



PARTITION COEFFICIENTS OF ORGANOCHLORINE PESTICIDES ON SOIL AND ON THE DISSOLVED ORGANIC MATTER IN WATER

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ABSTRACT

The partition coefficients of organochlorine pesticides (OCPs) between the organic matter of Taichung soil and water (K_{oc}) were evaluated with batch-type experiments. The partition coefficients of OCPs between Aldrich humic acid and water (K_{doc}) were estimated with solubility enhancement method as well. In this study, the K_{ocs} of aldrin, heptachlor, and *p,p'*-DDT are greater than their K_{docs} , and the relationship of dieldrin and heptachlor epoxide are opposite. The variations of partition coefficients are discussed. For predicting K_{doc} , a log-log regression relationship of K_{doc} and K_{ow} is determined.

INTRODUCTION

Hydrophobic organic contaminants were considered moving slowly in the environment, owing to their high trend to associate with soils and sediments. The factors controlling the uptake of hydrophobic organic contaminants by soil include adsorption and partition. Mingelgrin and Gerstl (1983) considered that the interaction between an organic solute and soil was adsorption, and the linear relationship was only observed at significantly low bulk concentrations. On the contrary, there were some investigations (Karickhoff *et al.*, 1979; Briggs, 1981; Chiou *et al.*, 1983; Wershaw, 1986) indicated that the distribution of nonionic organic solutes between soils/sediments and water was partition. Karickhoff *et al.* (1979) showed that the sorption isotherms for all the hydrophobic compounds studied were linear over a broad range of aqueous concentration. In addition, the linear partition coefficients were directly related to organic carbon content of the studied sediments. Chiou and Shoup (1985) demonstrated that the soil behaved as a dual sorbent, in which the mineral matter functioned as a conventional solid adsorbent and the organic matter as a partition medium. In aqueous system, owing to the strong ability of water to compete against hydrophobic organic solute for mineral surface, the solute partitioning into the soil organic phase is the primary mechanism of soil uptake (Chiou *et al.*, 1985).

Briggs (1981) indicated that despite the complexity of soil organic matter, K_{om} for a particular chemical is virtually constant. On the contrary, Gauthier *et al.* (1987) reported that the magnitude of the K_{oc} values correlated strongly with the characteristics of the humic material. Similarly, Kile and Chiou (1989) showed that the

magnitude of the partition coefficient (K_{dom} or K_{doc}) was a function of the physical properties of the solute and the nature of the dissolved organic matter.

However, recent investigations (Enfield *et al.*, 1989; Magee *et al.*, 1991; Dunnivant *et al.*, 1992; Ding and Wu, 1993) indicated that when there was a significant amount of free-moving dissolved organic matter (DOM) in the system, the transport of hydrophobic organic contaminants would be enhanced. Dissolved organic matter (DOM) or dissolved organic carbon (DOC), including dextran, humic acid, could form a third medium for the hydrophobic organic pollutants to associate with and carry these pollutants in the moving water (Enfield *et al.*, 1989; Magee *et al.*, 1991; Dunnivant *et al.*, 1992; Ding and Wu, 1993).

The partition coefficient between the dissolved organic matter and water is one of the important parameters in modelling the transport and fate of hydrophobic organic contaminants in the environment. The objective of this study is to evaluate the partition coefficients (K_{oc} and K_{doc}) of some model compounds as an indicator to quantify the enhancement of these compounds on the transport of trace organic pollutants.

MATERIALS AND METHODS

Properties of soil. The soil for experiments was sampled from an agricultural research station located at Taichung. Soil was air-dried for 14 days, then ground and sieved. All material passing through the sieve with 2-mm cutoff of particle diameter was retained for experimental use. Soil analyses were performed in duplicate and included pH (at 1:1 soil/water ratio), organic carbon (Walkley-Black method, in Nelson and Sommers, 1982), and particle-size distribution (pipette method, in Gee and Bauder, 1986). The water content of air dried soil was less than 1%. The characteristics of the soil is shown in Table 1.

