

DETERMINATION OF AQUEOUS SOIL SORPTION COEFFICIENT ( $K_{oc}$ ) OF  
STRONGLY HYDROPHOBIC ORGANIC CHEMICALS (SHOCs) USING MIXED  
SOLVENT SYSTEMS AND THE SOLVOPHOBIC MODEL

By

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To my Mom and Dad. Thanks go to them for their encouragement and interest in my education  
since first grade.

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Abstract of Thesis Presented to the Graduate School  
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Determination of the sorption coefficients ( $K_{oc}$ ) of strongly hydrophobic organic chemicals (SHOCs) in aqueous systems is difficult due to their very low solubility and the potential to adsorb on container walls and vessels.  $\beta$ -endosulfan, dieldrin, DDT, and anthracene were used in this study as probe compounds. Sorption of dieldrin and  $\beta$ -endosulfan on Teflon lined centrifuge tubes (TLCT) and HPLC vials (HPLCV) was measured in methanol-water systems. Similarly, DDT and anthracene sorption on TLCT was also measured. The volume fraction of methanol ( $f^c$ ) ranged from 0.01 to 1. The solution concentrations of  $^{12}\text{C}$ -dieldrin and  $^{12}\text{C}$ - $\beta$ -endosulfan were analyzed using high pressure liquid chromatography (HPLC) with UV detection. Liquid scintillation counting (LSC) was used to measure solution concentrations of  $^{14}\text{C}$ -DDT and  $^{14}\text{C}$ -anthracene.

The container sorption coefficients ( $K^W$ ) in aqueous systems were obtained by use of the Solvophobic model and extrapolating the sorption coefficient to zero fraction cosolvent ( $f^c = 0$ ). Using the Solvophobic model, the calculated percent recovery of  $\beta$ -endosulfan due to sorption on TLCT and HPLCV in aqueous system was 30%. Dieldrin recovery at  $f^c = 0$  was 6 and 32% from HPLCV and TLCT, respectively. DDT adsorbed most on TLCT followed by dieldrin and least

anthracene, with calculated recoveries in aqueous system of 29, 32, and 52%, respectively.

Negligible adsorption was detected for dieldrin at  $f^c \geq 0.45$  in TLCT and at  $f^c \geq 0.70$  in HPLCV.

Similarly negligible adsorption was detected for DDT and anthracene at  $f^c \geq 0.45$  in TLCT. It is important to point out that most researchers assume that Teflon lined centrifuge tubes and HPLC vials do not adsorb organic chemicals

The sorption coefficients of dieldrin, DDT, and anthracene by 3 carbonatic soils, one organic soil, and one spodosol, were then determined in methanol-water systems that eliminated sorption on the TLCT and HPLCV. The soil sorption coefficients ( $K^W$ ) in aqueous systems were extrapolated at volume fraction methanol ( $f^c = 0$ ). The  $K^W$  values were then normalized with soil organic carbon content (OC) to obtain [ $K_{OC} = K^M/OC$ ] values. The  $K_{OC}$  values for DDT, dieldrin, and anthracene obtained in this study were much lower than literature values and did not drastically vary across soil as it is reported in the literature. The  $K_{OC}$  values for dieldrin obtained in this study varied within a factor of 2 compared to the literature factor of 4. For DDT, the  $K_{OC}$  values varied within a factor of 4 compared to the reported literature factor of 13. The  $K_{OC}$  data from this study strongly indicate that sorption on container walls if neglected is a potential source of error while determining adsorption of strongly hydrophobic chemicals in aqueous systems. It is therefore recommended that sorption experiments of strongly hydrophobic chemicals be carried out in TLCT above 45% cosolvent in a mixture with water and at and above 70% cosolvent in HPLC vials. The sorption coefficients in aqueous systems can then be calculated using the Solvophobic model eliminating errors due to sorption on container walls and over estimation of sorption coefficients.

The hydrocarbonaceous surface area (HSA) of SHOCs calculated from sorption on TLCT, HPLCV, and by soils gave similar values as predicted by the Solvophobic theory.

## CHAPTER 1 INTRODUCTION

Experimental determination of soil sorption coefficients ( $K_{oc}$ ) values of strongly hydrophobic organic chemicals (SHOCs) has been traditionally done in aqueous systems assuming that there is no sorption on container walls and vessels. This might have led to a lot of variability in literature data reported on  $K_{oc}$  of strongly hydrophobic organic chemicals. Although there are other losses through evaporation of volatile compounds (physical processes), photolysis, oxidation, reduction and complexing (chemical reactions) and biodegradation (Namiesnik et al., 2002; Namiesnik et al., 2000), adsorption of these chemicals on container walls plays a significant role in variability of literature  $K_{oc}$  values (Lung et al., 2000)

Strongly hydrophobic organic chemicals have low water solubility ( $S_w$ ) of less than  $10^{-5}$  mol/L, have  $\log K_{ow}$  values  $\geq 5-6$  (Pontolillo and Eganhouse, 2001) and  $\log K_{oc}$  values  $> 4$  (Karickhoff, 1981). More than 700 publications from 1944 to 2001 for DDT and DDE, aqueous solubility and  $K_{ow}$  values revealed a variation of up to 4 orders of magnitude (Pontolillo and Eganhouse, 2001). This variability in the literature has been observed also for other persistent organic pollutants (POPs), (Table 2-2).

Based on The Stockholm Convention (2002), 9 of the 12 persistent organic pollutants are pesticides (Table 1-1). These pesticides can also be classified as SHOCs. POPs are typically water hating and fat loving chemicals (i.e. hydrophobic and lipophilic) and are persistent in the environment having long half lives in soils, sediments, air or biota. In soil/sediment, a POP could have a half life of years or decades and several days in the atmosphere (Jones et al., 1999). POPs have become ubiquitous in nature.

Use of Solvophobic theory has helped in prediction of sorption of hydrophobic organic compounds by soils and sediments. The model stipulates that the sorption of neutral hydrophobic

organic chemicals decreases exponentially as the cosolvent fraction increases (Rao et al., 1985). Extrapolating sorption coefficient at zero cosolvent in mixed solvents determines sorption of strongly hydrophobic organic pesticides in aqueous systems (Nkedi-Kizza et al., 1985).

A range of volume fraction of methanol ( $f^c$ ) in water where there was no sorption of anthracene, DDT,  $\beta$ -endosulfan, and dieldrin on Teflon lined centrifuge tubes (TLCT) and HPLC vials was determined. Above that range of methanol, sorption coefficients ( $K_{oc}$ ) of anthracene, dieldrin and DDT were determined using five soil series (Chekika, Perrine, Krome, Monteocha, and Lauderhill). Anthracene was used as a reference compound because it has no functional groups and its total surface area (TSA) is equal to the hydro carbonaceous surface area (HSA). Dieldrin and DDT are among the strongly hydrophobic organic pesticides (SHOPs) and are also POPs (The Stockholm Convention, 2001).  $\beta$ -endosulfan is a strongly hydrophobic organic pesticide that has been detected in canals in South Dade County, Florida (Zhou et al., 2003).

### **Hypotheses**

1. Strongly hydrophobic organic chemicals (SHOCs) adsorb on container walls and vessels during determination of  $K_{oc}$  values in aqueous systems.
2. Mixed solvent systems can eliminate sorption of strongly hydrophobic organic chemicals on container walls and vessels.
3. The Solvophobic model can be used to calculate aqueous  $K_{oc}$  of strongly hydrophobic organic chemicals by using sorption coefficients measured in mixed solvent systems where there is no sorption on container walls.
4. Sorption data of SHOCs on container walls and by soils can be used to calculate the hydrocarbonaceous surface area (HSA) of SHOCs.

### **Study Objectives**

1. Determine the range of mixed solvents (water plus methanol) in which sorption on container walls is eliminated for selected strongly hydrophobic chemicals (SHOCS) that include persistent organic pollutants (POPs).

2. Measure sorption coefficients ( $K^M$ ) values in mixed solvents for SHOCs and extrapolate the sorption coefficients ( $K^W$ ) in aqueous systems using the Solvophobic model. Normalize  $K^W$  values with soil organic carbon content (OC) to calculate [ $K_{OC} = K^W/OC$ ] values of selected SHOCs.
3. Compare  $K_{oc}$  values obtained in this study to literature values for various SHOCS used in this research.

Table 1-1. <sup>‡</sup>The dirty dozen: Persistent Organic Pollutants (POPs)

Pesticides	Aldrin, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Chlordan, Mirex, Toxaphene
Industrial chemical by products	Polychlorinated biphenyls(PCBs) Poly chlorinated dibenzo-p-dioxins(Dioxins) and Furans

<sup>‡</sup>The Stockholm Convention (2001)

## CHAPTER 2 LITERATURE REVIEW

Variability in literature data for aqueous sorption coefficients ( $K_{oc}$ ) of strongly hydrophobic organic pesticides (Table 2-2) can partly be attributed to losses (source of error) that occur while conducting experiments for  $K_{oc}$  determination and partly to variability (Karapanagioti et al., 2000) in the source and nature of soil organic matter. Losses occur through: adsorption of chemicals on the walls of samplers and vessels, evaporation of volatile compounds (physical processes), photolysis, oxidation, reduction and complexing (chemical reactions) and biodegradation (Namiesnik et al., 2002, Namiesnik et al., 2000). Sorption on container walls plays a significant role in variability of  $K_{oc}$  literature data (Manoli et al., 1999, Baltussen et al., 1998).

Several researchers have shown that 40-80% of the poly chlorinated biphenyls (PCBs) in a sample may be adsorbed on to the poly tetrafluoroethylene (PTFE) surface (Baltussen et al., 1999, Lung et al., 2000). Glass containers may be responsible for a 10-25% drop in water sample content of polychlorinated biphenyls (PCBs) and poly aromatic hydrocarbons (PAHs) causing drops in analyte concentration (Manoli et al., 1999, Baltussen et al., 1998).

Nine of the 12 chemicals which belong to the class of most hazardous environmental pollutants enlisted as persistent organic pollutants (POPs) under the Stockholm Convention (2001) are pesticides. These POPs are also strongly hydrophobic organic chemicals (SHOCs). POPs are typically water hating and fat loving chemicals (i.e. hydrophobic and lipophilic) and are persistent in the environment having long half lives in soils, sediments, air or biota. In soil/sediment, a POP could have a half life of years or decades and several days in the atmosphere (Jones et al., 1999).

According to Webster et al. (1998), persistence in the environment is defined operationally from a model calculated overall residence time at steady state in a multimedia environment. In aquatic systems and soils, POPs partition strongly to solids, mainly organic matter, avoiding aqueous phase. They also partition in to lipids in organisms rather than entering the aqueous milieu of cells and become stored in fatty tissue. This leads to their accumulation in food chains since their metabolism in biota is slow. POPs have a potential to enter the atmosphere through volatilization from soils, vegetation and water because of their resistance to breakdown reactions in air, they travel long distances before being redeposited (Ritter et al., 1995). Repeated volatilization and deposition leads to their accumulation in areas far removed from where they were used or emitted.

An important class of persistent organic pesticide is the organo chlorine pesticides like DDT, aldrin, endrin, dieldrin, hexachlorobenzene, heptachlor, mirex, chlorodane and toxaphene (Table 1-1). Some POPs are accidental byproducts of combustion or the industrial synthesis of other chemicals for example polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (Dioxins), chlorinated paraffins, and dibenzo- p- furans (Furans), (Ritter et al., 1995).

The properties of unusual persistence and semi-volatility, coupled with other characteristics, have resulted in the presence of compounds such as PCBs all over the world, even in regions where they have never been used. They have become ubiquitous in nature. They have been measured on every continent, at sites representing every major climatic zone and geographic sector throughout the world (Ritter et al., 1995). These include remote regions such as the open oceans, the deserts, the arctic and the Antarctic, where no significant local sources exist and the only reasonable explanation for their presence is long-range transport from other parts of the globe. Some POPs have been reported in air, in all areas of the world, at

concentrations up to 15ng/m<sup>3</sup>; in industrialized areas, concentrations may be several orders of magnitude greater. POPs have also been reported in rain and snow (Ritter et al., 1995)

Properties of DDT (Fig. 2-1), dieldrin (Fig. 2-2),  $\beta$ -endosulfan (Figure 2-3) and anthracene (Fig. 2-4) are shown in table 2-1.

Anthracene was used to show the validity of Solvophobic model. It served as an ideal sorbate for evaluating the Solvophobic theory because its sorption is characterized by Solvophobic interactions (hydro carbonaceous surface area (HSA) is equal to total surface area (TSA-202 Å<sup>2</sup>).

### **Harmful Effects of Persistent Organic Pesticides (POPs) that are also (SHOCS)**

The concern of POPs concentrates around their impact on top predator species, humans inclusive. Clear evidence of their effects is in birds and marine mammals. In great lakes (Giesy et al., 1994) and in Europe (Bosveld and Van den Berg, 1994), numerous subtle but far reaching effects on the reproductive potential of fish eating birds are reported. POP residues have increased in some top predators for instance harbor seals in the Southeast North Sea (Reijnders et al., 1997), white- tailed eagles in the Baltic and piscivorous birds in the great lakes (Munro et al., 1994).

POPs, principally PCBs, have also been reported to cause reproductive impairment and this has been shown in seals in the Baltic sea (Bergman and Olsson, 1985) and the Dutch Wadden Sea (Reijnders, 1986) and in beluga whales in the St. Lawrence sea way, Canada (Beland et al. 1993). In addition to being carcinogens, POPs are among the chemicals responsible for sex hormone or endocrine disruption in humans and wild life (Harrison et al, 1995; Kavlock et al., 1996).

DDE a metabolic break down product of DDT affects egg shell thickness (thinning) in birds of prey for example wild fowls (Ratcliffe, 1967 and 1970, Pearce et al., 1979). Man's

exposure to DDT lies in taking contaminated food including maternal milk. Long term exposure leads to chronic illness and breast cancer risk. Toxicity of DDT spreads to fish too. 50% of initial amounts of DDT are found in soil, even 10-15 years after use (Smith, 1991).

Man is exposed to dieldrin through eating contaminated fish and shell fish. Infants are exposed from breast milk. Dieldrin decreases the effectiveness of our immune system, cause cancer, increase infant mortality, reduces reproductive success, causes birth defects and damages the kidneys (Smith, 1991). Harmful effects of  $\beta$ -endosulfan are not clearly understood however excess levels of endosulfan are toxic to both humans and animals (Smith, 1991).

### **Concept of Koc**

The soil sorption coefficient (Koc) is the ratio between the concentrations of a given chemical sorbed by the soil and that dissolved in the soil water normalized to the total organic carbon content of the soil. It is used to quantify soil sorption and the advantage of this is that Koc for a particular pesticide is assumed to be independent of the soil pesticide combination (Nkedi-Kizza et al., 1983, Rao and Davidson 1980). Sorption is among the major processes that affect the fate of pesticides in the soil environment. It also regulates the rates and magnitudes of other processes that govern the fate and transport of organic contaminants in soils and sediments. Sorption of pesticides decreases their biological activities and rates of biological degradation. However, due to surface catalyzed hydrolysis, sorption may enhance non biological degradation (Stevenson, 1994).

Adsorption of hydrophobic organic pollutants by soil is strongly dependent on the soil organic matter content (Means et al., 1980; Xing et al., 1994). Organic matter can be humic or nonhumic (Morrill et al., 1982) and humified material is often a stronger sorbent for non-ionic pesticides due to the presence of oxygen –containing functional groups like –COOH, phenolic, aliphatic, enolic, -OH, and C=O. However this is not true for ionic pesticides, due to the range

of possible sorption mechanisms (Hance, 1988). The chemistry of soil organic matter in soils from different geographical regions varies. Soil organic matter may vary from soil to soil in its polarity, elemental composition, aromaticity, condensation, and degree of diagenetic evolution from a loose polymer to condensed coal-like structures (Garbarini and Lion, 1986; Gauthier et al., 1987; Grathwohl, 1990; Karapanagioti et al., 2000). Therefore land variations, such as type and age of soil organic matter may affect sorption of non-ionic pesticides.

Three different processes; film diffusion, retarded intra particle diffusion and intrasorbent diffusion, that involve diffusion mass transfer cause sorption related nonequilibrium. Retarded intraparticle diffusion is aqueous phase diffusion of solute within pores of micro porous particles; forexample, sand grains mediated by retardation resulting from instantaneous sorption to pore walls. Intra sorbent (intra organic matter) diffusion involves the diffusive mass transfer of sorbate with in the matrix of the sorbent. It involves diffusion within organic matter matrix. The major assumption in intra organic matter diffusion model is that sorbet organic matter is a polymeric type substance within which sorbate can diffuse. The organic matter associated with natural sorbents is reported to be a flexible, cross-linked, branched, amorphous (noncrystalline), polyelectrolytic polymeric substance (Brusseau et al., 1991).

The amount of chemical adsorbed is a function of both the soil and the solute. The distribution coefficient or partition coefficient,  $K^W$  (L/kg), is estimated by  $K^W = f_{oc} K_{oc}$ , where  $f_{oc}$  is a function of the soil and is the fraction of naturally occurring organic carbon measured in the soil and  $K^W$  is a function of the solute and is the partition coefficient of the solute between water and organic carbon.

A linear model of the following form is employed to approximate sorption data for soils and sediments.

$$S_e = K^W C_e \quad 2-1$$

Where  $S_e$  (mg/kg) is the mass of solute sorbed per unit mass of solid at equilibrium,  $C_e$  (mg/L) is solute concentration and  $K^W$  (L/kg) is the distribution coefficient in aqueous systems.

The parameter, octanol-water partitioning coefficient ( $K_{OW}$ ) which is the measure of hydrophobicity (water repulsing) of an organic compound (solute) is given by:

$$K_{OW} = C_O/C_W \quad 2-2$$

Where  $C_O$  (mg/L) is the concentration in the octanol phase and  $C_W$  (mg/L) is the concentration in aqueous phase.  $K_{OW}$  is used in assessment of environmental fate and transport for organic chemicals because the octanol phase is a surrogate for the lipid phase or organic carbon content of environmental compartments.  $K_{OW}$  is correlated to water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life (Lyman et al., 1990) and this makes it a key variable in estimation of these variables. The less hydrophobic (small  $K_{OW}$ ) a compound is, the more soluble it is in water and less likely it will adsorb to soil particles (Bedient, 1994).

Several relations have been developed between  $K_{OC}$  and  $K_{OW}$ :

$$\text{Log } K_{OC} = a \text{ log } K_{OW} + b \quad 2-3$$

Values reported for  $a$  and  $b$  in Eq. 2-3 include ( $a = 1$  and  $b = 0.48$ ) for polycyclic aromatic hydrocarbons, ( $a = 0.52$  and  $b = 4.4$ ) for certain group of pesticides and ( $a = 0.72$  and  $b = 3.2$ ) for alkylated and chlorinated benzenes (Jones and de Voogt, 1999). Conclusion from the available data is that, values of  $a$  and  $b$  are determined by the type of compounds that is compound classes and range of lipophilicity on which the relationship is established and only to a smaller degree by the type of natural sorbents used (Jones and de Voogt, 1999).

According to Karickhoff et al. (1981), the following relationship was found;

$$\text{Log } K_{OC} = 0.989 \text{ log } K_{OW} - 0.346 \text{ (5PAHs, } r^2 = 0.997) \quad 2-4$$

Equation 5 was for 13 methylated and halogenated benzenes (Schwarzenbach and Westall, 1981)

$$\text{Log } K_{OC} = 0.72 \log K_{OW} + 0.49 \quad (r^2=0.95) \quad 2-5$$

Vowles and Matoura (1987) proposed that different classes of solutes don't have similar affinities for octanol and natural organic matter. After arranging hydrocarbons into homologous groups, they came up with the following relationships:

$$\text{Log } K_{OC} = 0.774 \log K_{OW} + 0.37 \quad (\text{alkylnaphthalenes, } r^2=0.992) \quad 2-6$$

$$\text{Log } K_{OC} = 1.20 \log K_{OW} - 1.13 \quad (4 \text{ PAHs, } r^2 = 0.998) \quad 2-7$$

$$\text{Log } K_{OC} = 0.904 \log K_{OW} - 0.46 \quad (\text{alkyl benzenes, } r^2 = 0.992) \quad 2-8$$

Chiou (1990) reported a relationship between  $K_{OM}$  and  $K_{OW}$  for sorption of various organic compounds, including several pesticides, by different soils and sediments as;

$$\text{Log } K_{OM} = 0.94 \log K_{OW} - 0.779 \quad (r^2=0.989) \quad 2-9$$

Where  $K_{OM}$  is the partition coefficient for the organic compound between soil organic phase (based on organic matter) and water.

