) cultivated with cotton. The plain has 141,500 ha of irrigable land and is located between 36°43'–37°10' North latitudes and 38°47'–39°10' East longitudes. The plain has a semi-arid climate with almost no precipitation between June and September. The long-term mean annual precipitation is about 284.2 mm, the mean annual atmospheric temperature is about 18 °C, and the evaporation is 1884 mm (Yeşilnacar and Güllüoğlu, 2007).

The soils of the plain are mainly clayey, and pH values are slightly alkaline (pH 7.50–8.00). The minimum permeability values of the soils are between 0.22 and 3.51 m/day (DSI, 2003). Majority of soils in the plain are classified as Vertisol according to Soil Survey Staff (1999).

Soil samples were taken from the Ap (0–27 cm) and Bw2 (40–55 cm) horizons in a profile excavated on the Haran soil series map unit. Adsorption–desorption tests were applied on the samples from Ap and Bw2 horizons to establish the fate of endosulfan in the solum. The Ap is the horizon that receives the endosulfan and Bw2 horizon is an intermediate transition zone to subsoil horizons and groundwater.

Air-dried, sieved (<2 mm) samples were processed for the analysis of basic soil characteristics. Particle size distribution was determined using Bouyocus hydrometer method. Soil pH was measured in a 1:1 (w/v) soil to 0.01 M CaCl₂ solution mixture (Hendershot et al., 1993). The organic matter content was determined using modified Walkley–Black method. Cation exchange capacity (CEC) was measured using sodium-acetate method. The bulk density and lime (carbonate) content were determined using cylinder method and a calimeter, respectively (Tüzüner et al., 1990). Total and dithionite–citrate extractable iron-oxide (Fe₂O₃)_D were determined according to the method described by Sheldrick (1984).

2.2. Chemicals

Analytical grade endosulfan isomers were provided by Sigma–Aldrich with a chemical purity of 99%. All organic solvents used were HPLC grade; standard solutions of α and β endosulfan were prepared in an acetone matrix. Endosulfan stock solutions were

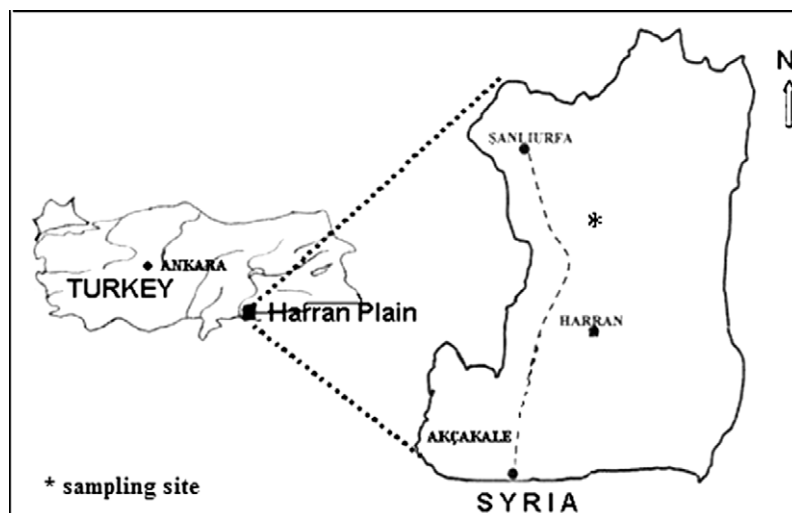


Fig. 2. Location map of the Harran plain.

prepared in 0.01 M CaCl₂ with methanol as co-solvent (1%). Methanol was used to prepare the endosulfan aqueous solutions due to its very low water solubility (0.335 μg mL⁻¹). All solutions were stored at 4 °C.

