Adsorption Behavior of Endosulfan on Alluvial Soil

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Summary: The present study was carried out to assess the behavior of endosulfan pesticide in alluvial soil under laboratory conditions. Sandy loam soil was studied to evaluate the fate of applied endosulfan with respect to soil properties. Known amount of endosulfan was added on alluvial soil in PVC column and eluted with 1000 ml of water. Eluents were collected in 10 parts, each of 100 ml. The soil in the column was divided in to three equal parts, each of 10 cm. Each part of the soil and eluents were analyzed for the determination of Endosulfan level using GC-μECD and GC-MS techniques. The kinetic and equilibrium adsorption characteristics of endosulfan on sandy loam soil was also studied and found that it follows Ho's pseudo second order and Freundlich isotherm. The present study revealed that α-and β-Endosulfan was determined efficiently with their degraded products in alluvial soil under laboratory conditions with above mentioned instruments.

Introduction

Endosulfan is an organochlorine insecticide. It is a highly toxic chemical, poisonous to most living organisms and is a 'persistent organic pollutant' or 'POP' [1-4], it persists in the environment, is bioaccumulative and can spread from the original source affecting remote human and wildlife populations [5, 6]. It has been banned in developed countries but its use is still common in developing countries including Pakistan. Endosulfan is cheaper pesticide with effective pest control in vegetables. It is still recommended for vegetable pest control specially okra. Most farmers are only interested in cheaper pesticides for protecting their vegetables from ravages by pests in order to get good harvest but have little concern for the detrimental effects of these pesticides on the soil environment.

When pesticides are applied to destroy pests and pathogens, only 15% of the applied amount hits the target, with the remaining 85% being distributed in the soil and air. The soil is the main matrix for pesticide disposition, and the bulk of pesticide residues are generally confined to the upper 5cm of the top soil [7]. Pesticide residues in the soil can move from the surface when they dissolve in runoff water, or percolate down through the soil, and eventually reach the groundwater [8]. Endosulfan has also been detected in the atmosphere, soils, sediments, estuaries, surface and rain waters, and food stuffs. Studies in conducted Swat soils have endosulfan residues up to 12.67 mg/kg in soil [9]. Endosulfan was detected in 8% wells of Punjab with maximum concentration of 3ppb [10]. Since this pesticide is found in ground waters, it is apparent that there is significant mobility of these chemicals through the soil [11]. The displacement of pesticides from soil to water strongly depends on the extent to which they are retained in soils, which in turn depends on the adsorption and desorption properties of the soil [12]. Above studies have been conducted in acidic soils whereas Sindh soils are sodic and alkaline in nature. Although endosulfan is still being extensively used in vegetables in Sindh, no studies have been conducted on its adsorption behavior in this type of soil. The present study is undertaken to evaluate the adsorption, and leaching of endosulfan in soil.

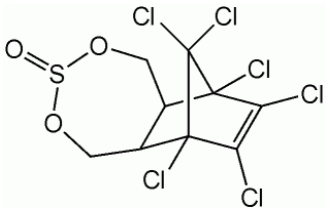

Fig. 1: Structure of endosulfan.

Results and discussion

Physicochemical Properties of the Soil

The physicochemical properties of the soil are shown in table-1. The pH of soil is approximately neutral (7.79), however, the slight tendency to be acidic in the presence of a salt may favour the stronger cation exchange mechanisms of chemisorption. The EC measurement of soil (808 $\mu S.cm^{-1}$) indicates saline conditions, when considered in relation to the effect on plants. The electrical conductivity between 0 and 200 $\mu S.cm^{-1}$ is

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considered to have negligible effects. The higher EC value of soil enhances water retention by increasing the osmotic potential of the soil, thereby increasing the contact-time for adsorption. As our soil is sandy loam in texture (sand 76.75 %), therefore adsorption may thus be limited because sand particles have less vacant sites as compared to silt or clay. Soil adsorption, presence of organic matter, soil texture, electrical conductivity, pH, bulk density all directly influence the degradation of endosulfan in soil. As Sindh soil has low organic matter (1.144 %), and this is expected to reduce the soil's ability to immobilize endosulfan in the soil profile [13].