There are propositions that solubility relationships for aliphatic and aromatic solutes are different because of their dependence on solute's polarizability and basicity (Kamlet et al., 1987) and additions of ring fragments and functional groups on the aromatic ring (Karickhoff, 1985).

Experimental determination of  $K_{oc}$  values is difficult, costly and time consuming. For compounds of low solubility such as DDT, lindane, and PCB's,  $K_{oc}$  values are inaccurate (Chiou et al., 1979; Kenaga and Goring, 1980). Therefore, correlations between  $K_{OC}$  and  $K_{OW}$  listed in Eqs. 2-3 to 2-9 might be questionable due to experimental errors made when measuring  $K_{OC}$  values in aqueous systems for strongly hydrophobic organic chemicals (SHOCs).

## **Variability of K<sub>oc</sub> Values in Literature for Persistent Organic Pollutants (POPs) that are also (SHOCS)**

Recently research scientists have questioned the reliability of chemical property data in the literature especially for SHOCs (Pontolillo and Eganhouse, 2001). Since this class of chemicals is sparingly soluble in water, direct determination of  $S_w$ ,  $K_{ow}$  and  $K_{oc}$  is problematic. Therefore indirect estimation based on correlations between  $S_w$ ,  $K_{ow}$  or  $K_{oc}$  with measurable molecular parameters (connectivity indices, HPLC capacity factors etc) have been used in the literature (Sangster, 1997, Karickhoff, 1981). However, these techniques depend on various assumptions that produce results that are not always comparable ((Pontolillo and Eganhouse, 2001). A literature search from 700 publications from 1944 to 2001 for DDT and DDE,  $S_w$  and  $K_{ow}$  values revealed a variation of up to 4 orders of magnitude (Pontolillo and Eganhouse, 2001). This trend in parameter variability in the literature is true for other POPs (Table 2-2).

Environmental risk assessment, fate and transport models, and sediment quality guidelines may not be accurate because of the variability of basic data needed to predict the fate of contaminants (POPs) in the environment (Renner, 2002). This problem is clearly demonstrated in Table 2-1. For example the  $K_{oc}$  values for dieldrin vary within a factor of 4 and for DDT the  $K_{oc}$  values vary within a factor of 13. Karickhoff (1981) reported  $K_{oc}$  values for weakly hydrophobic chemicals ( $K_{oc} < 1000$ ) to vary within a factor of 2. The variation in the literature values of the three parameters ( $K_{ow}$ ,  $K_{oc}$ , and  $S_w$ ) for SHOCs has been attributed to measurement uncertainty due to different analytical methods, temperature differences, lack of equilibrium and impurities of test compounds (Linkov et al., 2005; Chiou et al., 2005). However, one process that damages sample integrity before analysis is analyte adsorption onto the walls of samplers and vessels. This process has been ignored in the literature especially for SHOCs. Wolska et al. (2005) reported up to 70% of adsorption of PAHs and PCBs on walls of containers.

The adsorption on walls of containers increased as  $\log K_{OW}$  of the chemicals increased from 6.5 to 8.5.

### **The Solvophobic Theory**

Rao et al., (1985) and Nkedi-Kizza et al., (1985) showed that the Solvophobic model can be used to estimate (in aqueous systems) the sorption coefficient normalized to soil organic carbon content ( $K_{OC}$ ) of hydrophobic organic chemicals. Nkedi-kizza et al., (1985) suggested that sorption of SHOCs in aqueous systems can be determined in mixed solvents by extrapolating  $K_{OC}$  at zero co-solvent. Data for one SHOC (Anthracene) and two pesticides (Atrazine and Diuron) were presented that showed the validity of the Solvophobic model (Table 2-3).

Table 2-1. Properties of the chemicals used in the study

Property	Chemical			
	DDT	Dieldrin	$\beta$ -endosulfan	Anthracene
Melting point( $^{\circ}$ C)	108.5	175-176	70-100	217
Aqueous solubility at 25 $^{\circ}$ C( $\mu$ g/L)	1.2 - 5	140	320	75
Log $K_{OC}$	5.15 – 6.26	4.08 – 4.55	4.06	4.22
Boiling point( $^{\circ}$ C)	260	385	106	340
Appearance	White powder	White crystals	Colorless crystals	Yellow crystals

Source: Nkedi-Kizza et al., 1985; Kidd et al., 1991.

Table 2-2.  $S_w$ ,  $K_{OW}$  and  $K_{OC}$  values from the literature for selected POPs

<u>Pesticide</u>	*Log $K_{OW}$	$K_{OW}$	<u>Source</u>
Aldrin	5.17 to 7.40	147,910 to 25,118,864	a
DDT	4.89 to 6.91	77,624 to 8,128,305	a and b
Dieldrin	3.69 to 6.20	4,897 to 1,584,893	a
HCB	3.03 to 6.42	1,071 to 2,630,267	a
<u>Pesticide</u>	*Log $K_{OC}$	$K_{OC}$	
Aldrin	2.61 to 4.69	407 to 48,978	a
Chlordane	4.58 to 5.57	38,019 to 371,535	a
DDT	5.14 to 6.26	138,038 to 1,819,701	a
Dieldrin	4.08 to 4.55	12,023 to 35,481	a
HCB	2.56 to 4.56	363 to 36,308	a
<u>Pesticide</u>	* $S_w$ ( $\mu$ g/L)	Temperature ( $^{\circ}$ C)	
Aldrin	17 to 180	25	a
DDT	1.2 to 5.5	25	a
Endrin	220 to 260	25	a

Source:\* a. Ritter et al., 1995; b. Pontolillo and Eganhouse, 2001.

Table 2-3. Comparison of measured and calculated KOC values in four soils

Sorbate	Literature $K_{OC}$	Measured $K_{OC}$ in water ( $f^c = 0$ )	Measured $K_{OC}$ in methanol-water. Calculated with Solvophobic model	Measured $K_{OC}$ in acetone-water. Calculated with Solvophobic model
Anthracene	15849	16032	16560	16912
Atrazine	146	96	90	89
Diuron	426	426	417	351
Source:	Nkedi-Kizza et al., 1985			

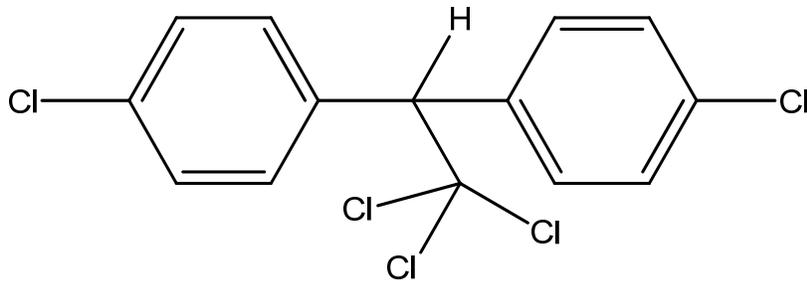


Figure2-1.DDT : $(C_{14}H_9Cl_{15})_1$ , 1, 1'-(2, 2, 2-Trichloroethylidene) bis (4-chlorobenzene)

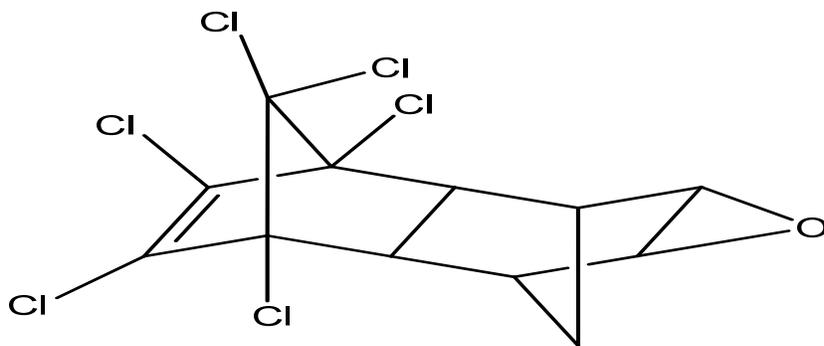


Figure2-2.Dieldrin: $(C_{12}H_8Cl_6O)$ 3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimetanonaph[2,3-b] oxirene.

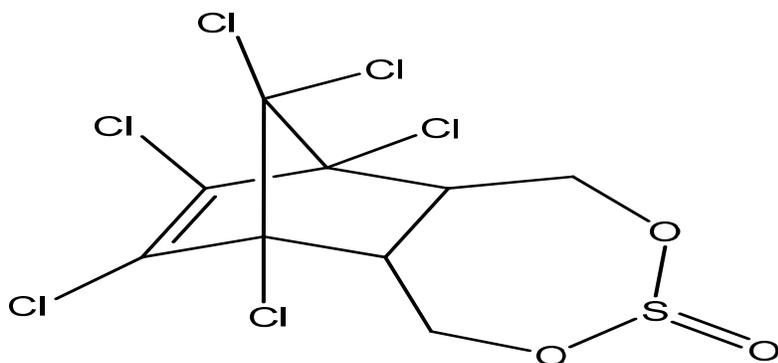


Figure2-3.β-endosulfan:6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2;4,3-benzadioxahepin 3-oxide.

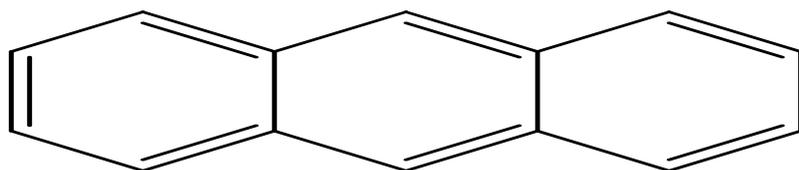


Figure 2-4. Anthracene:  $C_{14}H_{10}$

## CHAPTER 3 MATERIALS AND METHODS

### Soils

Five soils were used of which three were carbonatic (Perrine, Chekika and Krome) and two non carbonatic (Lauderhill, organic) and (Monteocha, Spodosol). The soils were taken from 0-15 cm of top soil. The Spodosols were collected from Alachua County, Florida. Carbonatic soils are defined as soils containing 40% carbonates (calcite and/or dolomite). The carbonatic soils in South Florida are classified as Entisols and the associated organic soils (Histosols) are mainly sapristis and fibrists (NRCS, 1987). Organic soils are defined as soils containing a minimum of 12% organic carbon when the mineral portion contains no clay or 18 % organic carbon if the soil has 60% or more clay (Lucas, 1982). The soils were selected to represent different geographical conditions and organic matter content. The soil series are presented in Table 3-1. The organic carbon content of the soils was determined by the dichromate method (Walkley and Black, 1934).

### Solvents and Sorbates

The binary solvents used in this study were various mixtures of methanol and 0.01M $\text{CaCl}_2$ . Methanol was chosen to represent an organic cosolvent that is completely miscible with water. The properties of the solvents are shown in Tables 3-2.

Anthracene was selected to represent an ideal strongly hydrophobic organic chemical (sorbate) without any polar functional groups. Its total surface area (TSA) is equal to hydrocarbonaceous surface area (HSA). Radio-labeled  $^{14}\text{C}$ - anthracene was used as a tracer for  $^{12}\text{C}$ -anthracene. Dieldrin,  $\beta$ -endosulfan, and DDT are strongly hydrophobic organic chemicals (SHOCs). Radio-labeled  $^{14}\text{C}$ -DDT was used as a tracer for  $^{12}\text{C}$ -DDT. Dieldrin,  $\beta$ -endosulfan ,

methanol, and water all of HPLC grade were obtained from Fisher Scientific. All chemicals were of 99.9% purity.

### **Teflon Lined Centrifuge Tubes, High Pressure Liquid Chromatography (HPLC) Glass Vials, High Pressure Liquid Chromatography (HPLC), and Liquid Scintillation Counting (LSC)**

Teflon lined centrifuge tubes are widely used in many experiments. They are made up of a polymer called poly tetraflouroethylene (PTFE). The tubes were obtained from Fisher scientific.

Before samples are analyzed by HPLC-UV, they are first put in HPLC vials and then put in autosampler for injection. They are made up of borosilicate (glass). The vials were bought from Fisher scientific. The HPLC system consisted of a pump: SP8800, an Intergrator: Dionex4270, Detector: Waters 490 programmable multivalent detector, and Autosampler: SP8780. Column: Nova-Pak C18.

The Liquid scintillation counter (Beckman LS 100-C model) was used to determine the  $^{14}\text{C}$  activity in 1-mL aliquots of solutions added to (Scinti-Verse II scintillation liquid, Fisher Scientific).

### **Sorption Experiments**

Before conducting sorption experiments, the following were put in to consideration.

#### **Reduced Sample Integrity Due to Sorption on container walls:**

The three possible steps where a chemical is sorbed before HPLC analysis when working in aqueous systems are:

1. Preparation of a stock solution in containers
2. Transfer of solution with plastic pipette to centrifuge tubes
3. Transfer of solution with plastic pipette to HPLC vials after centrifugation.

These three steps are illustrated in Fig. 3-1.

These sources of errors also occur when using LSC (Fig. 3-2). Unlike in HPLC analysis where some of its parts can sorb the chemical, LSC parts are excluded in the LSC analysis. The solution sample to be analyzed is directly added to the scintillation liquid which is a mixture of organic solvents. The possible error is due to the pipette used to transfer the solution.

All the stock solutions of the chemicals that were used in this research were prepared in pure methanol to eliminate sorption on the containers. Pipette tips were first rinsed with 1- mL methanol before being used in any step of the procedure. For the LSC analysis, after the sample had been transferred into the scintillation vial the pipette was rinsed with 1-mL of the scintillation liquid and then added to the scintillation vial.

#### **Determination of Surface Areas of Teflon Lined Centrifuge Tubes and HPLC Glass Vials**

Since 1 mL of solution was added to square flat bottom HPLC vials when analyzing solutions from sorption experiments, the area of the HPLC vials covered by the solution was calculated. It was calculated to be 4.76 cm<sup>2</sup> using the dimensions of the vial (Fig. 3-3).

The area of the Teflon Lined Centrifuge tube covered by the solution was calculated by a scanning model (Rhinoceros 3D SR410, 2006). The area of the tube covered by 10 mL of the solution was calculated to be 38.5 cm<sup>2</sup> (Fig. 3-4).

#### **The Solvophobic Theory**

Solvophobic theory was used to carry out the following;

#### **Sorption of Persistent Organic Chemicals on Container Walls and Soils**

During batch sorption experiments the main processes that would damage sample integrity would include sorbate adsorption on the walls of samplers, vessels, tubing, components of the pump, and injector valves; chemical reactions (photolysis, oxidation, reduction, and complexing) and biodegradation. To reduce sorbate loss before analysis, steps were taken to analyze the samples quickly. Also working in mixed solvents would reduce sorption on container walls. In

mixed-solvents, biological degradation is also reduced due to microbial toxicity of the organic solvents.

For sorption of SHOCs on container walls, the following equations were developed based on the Solvophobic model in Eq. 3-1 (Rao et al., 1985; Nkedi-Kizza et al., 1985)

$$K^M = K^W \exp(-\alpha^c \sigma^c f^c) \quad 3-1$$

$$R^M = C_e/C_o \quad 3-2$$

$$S_e = V/A (C_o - C_e) \quad 3-3$$

$$K^M = S_e/C_e = V/A (C_o/C_e - 1) \quad 3-4$$

$$K^M = V/A (1/R^M - 1); K^W = V/A (1/R^W - 1) \quad 3-5$$

$$R^M = 1 / (1 + (A/V) K^W \exp(-\alpha^c \sigma^c f^c)) \quad 3-6$$

$$R^W = 1 / (1 + (A/V) K^W) \quad 3-7$$

Where  $K^M$  and  $K^W$  are sorption coefficients ( $\text{mL}/\text{cm}^2$ ) in co-solvent and in aqueous systems, respectively;  $R^M$  = fraction of chemical recovered at each  $f^c$ ;  $C_e$  = equilibrium solution concentration ( $\mu\text{g}/\text{mL}$ );  $C_o$  = initial solution concentration ( $\mu\text{g}/\text{mL}$ );  $S_e$  = adsorbed concentration ( $\mu\text{g}/\text{cm}^2$ );  $V$  = volume of solution added to the tube ( $\text{mL}$ );  $A$  ( $\text{cm}^2$ ) = area of the tube covered by volume  $V$ ;  $R^W$  and  $R^M$  = fraction of chemical recovered in water and mixed solvents, respectively. Equation 3-1 can be used to calculate  $K^W$  at  $f^c = 0$  and Eq. 3-6 to calculate  $R^W$  also at  $f^c = 0$ .

The sorption on container walls was carried out as one-point isotherm in triplicate.

The value of  $\sigma^c$  in Eqs. 3-1 and 3-6 is the cosolvency power and can also be equated to the hypothetical liquid-liquid partition coefficient. Therefore it may be approximated as:

$$\sigma^c = \ln [S^C/S^W] \quad 3-8$$

Where  $S^C$  and  $S^W$  are the hydrophobic chemical mole fraction solubility in neat cosolvent and water, respectively. The value of  $\sigma^c$  is strongly correlated to solute properties such as

octanol-water partition coefficient ( $K_{OW}$ ) and molecular hydrophobic surface area (HSA), and to solvent properties such as dielectric constant, interfacial tension and bulk surface tension (Yalkowsky et al., 1976)

$$\sigma^c = [\Delta\gamma^c HSA] / (kT) \quad 3-9$$

$\Delta\gamma^c = \gamma^w - \gamma^c$  (ergs/Å<sup>2</sup>) = difference in interfacial free energy at the aqueous interface and the organic co-solvent interface with the hydro carbonaceous surface area (HSA, Å<sup>2</sup>) of SHOC molecule; k (ergs/K) is Boltzmann constant ; T is temperature in K.

For sorption of SHOCs on soils Eqs.3-3 and 3-4 are modified as follows:

$$K^M = S_o/C_e = V/m (C_o/C_e - 1) \text{ in mixed solvents} \quad 3-10$$

$$K^W = S_o/C_e = V/m (C_o/C_e - 1) \text{ in water} \quad 3-11$$

Where  $K^M$  and  $K^W$  are sorption coefficients (L/kg) in co-solvent and in aqueous systems, respectively; m = mass of soil (kg). Other parameters have been defined earlier.  $K^W$  can be estimated at  $f^c = 0$  using Eq. 3-1 and  $K^M$  data obtained in the range of co-solvent, where sorption on container walls is eliminated.

### **Sorption of $\beta$ -endosulfan on teflon lined centrifuge tubes (TLCT) and HPLC vials (HPLCV)**

Appropriate volumes of 11  $\mu$ g/mL solution of  $\beta$ -endosulfan were added to 50 mL Teflon lined centrifuge tubes and volumes of 0.01M CaCl<sub>2</sub> solutions were added to make a total of 10 mL thus obtaining fractions of methanol ( $f^c$ ) increasing from 0.1 to 0.8. The range of maximum equilibrium concentration ( $C_e$ ) at each  $f^c$  was predetermined to be the same by varying the amount of  $C_o$  added to make the 10 mL of solution. Each co-solvent was prepared in triplicates. The solutions were sampled after 24 hours without shaking (batch method). A sub-sample (1 mL) of each triplicate was put in HPLC vials. The solutions were analyzed by high pressure liquid chromatography (HPLC) with UV detection. All the standards were prepared in methanol.