Table 1. The characteristics of Taichung soil

soil pH	6.8
organic carbon content (%)	1.8
solid density (g/cm ³)	2.62
sand (%)	25
silt (%)	40
clay (%)	35
texture	clay loam

Chemicals and solvents. Test solutes (aldrin, dieldrin, heptachlor, heptachlor epoxide, and *p,p'*-DDT) were analytical standards purchased from commercial sources (Riedel-de Haën, Germany) and were used as received. Organic solvents (methanol, n-hexane, and acetone) were residue analysis grade (Baker, U.S.A.).

Organochlorine pesticides analyses. The stock solution of organochlorine pesticides spiked with hexachlorobenzene (EP grade, Tokyo Chemical Inc., Japan) as the internal standard was analyzed with a gas chromatography (Hewlett Packard, HP5890II, Avondale, PA., U.S.A.) with an electron capture detector (ECD). A DB-608 capillary column (30 m × 0.32 mm × 0.5 μm) (J&W Scientific, Folsom, CA., U.S.A.) was used. Carrier gas was nitrogen at 2.58 mL/min; makeup gas was nitrogen at 34.5 mL/min; injector was set splitless; temperature

programmed as 50°C for 1 min, 50°C/min to 200°C for 3 min, 5°C/min to 250°C for 5 min, 8°C/min to 270°C for 1 min; injector temperature was 250°C; detector temperature was 300°C (total run time 25 min).

Evaluation of K_{oc} . The partition coefficients of the solutes of interest between soil organic matter and water were evaluated with batch experiments. A liter of Milli-Q water (Millipore Corp., Bedford, MA., U.S.A.) in a 2-liter cylindrical glass bottle with glass stopper was added 10 grams of air dried soil. Test solutes (aldrin, dieldrin, heptachlor, heptachlor epoxide, and *p,p'*-DDT) were dissolved in methanol, and spiked into the suspended solution. The volume fraction of methanol was only 1×10^{-5} . The spiked amounts of aldrin, dieldrin, heptachlor, heptachlor epoxide, and *p,p'*-DDT were 3.81, 0.36, 3.27, 4.41, and 2.00 μg , respectively. After that, the bottle was shaken at 25°C for 60 hours. It had been tested that the equilibrium states were achieved. Finally, the soil solution was centrifuged at 10500g (Hettich-Zentrifugen Universal 30F, Germany) with Teflon centrifuge tubes with Teflon caps (Nalge Company, Rochester, NY., U.S.A.) for 1 h to separate the solid and liquid phases. The organic carbon content of liquid phase was measured with TOC analyzer (OI Company model 700, College Station, TX., U.S.A.). A 900 mL of liquid phase was extracted for 20 min with 300 mL of n-hexane in separating funnel. All solid phase was placed in the extraction thimble (Whatman, England) and extracted for 24 h with 300 mL of 1:1 n-hexane/acetone mixed solvent. Each used vessel (glass bottle, Teflon centrifuge tubes, separating funnel and so on) was washed with 10 mL n-hexane to remove the solutes adsorbed. Each wash was mixed as a sample. The resultant extracts were concentrated to about 3 mL with a rotary evaporative concentrator and cleaned on a 1-g Florisil column (J&W Scientific, Folsom, CA., U.S.A.).

Evaluation of K_{doc} . The partition coefficients of solutes between Aldrich humic acid and water (K_{doc}) were estimated with water solubility enhancement method which has been used by Chiou *et al.* (1986). Aldrich humic acid sodium salt (Aldrich Chemical Company, Milwaukee, WI., U.S.A.) was dissolved in Milli-Q water, and centrifuged at 5150g for 15 minutes. The centrifuged solution was diluted with Milli-Q water to different concentrations which were measured with TOC analyzer. 20 mL solutions were placed in 50-mL Teflon centrifuge tubes, and either aldrin, dieldrin, heptachlor, heptachlor epoxide, or *p,p'*-DDT was added to each tube in an amount slightly more than required to saturate the solution. Duplicate samples were prepared for each Aldrich humic acid concentration; they were then equilibrated on a reciprocating shaker for 48 h at 25°C. The samples were subsequently centrifuged at 5150g for 30 min to separate the undissolved solute. Solute particles adhering to the walls above the liquid level were carefully removed with tissue paper; the meniscus was aspirated to remove any particles on the surface. This centrifugation/cleaning procedure was repeated once more. A 5 mL sample of the supernatant was withdrawn and extracted for 30 min with 5 mL of n-hexane. The samples were gently reduced under nitrogen to about 1 mL and cleaned on a 1-g Florisil column.

