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# PARTITION KINETICS OF CHLOROBENZENES IN A SEDIMENT-WATER SYSTEM

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## ABSTRACT

The partition kinetics of chlorobenzenes (CBs) in a sediment-water system were studied to provide a basis for understanding the compounds' behaviour in the natural aquatic environment. A series of chlorobenzenes (CBs) 1,4-dichlorobenzene (DCB), 1,3,5-trichlorobenzene (TCB), 1,2,4,5-tetrachlorobenzene (TeCB), pentachlorobenzene (QCB), and hexachlorobenzene (HCB) were spiked to the sediment, and the concentrations of CBs both in sediment and water were measured at six different mixing time periods (0.17, 1, 4, 12, 24 and 48 hours). A partition kinetics model was developed to determine kinetics rate constants. Adsorption rate constants increased (DCB 15.3; HCB 26.3 L.kg<sup>-1</sup>.h<sup>-1</sup>) while desorption rate constants decreased (DCB 0.41; HCB 0.01 h<sup>-1</sup>) with  $K_{OW}$  values. The times to reach equilibrium in the system were between 6.7 h (HCB) and 14.3 h (TeCB), with no specific pattern related to the  $K_{OW}$  values of CBs. The kinetics of CBs were fitted to a first-order kinetics with a single-compartment model. QSAR analysis showed strong linear relationships between kinetics rate constants and physicochemical properties.

**Keywords:** chlorobenzenes, partition kinetics, QSAR, sediment-water system

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## 1. Introduction

Chlorobenzenes (CBs), with 1 to 6 chlorine atoms comprising 12 congeners, have been used in industry, agriculture and households. For example, 1,4-dichlorobenzene has been used as a toilet deodoriser, 1,2,4-tetrachlorobenzene as a component of dielectric fluids, and pentachlorobenzene as a pesticide to combat snails infesting oysters (IPCS, 2004). CBs are persistent hydrophobic organic compounds that are widely distributed in the environment such as soil in the vicinity of landfill sites (Dong et al., 2015), river sediment and water (Gotz et al., 2007), marine sediment and water (Hong et al., 2006), vegetables (Song et al., 2012), birds (Braune and Malone, 2006), and human blood (Kielb et al., 2010). The occurrences of CBs also have been found in dated sediment cores since the 1940's (Gotz et al., 2007). Occurrence of 11 of the possible 12 congeners of the CBs in sediment and water from Tonghui River near Beijing, China was reported by Zhou et al. (2009). The highest concentration of all reported results was measured for 1,2-DCB with  $1,029 \text{ ng.g}^{-1} \text{ d.w.}$  in sediment and  $4,981 \text{ ng.L}^{-1}$  in water.

Sediment-water partition coefficients of CBs derived from partition isotherm experiments have been reported (McPhedran et al., 2013; Djohan et al., 2005; Schrap et al., 1994a; Paya-Perez et al., 1991; and Brusseau et al. 1990). As the dynamics of CBs in sediments has been investigated and reviewed, there have been limited data on adsorption and desorption rate constants of CBs reported. In addition, variations in the kinetic model used in the experiments may limit the comparison among rate constants. Gschwend and Wu (1985) described three kinetic models in a sediment-water system, which were single-box kinetics, two-box kinetics, and radial diffusion kinetics models. A two-box kinetics model (fast and slow fraction) was applied by Schrap et al. (1994b). Also Cornelissen et al. (2000) developed a three action model (fast, slow, very slow) to obtain values of desorption rate constants of CBs from sediments.

The times for CBs to attain equilibrium in the sediment-water system have been reported but are highly variable. For example, fast equilibrium times for MCB were determined as less than 24 hours (Sharer et al., 2003) and 10 – 15 hours (Yu et al., 2000).

Quantitative structure activity relationships (QSARs) for 5 congeners of CBs were evaluated by Djohan et al. (2005) in terms of relationships between sediment-water partition coefficients and molar volume,  $K_{OW}$  and solubility in water. QSAR between rate constants of CBs and these three parameters may further enhance the understanding of behavior of CBs in the sediment-water system. However, the rate constants of CBs in the sediment-water system have not been quantified.