2.3. Adsorption–desorption studies

Adsorption–desorption isotherms of endosulfan on the soil were obtained by batch equilibration method (OECD, 2000) using a solid-to-liquid ratio of 1:5 for endosulfan adsorption–desorption studies. A preliminary kinetic experiment was tested to establish the equilibration time for endosulfan adsorption–desorption by soil fundamental particles. Tests were conducted in duplicate soil samples which was initially conditioned with 0.01 M CaCl₂ solution for 16 h. Soil samples (5 g) were shaken with 25 mL of endosulfan solutions in 0.01 M CaCl₂ with initial concentrations of 0.020, 0.050, 0.080, 0.120, and 0.144 μg mL⁻¹ for α endosulfan; 0.010, 0.025, 0.040, 0.060, and 0.075 μg mL⁻¹ for β endosulfan. All the experiments were executed with controls—with only endosulfan in 0.01 M CaCl₂ (no soil) and blanks—with the same amount of soil in 0.01 M CaCl₂ (without endosulfan).

In the preliminary kinetic experiment, soil suspensions were shaken on a reciprocating shaker (105 rpm) for 1–2–3–6–10–24 h (α endosulfan for both soils) and 1–2–3–4–6–8–12–24 h (β endosulfan for both soils) to attain the equilibration time for α and β endosulfan at 25 ± 1 °C in the dark and then centrifuged at 3100 rpm for 15 min. In the equilibrium studies, soils which treated with α endosulfan were shaken 3 h for both soil samples and soils which treated with β endosulfan were shaken 3 h for soil from the Ap horizon and 6 h for soil from the Bw2 horizon. Alpha and β-endosulfan were extracted from the aqueous supernatant, analyzed, and all reported results constituted the mean of duplicate measurements.

Obtaining desorption isotherms followed the same experimental conditions and procedures used for the adsorption isotherm studies. After completion of the adsorption study, the entire reaction mixture was centrifuged and the supernatant was decanted carefully and analysed for the residual endosulfan concentration. The same amount of decanted supernatant was replaced with 25 mL of endosulfan-free 0.01 M CaCl₂ solution. The suspensions were agitated for 1–2–3–6–10–24 h for both soil samples in the preliminary kinetic experiment to attain the desorption equilibria.

2.4. Extraction and chromatographic analysis of endosulfan

Alpha and β-endosulfan were extracted from the aqueous samples using solid phase extraction (SPE) and US Environmental Protection Agency (EPA) method 3535A (US EPA, 1992). SPE cartridges and the processing unit (a disc holder consists of a conical flask and a glass top) were used in the extraction process. Solid phase extraction cartridges (Varian SPEC 47 C₁₈AR Cat. No. A74819) were pre-conditioned with 5 mL of methanol, followed by 5 mL of deionized water, before the aqueous solution (supernatant) was loaded. Elution of endosulfan was obtained with 5 mL of acetone. The eluate was evaporated to dryness under a gentle stream of nitrogen, and the residue taken up in acetone prior to injection into the gas chromatograph (GC) for detection.

EPA method 8081 was used for endosulfan analyses (US EPA, 1996). The extracts were analysed in HP 6890 Series GC with an electron capture detector (ECD) equipped with autosampler and with HP 19091 J-413 max 325 °C, HP-S 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm). The operating conditions were as follows: The injector temperature was set at 275 °C and the detector temperature was 300 °C. The oven was programmed to increase from 200 °C to 240 °C at a rate of 3 °C min⁻¹ and to 290 °C (hold for 1.17 min) at a rate of

100 °C min⁻¹. Nitrogen (N₂) was used as the carrier gas at a flow rate of 80 mL min⁻¹. Retention time for α and β endosulfan was 7.14 and 8.90 min, respectively. Calibration curves were prepared using standard solutions of α and β endosulfan in acetone.