RESULTS AND DISCUSSION

Partition coefficient between soil and water. Backhus and Gschwend (1990) did not believe that low levels of methanol (5×10^{-3} volume fraction) would affect PAH aqueous activity enough to cause observable effects on PAH sorption by organic carbon. Similarly, the volume fraction of methanol in this study was only 1×10^{-5} . We believed that it would not affect the partition of solutes between organic carbon and water. In addition, the organic carbon concentration of the liquid phase was measured as 0.78 mg-C/L. Chiou *et al.* (1986) reported that the $\log K_{oc}$ of bulk organic carbon is 6-8 times more efficient than the soil fulvic acid extracts. These artificial water

soluble organic carbon in liquid phase may be more hydrophilic than fulvic acid extracted from soil. For relatively hydrophobic solutes, the partition coefficients between soil bulk organic carbon and water may be roughly 10 times more than the partition coefficients between the released water soluble organic carbon and water. Such a low concentration of organic carbon in liquid phase will reduce the partition coefficients less than 4 %, and its effect may be neglected.

p,p'-DDD and *p,p'*-DDE were absent in the spiked solution, but they were found in batch experiments. It indicated that a part of *p,p'*-DDT might be transferred to *p,p'*-DDD and *p,p'*-DDE in the soil/water system in this study. Therefore, we expressed the summation of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT as the total DDT. The mass adsorbed on all vessel (either glass or Teflon) walls was less than 1 % of the total spiked mass (data not shown). The percentage of the recovery of aldrin, dieldrin, heptachlor, heptachlor epoxide, and total DDT were 89.8, 103.9, 72.8, 90.7, and 110.0, respectively. The partition coefficients of organochlorine pesticides between soil and water (K_{ps}) were evaluated, and K_{ocs} were normalized from K_{ps} with organic carbon fraction of soil (1.8 %)(Table 2).

Table 2. The results of batch experiments and the partition coefficients of test solutes

Compound	Concentration of OCP on soil (μ g/g-soil)	Concentration of OCP in water (μ g/L-water)	K_p (mL/g)	K_{oc} (mL/g)
aldrin	0.3338	0.0768	4350	241500
dieldrin	0.0339	0.0347	980	54300
heptachlor	0.2178	0.1521	1430	79600
heptachlor epoxide	0.3142	0.8446	370	20700
<i>p,p'</i> -DDT	0.1942	0.0225	8640	479500
<i>p,p'</i> -DDD	0.0042	0.0018	2350	130600
<i>p,p'</i> -DDE	0.0164	0.0347	470	26300

Solubility enhancement experiments. Dissolved organic matter may enhance water solubility of hydrophobic solutes (Carter and Suffet, 1982; Landrum *et al.*, 1984; Gschwend and Wu, 1985; McCarthy and Jimenze, 1985; Chiou *et al.*, 1986). If one assumes that a partition-like interaction with dissolved organic carbon is responsible for solute water solubility enhancement, the magnitude of this effect for an organic solute with respect to a specific DOC can be expressed as (Chiou *et al.*, 1986)

$$S_w^* = S_w (1 + XK_{doc}) \quad (1)$$

where S_w^* is the apparent solute solubility in water containing DOC (as cosolute) at concentration X (in gram per milliliter of water), S_w is the solubility in pure water, and K_{doc} is the corresponding organic-carbon-based partition coefficient. Partition coefficients (K_{doc}) for the pairs of Aldrich humic acid and solutes were determined (according to equation 1) by plotting the apparent solubility (S_w^*) against the concentration of Aldrich humic acid. The slope gives $S_w K_{doc}$, and the intercept gives S_w . The results are shown in Figure 1.

The values of $\log K_{doc}$ of aldrin, dieldrin, heptachlor, heptachlor epoxide, and *p,p'*-DDT are 5.05, 4.89, 4.48, 4.46, and 5.53, respectively. The value of $\log K_{doc}$ of *p,p'*-DDT based on Aldrich humic acid in this study (5.53) is similar to the results of 5.44 measured from reverse-phase separation technique (Landrum *et al.*, 1984), 5.61

evaluated from equilibrium dialysis technique (Carter and Suffet, 1982), and 5.56 estimated from water solubility enhancement method (Chiou *et al.*, 1987).