The conditions for HPLC were: mobile phase, 80% acetonitrile: 20% water, wavelength, 214 nm, and flow rate of 1 mL/minute. For  $\beta$ -endosulfan sorption on container walls was not separately determined for TLCT and HPLC vials. The measured concentration of the aliquot was designated as  $C_e$  ( $\mu\text{g/mL}$ ). The  $C_e$  values at each  $f^c$  were then used to calculate  $R^M$  and  $K^M$  using Eqs. 2-2 and 2-4, respectively. However, the area of the TLCT covered by 10 mL was used in Eq. 3-4. Equations 3-1 to 3-6 and 3-9 were used to calculate properties of  $\beta$ -endosulfan (cosolvency power, percent of a chemical recovered from the HPLC vials plus TLCT, sorption coefficient in water, and HSA). The ratio of  $V/A$  was essentially equal for TLCT and HPLCV.

#### **Sorption of dieldrin on HPLC vials (HPLCV)**

Appropriate volumes of dieldrin initial concentrations of 2.5, 3.5, 4, 5, 6 and 7 ( $\mu\text{g/mL}$ ) were added to 0.01 M  $\text{CaCl}_2$  solution in HPLC vials to make up 1 mL of solution yielding 0.25, 0.35, 0.4, and 0.5 fractions of methanol ( $f^c$ ). The range of equilibrium concentration ( $C_e$ ) at each  $f^c$  was predetermined to be the same by varying the amount of  $C_o$  added to make the 10 mL of solution. Each cosolvent was used in triplicates. HPLC-vials of each cosolvent were prepared in triplicates. The 1 mL solution of each cosolvent was left to stand for 24 hours. Equilibrium concentration was analyzed using HPLC-UV. Conditions of the HPLC were; mobile phase of 80% methanol and 20% water, wavelength of 220 nm, sensitivity of 0.04 AUs and flow rate of 1.5 mL/min, and C-18 column. All the standards were prepared in methanol. Samples were injected thrice in the HPLC system. Percent recoveries ( $R$ ) were computed by dividing equilibrium concentration ( $C_e$ ) by original concentration ( $C_o$ ) then multiplying by hundred ( $R = (C_e/C_o) * 100$ ). The area covered with solution in HPLC vials was calculated from the vial dimensions and it was found to be  $4.76 \text{ cm}^2$ . Equations 3-1 to 3-6 and 3-9 were used to calculate properties of Dieldrin (cosolvency power, percent of a chemical recovered from the HPLC vials, sorption coefficient in water, and HSA).

### **Sorption of dieldrin on teflon lined centrifuge tubes (TLCT)**

Initial concentration ( $C_0 = 2 \mu\text{g/mL}$ ), was mixed with 0.01M  $\text{CaCl}_2$  solutions in a Teflon lined centrifuge tubes to make a total of 10 mL that yielded 0.10, 0.20, 0.25 and 0.30 fractions of methanol ( $f^c$ ). The range of equilibrium concentration ( $C_e$ ) at each  $f^c$  was predetermined to be the same by varying the amount of  $C_0$  added to make the 10 mL of solution. Centrifuge tubes of each cosolvent were prepared in triplicates. The 10 mL solution of each cosolvent was left to stand for 24 hours. Equilibrium concentration was analyzed using HPLC-UV. Conditions of the HPLC system were; wavelength of 220nm, sensitivity of 0.04Aufs, flow rate of 1.5mL/min; mobile phase of 80% methanol and 20% water, and C-18 column. All the standards and the samples were added to HPLC vials in methanol to make up 1 mL of at least 70% methanol. Samples were injected thrice in the HPLC system. Concentrations that were below detection limit after dilution of samples in HPLC vials with methanol were spiked with a known concentration of dieldrin in pure methanol. The measured concentration of the aliquot was designated as  $C_e$  ( $\mu\text{g/mL}$ ). The  $C_e$  values at each  $f^c$  were then used to calculate  $R^M$  and  $K^M$  using Eqs. 3-2 and 3-4, respectively. The area of the TLCT covered by 10 mL ( $A = 38.53 \text{ cm}^2$ ) was used in Eq.3- 4. Equations 3-1 to 3-6 and 3-9 were used to calculate properties of dieldrin (cosolvency power, percent of a chemical recovered from the TLCT, sorption coefficient in water, and HSA).

### **Sorption of anthracene on teflon lined centrifuge tubes (TLCT).**

A volume of  $^{12}\text{C}$ -Anthracene of initial concentration of 0.1  $\mu\text{g/mL}$  in methanol and a volume of  $^{14}\text{C}$ -Anthracene (10000 cpm/mL) also in methanol were pipetted into 50mL Teflon lined centrifuge tubes. A volume of 0.01M  $\text{CaCl}_2$  was added to make a total of 10 mL that resulted in 0.01, 0.06, 0.1, 0.20, 0.25 and 0.3 fractions of methanol. The range of equilibrium concentration ( $C_e$ ) at each  $f^c$  was predetermined to be the same by varying the amount of  $C_0$  added to make the 10 mL of solution. Each cosolvent was used in triplicates. The 10 mL solution

was left to stand for 24 hours. After 24 hours, equilibrium concentration was obtained by removing 1 mL of the supernatant from each cosolvent, put in a vial containing 5 mL of cocktail (Scinti-Verse II scintillation solution) and analyzed using a Beckman LS 100-C liquid scintillation counter (LSC). The analyzing time was 5 minutes. Back ground radioactivity from a blank of methanol + calcium chloride solution was subtracted from each LSC counts of the sample. Equations 3-1 to 3-6 and 3-9 were used to calculate properties of Anthracene (cosolvency power, percent of a chemical recovered from the Teflon lined centrifuge tubes, sorption coefficient in water, and HSA).

### **Sorption of DDT on Teflon lined centrifuge tubes**

A volume of  $^{12}\text{C}$ -DDT of initial concentration of 0.01  $\mu\text{g}/\text{mL}$  in methanol and a volume of  $^{14}\text{C}$ -DDT (10000 cpm/mL) also in methanol were pipetted into 50 mL Teflon lined centrifuge tubes. A volume of 0.01M  $\text{CaCl}_2$  was added to make a total of 10 mL that resulted in 0.1, 0.2, 0.3 and 0.4 methanol fractions. The range of equilibrium concentration ( $C_e$ ) at each  $f^c$  was predetermined to be the same by varying the amount of  $C_o$  added to make the 10 mL of solution. Each cosolvent was used in triplicates. The 10 mL solution was left to stand for 24 hours. After 24 hours, equilibrium concentration was obtained by removing 1 mL of the supernatant from each cosolvent, put in a vial containing 5 mL of cocktail (Scinti-Verse II scintillation solution) and analyzed using a Beckman LS 100-C liquid scintillation counter (LSC). The analyzing time was 5 minutes. Back ground radioactivity from a blank of methanol + calcium chloride solution was subtracted from each LSC counts of the sample. Equations 3-1 to 3-6 and 3-9 were used to calculate properties of DDT (cosolvency power, percent of a chemical recovered from the Teflon lined centrifuge tubes, sorption coefficient in water, and HSA).

## Sorption Isotherms on Soils

Before sorption isotherm experiments were done, an experimental design was carried out to make sure that a maximum equilibrium concentration ( $C_e$ ) was maintained at all  $f^c$  values and in all soils for a given chemical.

### Estimation of equilibrium concentrations

All sorption isotherms from soils were designed such that equilibrium concentrations ( $C_e$ ) at each  $f^c$  and in each soil were in the linear range of isotherms. This was achieved by using the Solvophobic model to calculate the solubility of each chemical at  $f^c$  values from 0 to 0.7. The model was also used to estimate sorption coefficients at each  $f^c$  based on literature  $K_{OC}$  values.

Using the linear isotherm model, the chemical's  $K_{OC}$  and  $f^c$  values the following equations were derived:

$$S_e = K^M C_e \quad 3-12$$

$$S_e = V/m (C_o - C_e) \quad 3-13$$

Parameters in Eqs. 3-12 and 3-13 have been defined earlier. Combining Eqs. 3-12 and 3-13 yield an equation that can be used to vary the soil: solution ration at all  $f^c$  values to maintain the required  $C_e$  range.

$$C_e = C_o / ((m/V * K^M) + 1) \quad 3-14$$

In order to maintain the same  $C_e$  range Eq.3-14 was used. This was achieved by adjusting  $C_o$ ,  $m$ , and  $K^M$  depending on  $f^c$  of methanol at which the isotherm was measured. A summary of the various parameters used during isotherm determination is given in Table 3-3.

### Sorption of anthracene on soils

Equilibrium sorption isotherms were measured from various mixtures of methanol and water using four soils (Krome, Perrine and Chekika, and Lauderhill). Isotherms were determined in the range of methanol ( $f^c = 0.5$  to  $0.7$ ) when there was no sorption on TLCT. The soil solution

ratios of 1:2, 1:1.2.5, and 1:1 were used for methanol fractions of 0.5, 0.6 and 0.7, respectively, for carbonatic soils. Initial concentrations of  $^{12}\text{C}$ -Anthracene were 0.1, 0.2, 0.4 ( $\mu\text{g}/\text{mL}$ ) for  $f^c = 0.5, 0.6$  and 0.7. The soil solution ratio at  $f^c = 0.5, 0.6$  and 0.7 were 1:1, 1:40, and 1:17, respectively for Lauderhill. The soil solution ratios at  $f^c = 0.5, 0.6$  and 0.7 were 1:67, 1:25, and 1:13, respectively, for Monteocha. All isotherms were run in triplicates for each initial concentration and at a given  $f^c$ . The solutions were spiked with  $^{14}\text{C}$ -Anthracene to give (10,000 cpm/mL).

Following a 24 h shaking and equilibration period, the solution phase was separated from the solid phase by centrifugation at 9000 rpm for 25 minutes and 1 mL of the supernatant was put in a 5 mL of cocktail in plastic vials. Liquid scintillation counting (LSC) was used to analyze  $^{14}\text{C}$ -Anthracene in solution. The counting time was 5 minutes. Background radioactivity from a blank of methanol + calcium chloride solution was subtracted from counts of the sample. The decrease in sorbate solution concentration was assumed to be due to sorption by the soil.

Additional sorption experiments by Krome soil were carried out at  $f^c = 0.1, 0.2,$  and 0.3 with soil solution ratios of 0.01, 0.02, and 0.1, respectively. The total volume of solution was 10 mL.

All isotherms were done in triplicates. The additional data were collected to test the linearity of the Solvophobic model by directly determining anthracene adsorbed on the soils. The initial  $^{12}\text{C}$ -Anthracene concentration was 0.1 to 0.2 ( $\mu\text{g}/\text{mL}$ ), and  $^{14}\text{C}$ -Anthracene was 40,000 cpm/mL. Due to potential sorption on TLCT, the batch slurry method was modified. The amount of  $^{14}\text{C}$ -Anthracene adsorbed on the soil was directly determined by combusting an oven dry sub-sample of the soil at the end of the equilibration period after centrifuging the samples at 9000 rpm for 25 minutes and determining  $C_e$  in the supernatant solution by LSC. The soil sample was

combusted in a Harvey Ox 500 Biological oxidizer, trapping the evolved CO<sub>2</sub> in a scintillation solution and quantifying <sup>14</sup>CO<sub>2</sub> by liquid scintillation as described earlier. The adsorbed concentration (S<sub>e</sub>) was calculated using Eq.3-13 and was plotted against the solution concentration (C<sub>e</sub>). The slope of the line is equal to the sorption coefficient (K<sup>M</sup>) based on Eq. 3-12. Equations 3-1, 3-9, and 3-10 were used to calculate properties of Anthracene (cosolvency power, σ<sup>c</sup>), sorption coefficient in water (K<sup>W</sup>), and HSA. The values of K<sup>W</sup> were normalized with soil organic carbon content to calculate K<sub>OC</sub> for each soil.

### **Sorption of DDT on soils**

Methanol fractions (f<sup>c</sup>) of 0.5, 0.55, and 0.6 were used for all soils. Initial concentrations of <sup>12</sup>C-DDT were 0.02 to 0.04 (μg/mL) for all methanol fractions used. The soil solution ratios at f<sup>c</sup> = 0.5, 0.55 and 0.6 were 1:3, 1:2 and 1:1 respectively for Krome, Chekika and Perrine. The soil solution ratios at f<sup>c</sup> = 0.5, 0.55 and 0.6 were 1:50, 1:29 and 1:20, respectively for Montechoa soil. The soil solution ratios at f<sup>c</sup> = 0.5, 0.55 and 0.6 were 1:100, 1:67 and 1:50, respectively for Lauderhill soil. The total volume of solution was 10 mL, and the samples were spiked with <sup>14</sup>C-DDT to give 40,000 cpm/mL.

Following a 24hr shaking and equilibration period, the solution phase was separated from the solid phase by centrifugation at 9000 rpm for 25 minutes and 1 mL of the supernatant was put in a 10mL of cocktail in plastic vials. Liquid scintillation counting (LSC) was used to analyze the solution. The analyzing time was 5 minutes. The decrease in sorbate solution concentration was assumed to be due to sorption by the soil.

The adsorbed concentration (S<sub>e</sub>) was calculated using Eq. 3-13 and was plotted against the solution concentration (C<sub>e</sub>). The slope of the line is equal to the sorption coefficient (K<sup>M</sup>) based on Eq.2-12. Equations 3-1, 3-9, and 3-10 were used to calculate properties of DDT

(cosolvency power ( $\sigma^c$ ), sorption coefficient in water ( $K^W$ ), and HSA). The values of  $K^W$  were normalized with soil organic carbon content to calculate  $K_{OC}$  for each soil.

### **Sorption of dieldrin on soils**

Equilibrium sorption isotherms were measured from various mixtures of methanol and water. Methanol fractions of 0.4, 0.45, 0.5 and 0.6 were used. Soil solution ratios of 1:2.5, 1:2, 1:1.3, and 1:1 for  $f^c = 0.4, 0.45, 0.5$  and  $0.6$ , respectively, were used for Perrine, Krome and Chekika soils. Methanol fractions of 0.4, 0.5 and 0.6 were used for Lauderhill and Monteocha soils at solution ratios of 1:17, 1:6, and 1:3. The three initial concentrations of dieldrin were between 4 to 8  $\mu\text{g/mL}$ . The total volume of solution in TLCT was 10 mL. At each  $f^c$  and initial concentration, triplicate soil samples were used.

Following a 24h shaking and equilibration period, the solution phase was separated from the solid phase by centrifugation at 9000 rpm for 25 minutes. The supernatant was added to HPLC vials and diluted by methanol to reach ( $f^c = 0.7$ ) when there was no sorption on HPLC vials. The solution was analyzed by HPLC with UV detection. Conditions of the HPLC system were; wavelength of 220nm, sensitivity of 0.04Aufs, flow rate of 1.5mL/min; mobile phase of 80%methanol and 20% water, and C-18 column. All the standards and the samples were added to HPLC vials in methanol to make up 1 mL of at least 70% methanol. Samples were injected thrice in the HPLC system. The run time was 8 minutes and retention time was 6 minutes. Concentrations that were below detection limit after dilution of samples in HPLC vials were spiked with a known concentration of dieldrin in pure methanol.

The adsorbed concentration ( $S_e$ ) was calculated using Eq.3-13 and was plotted against the solution concentration ( $C_e$ ). The slope of the line is equal to the sorption coefficient ( $K^M$ ) based on Eq.12. Equations 3-1, 3-9, and 3-10 were used to calculate properties of Dieldrin (cosolvency

power ( $\sigma^c$ ), sorption coefficient in water ( $K^W$ ), and HSA). The values of  $K^W$  were normalized with soil organic carbon content to calculate  $K_{OC}$  for each soil.

Table 3-1: Characteristics of the soils used

Soil series name	Location	Classification
Chekika	Miami Dade County, Florida	Loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents.
Krome	Miami Dade County, Florida	Loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents
Perrine, marl	Miami Dade County, Florida	Coarse-silty, carbonatic, hyperthermic Typic Fluvaquents
Lauderhill	Miami Dade County	Euic hyperthermic Lithic Haplosaprists
Monteocha	Alachua County, Florida	Sandy, siliceous hyperthermic Ultic Alaquods Monteocha

Table 3-2. Some properties of the solvents (at 25°C) used

Solvent	Boiling Point (°C)	Viscosity (cP)	Surface Tension (dyne/cm)	Density (g/mL <sup>3</sup> )	Rohrschneider Polarity index	Dipole Moment (D)	Dielectric constant
Water	100	0.89	73	1.0	9.0	1.84	80.0
Methanol	65	0.54	22	0.77	6.6	1.66	32.7

**Source:** Snyder et al. (1978)

Table 3-3. Summary of initial and equilibrium concentrations used for sorption isotherms

Chemical	Type	f <sup>e</sup> range for isotherm	C <sub>o</sub> (ug/mL)	C <sub>e</sub> range (ug/mL)	Sorbent(s)
β-endosulfan	<sup>12</sup> C	0.1 – 1	11	5 – 9	HPLCV + TLCT
Dieldrin	<sup>12</sup> C	0.25 – 0.4	2.5 – 5	1- 2.5	HPLCV
Dieldrin	<sup>12</sup> C	0.1 – 0.6	2 – 3	1 – 2.5	TLCT
Dieldrin	<sup>12</sup> C	0.3 - 0.6	4 - 8	1.3 – 2.6	Soils
Anthracene	<sup>12</sup> C and <sup>14</sup> C	0.01 – 0.6	0.1	0.05 – 0.09	TLCT
Anthracene	<sup>12</sup> C and <sup>14</sup> C	0.5 – 0.7	0.1	0.01- 0.06	Soils
DDT	<sup>12</sup> C and <sup>14</sup> C	0.05 – 0.5	0.01 – 0.02	0.009 – 0.02	TLCT
DDT	<sup>12</sup> C and <sup>14</sup> C	0.5 – 0.6	0.02 – 0.04	0.009 – 0.02	Soils