Table-1: Selected physicochemical properties of soil samples (mean ± standard deviation; n = 3).

Parameter	Value
Ph	7.79 ± 0.01
Electrical Conductivity (µS/cm)	808 ± 0.32
Total Dissolved Solids (mg/l)	395 ± 0.45
Cation exchange capacity (meq/100g)	12 ± 0.01
Organic matter content (%)	1.44 ± 0.01
Total Organic Carbon	0.664 ± 0.001%
Specific Gravity	2.912 ± 0.01
Bulk Density (g/ml)	1.117 ± 0.01
Sand (%)	74.75 ± 0.68
Slit (%)	18.15 ± 0.24
Clay (%)	7.1 ± 0.17
Classification	Sandy Loam

Percent Recovery

For percent recovery five standard endosulfan solutions from 1 to 5ng/µl were run on GC-µECD. These all standard endosulfan concentrations were in linear range, giving R^2 value 0.998 and 0.995 for α- and β-endosulfan respectively. The percent recovery of α-endosulfan and β-endosulfan in soil was 96.19± 1.2% and 96.16± 1.2 %, while in water 93.47 % and 93.07 % respectively.

Limits of Detection and Quantification

The limits of detection for α- and β-endosulfan from soil samples were 0.00026 mg/kg and 0.00013 mg/kg respectively while limits of quantification of these samples for α- and β-endosulfan were 0.00089 mg/kg and 0.00073 mg/kg respectively.

Kinetic Adsorption Study

Adsorption kinetic is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface. Kinetic adsorption of both alpha and beta endosulfan was studied and result is indicated in Fig 2(a) and (b). The adsorption kinetic exhibited two distinct regions, a very rapid adsorption in the initial stages (within 2 h) followed by a slow adsorption. The pseudo equilibrium was reached within 5 h, after that a little variation of endosulfan concentration in the adsorbate was observed. Similar trend was observed while studying the adsorption of lindane [14], and carbofuran [15] in different soils. There is no significant change of behaviour by alpha and beta endosulfan on reaching the equilibrium was observed. The rapid initial adsorption of endosulfan is a surface phenomenon. Due to hydrophobic nature of endosulfan, the vacant sites in the soil particles were filled up rapidly in the initial stages and followed by a slow migration and diffusion of endosulfan molecules in soil as reported by other researchers [16, 17]. From the results it was observed that rapid adsorption is more significant as compared to slow adsorption..Langergreen [18] and Ho [19] kinetic models were used to examine that adsorption follows either pseudo first or pseudo second order reaction respectively.Fig. 2(a)(b).

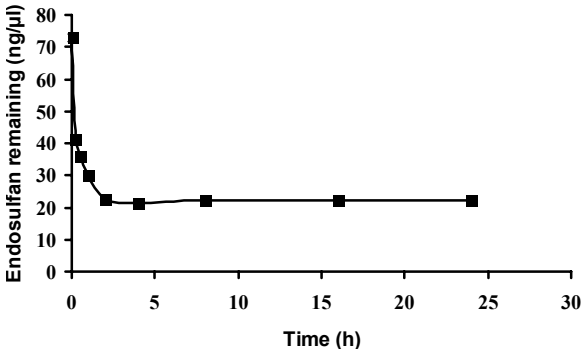

Fig. 2: Adsorption kinetics of (a) α- endosulfan and (b) β-endosulfan.

Langergreen Pseudo First Order Model

Pseudo first order rate constant was determined through equation 1.

$$\log (qe-qt) = \log qe - k.t/2.303 \qquad (1)$$

where qe and qt are the amount of endosulfan adsorbed ($mg.g^{-1}$) at equilibrium and at time t (min) respectively while k (h^{-1}) is the first order rate constant. Langergreen equation 1 had R^2 values 0.889 and 0.903 for α and β endosulfan respectively. This model did not give as good fit as Ho's pseudo second order model, therefore it is inferred that kinetic adsorption of endosulfan on this soil has followed pseudo second order model.

Ho's Pseudo Second Order Model

Data was also investigated through pseudo second order model given by Ho and McKay. Pseudo second order rate is given as in equation 2.