2.5. Data analysis

Adsorption–desorption data were analysed for each horizon using linearized form of the Langmuir and Freundlich isotherms:

$$\frac{C_e}{C_s} = \frac{1}{k_b} + \frac{C_e}{b} \quad (1)$$

$$\log C_s = \log K_f + \frac{C_e}{n_f} \quad (2)$$

where k is the Langmuir constant (mL μg⁻¹) and b is the maximum amount of adsorbent (μg g⁻¹) that can be adsorbed. Plotting C_e/C_s versus C_e , the slope is $1/b$ and the intercept is $1/k_b$. K_f (mL g⁻¹) and $1/n_f$ (non-dimensional) are the empirical Freundlich constants. By plotting $\log C_s$ (amount adsorbed to the soil, μg g⁻¹) versus $\log C_e$ (amount of pesticide in solution, μg mL⁻¹), $1/n_f$ is calculated as the slope of the curve and the intercept is equal to $\log K_f$ (Sparks, 1995).

3. Results and discussion

3.1. Soil samples

Selected properties of the soil samples used in this study are presented in Table 1. The lime content and pH of the soils from both horizons were similar. The Ap horizon had a slightly higher organic matter and CEC and the Bw2 horizon contained more dithionite extractable Fe and slightly higher clay. Based on our unpublished data, clay minerals consisted of predominantly smectite, however, paligorskite content was also considerable in addition to illite and kaolinit.

3.2. Adsorption of α and β endosulfan

3.2.1. Adsorption kinetics

The adsorption kinetics exhibited an immediate rapid adsorption by which about 72–78% of the added pesticide was adsorbed within 1 h. Alpha endosulfan adsorption leveled off 3 h for the Ap and Bw2 horizons. Beta endosulfan reached adsorption equilibrium within 3 h in the Ap and 6 h in the Bw2 horizon (Fig. 3a and b). The rapid sorption was followed by a slow sorption of the two endosulfan isomers in the Ap and Bw2 horizons. As pointed out by Von Oepen et al. (1991), there is likely an initial quick sorption, a surface phenomenon, followed by slow migration and diffusion of the pesticides into the organic matter or clay mineral interlayers and surfaces. Because the changes in solution concentration were rather small after equilibration period of α and β

Table 1
Basic properties of soil used in adsorption–desorption tests.

Horizon and depth (cm)	Ap (0–27)	Bw2 (40–55)
Bulk density (Mg m ⁻³)	1.30	1.49
Soil texture		
% clay	60	63
% sand	16	17
% silt	24	20
Texture class	Clay	Clay
CEC (cmol kg ⁻¹)	32.53	28.65
Organic matter (%)	1.00	0.80
pH	7.60	7.50
Lime content (% CaCO ₃)	17.10	17.25
(Fe ₂ O ₃)T (%)	3.54	5.47
(Fe ₂ O ₃)D (%)	1.30	1.71