The aims of this paper were to measure kinetics rate constants of chlorobenzenes in a sediment water system experimentally and to evaluate of the experimental data with a single-compartment partition kinetics model of CBs in a sediment-water system. Five congeners of CBs (1,4-DCB; 1,3,5-TCB; 1,2,4,5-TeCB, QCB, and HCB) were used for kinetics experiments to obtain adsorption and desorption rate constants of CBs in the sediment-water system. Then the first-order kinetics model was used to determine the rate constants by using experimental constants and a single sediment to water ratio in the system. QSARs were also developed to analyse relationships between the adsorption and desorption rate constants and physicochemical properties of the CBs which are molar volume ( $v$ ), solubility in water ( $S_w$ ), octanol-water partition coefficient ( $K_{OW}$ ), and sediment organic carbon – water partition coefficient ( $K_{OC}$ ).

## 2. Theory

The changes of concentrations of a compound in sediment over time can be described by using the first-order kinetics model with a single-compartment (Fig. 1) as,

$$dC_s/dt = k_1 C_w - k_2 C_s \quad (1)$$

where  $C_s$  is the concentration in sediment ( $\mu\text{g.kg}^{-1}$ ),  $C_w$  is the concentration in water ( $\mu\text{g.L}^{-1}$ ),  $k_1$  is a first-order adsorption rate constant ( $\text{L.kg}^{-1}.\text{h}^{-1}$ ),  $k_2$  is a first-order desorption rate constant ( $\text{h}^{-1}$ ), and  $t$  is time (h).

Since the ratios between  $k_1$  and  $k_2$  is the sediment-water partition coefficient ( $K_D$ ),

$$k_1/k_2 = K_D \quad (2)$$

Eq. (1) can be written as

$$dC_s/dt = -k_1[(C_s/K_D) - C_w] \quad (3)$$

The mass balance of the compound in the sediment-water system can be expressed as,

$$C_s M + C_w V = C_{wo} V + C_{so} M \quad (4)$$

where  $M$  is the mass of sediment (kg),  $V$  is the volume of water (L),  $C_{so}$  ( $\mu\text{g.kg}^{-1}$ ) and  $C_{wo}$  ( $\mu\text{g.L}^{-1}$ ) are the initial concentrations of the compound in sediment and water, respectively.

Substitution of Eq. (4) into Eq. (3) results in,

$$dC_s/dt = -k_1[1/K_D + (M/V)]C_s + k_1[C_{wo} + C_{so}(M/V)] \quad (5)$$

and further re-arrangement of Eq. (5) gives

$$dC_s / \{C_s - (C_{wo} + C_{so} M/V) / \{1/K_D + M/V\}\} = -k_1 \{1/K_D + M/V\} dt \quad (6)$$

which can be integrated to give

$$\ln \left| \frac{C_s - \{C_{w0} + C_{so} M/V\}/1/K_D + M/V}{C_{so} - \{C_{w0} + C_{so} M/V\}/\{1/K_D + M/V\}} \right| = -k_1 \{1/K_D + M/V\} t \quad (7)$$

If we define,

$$\alpha = 1/K_D + (M/V) \quad (8)$$

and

$$\beta = \{C_{w0} + C_{so} M/V\}/\{1/K_D + (M/V)\} \quad (9)$$

then Eq. (7) can be written as

$$\ln[\{C_s - \beta\}/\{C_{so} - \beta\}] = -k_1 \alpha t \quad (10)$$

where  $\alpha$  ( $\text{kg.L}^{-1}$ ) and  $\beta$  ( $\mu\text{g.kg}^{-1}$ ) are experimental constants for each of CBs in a given sediment-water system. Constant  $\beta$  represents the concentration of the compound in sediment at equilibrium time. Both  $\alpha$  (Eq. 8) and  $\beta$  (Eq. 9) constants contain sediment-water ratio ( $M/V$ ). If we define,

$$\phi = (C_{so} - \beta)/(C_s - \beta) \quad (11)$$

Eq. (10) can be written in another way as,

$$\ln \varphi = \ln \left[ \frac{C_{so} - \beta}{C_s - \beta} \right] = k_1 \alpha t \quad (12)$$

When  $K_D$ ,  $\alpha$ , and  $\beta$  values are known, the adsorption rate constant ( $k_1$ ) can be obtained as the slope of the plot of  $\ln \varphi$  versus  $\alpha t$  by using linear regression analysis.