$t/q_t = 1/h + t/q_e$ (2)

Here $h = k.q^2$. Plot of t/qt versus t exhibit straight line with R^2 value 0.999 for both α and β endosulfan as shown in Fig.3(a) and (b), from which it was concluded that sorption of endosulfan completely follows pseudo second order kinetics. In chemisorption process, the pseudo second order is superior to pseudo-first order model because it deals with interaction of adsorbent-adsorbate through their valency forces [20, 21].

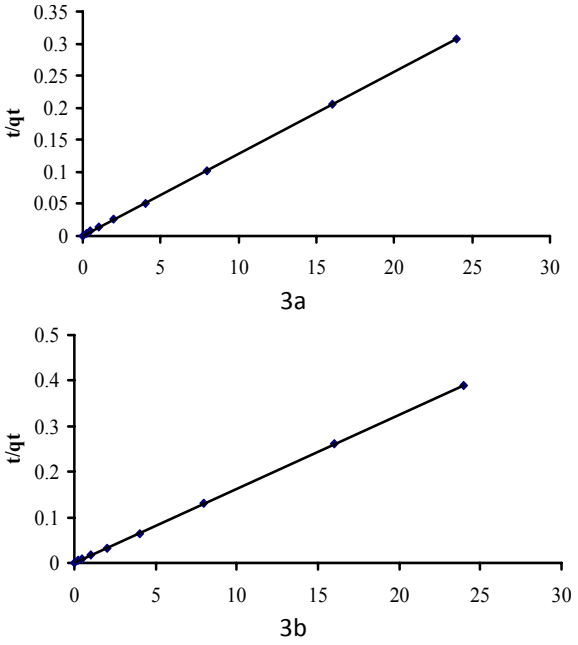

Fig. 3: Ho's pseudo second order plot for (a) α-endosulfan and (b) β-endosulfan.

The rate constants for alpha and beta endosulfan were calculated and shown in table-2.

Table-2: Adsorption rates of alpha and beta endosulfan.

Models applied	Rate of adsorption ($mg.g^{-1}.h^{-1}$)	
	Alpha endosulfan	Beta endosulfan
Lagergren pseudo first order	23.373	13.535
Ho's pseudo second order	21.333	8.539

Equilibrium Adsorption Study

Adsorption isotherm studies were conducted at 28 ^{0}C with an equilibrium time of 5 h. Langmuir and Freundlich isotherm models were used to calculate the isotherm constants and the maximum adsorption capacity of endosulfan at nine different concentrations to understand its behavior clearly. These concentrations were 0.15, 0.25, 1, 2, 5, 10, 25, 50 and 100 ng/µl.

Langmuir Isotherm Model

This model assumes monolayer and homogeneous adsorption because each molecule possess constant enthalpies and sorption activation energy, therefore the adsorbed layer is one molecule in thickness, with adsorption occurring at fixed sites, which are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules[22, 23]. Linear form of this model is given as in equation 3.

$Ce/Cads = 1/Qb + Ce/Q$ (3)

Where Ce is the equilibrium concentration of endosulfan in solution (mol $L^{-1)}$ and Cads is the amount of endosulfan (mol g^{-1}) on soil surface, Q is the monolayer adsorption capacity, and b is Langmuir constant. This model did not give good fit (R^2 value 0.968 and 0.83 for α- and β-endosulfan respectively) as Freundlich gives, therefore it is inferred that equilibrium adsorption of endosulfan on this soil has followed Freundlich isotherm

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Freundlich Isotherm Model

Freundlich isotherm is related to the non-ideal and reversible adsorption, not restricted to the formation of monolayer. Therefore it is applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Linear form of this model is given as in equation 4.

$\log Cads = \log A + (1/n) \log Ce$ (4)

Where A is multilayer adsorption capacity and n is adsorption intensity. A plot of log Cads against Ce gives straight line as shown in Fig. 4. The lower concentration includes 0.15, 0.25 and 1 ng/µl, while higher 2, 5, 10, 25, 50 and 100 ng/µl endosulfan.