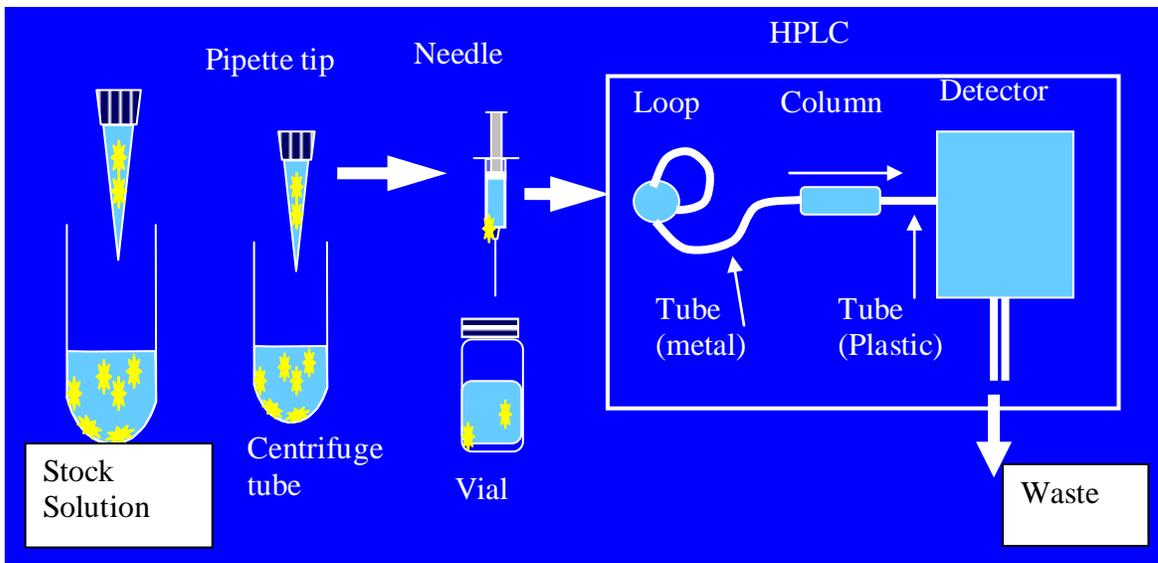


Figure 3-1. Sorption of a chemical up to HPLC analysis

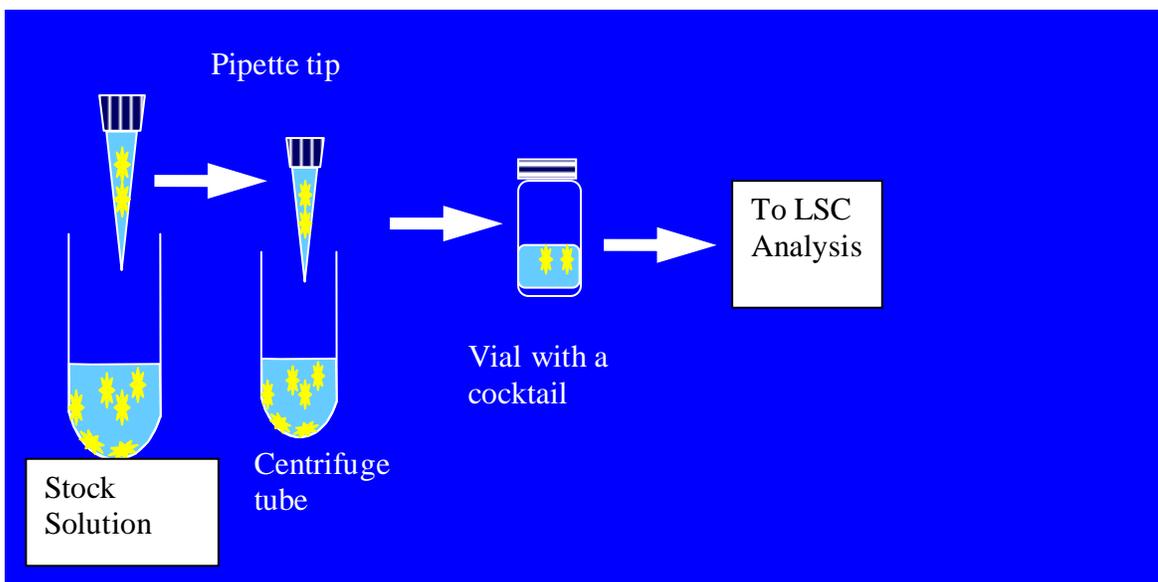


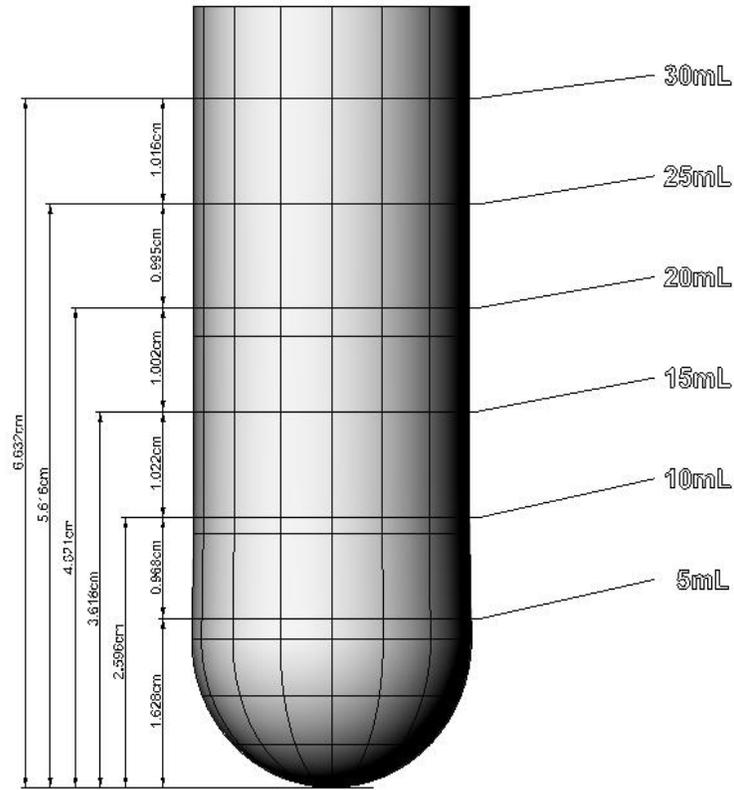
Figure 3-2. Sorption of a chemical up to LSC analysis



**Area:  $4.76\text{cm}^2$**   
**Volume = 1mL**  
**Radius = 0.5cm**  
**Height = 1.25cm**

Figure 3-3. Calculation of the area of HPLC vials covered by solution

# FEP



5mL = 22.26cm<sup>2</sup>  
10mL = 38.53 cm<sup>2</sup>

Figure 3-4. Calculation of the area of Teflon Lined Centrifuge Tubes covered by solution

## CHAPTER 4 RESULTS AND DISCUSSION

In this study, initially, sorption of  $\beta$ -endosulfan, dieldrin, anthracene, and DDT, on container walls (Teflon lined centrifuge tubes and HPLC vials) in methanol-water systems with methanol ranging from ( $f^c = 0.01$  to 1) were determined. Then the range of fraction of methanol ( $f^c$ ) where there was no sorption on container walls was identified. Above that range of methanol  $f^c$ , sorption coefficients ( $K^M$ ) of anthracene, DDT, and dieldrin, were determined in five soils (Perrine, Krome, Chekika, Lauderhill and Montechoa). The aqueous ( $f^c = 0$ ) sorption coefficient ( $K^W$ ) of each chemical was calculated using the Solvophobic model. The  $K^W$  values were normalized with soil organic carbon content to obtain  $K_{OC}$  values for each chemical in all soils. The parameters that were used to calculate HSA,  $K_{OC}$ , and  $K^M$  of each chemical are listed in Table 4-1.

### Sorption on Container Walls

#### Sorption of $^{12}\text{C}$ - $\beta$ -endosulfan on Teflon Lined Centrifuge Tubes (TLCT) and HPLC Vials (HPLCV).

Data in Figs. 4-1 and 4-2 show that  $\beta$ -Endosulfan adsorbed on the container walls (TLCT and HPLCV) up to 0.5  $f^c$  with little sorption at  $f^c = 0.7$ . Data in Figs. 4-1 and 4-2 also reveal that the Solvophobic model describe the data reasonably well. The percent recovery in water ( $f^c = 0$ ) was calculated as 30%. The sorption coefficient of  $\beta$ -endosulfan in an aqueous system ( $K^W$ ) from Figure 4-1 was  $0.60 \mu\text{g}/\text{cm}^2$ . Although sorption on container walls is not needed, sorption on container walls was used to calculate HSA for  $\beta$ -endosulfan of  $176 \text{ \AA}^2$  using Eq. 3-9 and parameters listed in Table 4-1. No data are available in the literature for  $\beta$ -endosulfan HSA or TSA. Nkedi-Kizza et al., (1985) pointed out that the value of the slope of the line in Fig. 4-1 depends on the properties of methanol, water, and  $\beta$ -endosulfan, and therefore the HSA calculated should not be affected by the nature of the sorbent. However, the magnitude of  $K^W$

calculated depends on the properties of the sorbing materials, in this case TLCT and HPLC vials. In many studies of organic chemicals, TLCT and HPLCV are assumed not to adsorb chemicals such as  $\beta$ -endosulfan. The data presented show that the concentration of  $\beta$ -endosulfan if measured in aqueous system with HPLC-UV would be reduced by 70%.

### **Sorption of $^{12}\text{C}$ -Dieldrin on Container Walls**

#### **Sorption on HPLC vials (HPLCV) and Teflon lined centrifuge tubes (TLCT)**

The dependence of  $K^M$  on  $f^c$  for dieldrin sorption by two container walls (TLCT and HPLCV) is shown in Fig. 4-3. As predicted by the Solvophobic theory (Eq. 3-1) a log-linear relationship describes the data over the range of  $0.1 \leq f^c \leq 0.5$ . The slopes of the lines in Fig. 4-3 are essentially the same, indicating that the value of  $\sigma^c$  (Table 4-1) is independent of the sorbent as predicted by Eq. 3-1. Similar trend in data was reported for anthracene sorption on 4 soils in methanol-water systems (Nkedi-Kizza, et al., 1985).

The calculated aqueous sorption coefficient values ( $K^W$ ) for Dieldrin were 0.57 and 3.24  $\mu\text{g}/\text{cm}^2$  on TLCT and HPLV container walls, respectively. Data in Figs. 4-4 and 4-5 further emphasize that HPLCV sorb more dieldrin than TLCT. The percent recovery in aqueous systems was estimated as 6 and 32% for HPLCV and TLCT, respectively. Another observation is that dieldrin is not adsorbed on HPLCV at  $f^c \geq 0.70$  compared to TLCT in which there is no sorption of dieldrin at  $f^c \geq 0.45$ . The implications are that sorption experiments of dieldrin should be determined in methanol at  $f^c \geq 0.45$  to eliminate sorption on TLCT. However, for the analysis of dieldrin with HPLC-UV, the analyte in HPLC glass vials should be in methanol at  $f^c \geq 0.70$ . The data in Figs. 4-4 and 4-5 describe the percent recovery well as predicted by the theory (Eq. 3-6).

In Fig. 4-6, the plot of the relative sorption coefficient [ $\ln(K^M/K^W)$ ] VS.  $f^c$  is shown for Dieldrin sorption on HPLCV and TLCT container walls. The sorption data from TLCT and HPLC vials are described by one line as expected from Eq. 3-1. The  $\sigma^c$  value calculated from the

slope of the line in Fig. 4-6 (using  $\alpha^c = 0.83$ ) was 10.69 which was close to  $\sigma^c$  value of 10.67 and 10.75 for HPLCV and TLCT, respectively. The  $\sigma^c$  values were used to calculate HSA of dieldrin using Eq. 3-9 and appropriate values of ( $\Delta\gamma^c$ ,  $k$ , and  $T$ ) listed in Table 4-1. The HSA for dieldrin was 221 Å<sup>2</sup> (Table 4-2).

### **Sorption of <sup>14</sup>C-Anthracene on Teflon Lined Centrifuge Tubes (TLCT)**

The dependence of  $K^M$  on  $f^c$  for anthracene sorption by container walls of TLCT is shown in Fig. 4-7. As predicted by the Solvophobic theory (Eq. 3-1) a log-linear relationship describes the data over the range of  $0.1 \leq f^c \leq 0.25$ . The line was extended to  $f^c = 0$  to estimate  $K^W$ . The calculated aqueous sorption coefficient ( $K^W$ ) value for anthracene on TLCT container walls was 0.54 µg/ cm<sup>2</sup>. The percent recovery (in aqueous systems) for sorption of anthracene on TLCT container walls was estimated to be 52% (Fig. 4-8). Anthracene is not adsorbed on TLCT at  $f^c \geq 0.45$ . This implies that sorption experiments on anthracene should be determined in methanol-water mixtures at  $f^c \geq 0.45$  to eliminate sorption on TLCT.

The  $\sigma^c$  value calculated from the slope of the line in Fig. 4-6 (using  $\alpha^c = 0.83$ ) was 9.83. The  $\sigma^c$  values were used to calculate HSA of anthracene using Eq. 3-9 and appropriate values of ( $\Delta\gamma^c$ ,  $k$ , and  $T$ ) listed in Table 4-1. The HSA for anthracene was 203 Å<sup>2</sup> very close to the literature value of 202 Å<sup>2</sup> (Nkedi-Kizza et al., 1985). Since anthracene has no functional groups, its TSA is equal to HSA. This gives credibility to the use of the Solvophobic model in this study.

### **Sorption of <sup>14</sup>C-DDT on Teflon Lined Centrifuge Tubes (TLCT)**

The dependence of  $K^M$  on  $f^c$  for DDT sorption by container walls of TLCT is shown in Fig. 4-9. As predicted by the Solvophobic theory (Eq. 3-1) a log-linear relationship describes the data over the range of  $0.05 \leq f^c \leq 0.30$ . The line was extended to  $f^c = 0$  to estimate  $K^W$ . The calculated aqueous sorption coefficient ( $K^W$ ) value for DDT on TLCT container walls was 0.67 µg/ cm<sup>2</sup>. The percent recovery (in aqueous systems) for sorption of DDT on TLCT container

walls was estimated to be 29% (Fig. 4-10). DDT is not adsorbed on TLCT at  $f^c \geq 0.45$ . This implies that sorption experiments on DDT can be determined in methanol-water mixtures at  $f^c \geq 0.45$  to eliminate sorption on TLCT.

The  $\sigma^c$  value calculated from the slope of the line in Fig. 4-6 (using  $\alpha^c = 0.83$ ) was 12.94. The  $\sigma^c$  values were used to calculate HSA of DDT using Eq. 3-9 and appropriate values of ( $\Delta\gamma^c$ ,  $k$ , and  $T$ ) listed in Table 4-1. The HSA for DDT was  $322 \text{ \AA}^2$ . No data in the literature are available for comparison.

### Conclusions

Sorption of four strongly hydrophobic chemicals on container walls of Teflon lined centrifuge tubes and HPLC vials has been demonstrated. Using dieldrin sorption data on HPLC vials and Teflon lined centrifuge tubes; HPLC vials sorb more dieldrin than Teflon lined centrifuge tubes in aqueous systems. This was confirmed by low recovery of  $\beta$ -endosulfan that was sorbed on both TLCT and HPLCV. In aqueous systems, the sorption on TLCT container walls was predicted to be in the order DDT > Dieldrin > Anthracene (Table 4-2). For all three SHOCs there was negligible sorption on TLCT at  $f^c \geq 0.45$ . However, it is clear that glass HPLC vials sorb these chemicals at  $f^c < 0.7$ .

To eliminate sorption on Teflon lined centrifuge tubes and to determine soil sorption coefficients of dieldrin, DDT, and anthracene in these tubes, experiments should be conducted in methanol-water mixtures at  $f^c \geq 0.45$ . If HPLC-UV is the method of detection of SHOCs in solution, the analyte should be prepared in methanol or other miscible solvents at  $f^c \geq 0.7$ . Literature data that support findings in this study have reported that 40-80% of the polychlorinated biphenyls (PCBs) in a sample may be adsorbed on to the poly tetrafluoroethylene (PTFE) surface (Baltussen et al., 1999, Lung et al., 2000).

It was interesting to find that the hydrocarbonaceous surface areas of  $\beta$ -endosulfan, dieldrin, DDT, and anthracene could be calculated from sorption data on container walls. The HSA values are summarized in Table 4-2. It appears that the Solvophobic model was appropriate for this study.

### **Sorption Isotherm Experiments**

Sorption isotherm experiments for sorption of chemicals by soils were carried out to determine sorption coefficients in mixed solvents ( $K^M$ ) and there after extrapolate to aqueous systems using the Solvophobic model to obtain sorption coefficients ( $K^W$ ). Then soil sorption coefficient values ( $K_{oc}$ ) were calculated by dividing  $K^W$  with organic carbon fractions (OC) of soils. Sorption data on soils were also used to calculate hydrocarbonaceous surface areas (HSA) of the chemicals.

#### **Sorption of Dieldrin on Soils**

The exponential decrease in sorption coefficients ( $K^M$ ) of dieldrin in mixed solvents with increasing methanol fractions ( $f^c$ ) is shown in Fig. 4-11, for 5 soils. The slopes of these lines are essentially the same because the cosolvency power ( $\sigma^c$ ) is independent of the sorbents (soils) used. Plots of relative sorption coefficients ( $K^M/K^W$ ) for all soils were therefore described as a single line (Fig. 4-12) from which effective HSA was calculated. The soil sorption coefficients in aqueous systems ( $K^W$ ) were calculated from the intercepts of the plots (Fig. 4-11). Similar trend in data were reported for sorption of diuron and atrazine in soils (Nkedi-Kizza et al., 1985).

The ( $\sigma^c$ ) values from sorption of dieldrin by Chekika, Krome, Perrine, Lauderhill, and Montechoa, were used to calculate HSA values. The HSA values were very close to the effective HSA calculated from all soils of  $222 \text{ \AA}^2$ . The data are summarized in Table 4-3. The HSA values are also close to those determined for dieldrin sorption on container walls (Table 4-2).

From literature, sorption is directly proportional to organic carbon content of the soil. The trend of sorption coefficients in aqueous systems ( $K^W$ ) as shown in Table 4-3 is proved to be true for all soils. When sorption coefficients in aqueous systems ( $K^W$ ) were normalized with organic carbon content of the soils to obtain soil  $K_{oc}$  values, all soils except Krome gave values close to each other (Figure 4-13). However, dieldrin sorption coefficient value in Krome is within a factor of two (Karickhoff, 1981). The low organic carbon content (Karickhoff, 1984) of Krome can explain the deviation of dieldrin  $K_{oc}$  value from other soils. Data in Fig.4-14 show an average  $K_{oc}$  of 4803 for all soils. The  $K_{oc}$  values obtained in this study are much less than what is reported in the literature (Table 2-2) which implies that sorption on container walls is a factor for the variation of  $K_{oc}$  values of strongly hydrophobic organic chemicals.

### **Sorption of Anthracene on Soils**

Sorption of anthracene on soils was done to show the validity of Solvophobic model. Anthracene served as an ideal sorbate for evaluating the Solvophobic theory because its sorption is characterized by solvophobic interactions since the hydrocarbonaceous surface area, HSA, is equal to total surface area, TSA. The exponential decrease in sorption coefficients ( $K^M$ ) in mixed solvents with increasing methanol fractions ( $f^c$ ) is shown in Fig. 4-15 for Krome soil. The  $K^M$  data in Fig. 4-15 were obtained at  $0.45 \leq f^c \leq 0.8$  where there is negligible sorption of anthracene on TLCT container walls. These data were used in the model. The  $K^M$  values for anthracene sorption at  $f^c = 0.1, 0.2$  and  $0.3$  were directly measured by combusting  $^{14}\text{C}$ -Anthracene to determine the amount adsorbed on the soil. The  $K^M$  values at  $f^c = 0.1, 0.2,$  and  $0.3$  are also described by the theory (Eq. 3-1). This emphasizes that  $K^M$  data collected at  $f^c \gg 0$  can be used to estimate  $K^W$  at  $f^c = 0$ . However, if sorption on container walls is ignored, the  $K^M$  values measured at  $f^c = 0.1, 0.2,$  and  $0.3$  will give a very high  $K^W$  (1012 mL/g) resulting in anthracene  $K_{OC}$  of 101, 200. This  $K_{OC}$  value is about 5 times larger than the  $K_{OC}$  of 18752 that was obtained

for anthracene sorption by Krome that when there was no sorption on container walls on container walls (Table 4-4).

The dependence of  $K^M$  values on  $f^c$  for Anthracene sorption by four soils from methanol-water mixtures at which there no sorption on TLCT walls is shown in Fig. 4-16. As predicted by the Solvophobic theory (Eq. 3-1), a log-linear relationship describes the data for all soils. The slopes of the lines are essentially the same because the cosolvency power ( $\sigma^c$ ) is independent of the sorbents (soils). Plots of relative sorption coefficients ( $K^M/K^W$ ) for all soils were therefore described as a single line (Figure 4-17) from which effective HSA was estimated as  $203 \text{ \AA}^2$ . The HSA values from sorption of anthracene on Krome, Chekika, Perrine, Monteocha, and Lauderhill (Table 4-4) were very close to the value of  $202 \text{ \AA}^2$  that is reported in the literature (Yalkowsky et al., 1979). The HSA values are also close to the values obtained for the sorption of Anthracene on TLCT container walls (Table 4-2).

As was observed for dieldrin sorption in soils, sorption is proportional to organic carbon content of the soil. The trend of sorption coefficients in aqueous systems ( $K^W$ ) can be seen (Table 4-4). Since soil organic carbon increases in the order Lauderhill > Perrine > Chekika > Krome, the  $K^M$  values also increase in the same order. When Sorption coefficients in aqueous systems ( $K^W$ ) were normalized with organic carbon content of the soils to obtain  $K_{OC}$  values, the values did not give constant figures across all the soils. Although most of the values are within the acceptable factor of two, some go beyond that factor. The low organic carbon content (Karickhoff, 1984) of the carbonatic soil Krome might have caused the difference in  $K_{OC}$  values as was also observed for dieldrin sorption in Krome. As was observed for dieldrin sorption, Perrine soil has the lowest  $K_{OC}$  value for Anthracene. The average anthracene  $K_{OC}$  value for all

the soils of 8886 was obtained from the slope of the plot of sorption coefficients in aqueous systems ( $K^W$ ) against the organic carbon content as shown in Figure 4-19.