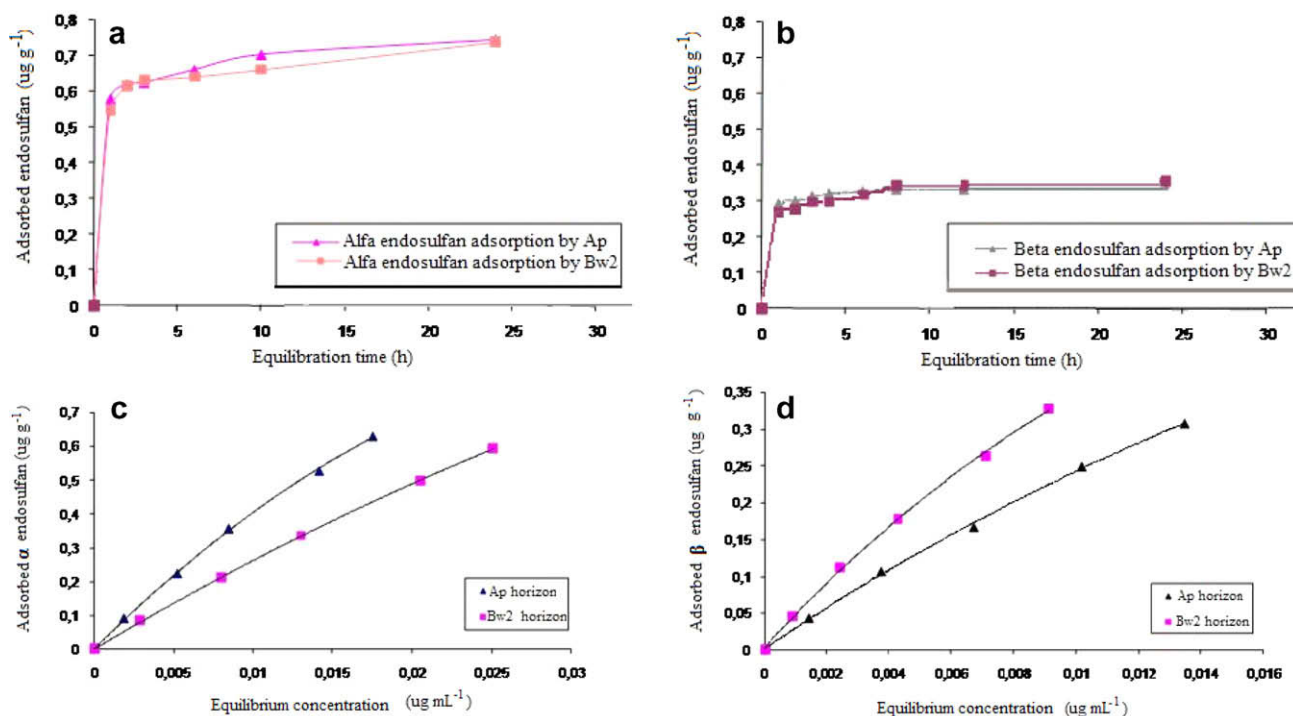


Fig. 3. Adsorption kinetics of (a) α and (b) β endosulfan and adsorption isotherms of (c) α and (d) β endosulfan for the Ap and Bw2 horizons.

endosulfan, equilibration times were used in the remaining adsorption studies. Parkpian et al. (1998) specified the initial rapid phase followed by a slower phase for endosulfan adsorption in the soil. It was mentioned that, the changes in solution concentration were quite small after equilibration time.

3.2.2. Adsorption isotherms

The Freundlich and Langmuir equation were used to describe the experimental data (Fig. 3c and d). The values of the Freundlich and Langmuir adsorption constants are given in Table 2a. Alpha and β endosulfan adsorption isotherms fitted well with Freundlich isotherm with a coefficient of determination >0.99 for the Ap and Bw2 horizons. According to the Giles classification (Giles et al., 1960), endosulfan adsorption isotherm was type L for both horizons which is typical of an adsorbent with a high affinity for the adsorbate. Hydrophobic nature of endosulfan caused to increase the attraction to the soil surfaces. The values of $1/n_f$ for endosulfan isomers were about 0.9 (<1.0) implying the L type isotherm. Therefore, Langmuir equation also showed a good fit to experimental data for endosulfan isomers (R^2 range 0.92–0.97). Kumar and Philip (2006) also, found that the experimental data for endosulfan adsorption in Indian soils fitted well with Langmuir equation. However, adsorption of α and β endosulfan in the Harran soil followed Freundlich isotherm better than Langmuir isotherm, because of the heterogeneous nature of the soil studied.

Alpha endosulfan adsorption was higher for the Ap horizon, with K_f (Freundlich adsorption coefficient) and k (Langmuir constant) values of 21.63 and 21.98, respectively. Beta endosulfan adsorption was higher, inversely in the Bw2 horizon with K_f and k values of 17.98 and 50.93, respectively. Alpha and β endosulfan exhibited the same adsorption tendency in the soil by both Langmuir and Freundlich isotherms.