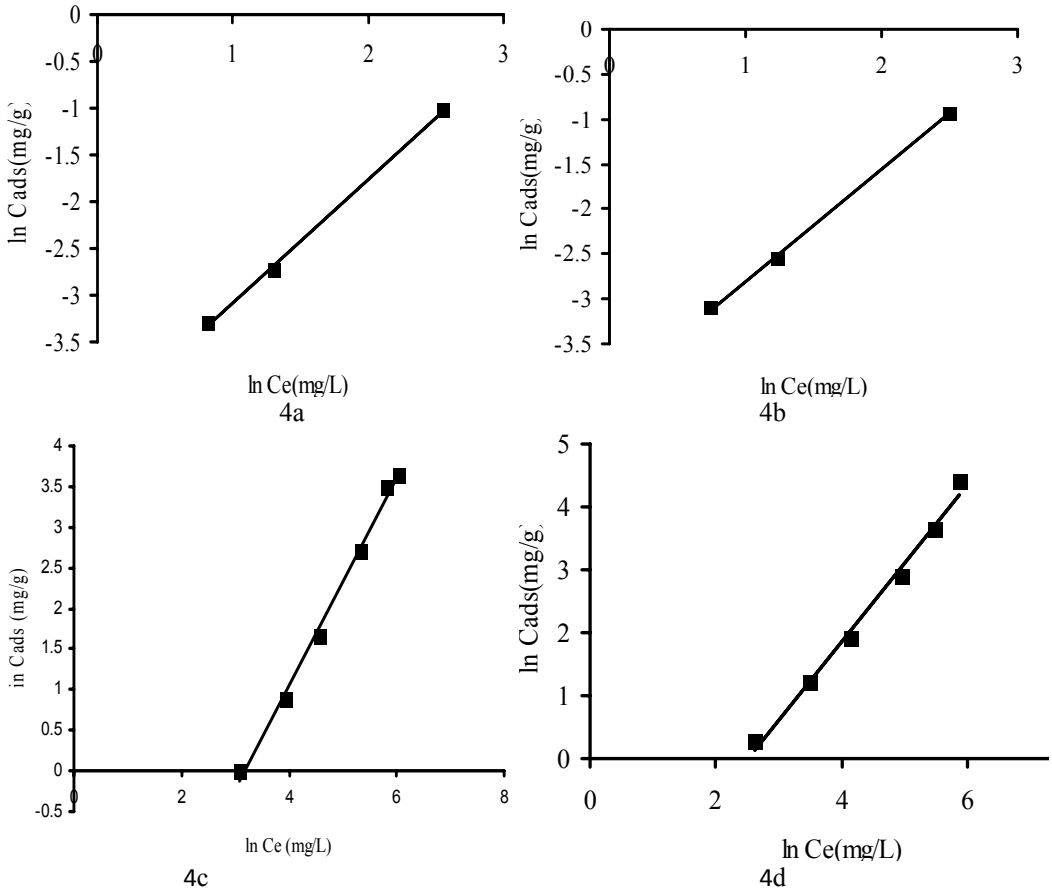

Fig.4: Freundlich isotherms: a and b represents α- and β-endosulfan at lower concentration, while c and d represents α- and β-endosulfan at higher concentration.

A dimensionless constant called separation factor (R_L) is given as in equation 5.

$$R_L = 1/1 + b.Ci \qquad (5)$$

Where b is a Langmuir constant, Ci is initial concentration. Magnitude of isotherm constants represent the adsorption process is favorable or not. R_L value indicates the adsorption nature to be either favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$). Here R_L value is <1, showing that adsorption of endosulfan on soil is favorable. Table-3 represents isotherm constant values of both models. The n value is 1.349 and 1.342 for α- and β-endosulfan respectively showing that adsorption process is favorable because $1< n < 10$ [24] represents that adsorption is favorable.

In our study, both linear and non-linear forms of Freundlich isotherm were applied. From which it was observed that non-linear method is a better way to achieve the isotherm parameters. The result is indicated in table-4 and 5.

Table 3: The adsorption isotherm values for alpha and beta endosulfan.

	Langmuir isotherm			Freundlich isotherm		
	Q (mol/g)	b	R_2	A (mol/g)	n	R^2
α-endosulfan	1.293	0.0541	0.968	5.385×10^{-5}	0.741	0.993
β-endosulfan	1.228	0.0274	0.83	2.698×10^{-4}	0.745	0.989

Table-4: Isotherm parameters obtained using the linear- Freundlich isotherm.