Eq. (12) can be re-written as,

$$C_s = \beta + (C_{so} - \beta) \exp^{-k_1 \alpha t} \quad (13)$$

Having obtained the rate constants, the concentrations of the compound in the sediment over time can be estimated by using Eq. (13). Further re-arrangement of Eq. (4) results in

$$C_w = \{C_{wo}V + C_{so}M - C_sM\}/V \quad (14)$$

and substitution of Eq. (13) into Eq. (14) leads to

$$C_w - C_{wo} = (M/V)(C_{so} - \beta)[1 - \exp^{-k_1 \alpha t}] \quad (15)$$

and by using the right side of Eq. (9), the  $(C_{so} - \beta)$  can be further written as

$$C_{so} - \beta = C_{so} - \{C_{wo} + C_{so} M/V\}/\{1/K_D + M/V\} \quad (16)$$

and further re-arrangement of Eq. (16) leads to

$$C_{so} - \beta = C_{so} - \{(C_{so}/K_D) - C_{wo}\} / \{1/K_D + (M/V)\} \quad (17)$$

Substitution of Eq. (17) into Eq. (15) gives Eq. (18), which can be used to estimate the concentrations of the compound in water over time.

$$C_w = C_{w0} + \{(C_{so} - K_D C_{wo})(V/M) + K_D\}(1 - \exp^{-k_1 \alpha t}) \quad (18)$$

The time required to establish equilibrium ( $t_{eq}$ ) can be obtained by assuming equilibrium is reached when  $C_s$  is equivalent to  $1.01 \beta$ . Substitution of  $C_s$  with  $1.01 \beta$  and  $t$  with  $t_{eq}$  to Eq. (12) results in

$$\ln \phi = \ln[(C_{so} - \beta)/0.01\beta] = k_1 \alpha t_{eq} \quad (19)$$

and finally, the time to establish equilibrium ( $t_{eq}$ ) can be calculated as

$$t_{eq} = \ln[(C_{so} - \beta)/0.01\beta] / k_1 \alpha \quad (20)$$

### 3. Materials and Methods

#### 3.1. Chemicals and Materials

Five CBs (1,4-DCB; 1,3,5-TCB; 1,2,4,5-TeCB; QCB; and HCB) were used as test compounds in this experiment. Two other congeners of CBs (1,2,3-TCB and 1,2,3,4-TeCB) were used as internal standards. All compounds were obtained from Aldrich, except 1,4-



DCB, which was obtained from the British Drug Houses (BDH). Based on GC-ECD analysis, all test compounds and internal standards were analysed and confirmed as  $\geq 97\%$  purity. Hexane and acetone, were obtained from Mallinckrodt with nanograde levels of purity, and were used in this experiment. Anhydrous sodium sulfate from BDH and Florisil® (AR grade 60/100 mesh) (Mallinckrodt) were used as a drying agent and clean up agent, respectively.

A natural sediment was collected from a creek in Brookfield, Brisbane (Queensland, Australia). The fraction of organic carbon content ( $f_{oc}$ ) in the sediment was 0.046. Distilled water was used as the aqueous phase in this experiment. The sediment to water ratio ( $M/V$ ) in this experiment was  $0.008 \text{ kg.L}^{-1}$  which was comparable to ranges of sediment to water ratios reported in the natural waters ( $10^{-5} - 10^{-2} \text{ kg.L}^{-1}$ ) (O'Connor and Connolly, 1980).

### *3.2. Experimental Method*

Six sets of sediment-water mixtures were used with each set representing different mixing times, which were determined as 0.17, 1, 4, 12, 24, and 48 hours. Each set consisted of two replicates of the sediment – water mixture. Five test CBs (in 100  $\mu\text{L}$  acetone) were spiked into 2 g dry sediment in a glass bottle (300 mL size). The amount of the test compounds spiked to the sediment were 600  $\mu\text{g}$  (DCB), 180  $\mu\text{g}$  (TCB), 88  $\mu\text{g}$  (TeCB), 40  $\mu\text{g}$  (QCB), and 1.2  $\mu\text{g}$  (HCB). The sediment was left for five minutes for the acetone to be volatilised. Then, 250 mL of 0.01 M  $\text{CaCl}_2$  (aqueous phase) was added to the sediment. Each set of the sediment-water mixtures was shaken in a vertical rotary shaker for its pre-determined mixing time. At the end of the mixing times, sediment and water were separated by centrifugation (3,000 rpm for 5 min). Internal standards were added into the separated sediment (70  $\mu\text{g}$  in 100  $\mu\text{L}$  acetone) and water (160  $\mu\text{g}$  in 100  $\mu\text{L}$  acetone) before extraction.