### Sorption of DDT on Soils

The exponential decrease in sorption coefficients ( $K^M$ ) in mixed solvents with increasing methanol fractions ( $f^c$ ) is shown in Fig. 4-20 for Krome soil. The  $K^M$  data in Fig. 4-19 were obtained at  $0.50 \leq f^c \leq 0.7$  when there is negligible sorption of DDT on TLCT container walls. These data were used in the model. The  $K^M$  values for DDT sorption at  $f^c = 0.3$ , and 0.4 were directly measured by combusting  $^{14}\text{C}$ -DDT to determine the amount adsorbed on the soil. The  $K^M$  values at  $f^c = 0.3$  and 0.4 are also described by the theory (Eq. 3-1). This implies that  $K^M$  data collected at  $f^c \gg 0$  can be used to estimate  $K^W$  at  $f^c = 0$ . A similar trend in data was observed for anthracene sorption in Krome soils.

The exponential decrease in sorption coefficients ( $K^M$ ) in mixed solvents with increasing methanol fractions ( $f^c$ ) is shown in Figures 4-21 with slopes of the lines essentially the same. This further demonstrates that cosolvency power ( $\sigma^c$ ) is independent of soils.

Plots of relative sorption coefficients ( $K^M/K^W$ ) for all soils were therefore described as a single line (Figure 4-22). The value of  $\sigma^c$  from Fig. 4-22 was used to calculate the HSA of DDT which was  $322 \text{ \AA}^2$ . The HSA values from sorption of DDT by Chekika, Krome, Perrine, Lauderdale, and Montechoa soils were 323, 326, 319, 319, 324, and  $319 \text{ \AA}^2$ , respectively, as shown in Table 4-5. Note that a similar HSA value of  $322 \text{ \AA}^2$  was obtained from DDT sorption on TLCT container walls.

From literature data, sorption is proportional to organic carbon content of the soil (Table 4-1). The trend of sorption coefficients in aqueous systems ( $K^W$ ) as shown in Table 4-2 is generally proved to be true for all soils. When Sorption coefficients in aqueous systems ( $K^W$ ) were normalized with organic carbon content of the soils to obtain Koc values, the data were within a

factor of two for three soils (Krome, Monteocha, and Lauderhill). The two other carbonatic soils had  $K_{OC}$  values lower than a factor of three. Such low  $K_{OC}$  values for Perrine and Chekika have been reported for diuron and atrazine (Nkedi-Kizza et al., 2006). The average  $K_{OC}$  from all soils was calculated to be 195,665. The  $K_{OC}$  values obtained from this study for DDT are much lower than those reported in the literature (Table 2-1). The  $K_{OC}$  values from this study varied within a factor of 4 compared to a factor of 13 reported in the literature (Table 2-1). This implies that sorption on container walls might be a serious cause of variability in literature  $K_{OC}$  values for DDT.

### **Conclusions**

DDT sorbed most on the soils followed by Anthracene and the least sorption was observed for dieldrin, which is a reflection of aqueous solubility of these chemicals. The three chemicals have very low aqueous solubility which makes it difficult to measure sorption in water. All three chemicals would strongly sorb on Teflon lined centrifuge tubes and HPLC vials in aqueous systems. Consistent sorption data in soils for SHOCs can be obtained while measuring sorption in mixed solvents that will eliminate sorption on container walls and vessels.

Table 4-1. Parameters used to calculate chemical properties (HSA,  $K_{OC}$ , and  $K^M$ )

Parameter/Soil	Value	Source
$\Delta\gamma_c$ (erg/ $\text{\AA}^2$ )	$1.99 \times 10^{-15}$	Nkedi-Kizza et al. (1985)
k (ergs/K)	$1.38 \times 10^{-16}$	
T	298 (K)	Room temperature
$\alpha^c$	0.83	Karickhoff, (1981)
Chekika-OC (g/g)	0.02	This study
Krome-OC (g/g)	0.01	This study
Perrine-OC (g/g)	0.03	This study
Monteocha-OC (g/g)	0.07	This study
Lauderhill-OC (g/g)	0.31	This study
TLCT-surface area for 10 mL (A, $\text{cm}^2$ )	38.53	This study
HPLCV-surface area for 1 mL (A, $\text{cm}^2$ )	4.76	This study

Table 4-2 Sorption of DDT,  $\beta$ -endosulfan, Anthracene and Dieldrin on containers.

Chemical (Sorbent)	$K^W$ ( $\mu\text{g}/\text{cm}^2$ )	% Recovery at $f^c = 0$	100 % recovery $f^c$	$\sigma^c$	HAS ( $\text{\AA}^2$ )
Endosulfan(HPLCV+TLCT)	0.60	30	70	8.65	176
Dieldrin(HPLCV)	3.24	6	70	10.67	221
Dieldrin(TLCT)	0.57	32	45	10.75	221
Dieldrin (TLCT and HPLCV)	NA	NA	NA	10.69	221
DDT(TLCT)	0.67	29	45	15.59	322
Anthracene (TLCT)	0.24	52	45	9.81	203

NA = Not applicable

Table 4-3. Sorption coefficients ( $K^W$  and  $K_{oc}$ ), cosolvency powers ( $\sigma^c$ ) and hydrocarbonaceous surface area (HSA) for Dieldrin

Parameter	Perrine	Chekika	Krome	Monteocha	Lauderhill	All soils
$K^W$ (L/kg)	119	99	86	314	1495	
$\sigma^c$	10.72	10.71	10.67	10.98	10.51	10.72
HSA ( $\text{\AA}^2$ )	222	221	221	227	217	222
$K_{oc}$ (L/kg)	3961	4,945	8,566	4,478	4,823	4,803

Table 4-4. Sorption coefficients ( $K^W$  and  $K_{oc}$ ), cosolvency powers ( $\sigma^c$ ) and hydrocarbonaceous surface areas (HSA) for Anthracene

Parameter	Perrine	Chekika	Krome	Lauderhill	All soils
$K^W$ (L/kg) for $f^c = 0.5, 0.6, 0.7$	110	128	188	2770	
$K_{oc}$ (L/kg) for $f^c = 0.5, 0.6, 0.7$	3,669	6,418	18,752	8,935	
$K^W$ (L/kg) for $f^c = 0.1, 0.2, 0.3$	NA	NA	1012	NA	
$K_{oc}$ (L/kg) for $f^c = 0.1, 0.2, 0.3$	NA	NA	101200	NA	
$\sigma^c$	9.83	9.78	9.86	9.78	9.81
HSA ( $\text{\AA}^2$ )	203	202	203	202	203
$K_{oc}$ (L/kg) for $f^c = 0.5, 0.6, 0.7$					8,886

NA = Not applicable

Table 4-5. Sorption coefficients ( $K_{oc}$ ), cosolvency powers ( $\sigma^c$ ) and hydrocarbonaceous surface areas (HSA) for DDT

Parameter	Perrine	Chekika	Krome	Monteocha	Lauderhill	All soils
$K^W$ (L/kg)	1,703	1,236	2,101	11,614	61,698	NA
$K_{oc}$ (L/kg)	56,758	61,823	210,065	165,920	196,489	195,665
( $\sigma^c$ )	15.43	15.58	15.76	15.43	15.67	15.59
HAS ( $\text{\AA}^2$ )	319	323	326	319	324	322

NA = Not applicable

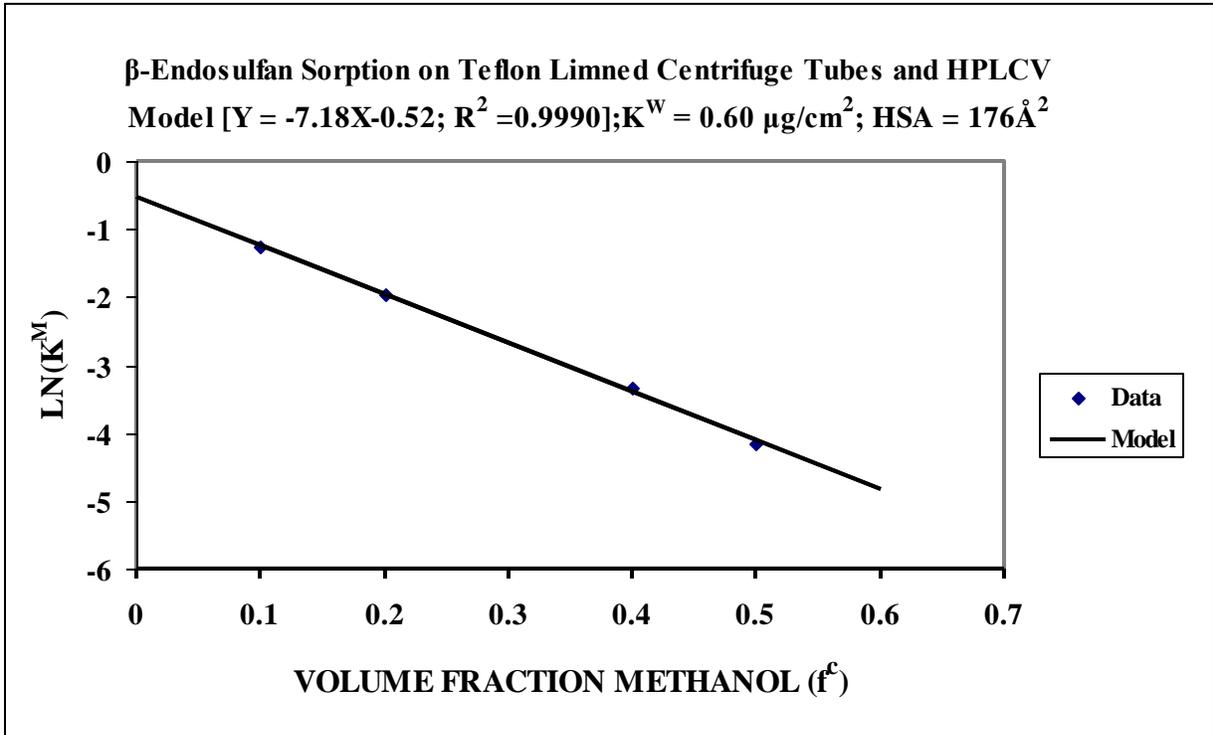


Figure 4-1. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of  $\beta$ -Endosulfan by Teflon Lined Centrifuge Tubes and HPLC Vials

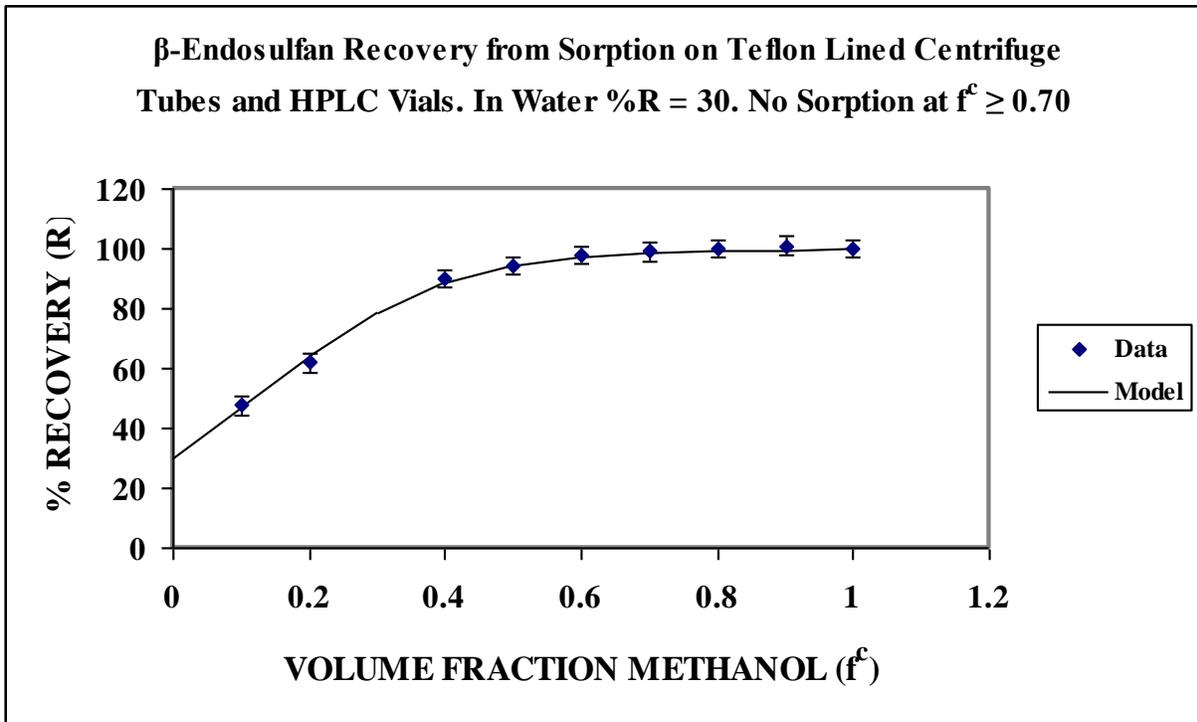


Figure 4-2 Percent recovery of  $\beta$ -Endosulfan sorption on Teflon Lined Centrifuge Tubes and HPLC Vials

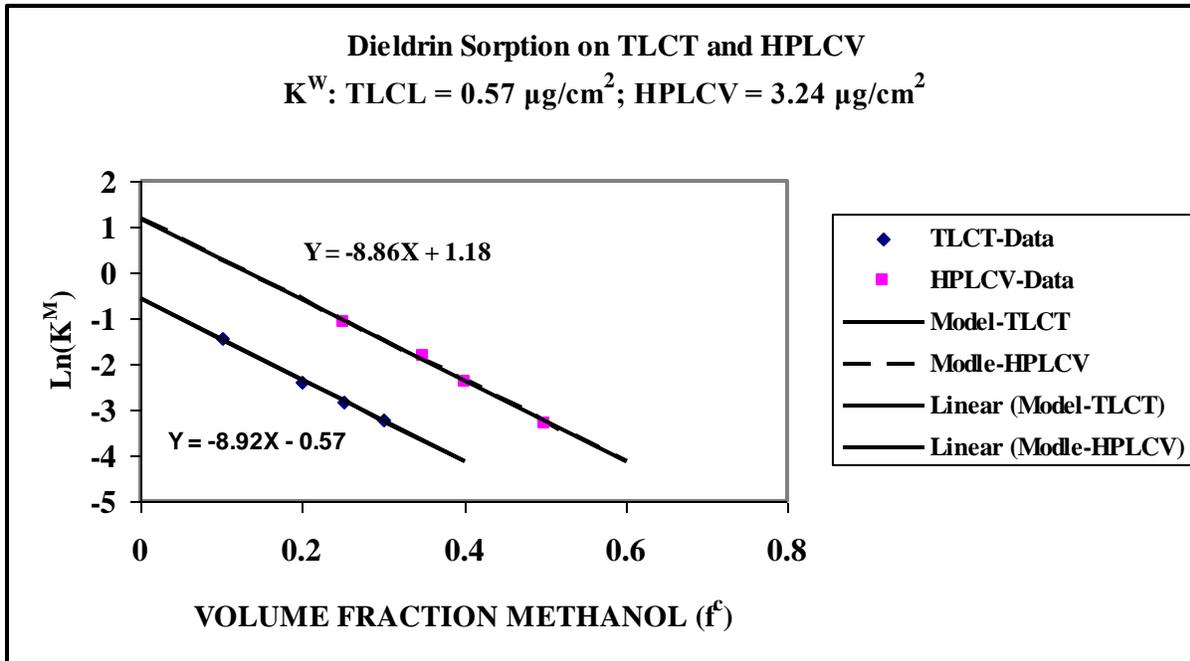


Figure 4-3. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of Dieldrin by Teflon Lined Centrifuge Tubes and HPLC Vials

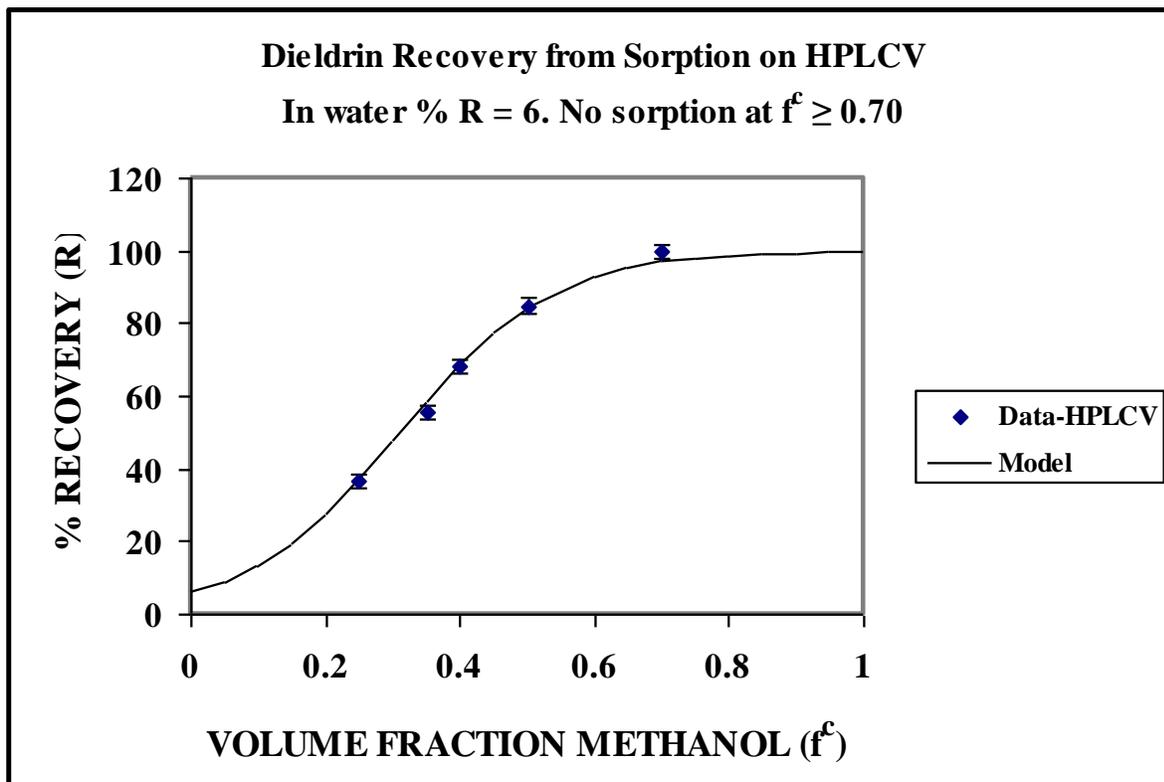


Figure 4-4. Percent recovery of Dieldrin sorption on HPLC Vials

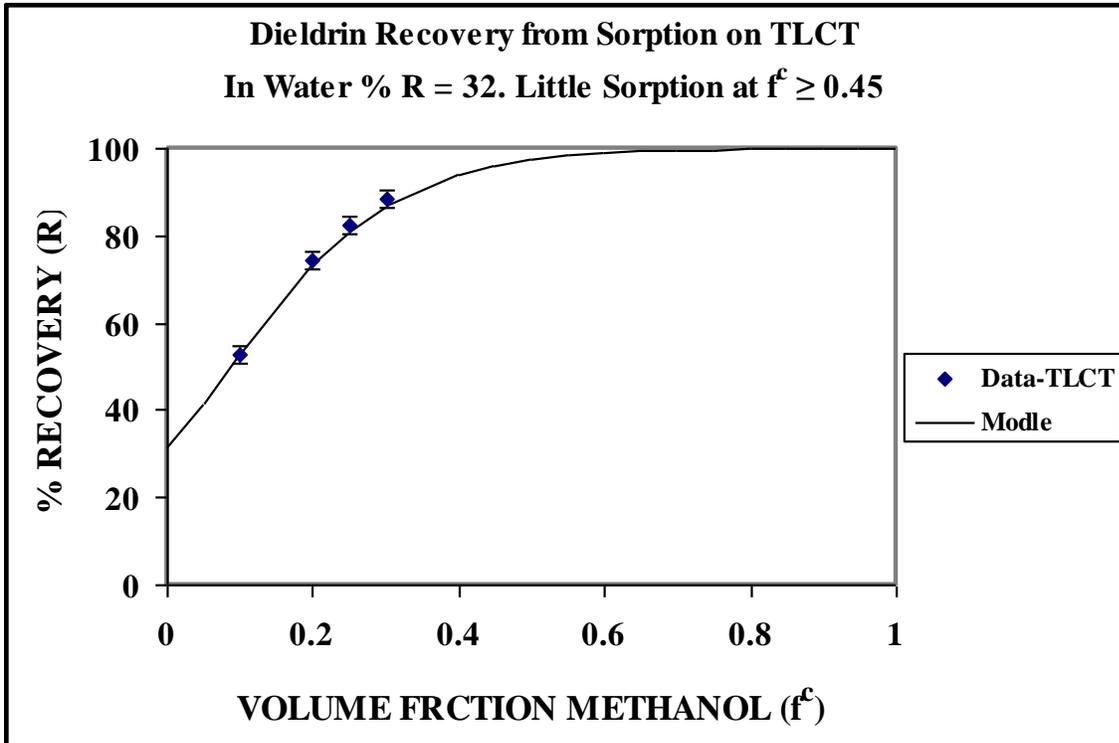


Figure 4-5. Percent recovery of Dieldrin sorption on Teflon Lined centrifuge Tubes (TLCT)