Pesticide	K_F $(mg/g)(dm^3/mg)^{1/n}$	K_{FOC}	1/n	R^2
α-endosulfan	42.882	6458.132	5.641	0.8701
β-endosulfan	20.843	3139.006	4.463	0.951

Table-5: Isotherm parameters obtained using the nonlinear- Freundlich isotherm.

Pesticide	K_F $(mg/g)(dm^3/mg)^{1/n}$	K_{FOC}	1/n	R^2
αendosulfan	1.854	279.202	1.349	0.993
βendosulfan	1.5499	233.419	1.342	0.989

Table-6: Ground water ubiquity score.

Pesticide	Linear(mg/l)	Freundlich(mg/l)	Half Life(days)	GUS -Linear	GUSFreundlich	Pesticide Movement
A-endosulfan	**6458.132**	**279.202**	**50**	**0.323**	**2.640**	**Moderate**
β-endosulfan	**3139.006**	**233.419**	**50**	**0.855**	**2.772**	**Moderate**

nd: not detected

Table-7: Endosulfan leaching through soil column (mg/kg).

Sample	α-Endosulfan	β-Endosulfan	Endosulfan ether	Endosulfan diol	Endosulfan sulphate
Soil- 0-4"	**1.451 ±0.18**	**0.968 ±0.04**	**-nd-**	**0.113 ±0.04**	**0.298 ±0.05**
Soil 4-8"	**-nd-**	**-nd-**	**-nd-**	**-nd-**	**0.387 ±0.15**
Water-01	**1.379 ±0.62**	**-nd-**	**-nd-**	**-nd-**	**-nd-**
Water-04	**-nd-**	**-nd-**	**0.081 ±0.02**	**-nd-**	**-nd-**

Therefore pesticides with a GUS (ground water ubiquity score) value less than 0.1-1.0 have very low potential to move towards groundwater, while values of 1-2 is low, 2-3 is moderate, 3-4 is high and >4 have very high potential to move towards groundwater . In our study the GUS value (shown in Table-6) indicates that the movement of endosulfan towards groundwater is moderate.

Soil Column Leaching Study

The result in Table-7 depict α-endosulfan, β-endosulfan, endosulfan diol and endosulfan sulfate were found in first portion of column soil, while in second portion of column soil only endosulfan sulfate was found and in third portion of column soil no metabolite of endosulfan was found. Chromatogram of elution pattern of endosulfan isomers and metabolites on GC-MS column is represented in Fig 5. α-endosulfan in first portion of water while endosulfan ether in fourth portion of water was found. In remaining water portions no any metabolite was found [25].

Experimental

Chemicals

High purity (99.4%) endosulfan was gifted from Bayer Crop Science, and commercial Endosulfan was purchased from local market Hyderabad-Sindh, Pakistan (35% EC). Other chemicals, reagents and solvents used in the present work were purchased from Sharlau (Barcelona, Spain). Endosulfan stock solution (1000 ng/µl) was prepared in ethyl acetate and stored in a freezer at -10°C. Working standard solutions were prepared by appropriate dilutions with ethyl acetate and stored under refrigeration (4°C). All the glassware were cleaned with soap water, rinsed with distilled water followed by acetone rinse and dried at 110 ◦C for 2 h.

Soil Sampling

Soil samples were collected from experimental field of National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Sindh-Pakistan. This field did not receive pesticide applications and samples were collected from the 0 to 15cm soil depth, air-dried, and ground to pass through a 2-mm sieve. Processed soil samples were stored in glass bottles till further analysis. Physical and chemical properties of the soil were measured with the methods described in *Methods of Soil Analysis* [26].

Extraction and cleanup of soil samples

50 g air dried soil was transferred to 250-ml stoppered conical flasks and 50-ml ethyl acetate was added. The samples were equilibrated on a rotary shaker for 2 h, the extract was filtered. Ethyl acetate extract was washed with 100 ml distilled water in separatory funnel. The water layer containing impurities was discarded and ethyl acetate layer containing residues was dried with anhydrous sodium sulphate and concentrated to 5ml gently with stream of nitrogen. The soil samples were ready for GS-MS analysis.