The K_{oc} values of α and β endosulfan, calculated using their K_f values, are 7155, 5646 and 4481, 9191 for the Ap and Bw2 horizons, respectively. The values of $\log K_{oc}$ which are often used as a measure of the pesticide adsorption capacity of soils were similar

for the selected two horizons, reflecting the fact that there was no significant difference in organic matter contents. As a general rule, we can say that for a given soil, the larger the pesticide's sorption coefficients (K_{oc}), the more slowly the pesticide moves downward through the soil and the less likely it is to contaminate ground waters (Pepper et al., 1996). Organic matter is likely the most important soil characteristic affecting the pesticide adsorption (Thorstensen et al., 2001). It is clear that, increasing of endosulfan adsorption through the soil profile decreases the probability of groundwater contamination in the Harran plain.

Two endosulfan isomers were exhibited a different adsorption tendency for the top and subsoils. The most important differences between the Ap and Bw2 horizons were the organic matter, clay, and Fe (total and dithionite extractable) contents. The A horizon is generally higher in organic matter; whereas the B horizon is a layer with an accumulation of clay, sesquioxides, and carbonates (Pierzynski et al., 1994). Organic matter content of Ap was higher than Bw2 horizon. However, clay content of the Ap was slightly lesser than the Bw2 horizon.

The α endosulfan adsorption was higher in the Ap horizon in which the organic matter was slightly higher. However, β endosulfan adsorption was more in the Bw2 horizon in which the Fe-oxyhydroxide was higher together with slightly higher clay content. Kumar and Philip (2006), found that the adsorption of both α and β endosulfans on the clay soil was higher than the composted soil. However, the composted clayey soil used by Kumar and Philip (2006) had different pH values (7.4 and 8.5).

The different behavior of α and β endosulfan in the selected two horizons is thought to be likely from the different atomic arrangement of two molecules and slightly different clay, organic matter and but considerable dithionite-citrate extractable Fe contents. Masutti and Mermut (2007) indicated that high adsorption rate of pesticide (fipronil) was due to the presence of poorly crystalline Fe-oxyhydroxides in the tropical soil they have studied.

The higher α endosulfan adsorption in the soil affects the agricultural efficiency of this pesticide for the crops. The α and β

Table 2
Freundlich and Langmiur (a) adsorption and (b) desorption constants for α and β endosulfan.

Sample	K_f (mL g ⁻¹)	log K_f (mL g ⁻¹)	1/ n_f	log K_{oc} (mL g ⁻¹)	K_{oc} (mL g ⁻¹)	R^2	
(a) ADSORPTION							
<i>Alfa Endosulfan</i>							
<i>Freundlich constants</i>							
Ap	21.63	1.34	0.87	3.85	7 155	>0.99	
Bw2	16.33	1.21	0.90	3.75	5 646	>0.99	
Sample	1/ kb (g mL ⁻¹)	1/ b (g μ g ⁻¹)	k (mL μ g ⁻¹)	b (μ g g ⁻¹)	R^2		
<i>Langmiur constants</i>							
Ap	0.020	0.44	21.98	2.25	0.97		
Bw2	0.034	0.36	10.53	2.81	0.92		
Sample	K_f (mL g ⁻¹)	log K_f (mL g ⁻¹)	1/ n_f	log K_{oc} (mL g ⁻¹)	K_{oc} (mL g ⁻¹)	R^2	
<i>Beta Endosulfan</i>							
<i>Freundlich constants</i>							
Ap	14.01	1.15	0.88	3.65	4 481	>0.99	
Bw2	17.98	1.26	0.85	3.96	9 191	>0.99	
Sample	1/ kb (g mL ⁻¹)	1/ b (g μ g ⁻¹)	k (mL μ g ⁻¹)	b (μ g g ⁻¹)	R^2		
<i>Langmiur constants</i>							
Ap	0.033	0.84	25.50	1.19	0.94		
Bw2	0.019	0.98	50.93	1.02	0.97		
Sample	K_{fd} (mL g ⁻¹)	log K_{fd} (mL g ⁻¹)	1/ n_{fd}	$K_{fd} - K_f$ (mL g ⁻¹)	log K_{ocd} (mL g ⁻¹)	K_{ocd} (mL g ⁻¹)	R^2
(b) DESORPTION							
<i>Alfa Endosulfan</i>							
<i>Freundlich constants</i>							
Ap	118.03	2.07	1.29	96.40	3.73	5 322	0.98
Bw2	48.08	1.68	1.15	31.75	3.73	5 362	>0.99
Sample	1/ kb (g mL ⁻¹)	1/ b (g μ g ⁻¹)	k (mL μ g ⁻¹)	b (μ g g ⁻¹)	R^2		
<i>Langmiur constants</i>							
Ap	0.046	-1.27	-27.61	-0.79	0.68		
Bw2	0.048	-0.66	-13.63	-1.52	0.73		
Sample	K_{fd} (mL g ⁻¹)	log K_{fd} (mL g ⁻¹)	1/ n_{fd}	$K_{fd} - K_f$ (mL g ⁻¹)	log K_{ocd} (mL g ⁻¹)	K_{ocd} (mL g ⁻¹)	R^2
<i>Beta Endosulfan</i>							
<i>Freundlich constants</i>							
Ap	45.81	1.66	1.17	31.80	3.53	3 371	>0.99
Bw2	68.71	1.84	1.19	50.73	3.74	5 535	>0.99
Sample	1/ kb (g mL ⁻¹)	1/ b (g μ g ⁻¹)	k (mL μ g ⁻¹)	b (μ g g ⁻¹)	R^2		
<i>Langmiur constants</i>							
Ap	0.063	-1.63	-25.88	-0.61	0.93		
Bw2	0.050	-1.70	-34.11	-0.59	0.92		