### 3.3. Chemical Analyses

Detail extraction procedures of chlorobenzenes from sediment and water were described in previous study (Djohan et al., 2005). Chemical analyses of chlorobenzenes by a gas chromatography (GC) (Hewlett Packard - 6890 model) equipped with a DB-5 capillary column (J & W Scientific) and a  $^{63}\text{Ni}$  Electron Capture Detector (ECD) were reported in previous study (Djohan et al., 2005). The recoveries for CBs in sediment by this procedure were 90% (DCB); 90% (TCB); 89% (TeCB); 86% (QCB); and 88% (HCB), while the recoveries in water were 91% (DCB); 95% (TCB); 93 % (TeCB); 92% (QCB); and 91% (HCB). The detection limits for DCB; TCB; TeCB; QCB; and HCB in sediment were 21.7; 16.4; 12.3; 10.7; and 8.1  $\mu\text{g.kg}^{-1}$ , respectively, and in water were 1.4; 0.3; 0.5; 0.5; and 0.06  $\mu\text{g.L}^{-1}$ , respectively.

## 4. Results and Discussion

### 4.1. Concentrations of chlorobenzenes in sediment and water over time

The initial concentrations of CBs in sediment ( $C_{so}$ ), concentrations in sediment at equilibrium time ( $C_{se}$ ), and concentrations in water at equilibrium time ( $C_{we}$ ) are listed in Table 1. Changes of concentrations of CBs over time in sediment and water are shown (Fig. 2), the concentrations of CBs in the sediment decreased rapidly for the first four hours and became steady for the remaining time. On the other hand, the concentrations of CBs in the water increased notably during the first four hours, followed by steady concentrations up to the end of the experiment at 48 hours.

The  $C_{se}$  and  $C_{we}$  were calculated as the means of the concentrations of CBs in the sediment and water at 12, 24, and 48 hours, time periods which showed the concentrations had plateaued. Initially,  $C_s$  for all CBs rapidly decreased followed by steady concentrations, while  $C_w$  for all CBs rapidly increased then became steady (Fig. 2) indicating transfer of CBs from the solid to the aqueous phase. The values of sediment-water partition coefficients ( $K_D$ ), determined as  $C_{se}/C_{we}$  are provided in Table 1. These values were comparable to the  $K_D$  values for similar CBs obtained from partition isotherm experiments (Djohan et al., 2005) with less than 10% difference.

At equilibrium, the concentrations of CBs in water could be expressed as relative concentrations to the compounds solubility in water or  $C_{we}/S_w$  (Table 1). The relative solubility values for DCB, TCB, and TeCB in this study were 0.03, 0.06 and 0.14, respectively (Table 1). The relative solubility in water can be related to the desorbed fraction ( $C_s/C_{so}$ ) in sediment. For example, the relative solubility of TeCB in this study (0.14) corresponds with a desorbed fraction of 0.64 ( $C_{se}/C_{so}$ , Table 1), while the relative solubility of TeCB in Xia and Ball (1999) corresponds with an adsorbed fraction between 0.3 and 0.4 or desorbed fraction between 0.6 and 0.7.

#### 4.2. Experimental constants $\alpha$ and $\beta$

The experimental constants  $\alpha$  and  $\beta$ , as previously described in Eq. (8) and Eq. (9), respectively, are listed in Table 1. It can be seen that the  $\alpha$  and  $\beta$  values decreased from DCB to HCB as the  $\alpha$  and  $\beta$  are inversely proportional to the  $K_D$ . The values of the constant  $\alpha$  (Table 1) decreased with the increase in the number of chlorine atoms. The value of constant  $\alpha$  for HCB was  $0.008 \text{ L.kg}^{-1}$  which was similar to sediment to water ratio used in this study.

This can be readily explained since the right side of Eq. (8) contains a  $K_D$  value for HCB of 3,200 L.kg<sup>-1</sup> (Table 1).

The values of  $\beta$  constants (Table 1) were comparable to the concentrations of CBs in sediment at equilibrium ( $C_{se}$ ) (Table 1). The percentages of difference between  $\beta$  and  $C_{se}$  values were relatively small, for example the differences were 5.5% for DCB and 0.9% for HCB. A regression line between paired data of  $\beta$  and  $C_{se}$  values of the 5 CBs, passing through the origin point at zero, resulted in a  $C_{se}$  value equivalent to 1.05  $\beta$ , while in the model it was assumed that  $C_{se}$  is equivalent to 1.01  $\beta$  (Eq. 19), or the differences between the measured and the estimated concentrations of the CBs were approximately 4%. This also implies that the first-order kinetics model is suitable to describe partition of CBs in the sediment-water system in this study.