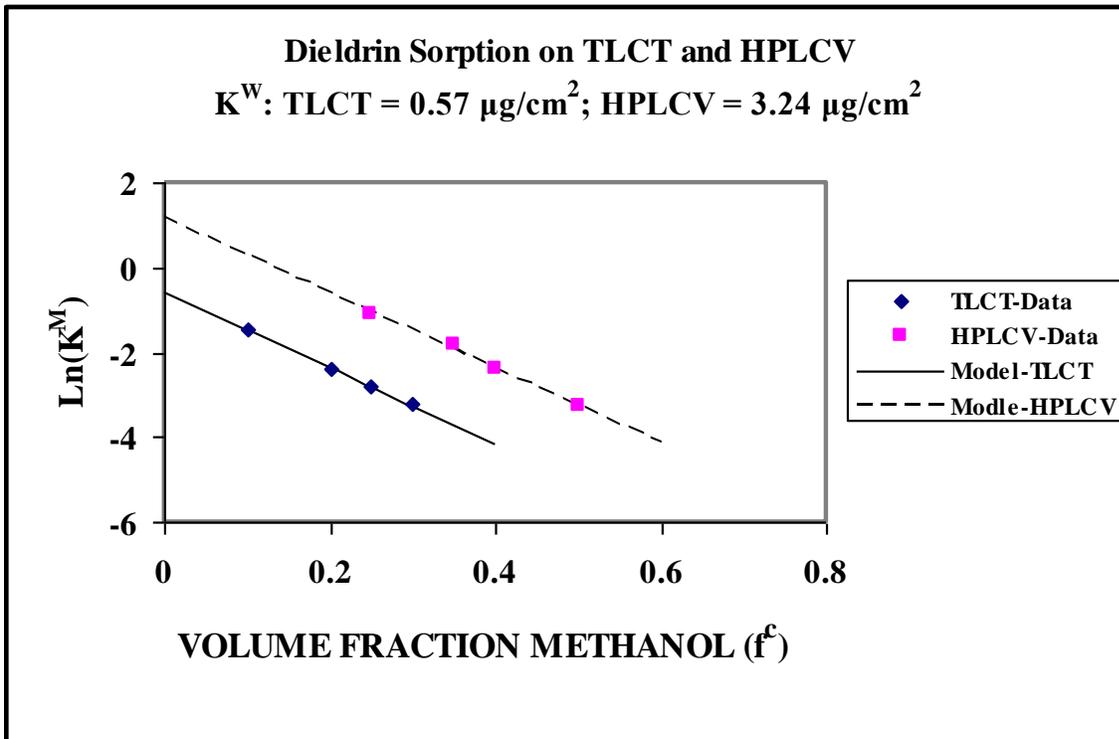


Figure 4-6. Relative sorption coefficient ( $K^M/K^W$ ) as a function of fraction of methanol ( $f^c$ ) for Dieldrin sorption by Teflon Lined Centrifuge Tubes and HPLC Vials.

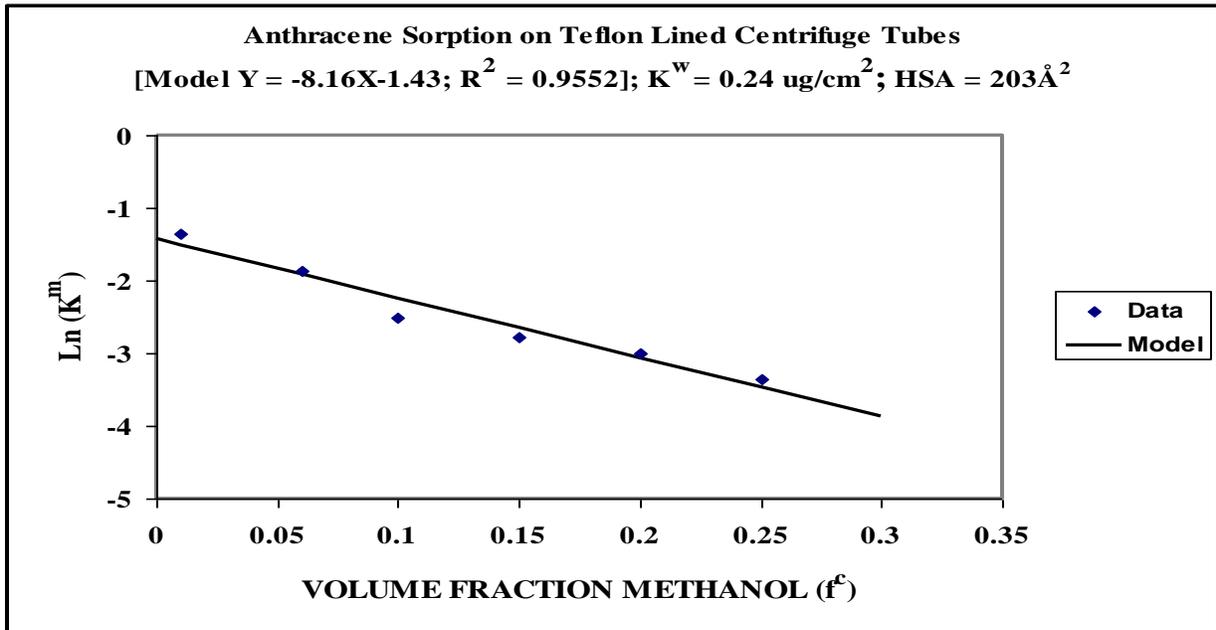


Figure 4-7. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of Anthracene by Teflon Lined Centrifuge Tubes.

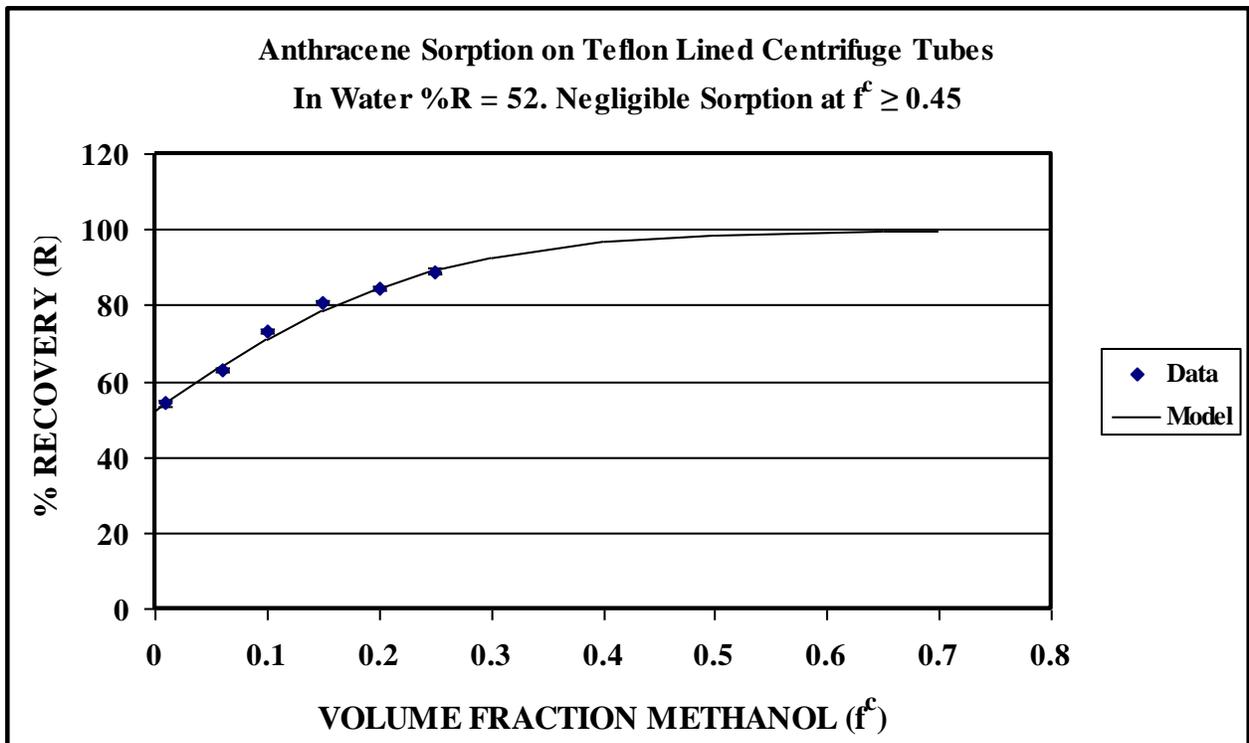


Figure 4-8. Percent recovery of Anthracene sorption on Teflon Lined centrifuge Tubes

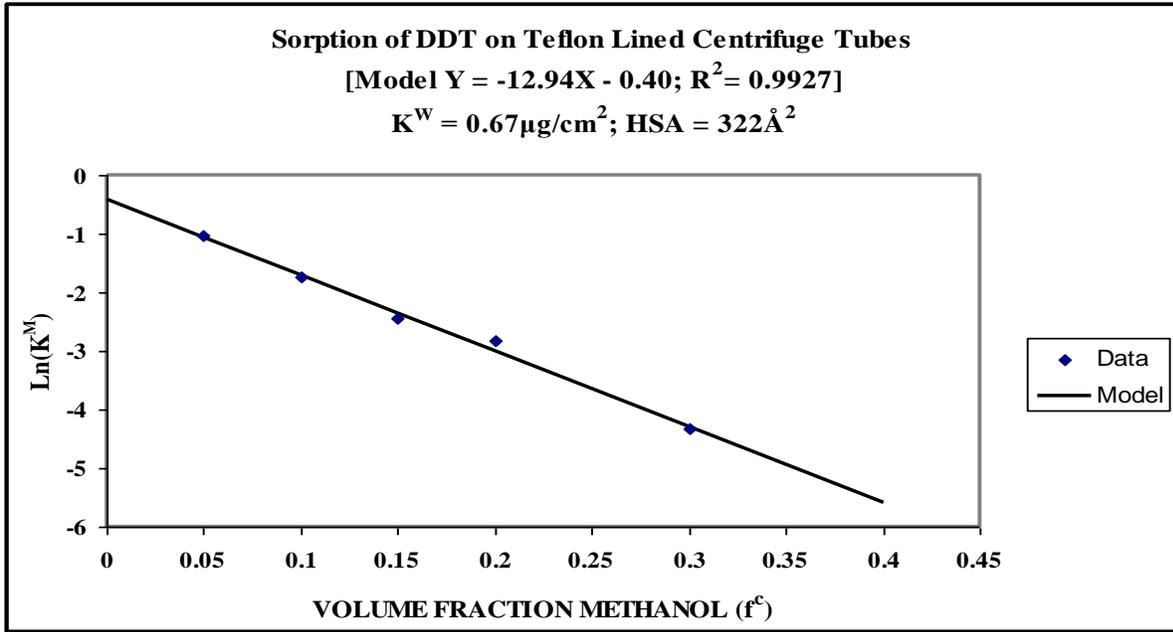


Figure 4-9. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of DDT by Teflon Lined Centrifuge Tubes

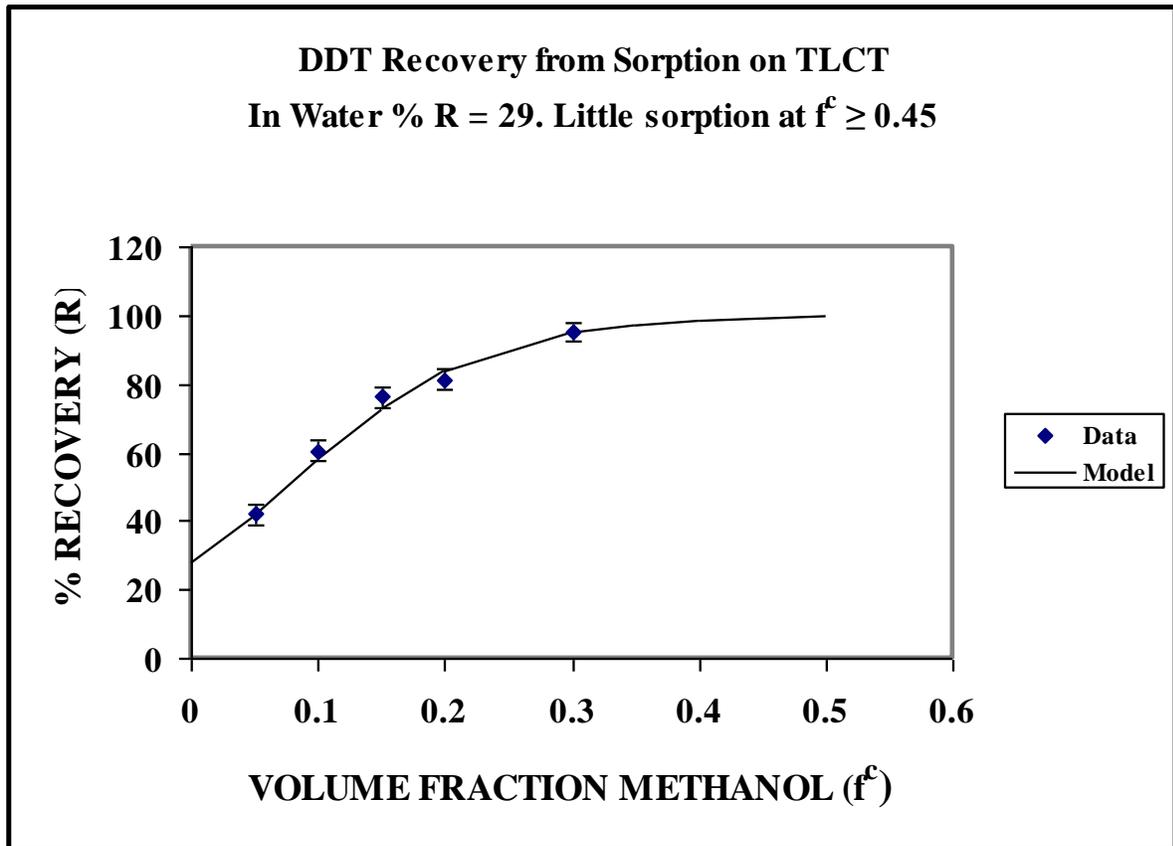


Figure 4-10. Percent Recoveries of Dieldrin sorption on Teflon Lined Centrifuge Tubes

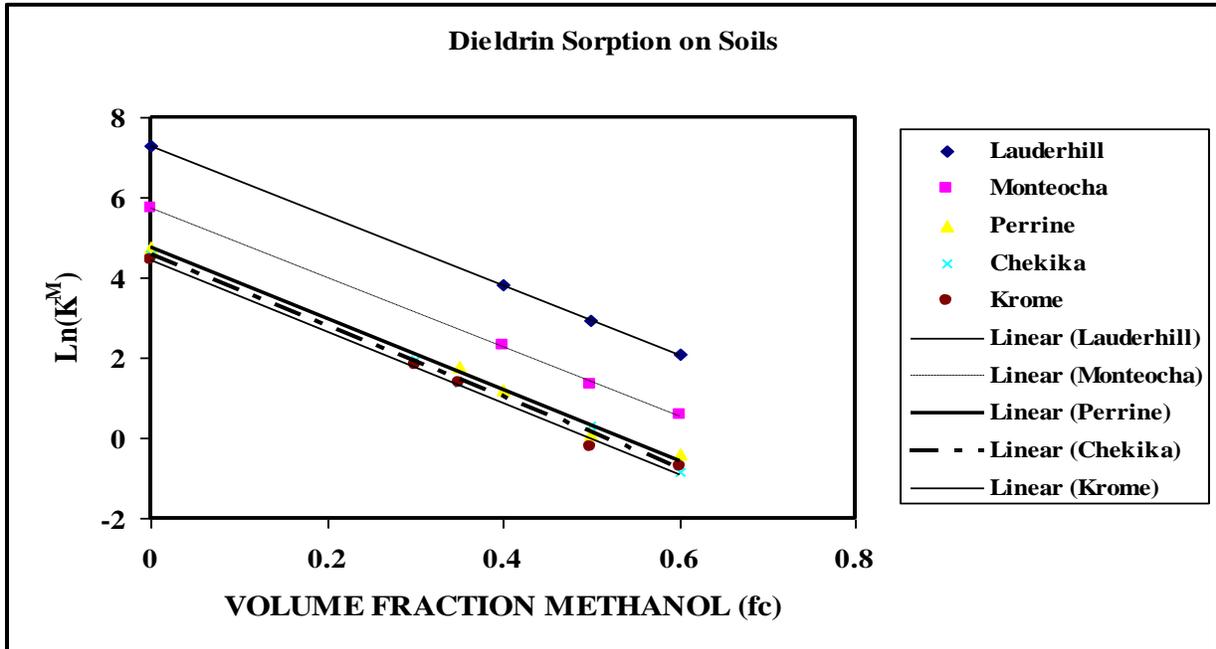


Figure 4-11. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of Dieldrin by soils

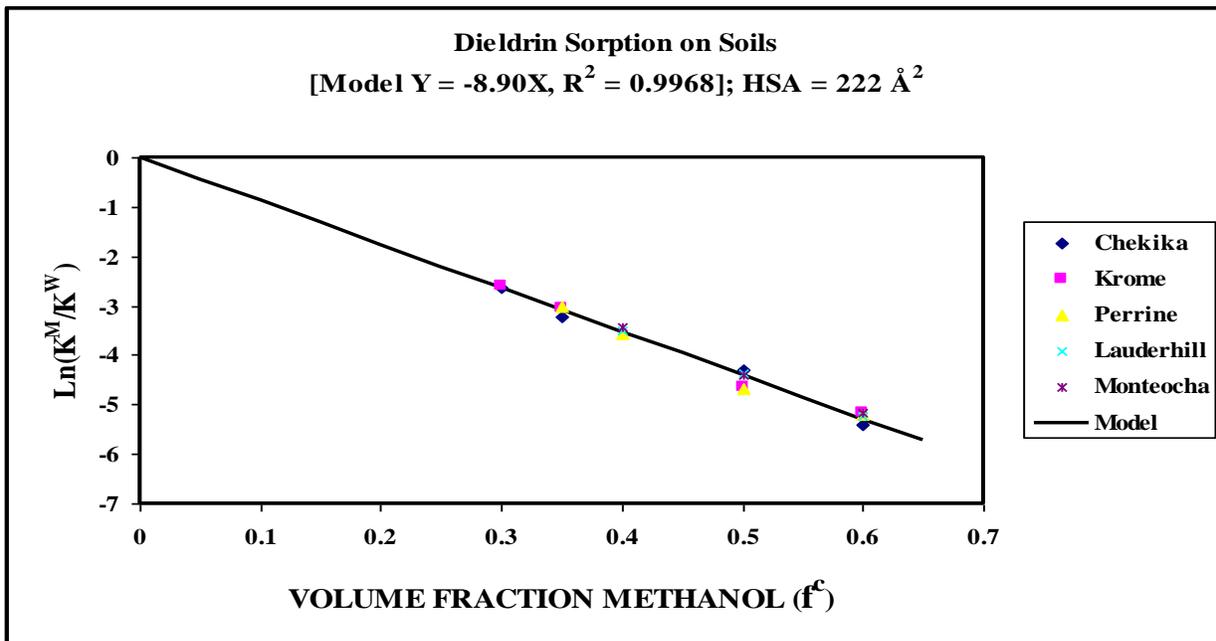


Figure 4-12. Relative sorption coefficient ( $K^M/K^W$ ) as a function of fraction of methanol ( $f^c$ ) for Dieldrin sorption by soils.