exists proportionally 70% and 30% in the commercial endosulfan. Different adsorption tendency of these pesticide isomers may affect the cost benefit on the target organisms.

Adsorption of α and β endosulfan in the Ap and Bw2 horizons, reduce their mobility and leaching potential through the soil profile. Si et al. (2006) also found that the leaching of pesticide is inversely related to adsorption and that the sorption controls the mobility of pesticide in the soil. In soils, clay size particles, metal oxides, and organic matter surfaces and silicate clay interlayers are the dominant sites responsible for the sorption of organic contaminants (Pierzynski et al., 1994). Monkiedje and Spiteller (2002) indicated that, the relatively high adsorption of pesticides in the soil they have studied which was under cotton plants could also be due to its high clay content. As suggested by Kumar and Philip (2006), the presence of clay and organic matter immobilizes both α and β endosulfan in the soil.

3.3. Desorption of α and β endosulfan

3.3.1. Desorption kinetics

Desorption is another important parameter to evaluate the endosulfan movement in soil. Desorption was negatively correlated with soil organic matter content (Felsot and Lew, 1989; Jenks et al., 1998). Desorption of endosulfan was rapid in the initial stage. Thorstensen et al. (2001) found that the desorption equilibrium of

bentazone, dichlorprop, and propiconazole was achieved almost immediately. Maximum α endosulfan desorption from the Ap horizon and Bw2 horizon, were 15% within 1 h and 13% within 2 h, respectively (Table 3). Alpha endosulfan desorption decreased with time, and levelled off within 4 h for both soils. About 15% of β endosulfan from Ap and 8% of β endosulfan from Bw2 horizon were desorbed maximum within 1 h. Beta endosulfan desorption decreased with time and leveled off within 6 h. Desorption of α endosulfan reached a stable condition more rapidly than β endosulfan.

Endosulfan desorption was faster initially. However, re-adsorption phenomena took place with time. High affinity of the soil on endosulfan molecules was effective on re-adsorption. Despite

Table 3
Desorption kinetics of endosulfan from the Ap and Bw2 horizons.