The use of experimental constants  $\alpha$  and  $\beta$  in this study could be compared with the use of experimental constants relating suspended particle concentration ( $SPM$ ) and  $K_D$  for HCB and several other organic compounds (Turner et al., 1999) as

$$K_D = a(SPM)^{-b} \quad (21)$$

The experimental constants “ $a$ ” and “ $b$ ” in Turner et al. (1999) refer to the particle concentration-normalised  $K_D$ , and the slope of the relationship, respectively. These authors also explained that the values “ $a$ ” and “ $b$ ” could be considered as site-specific constants and compound-specific constants, respectively. In a different manner, the constant  $\alpha$  was used in this study to include the influence of sediment-to-water ratio ( $M/V$ ) on  $K_D$  values (Eq. 8) while constant  $\beta$  was used in estimation of concentrations of CBs in sediment at equilibrium (Eq. 9). The  $M/V$  values can influence desorption, since at higher  $M/V$  values, collision among particles occur more often, consequently higher desorption is expected (Mackay and Powers, 1987). It was also reported that  $M/V$  values influenced desorption of HCB at lower

$M/V$  values ( $< 5 \times 10^{-4} \text{ kg.L}^{-1}$ ) but did not much have influence at higher  $M/V$  values (Jepsen et al., 1995).

#### 4.3. Partition rate constants ( $k_1$ and $k_2$ )

The  $k_1$  and  $k_2$  values of CBs in this study are listed in Table 1. The linear plots of  $\ln \varphi$  versus ( $\alpha t$ ) to calculate the adsorption rate constants ( $k_1$ ) are shown in Fig. 3. The  $k_1$  was determined as the slope of the linear plot passing through the origin point at zero. Five plots showed high linear regression coefficients ( $> 0.90$ ) and the  $k_1$  values increased with the number of chlorine atoms in the CBs molecule. The values of  $k_1$  in this study for TCB, TeCB, QCB, and HCB were 20.8; 23.2; 24.9; and 26.1  $\text{L.kg}^{-1}\text{h}^{-1}$ , respectively (Table 1). These values were one to two orders of magnitude higher compared to  $k_1$  values for the same CBs in the fast compartment of sediment, which were reported by Schrap et al. (1994b) as 0.35; 4.80; 3.40; and 5.30  $\text{L.kg}^{-1}\text{h}^{-1}$ , for TCB, TeCB, QCB, and HCB, respectively. This study used the batch experimental technique, while the study by Schrap et al. (1994b) used a gas-purge system which could possibly explain these differences.

The values of the adsorption rate constants ( $k_1\alpha$ ) measured in this study ranged from  $0.54 \text{ h}^{-1}$  (DCB) to  $0.21 \text{ h}^{-1}$  (HCB) (Table 1), decreasing with the increase of the number of chlorine atoms. The  $k_1\alpha$  values for DCB and HCB were in accord with those reported by Kan et al. (2000), as  $0.23$  and  $0.31 \text{ h}^{-1}$ , respectively. This study used fresh sediment while Kan et al. (2000) investigated desorption of CBs and other organic compounds from contaminated aged sediment.

The desorption rate constants ( $k_2$ ) for all CBs except HCB in this study ranged from  $0.03$  to  $0.41 \text{ h}^{-1}$  (Table 1) and can be categorized as *fast* ( $\sim 0.1 \text{ h}^{-1}$ ), according to ten Hulscher et al. (2002). The  $k_2$  of HCB ( $0.01 \text{ h}^{-1}$ ) can be classified as *slow*, the range of which was  $0.01$

– 0.001 h<sup>-1</sup> (ten Hulscher et al., 2002). The values of  $k_2$  in this study for TCB, TeCB, QCB, and HCB were 0.16; 0.10; 0.03; and 0.01 h<sup>-1</sup>, respectively (Table 1). These values were comparable to  $k_2$  values in the fast kinetic compartment of sediment, which was reported by Schrap et al. (1994b). The  $k_2$  values in Schrap et al. (1994b) for TCB, TeCB, QCB, and HCB were 0.06; 0.16; 0.07; and 0.04 h<sup>-1</sup>, respectively. The sediment to water ratio in Schrap et al. (1994b) was 10<sup>-2</sup> kg.L<sup>-1</sup> which was comparable to 8 x 10<sup>-3</sup> kg.L<sup>-1</sup> in this study. Schrap et al. (1994b) used three sets of experiments (variations in sediment-to-water ratio, adsorption period, and desorption period) but found that the rate constants were not influenced by the experimental conditions. The  $k_2$  values in this study were also comparable to estimated  $k_2$  values described by Karickhoff and Morris (1985) as