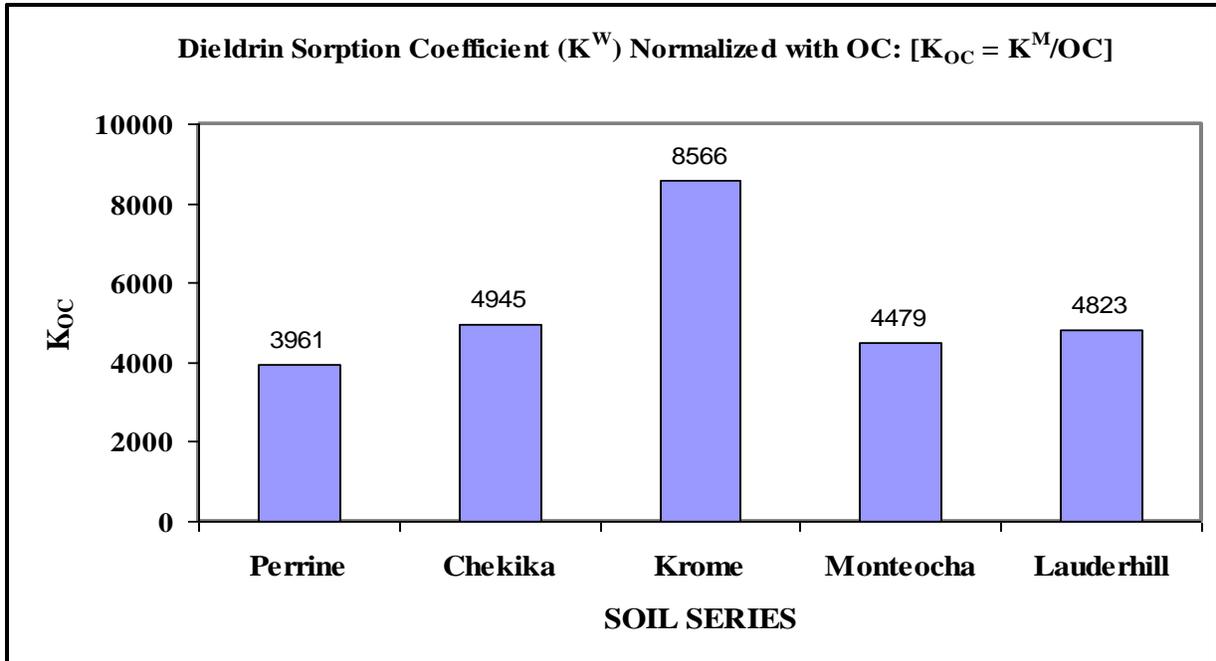


Figure 4-13. Dieldrin KOC from different soils

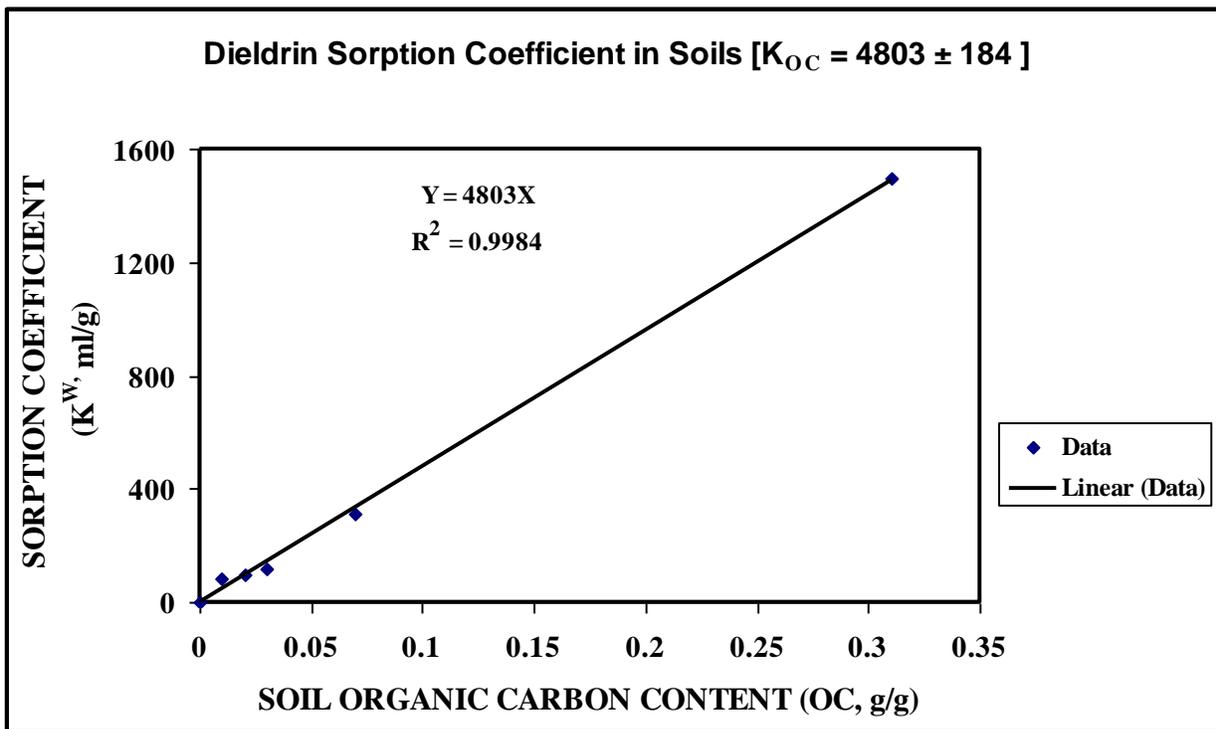


Figure 4-14. Relationship between the sorption coefficient ( $K^W$ ) and soil organic carbon content (OC) for sorption of Dieldrin by soils

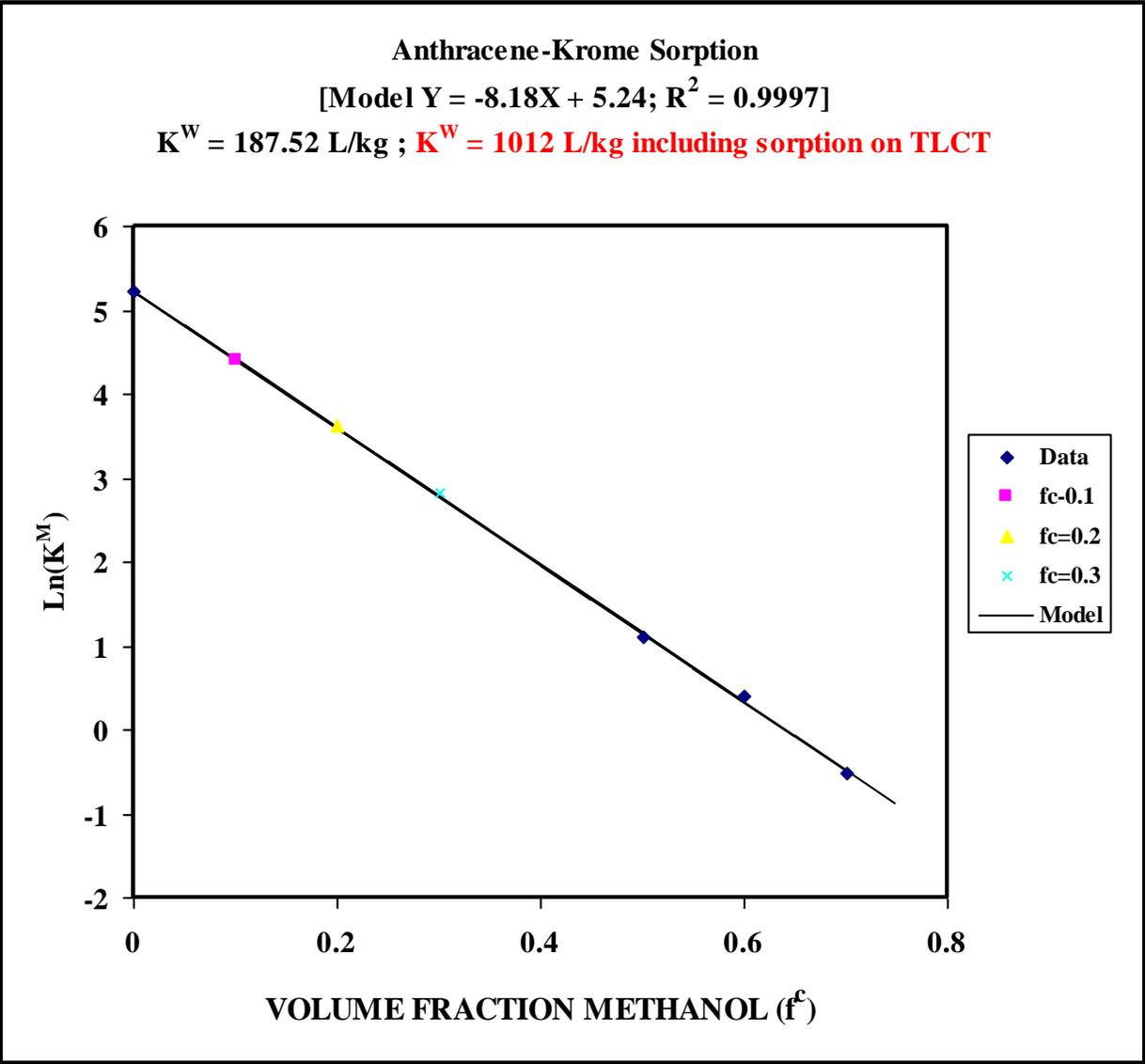


Figure 4-15. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of Anthracene by Krome soil.

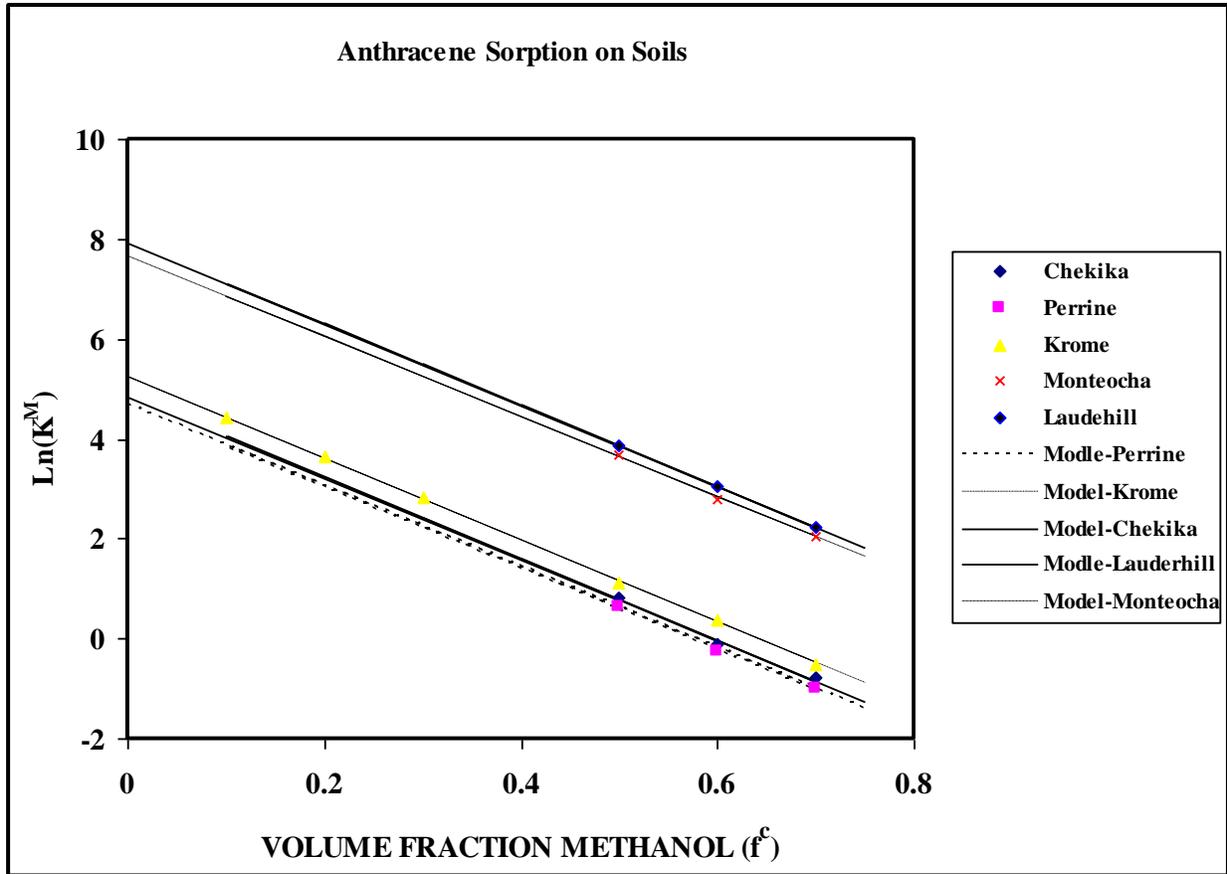


Figure 4-16. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of Anthracene by soils

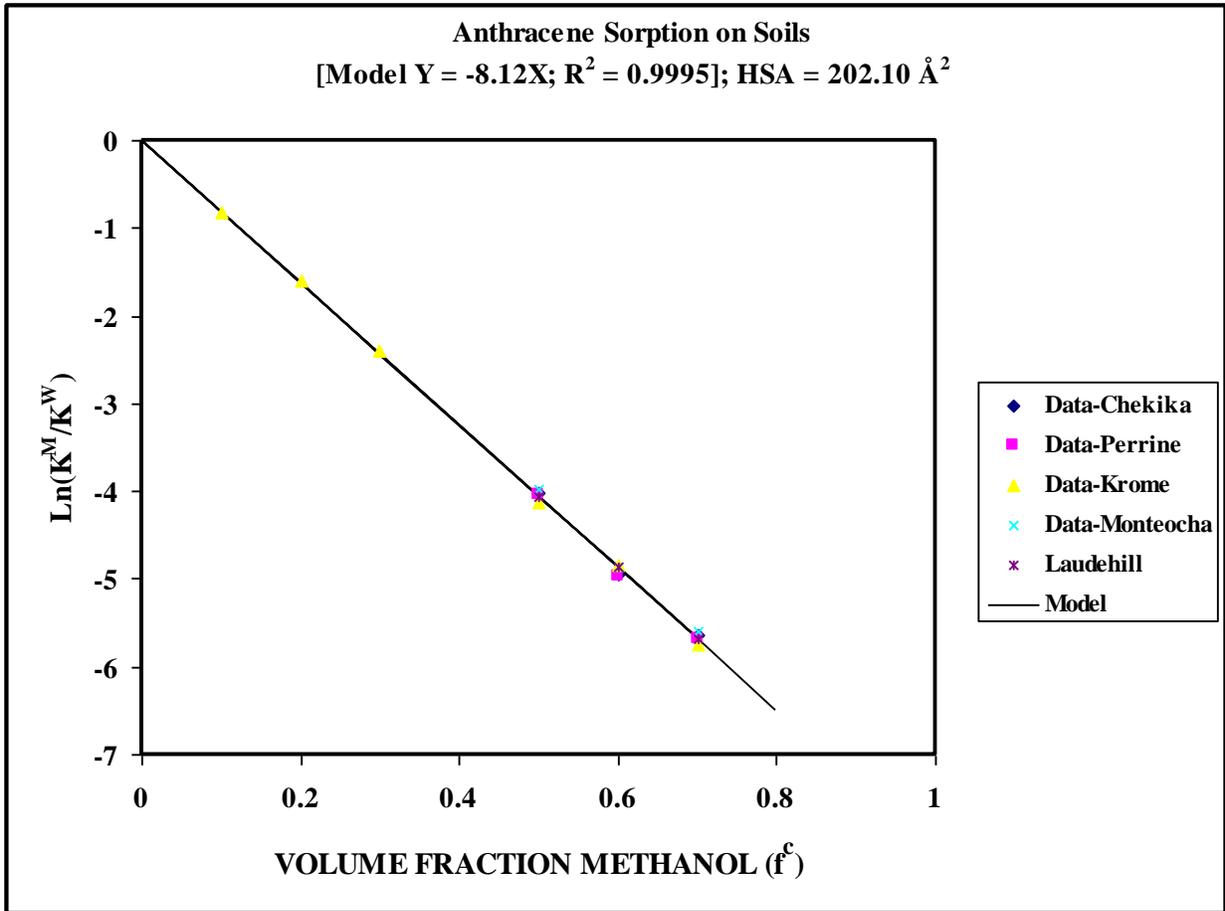


Figure 4-17. Relative sorption coefficient ( $K^M/K^W$ ) as a function of fraction of methanol ( $f^c$ ) for Anthracene sorption by soils.