Extraction of Water Samples

Each 100-ml water portion eluted from column was mixed with 50-ml ethyl acetate in a 250-ml separating funnel. The separating funnel was shaken vigorously for 5 minutes to ensure the complete mixing of two layers. The two layers were then allowed for clear separation. Lower aqueous layer was discarded and ethyl acetate layer containing residues was dried through anhydrous sodium sulphate and concentrated to 5 ml as described above.

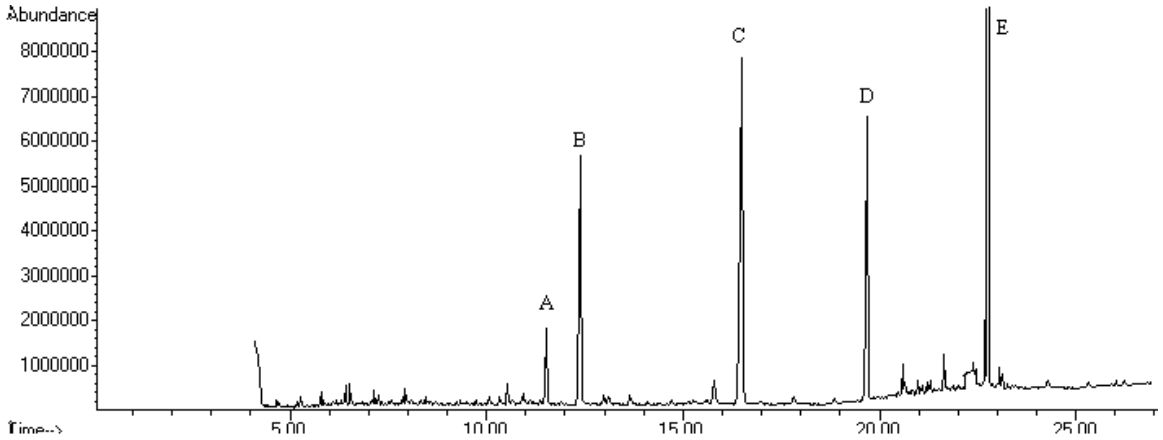

Fig. 5: Chromatogram showing (A) endosulfan ether (B) endosulfan diol (C) α-endosulfan (D) β-endosulfan and (E) endosulfan sulphate.

Instrumental Analysis

Endosulfan residues were analyzed GC-μECD and confirmed with GC-MS. An Agilent Technologies 7890A GC system equipped with μECD was used. The GC column used was HP-5 (30 m × 0.320mm × 0.25μm). The GC is fitted with 7683 series autosampler and 7683B series injector. The operating conditions were as follows: injector port temperature 250 °C, injection volume 2μl in a split mode (50:1), nitrogen as carrier gas at a flow rate of 60 mL/min; oven temperature program, initial 70 °C, increased at 30 °C/min to 210 °C (2 min), then increased to 250 °C at 25 °C/min (2 min) and finally increased at 30 °C/min to 290°C and held for 5 min. The total analysis time is 16.6 min. The temperature of μECD was 310 ^{0}C. All analyses were carried out by autosampler injection.

GC-MS analysis was performed with an Agilent Technologies 6890N network GC system equipped with a 5975 inert MSD operated in Electron Impact ionization mode (EI), and automatic split-splitless injector model Agilent 7683. HP-5MS 5% Phenyl Methyl Siloxane capillary column (30 m × 0.25 mm × i.d., 0.25μm film thickness) supplied by Agilent Technologies, was employed. The carrier gas used was Helium (with purity up to 99.9993%). The operating conditions were as follows: injector port temperature 280 °C, pressure 12.75 psi, injection volume 2μl in splitless mode, helium as carrier gas at a flow rate of 17.1 mL/min; oven temperature program, 80 °C (2 min), increased at 30 °C/min to 180 °C, then increased to 200 °C at 1.5 °C/min and finally increased at 20 °C/min to 280°C and held for 8 min, solvent delay, 4.00 min. The total analysis time is 30.67 min. The mass spectrometer was operated in electron impact ionization mode (ionizing energy = 70 eV) scanning from m/z 80 to 550. The ion source (EI) and quadrupole temperatures were 230 and 150 °C, respectively.