$$\frac{1}{k_2} = 0.03K_D \quad (22)$$

By using Eq. (22) and  $K_D$  values (Table 1), the estimated  $k_2$  values for TCB, TeCB, QCB, and HCB could be determined as 0.24; 0.15; 0.04; and 0.01 h<sup>-1</sup>, respectively, which were comparable for the measured  $k_2$  values in this study for TCB, TeCB, QCB, and HCB as 0.16; 0.10; 0.03 and 0.01 h<sup>-1</sup>, respectively (Table 1).

#### 4.4. Time to equilibrium

The time to attain equilibrium ( $t_{eq}$ ) of CBs increased with the increase in the number of chlorine atoms, for lower CBs, from DCB, TCB, and TeCB (10.8; 13.8; and 14.3 h, respectively) (Table 1). The time to reach equilibrium generally increased with hydrophobicity of the compound (Valsaraj and Thibodeaux, 1999). However, in this study

the  $t_{eq}$  values for higher CBs, QCB (12.1 h) and HCB (6.7 h) were faster than those of the other CBs, which is an unusual pattern which discussed below.

Characteristics of sediments may influence sorption of HOCs (Calvet, 1989) such as sediment mineral content and composition. This may influence the adsorption of QCB to sediment organic matter as the mineral affects the surface structure of organic matter (Calvet, 1989). The mineral surface interacts with the dissolved organic matter of sediment (Thimsen et al., 1998). Times to attain equilibrium of CBs are listed in Table 2. Generally, 80-90% of equilibrium is achieved within less than an hour and often in a few minutes or can be considered as effectively instantaneous (Voice and Weber, 1983). The effectively instantaneous sorption process is assumed to be the most simple situation in the partition process (Calvet, 1989). Times to attain equilibrium for CBs in solid – water system are listed in Table 2. Equilibrium times between 1 to 2 days were obtained from the application of a first-order kinetics model to estimate fate and transport of a hypothetical organic compound ( $\log K_{OW}$  of 5) in a sediment-water system matched to field conditions (Wu and Gschwend, 1988).

#### *4.5. Application of the first-order kinetics model*

The application of the first-order kinetics model in this study was based on Eq. (12) which indicated the changes of CB concentrations in the sediment from initial contact time ( $C_{so}$ ) to CB concentrations in sediment at equilibrium time ( $\beta$ ). The estimated concentrations of CBs by the model, provided as continuous lines (Fig. 2), were in accord with the experimental data sets. The first-order kinetics model in this study used CBs with  $\log K_{OW}$  ranging from 3.44 to 5.41 (Table 3), fresh sediment, sediment-water contact times of 48 hours, and two experimental constants containing sediment-water ratio in order to obtain kinetics rate constants and equilibrium times. The relatively short contact times used in this

study should minimise losses due to volatilisation and biodegradation. Rapid desorption of CBs in this study (0 – 12 hours) followed by relatively steady concentrations (12 – 48 hours) (Fig. 2) can be associated with partition from small particles in the rapid phase and partition from large particles in the steady phase (Smit et al., 2010).

A double-compartment model with three phases (water, fast fraction of sediment, and slow fraction of sediment) was proposed by Schrap et al. (1994b) for kinetics of CBs in the sediment-water system. The percentages of fast fractions in the sediment for 5 CBs obtained in one of the desorption experiments ranged from 72% (HCB) to 86% (TeCB) (Schrap et al., 1994b), and no clear relationship was found between the fast fractions and chlorine numbers of CBs. Some parameters used in the experiments by Schrap et al. (1994b) were comparable to this study such as sediment water ratio ( $10^{-2}$  to  $8 \times 10^{-3}$  kg.L<sup>-1</sup>), fraction of organic carbon (3 to 4.6%), and contact time (64 to 48 h).