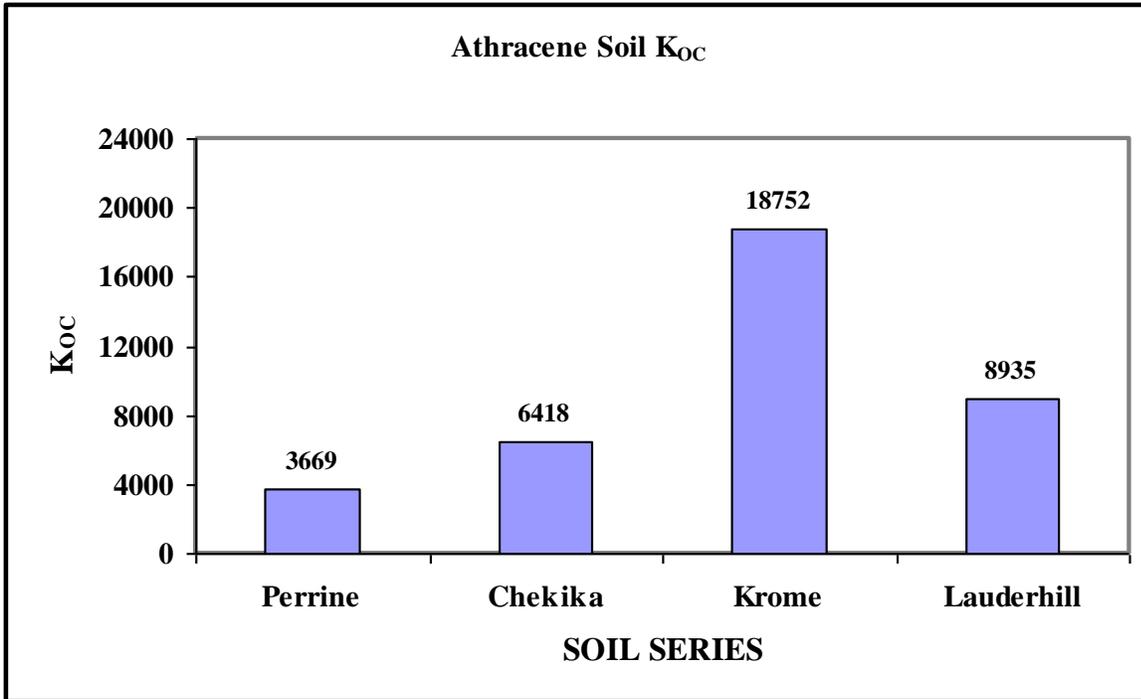


Figure 4-18. Anthracene  $K_{OC}$  values from different soils

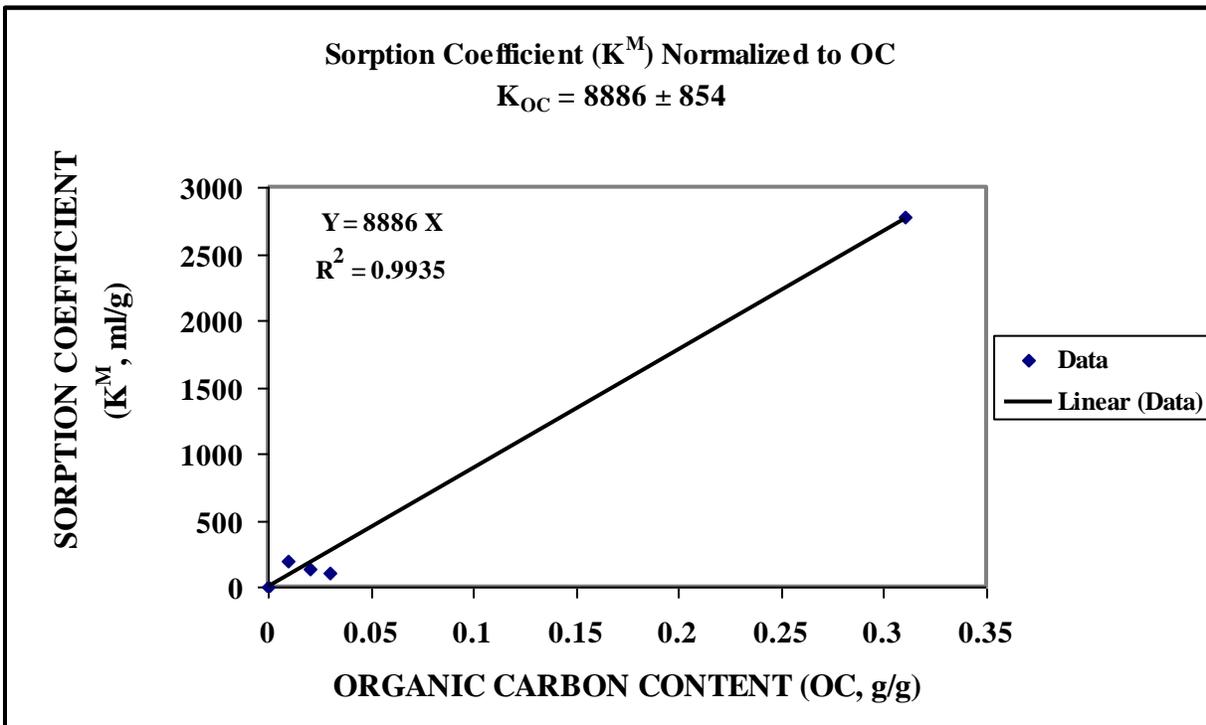


Figure 4-19. Relationship between the sorption coefficient ( $K^W$ ) and soil organic carbon content (OC) for sorption of Anthracene by soils

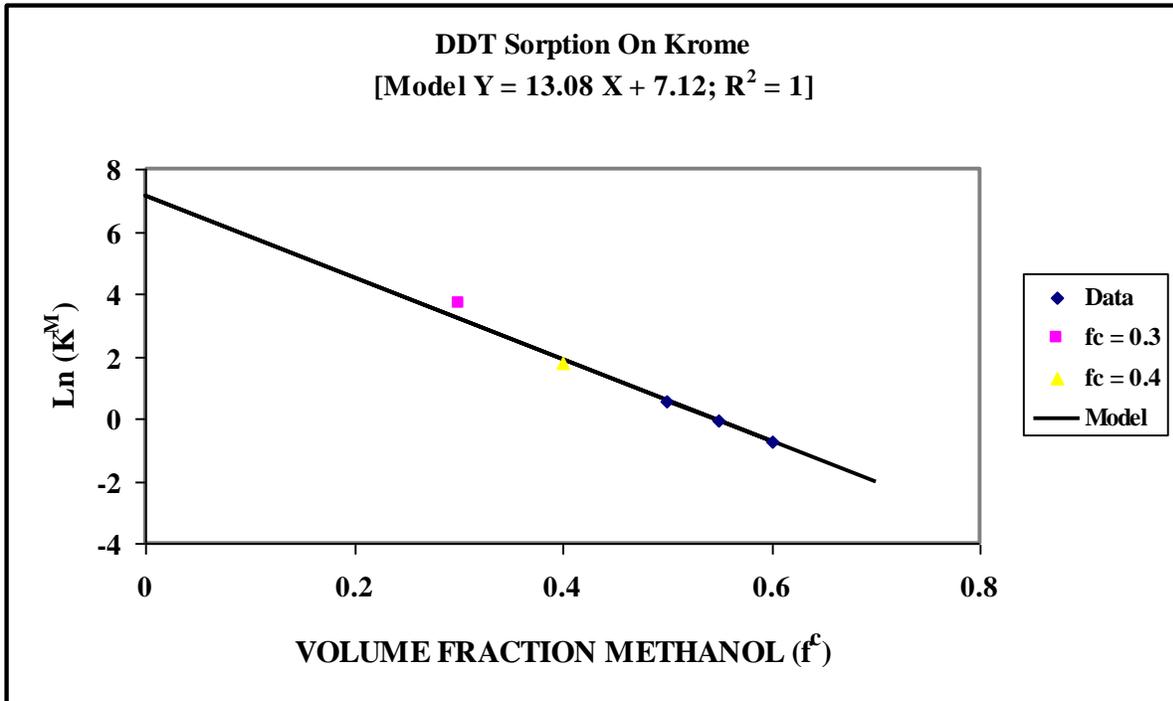


Figure 4-20. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of DDT by Krome soil.

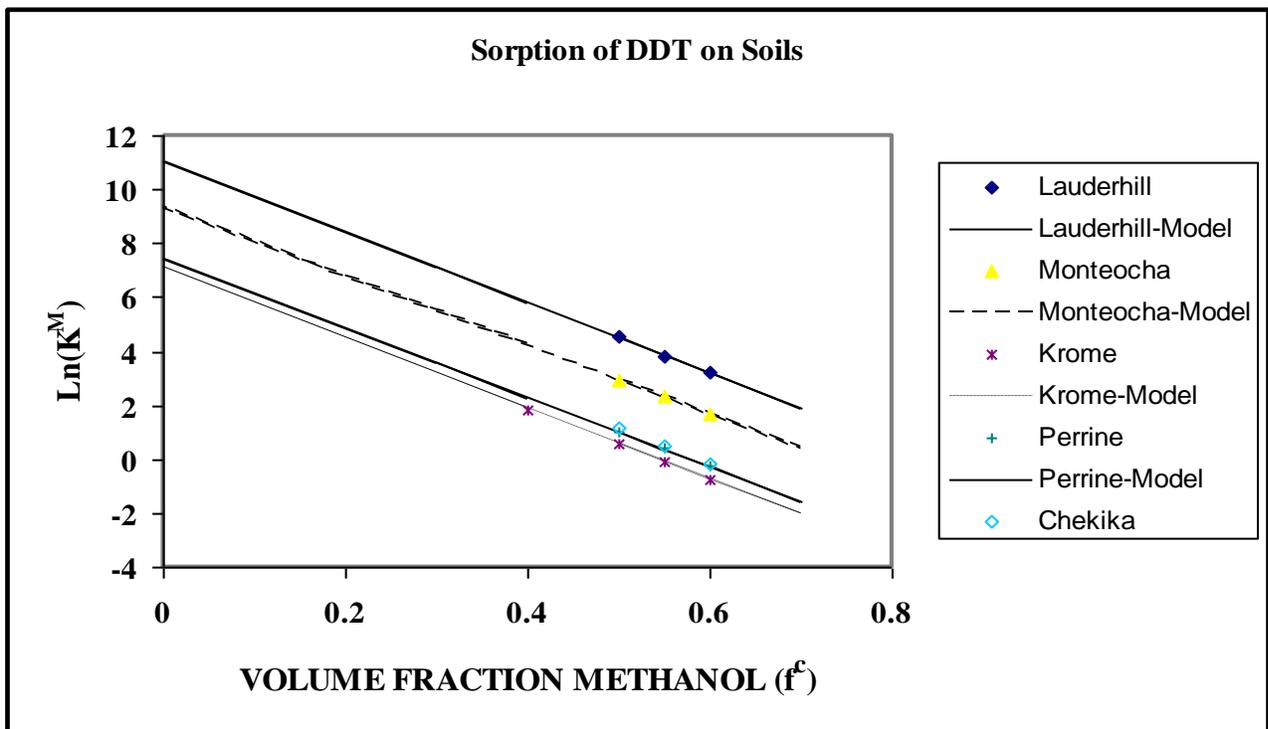


Figure 4-21. Log-linear relationship between sorption coefficient ( $K^M$ ) and fraction of methanol ( $f^c$ ) for sorption of DDT by soils.

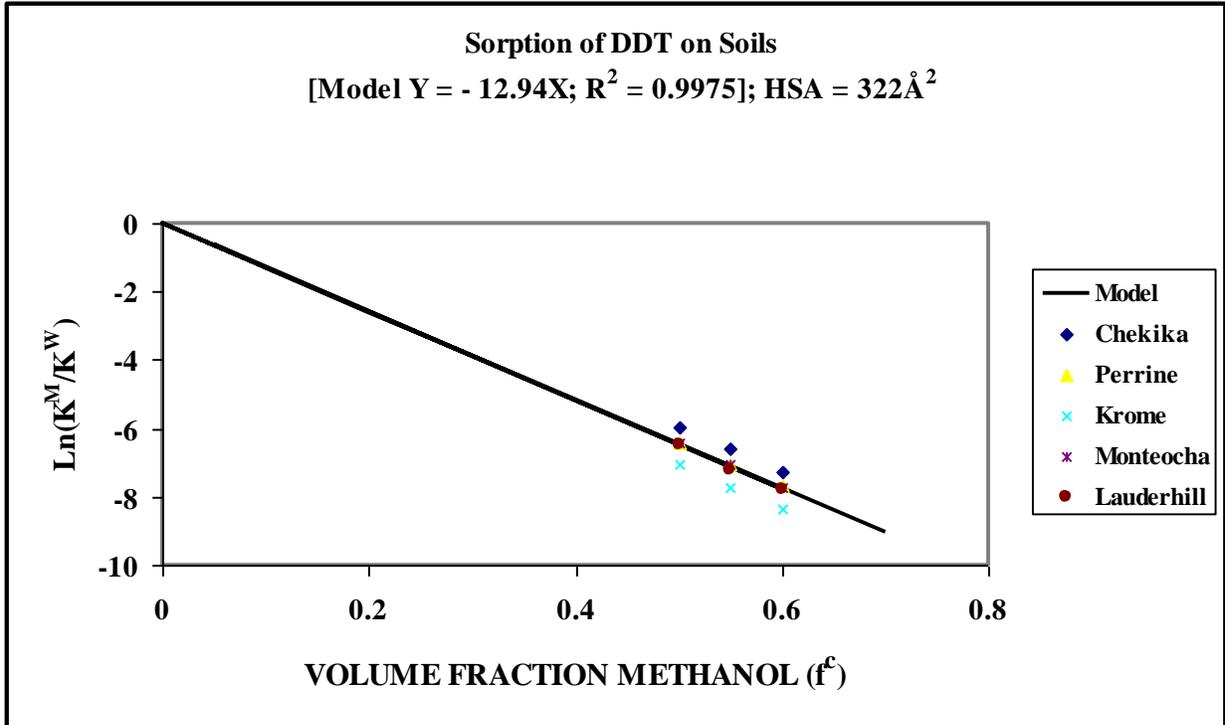


Figure 4-22. Relative sorption coefficient ( $K^M/K^W$ ) as a function of fraction of methanol ( $f^c$ ) for DDT sorption by soils.

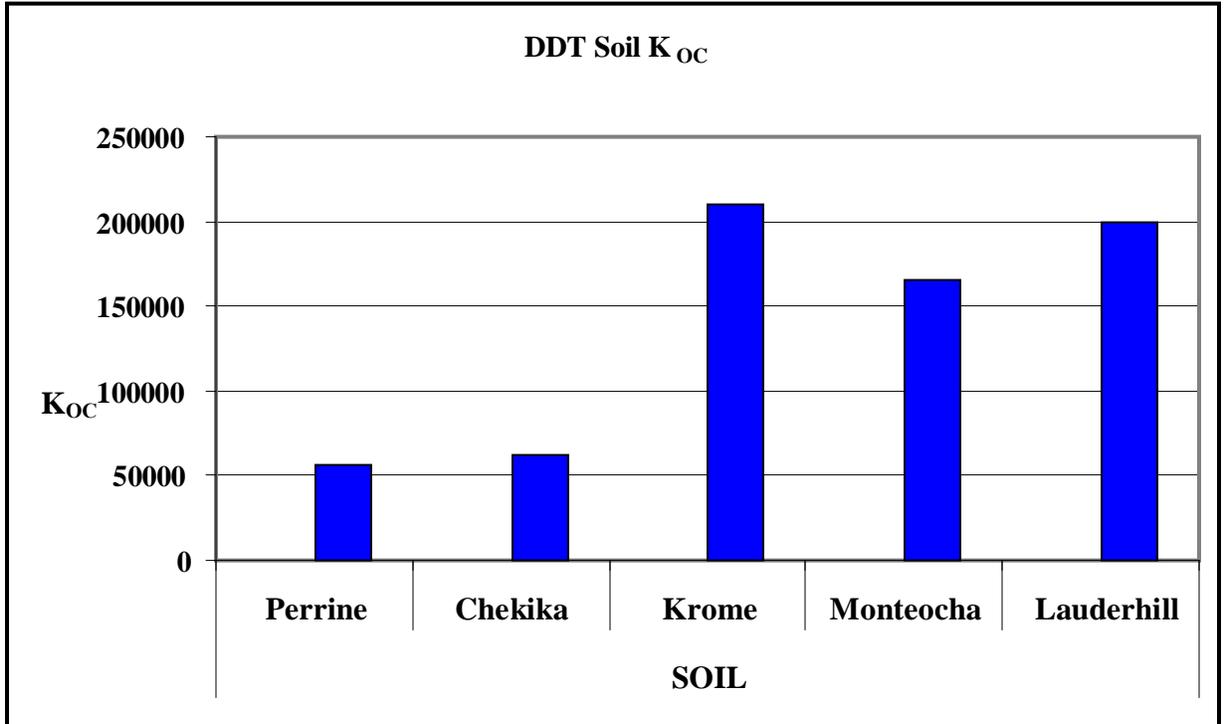


Figure 4-23. DDT  $K_{OC}$  values from different soils

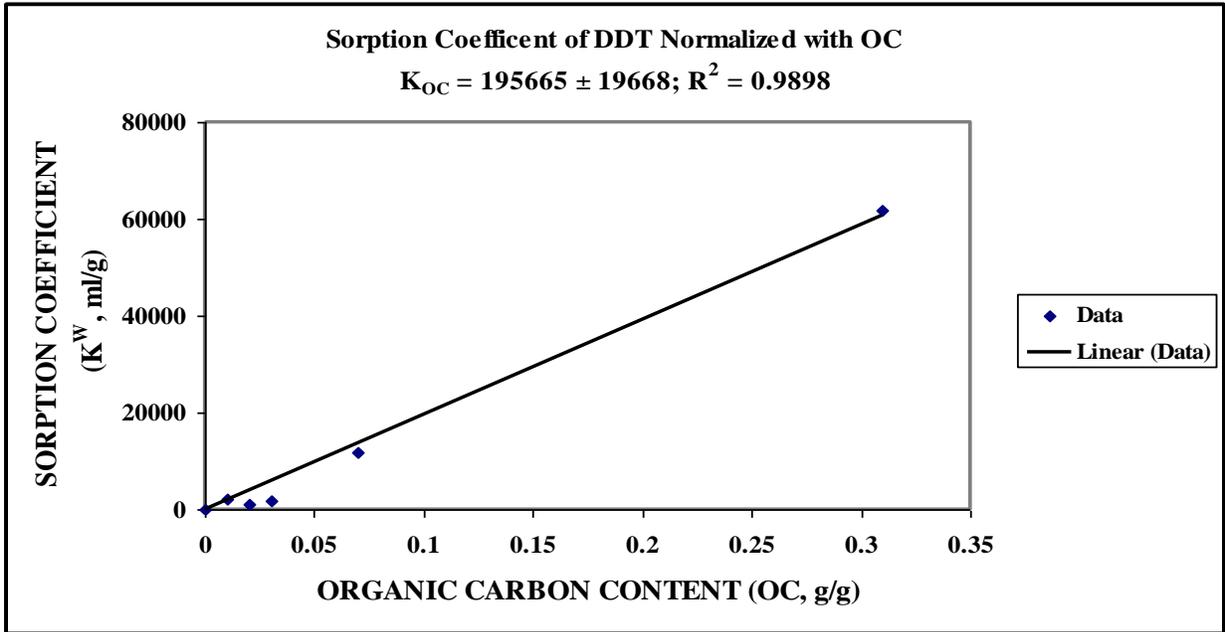


Figure 4-24. Relationship between the sorption coefficient ( $K^w$ ) and soil organic carbon content (OC) for sorption of DDT by soils.

## CHAPTER 5 CONCLUSIONS

Sorption on container walls (Teflon, glass, and polycarbonate) by strongly hydrophobic organic chemicals (SHOCs) was observed in this study. This experimental error plays a significant role in reducing analyte integrity before the actual sample concentration is measured by HPLC or TLC in aqueous systems. This is mainly due to the very low aqueous solubility of these chemicals. This research also alerts manufacturers of containers that all containers tested adsorb SHOCs during storage and multi-step analysis in aqueous systems.

Based on this research, storing Dieldrin and DDT dissolved in water for 24 hours in Teflon lined centrifuge tubes gives less than 40% recovery of original concentrations of dieldrin and DDT. Soil sorption isotherms therefore should be done in mixed solvents for example methanol and water that eliminate sorption on containers.

DDT sorbs more than dieldrin on Teflon lined centrifuge tubes in aqueous systems. Samples of SHOCs when put in HPLC glass vials before HPLC analysis are subject to adsorption on glass walls. This phenomenon was clearly demonstrated by sorption of dieldrin on HPLC vials. HPLC vials sorb more dieldrin than Teflon lined centrifuge tubes.

Reasonable values of cosolvency powers and hydrocarbonaceous surface areas of strongly hydrophobic organic chemicals can be calculated by fitting data for sorption on container walls and by soils using the Solvophobic model since cosolvency powers of these chemicals are independent of the sorbents.

The Koc values obtained in this study using mixed solvent system and thus eliminating sorption on container walls varied much less than those reported in the literature for dieldrin and DDT. This implies that sorption on container walls plays a significant role in the variability of the literature Koc values. It also shows that the Solvophobic model can be used to calculate the

aqueous sorption coefficient by extrapolating to zero fraction of cosolvent (methanol). However,  $K_{OC}$  values of carbonatic soils seem to be lower than values from non-carbonatic soil. This was attributed to the source and nature of organic matter in carbonatic soils that might be different from that of non-carbonatic soils.

Generally sorption of DDT, anthracene, and dieldrin was directly proportional to soil organic carbon content. The trend of sorption of the chemicals on the soils was in the same order as their aqueous solubilities (DDT > Anthracene > Dieldrin). The trend agrees with the literature data.

Although sorption of the chemicals on organic carbon is only examined, sorption on other soil components like clays and carbonates should be investigated in future research. This study has shown high  $K_{OC}$  values for Krome (OC = 1%) compared to organic soil, Lauderhill (OC = 31%) which emphasizes the argument that there could be other soil components sorbing SHOCs. Further examination of the hydrophobicity of the organic carbon of the carbonatic soils is needed. For example this study has consistently shown that sorption coefficients values ( $K_{OC}$ ) of Krome (OC = 1%) are higher than those of Perrine (OC = 3%) yet this would be the opposite according to literature data.

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