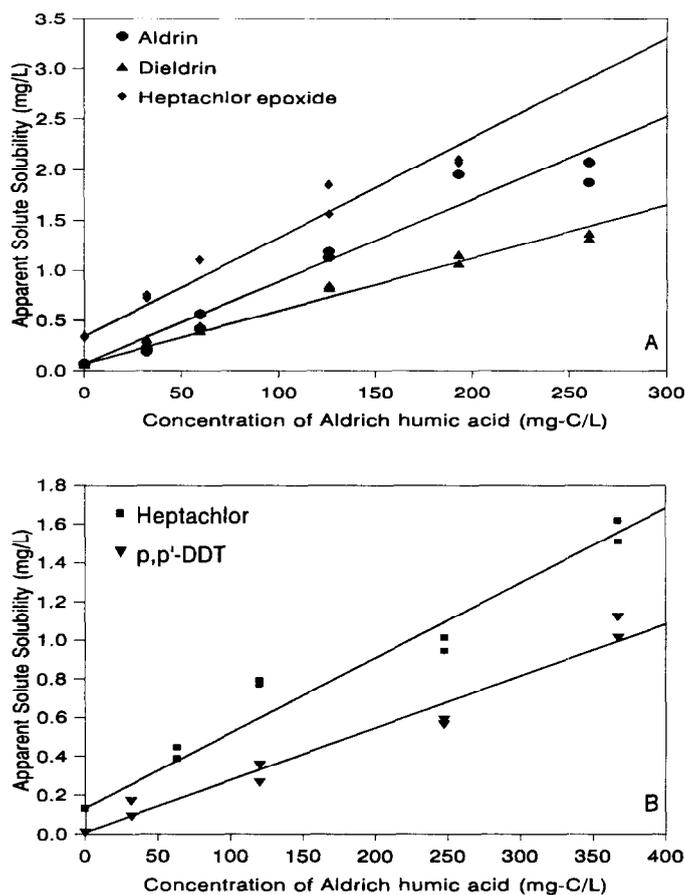


Figure 1. Dependence of the apparent water solubility of aldrin, dieldrin, heptachlor epoxide (A), heptachlor, and *p,p'*-DDT (B) on the concentration of Aldrich humic acid.

Variations of partition coefficients. Comparison of $\log K_{oc}$, $\log K_{doc}$ and $\log K_{ow}$ values of test solutes is shown in Table 3. The value of $\log K_{oc}$ is less than the value of $\log K_{ow}$ of each test solute. Chiou *et al.* (1983) indicated that soil organic matter is inferior to octanol as partition phase for relatively nonpolar organic compounds and that is quite reasonable as the organic matter is generally more polar than octanol. Similarly, it is the explanation for the lower value of $\log K_{doc}$ than the value of $\log K_{ow}$ of each test solute.

The K_{ocs} of aldrin, heptachlor, and *p,p'*-DDT are greater than their K_{docs} , and the relationships for dieldrin and for heptachlor epoxide are the opposite. The sources and the nature of the soil bulk organic carbon of Taichung soil and the dissolved Aldrich humic acid are different. The molecular polarities of dieldrin and heptachlor epoxide are greater than those of aldrin and heptachlor. We consider that this is one of the sakes for the variations of partition coefficients of the model solutes in this study.

Table 3. The comparison of partition coefficients of test solutes

Compound	log K_{oc}	log K_{doc}	log K_{ow}
aldrin	5.38	5.05	5.52 ^a
dieldrin	4.73	4.89	5.48 ^b
heptachlor	4.90	4.48	5.44 ^b
heptachlor epoxide	4.32	4.46	5.40 ^b
<i>p,p'</i> -DDT	5.68	5.53	6.36 ^c

^a cited from Garten and Trabalka (1983), ^b cited from Mackay (1982),

^c cited from Chiou *et al.* (1982)