Equilibration time (h)	α Endosulfan		β Endosulfan	
	% Desorption		% Desorption	
	Ap horizon	Bw2 horizon	Ap horizon	Bw2 horizon
1	15	11	15	8
2	10	13	12	6
3	9	9	10	7
6	9	7	7	6
10	11	8	7	5
24	9	9	6	5

Table 4
 α and β endosulfan desorption after equilibration.

Adsorbed		Desorbed		Desorption	
α ($\mu\text{g g}^{-1}$)	β ($\mu\text{g g}^{-1}$)	α ($\mu\text{g g}^{-1}$)	β ($\mu\text{g g}^{-1}$)	α (%)	β (%)
<i>Ap Horizon</i>					
0.0907	0.0428	0.0157	0.0099	17	23
0.2239	0.1063	0.0383	0.0234	17	22
0.3577	0.1664	0.0458	0.0329	13	20
0.5293	0.2491	0.0626	0.0481	12	19
0.6324	0.3075	0.0791	0.0565	13	18
<i>BW2 Horizon</i>					
0.0856	0.0455	0.0163	0.0086	19	19
0.2102	0.1128	0.0387	0.0206	18	18
0.3350	0.1784	0.0524	0.0286	16	16
0.4975	0.2645	0.0812	0.0396	16	15
0.5946	0.3294	0.0920	0.0485	15	15

the hydrophobic characteristic of endosulfan, the presence of electrolyte (CaCl_2) induced the re-adsorption mechanism. In the soil there is always some electrolyte to play role. After 24 h, α and β endosulfan desorption from the Ap horizon reduced to 9% and 6%, respectively from the maximum level of 15%. Alpha and β endosulfan desorption from the Bw2 horizon decreased to 9% and 5% from the maximum level of 13% and 8%. These reductions are attributed to the re-adsorption of β endosulfan in the Ap and Bw2 horizon as suggested by Johnson and Shaner (2000) and Masutti (2003).

3.3.2. Desorption isotherms

Alpha and β endosulfan desorption rates are shown on Table 4. Alpha endosulfan desorption ranged between 13% and 17% for the Ap horizon and 15% and 19% for the Bw2 horizon. It is interesting to note that Masutti and Mermut (2007) found that the fipronil desorption from a goethite sample was significantly higher than in the tropical soils they studied. Beta endosulfan desorption was slightly higher than α endosulfan desorption for the Ap horizon and ranged between 18% and 23%. Percentage of β endosulfan desorption was about the same as α endosulfan desorption for the Bw2 horizon and ranged between 15% and 19%. The range between 13% and 23% desorption rate exhibited the probability of endosulfan transfer or movement in the soil.

From the discussions it seems that α and β endosulfan probably move down the profile and they can reach to the subsoil and finally to the groundwater. We carried out the desorption studies at 25 °C and between the pH range of 7.0–7.5 in the laboratory. However, in the field, variations in soil characteristics (pH, temperature, moisture etc.) can change the desorption rate of endosulfan in the soil. Yen et al. (2000) noticed that, the mobility of acephate in the soil was somewhat faster than that of methamidophos, and thus acephate may lead to the contamination of groundwater much easily than methamidophos under normal conditions. Increased desorption of endosulfan rises the contamination risk of groundwater.

Values of the Langmuir and Freundlich desorption constants are summarized in Table 2b. The Langmuir equation yielded a poor fit to α and β endosulfan desorption on the Ap and Bw2 horizons (Table 2b). The coefficient of determination for the Langmuir equation for α endosulfan desorption was 0.68 and 0.73 for the Ap and Bw2 horizons, respectively. Beta endosulfan desorption was not defined with Langmuir equation, due to the negative Langmuir parameters. The Freundlich equation provided a good fit to the isotherms for α endosulfan desorption with R^2 of 0.98 for the Ap and >0.99 for the Bw2 horizons, respectively and β endosulfan desorption data followed Freundlich isotherm with $R^2 > 0.99$ for both the Ap and Bw2 horizons. The reversibility of adsorption was evaluated from the change in coefficient calculated for the adsorption (K_f) and

desorption (K_{fd}) experiments. Adsorption–desorption hysteresis occurred when $K_{fd} > K_f$ (positive hysteresis). The α and β endosulfan K_{fd} values were higher than their K_f values of both horizons (Table 2b).