Other partition studies of CBs have also applied first-order kinetics model but with different experimental designs. A comparison of three different kinetic models, which were one-compartment, two-compartment first-order kinetics model, and radial diffusion model was performed by Gschwend and Wu (1985). The radial diffusion model was considered better for comparison between model predicted concentrations of some CBs and experimental data. One-compartment first order kinetic model did not describe steady concentrations of CBs close to equilibrium time (Gschwend and Wu, 1985), while the first-order kinetic model in this study was supported by well fitted between experimental and estimated concentrations at times close to equilibrium (12 - 48 h).

Many partition studies of CBs in sediment or soil – water system have applied two-compartment first-order kinetic model (Birdwell et al., 2007), such as experiments performed by ten Hulscher et al. (2002), Lee et al. (2002), Cornelissen et al. (2000), Culver et al. (2000),



and Kan et al. (2000). Generally, two-compartment first order kinetics model of CBs are generally focused on slow desorption rate constants of CBs. Three-compartment first-order kinetic model to describe partition of some CBs has been successfully used by McPhedran et al. (2013) and van den Heuvel and van Noort (2005). There is no model which can be used to describe kinetics of lipophilic organic chemicals in varied conditions of sediment-water systems (Birdwell et al., 2007).

#### 4.6. QSAR of partition kinetics rate constants

QSAR evaluations based on adsorption rate constants ( $\log k_1$ ) ( $\text{L.kg}^{-1}.\text{h}^{-1}$ ) and desorption rate constants ( $\log k_2$ ) ( $\text{h}^{-1}$ ) were carried out using molar volume ( $v$ ), solubility in water ( $\log S_w$ ),  $\log K_{OW}$ , and  $\log K_{OC}$  (Table 3). The relationship between molar volume and  $\log k_1$  was better described by a linear regression plot (Eq.23). Two plots of  $\log k_2$  were well described by linear regression plots (Eq.25 and Eq.28), so no polynomial second-order regression plot was provided. However, the relationships between uptake rate constants and molar volume of CBs were better described by polynomial second order regression (Eq.24). A moderate ( $R^2$  0.89) linear regression relationship between  $\log k_2$  and molar volume of CBs has been reported by Cornelissen et al. (1997), while the value of  $R^2$  for a similar plot in this study was 0.98 (Eq.25).

The inverse relationship between  $\log S_w$  and  $\log k_1$  was well described ( $R^2$  0.99) by using a polynomial second-order equation (Eq.27) rather than by using a linear regression equation ( $R^2$  0.82, Eq.26). However, the positive relationship between  $\log S_w$  and  $\log k_2$  was well described ( $R^2$  0.96) by a linear regression equation (Eq.28). The relationships between  $\log K_{OW}$  and  $\log k_1$  and  $\log k_2$  were well described ( $R^2$  0.99) by polynomial second-order equations (Eq. 30 and Eq. 32). Compared to molar volume and solubility in water,  $\log K_{OW}$  had the strongest relationships with the two rate constants. The range of the  $\log K_{OW}$  values of

CBs in this study was 1.58 log units, while that of  $\log S_w$  was 4.2 log units, with HCB showing the lowest  $\log S_w$  compared to the other CBs (Table 3). Such differences were not found for molar volumes, which increased regularly by  $20.9 \text{ cm}^3 \cdot \text{mol}^{-1}$  for each chlorine atom (Table 3).

Relationships between log rate constants ( $k_1$  and  $k_2$ ) in this study with  $\log K_{OC}$  (Djohan et al., 2005) were described in Eq. (33) to Eq. (36) and provided in Table 3. Similar to discussions above, the highest regression coefficient of 0.99 was obtained from the linear regression relationship between  $\log k_2$  and  $\log K_{OC}$  (Eq. 35). The  $\log k_2$  and  $\log K_{OC}$  plot (slope -0.88,  $R^2$  0.99) (Eq. 35) is comparable to a similar plot obtained in a sediment colloidal organic carbon system (slope -0.76,  $R^2$  0.93) (Eq. 36) as reported by McPhedran et al. (2013). Another plot, which related  $\log k_2$  with  $\log K_{OW}$  in this study (slope -0.79,  $R^2$  0.93) (Eq. 37) had a comparable slope (-0.82,  $R^2$  0.91) to a similar plot obtained in a bioconcentration kinetics study of CBs in pond snail (Eq. 38) (Legierse et al., 1998). The values of  $k_2$  (elimination rate constant in pond snail) in Legierse et al. (1998) for TCB, TeCB, QCB, and HCB were 3.99; 1.52; 0.24; and  $0.25 \text{ d}^{-1}$  which were higher than the values of  $k_2$  in this study ( $0.16$ ;  $0.10$ ;  $0.03$  and  $0.01 \text{ h}^{-1}$ ) (Table 1).