Percent Recovery

For percent recovery study, 50g blank soil was spiked with endosulfan standard solution prepared in ethyl acetate so as to make final concentration of 0.1 and 1 ug/mg in soil sample. Soil was mixed thoroughly for even distribution of endosulfan and was left for 24 hours so that the pesticide can be adsorbed completely. After that endosulfan was extracted by placing soil in 250-mL stoppered conical flasks and 50ml ethyl acetate was added. The sample was equilibrated on a rotary shaker for 2 h, filtered and filtrate was concentrated by evaporating ethyl acetate up to 5ml. This final volume of sample was analyzed by GC-μECD. For calibration the endosulfan standards from 1 to 5 ng/μl were run on GC-μECD.

Limits of Detection and Quantification

Limit of detection (LOD) of endosulfan was calculated at a signal-to-signal ratio of 3, while the limit of quantification (LOQ) was obtained at a signal-to-signal ratio of 10.

Adsorption Experiments

Kinetic Study

For kinetic adsorption study, 5 g of soil was mixed with 100 ml of 100 ng/μl standard endosulfan

solution in a 250 ml conical flask. This mixture was shaken on an orbital shaker at the speed of 150 rpm for a period of 24 hours at room temperature. 5 ml of sample was collected from flask at time intervals of 0, 0.25, 0.5, 1, 2, 4, 8, 16 and 24 hours. The collected samples were extracted with 10 ml of ethyl acetate solution in separating funnel. The water layer was decanted carefully and the supernatant was extracted with 5 ml of ethyl acetate for two more times. Finally, extracted samples were filtered through anhydrous sodium sulfate to remove moisture content and were analyzed for residual pesticide concentration using GC-μECD [13].

Equilibrium Study

For equilibrium adsorption study, 5 g of soil was mixed with different endosulfan concentrations as 0.15, 0.25, 1, 2, 5, 10, 25, 50 and 100ng/μl in 250 ml conical flasks. Then reaction mixtures were shaken on an orbital shaker at the speed of 150 rpm for 5 hours (equilibrium time) at room temperature. After 5 hours, 5 ml of sample was taken from each conical flask and centrifuged at 5000 rpm for 15 min; the supernatant was extracted with ethyl acetate solution (as described above). Extracted samples were filtered through anhydrous sodium sulfate to remove moisture content and analyzed by GC-μECD. Same way a blank solution was also prepared to know the effect of endosulfan adsorption on walls of conical flask.

Soil Column Leaching Study

Column (30-cm length × 6-cm i.d.) was constructed from polyvinyl chloride (PVC) pipe. The PVC column was rested in iron stand fitted with a 0.60-um nylon membrane. Wool was placed on nylon membrane to prevent the flow of soil from column to outside. The column was filled with soil, one day before endosulfan application the column was pretreated with 500-mL of distilled water to minimize the variation in soil water content between the column. Water was allowed to drain naturally and column was left overnight. Endosulfan (1 mg) was applied to the column surface in 6-mL ethyl acetate in a drop-wise manner and column was left overnight to assure even endosulfan distribution. The column surface was covered with a paper to minimize the disturbance of soil and to provide an even distribution of leaching water. The next day column was eluted with 1000-ml of distilled water. The water was applied on the column surface at the rate of $100ml.h^{-1}$ with the help of peristaltic pump and gravitational drainage was allowed. The eluate fractions were collected in ten portions of 100-ml each. After elution was over the soil was carefully removed from column and the soil block was divided into three sections of 10-cm increments. Each soil section was spread as thin film in a glass tray 12" x 24" and allowed to air-dry at room temperature. The dried soil was kept in a teflon capped glass jar and kept in freezer until extraction. Above procedure was repeated for untreated control (blank) soil samples also [27-29].

Conclusions

From column leaching study it was observed that along with adsorption of endosulfan on soil, it also leached with water indicating its toxicity to soil and ground water in the areas where it is repeatedly sprayed. Therefore soil with low organic matter and heavy rain water will be best medium for mobility/leaching of endosulfan pesticide. Kinetic adsorption revealed that endosulfan adsorption on soil followed pseudo second order model while equilibrium adsorption showed that Freundlich isotherm is fitted well hence adsorption was multilayer.

Acknowledgments

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