Alpha endosulfan desorption from the Ap and β endosulfan desorption from the Bw2 was higher with Freundlich desorption coefficients (K_{fd}) of 118.03 and 68.71, respectively. This fact confirmed that the α endosulfan has higher affinity for Fe-oxyhydroxides and silicate clay mineral surfaces, which are higher in the Bw2 horizon, while the β endosulfan has higher affinity for organic matter which is slightly higher in the Ap horizon. Alpha endosulfan adsorption and desorption for the Ap horizon was higher than the Bw2 horizon. However, β endosulfan adsorption and desorption for the Bw2 horizon was higher than the Ap horizon.

Higher adsorption and desorption behavior of the soil was attributed to poor physical bonding (as Van der Waals force) between endosulfan isomers and the soil particles. This fact is in line with the use of endosulfan in agriculture but also brings its movement in the environment, especially contamination of the surface and ground waters. The large size of endosulfan molecules arranged as a chain circle around the adsorptive site in the soil. The attraction forces between the last circle and soil molecule are weak. Therefore, desorption of endosulfan molecules should be rather easy. However, it is the re-adsorption phenomenon that restricts the high desorption of endosulfan. The difference between K_{ocd} values (based on Freundlich coefficients) for α endosulfan desorption from the Ap and Bw2 horizons and β endosulfan desorption from the Bw2 horizon (Table 2b) is rather small. K_{ocd} value of β endosulfan desorption from the Ap horizon was lower than the Bw2 suggesting its tighter bonding with the topsoil.

Endosulfan desorption from the Ap and Bw2 horizons in the Vertisol of the Harran plain supports the view that endosulfan could move through the soil profile. During the dry season Vertisol may form cracks and soil particles from the surface may get into the subsoil through the cracks. Therefore, adsorbed pesticide by the soil may be transported to the subsoil. Just as the pesticide may move horizontally to nontarget areas, they may also be moved vertically to the subsoil by pedoturbation (Mermut et al., 1996). With regard to this typical characteristic of the Harran soils, adsorbed pesticide molecules in the surface soil may reach to the subsoil and even ground waters.

4. Conclusions

Alpha endosulfan was adsorbed more in the Ap, whereas β endosulfan was adsorbed more in the Bw2 horizons. These suggest that the endosulfan isomers have affinity to Fe-oxyhydroxides and organic matter. Desorption from the Bw2 horizons for both isomers even less is suggesting that Fe-oxyhydroxides make an organo mineral complex with endosulfan. Iron-oxyhydroxides seem to play an important role in the adsorption and desorption processes in the Vertisol studied. The amount of desorbed α isomers is higher in the Bw2 horizon, however, β endosulfan desorption is higher in the Ap horizon. Different atomic arrangement of the two endosulfan isomers results in different affinity for the clay, organic matter, and Fe-oxide contents of the soil studied. High adsorption rate supports the view of the immobility of endosulfan in the soil. However, about of 13–23% desorption rate of endosulfan especially in the Vertisol with pedoturbation and deep crack formation may create conditions for groundwater contamination. Higher adsorption and then desorption behavior on a soil horizon increases the agricultural value of endosulfan but also its movement towards the surface and ground waters. The extensive use of endosulfan should be avoided, farmers training must be carried out and the pest management techniques/practices must be improved.

Acknowledgements

This study was funded by the Scientific & Technological Research Council of Turkey (TUBITAK project No.: 1040138 was executed by A.R. Mermut) and the Scientific Research Projects of Harran University (HUBAK project No.: 568). The authors thank to Dr. Güzel Yılmaz and Dr. Nurcan Köleli for their advice.

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