When the nature of the dissolved organic matter released from the soil/sediment bulk organic matter is similar to that of the soil/sediment bulk organic matter, the ratios of K_{doc}/K_{oc} of solutes will be close to 1. If the dissolved organic matter is more hydrophilic than the soil/sediment bulk organic matter, they tend to escape from soil/sediment particles to the aqueous phase, and the ratios of K_{doc}/K_{oc} of these solutes will be less than 1. The K_{docs} to nonsettling colloids were 0.5-1 times the K_{ocs} to sediments of the Lake Superior for PCB congeners (Gschwend and Wu, 1985; Baker *et al.*, 1986). When the sources and nature of the dissolved organic matter and soil/sediment organic matter are different, the ratios of K_{doc}/K_{oc} of solutes will have a broad range. For 2,4,4'-PCB, the value of $\log K_{oc}$ was measured as 4.38 (Chiou *et al.*, 1983), and the values of $\log K_{doc}$ were measured as 3.53-4.83 (Chiou *et al.*, 1987); the ratios of K_{doc}/K_{oc} were 0.14-2.88. For 2,2',5,5'-PCB, the values of $\log K_{oc}$ were measured as 5.35 (Baker *et al.*, 1986), and the values of $\log K_{doc}$ were measured as 3.23-5.68 (Landrum *et al.*, 1984); the ratios of K_{doc}/K_{oc} were 0.008-2.14. For *p,p'*-DDT, the values of $\log K_{oc}$ were measured as 4.97-5.63 (Vinten *et al.*, 1983; Gerstl, 1990), and the values of $\log K_{doc}$ were measured as 4.23-5.74 (Chiou *et al.*, 1987; Landrum *et al.*, 1984; Carter and Suffet, 1982); the ratios of K_{doc}/K_{oc} were 0.04-5.9.

A log-log regression equation of K_{doc} and K_{ow} from this study is determined as:

$$\log K_{doc} = 0.96 \log K_{ow} - 0.51 \quad (n=5, r^2=0.76) \quad (2)$$

The correlation between K_{doc} and K_{ow} of some hydrophobic solutes is shown in Figure 2. The magnitudes of K_{doc} of a particular solute to the relatively hydrophilic and more hydrophobic DOCs may show about one to two orders of variation. The data collected from the literatures are shown in Figure 2, including some hydrophilic DOCs. For predicting the K_{docs} , equation 2 will be adaptable for relatively hydrophobic DOCs, however, may have larger error toward overestimation.

CONCLUSIONS

According to the results in the literatures and this study, in aqueous system, the interactions of hydrophobic organic solutes between soil organic matter and water or dissolved organic matter and water are partition. The variations of the partition coefficients are dependent on the characteristics of the solutes and the sources and nature of the organic carbons. For predicting the K_{docs} , A log-log regression equation of K_{doc} and K_{ow} is determined. It is also adaptable for relatively hydrophobic DOCs.

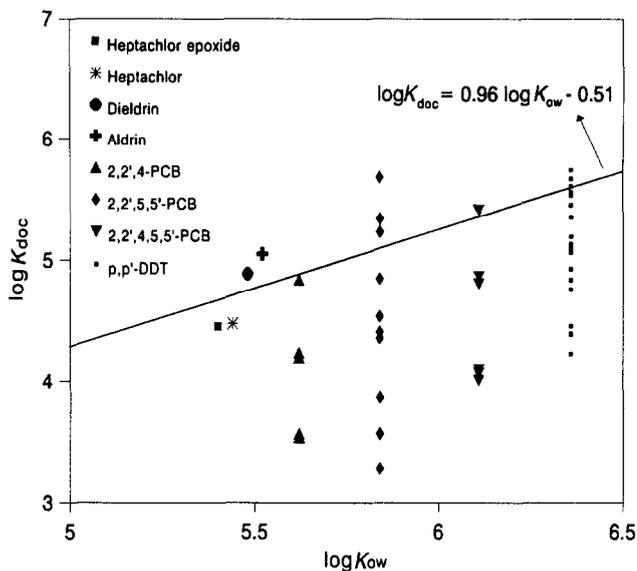


Figure 2. Correlation between K_{doc} and K_{ow} . The data are cited from Mackay (1982), Garten and Trabalka (1983), Carter and Suffet (1982), Landrum *et al.* (1984), Chiou *et al.* (1982, 1986, 1987), and this study.

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