## 5. Conclusions

Partition kinetics rate constants of chlorobenzenes in a sediment-water system were measured experimentally. Adsorption rate constants of CBs increased (DCB 15.3; HCB 26.3  $\text{L} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$ ) with the increase of  $\log K_{OW}$  values of CBs, while desorption rate constants decreased (DCB 0.41; HCB  $0.01 \text{ h}^{-1}$ ) with the increase of  $\log K_{OW}$  values. The values of kinetics rate constants were comparable to the values reported in literature. The times to reach equilibrium was obtained between 6.7 (HCB) to 14.3 h (TeCB), with no specific pattern related to the  $\log K_{OW}$  values of CBs.

The experimental constants  $\beta$  in the model, which were the estimated concentrations of CBs in the sediment at equilibrium, were comparable to the measured concentrations at equilibrium ( $C_{se}$ ). The differences between  $\beta$  and  $C_{se}$  for individual CBs were of a low order, between 0.9% (HCB) to 5.5% (DCB). A correlation analysis between the set of constant  $\beta$  values and the set of  $C_{se}$  values gave a high value of correlation coefficient ( $R^2$  0.99).

QSAR analysis showed high linear regression coefficients ( $R^2 \geq 0.90$ ) between kinetics rate constants and physicochemical properties (molar volume, solubility in water,  $K_{ow}$ , and  $K_{oc}$ ). The measured kinetics rate constants, the observed times to attain equilibrium, and strong QSAR relationships provide a basic understanding of the partition behaviour of CBs in the sediment-water system.

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**Table 1. Concentrations of chlorobenzenes, experimental constants, kinetics rate constants and times required to establish equilibrium in the sediment-water system.**

Parameter	Unit	1,4-DCB	1,3,5-TCB	1,2,4,5-TeCB	QCB	HCB
$C_{so}$	$\mu\text{g.kg}^{-1}$	300,000	90,000	44,000	20,000	600
$C_{se}$	$\mu\text{g.kg}^{-1}$	$63,000 \pm 3,600$	$46,000 \pm 1,700$	$28,000 \pm 1,100$	$17,000 \pm 350$	$580 \pm 5.3$
$C_{we}$	$\mu\text{g.L}^{-1}$	$1,800 \pm 120$	$330 \pm 30$	$120 \pm 10$	$20.6 \pm 2$	$0.18 \pm 0.02$
$C_{se}/C_{so}$	-	0.21	0.51	0.64	0.85	0.97
$C_{we}/S_w$	-	0.03	0.06	0.14	0.05	0.02
$\alpha$	$\text{kg.L}^{-1}$	0.035	0.016	0.012	0.009	0.008
$\beta$	$\mu\text{g.kg}^{-1}$	68,500	45,900	28,500	17,200	575
$k_1$	$\text{L.kg}^{-1}.\text{h}^{-1}$	15.3	20.8	23.2	24.9	26.1
$k_1.\alpha$	$\text{h}^{-1}$	0.54	0.33	0.28	0.23	0.21
$k_2$	$\text{h}^{-1}$	0.41	0.16	0.10	0.03	0.01
$t_{eq}$	h	10.8	13.8	14.3	12.1	6.7
$K_D = k_1/k_2$	$\text{L.kg}^{-1}$	37	130	230	830	2,600

$C_{so}$  concentration in sediment at time zero;  $C_{se}$  concentration in sediment at equilibrium;  $C_{we}$  concentration in water at equilibrium;  
 $S_w$  solubility in water, Log  $S_w$  from Dannenfelser et al. (1991) DCB -3.32; TCB -4.54; TeCB -5.34; QCB -5.74, HCB -7.52 ( $\text{mol.L}^{-1}$ )  
 $\alpha$  experimental constant;  $\beta$  experimental constant;  $k_1$  adsorption rate constant;  $k_2$  desorption rate constant;  
 $t_{eq}$  time to establish equilibrium

**Table 2. Times required to establish equilibrium ( $t_{eq}$ ) of chlorobenzenes in the sediment-water system in this study and literature.**

Compound	Solid phase	$t_{eq}$ (h)	Reference
MCB	Soil	24	Sharer et al.(2003)
MCB	Sediment	3	Zhao et al.(2001)
1,4-DCB	Sediment	10.8	Present study
1,3-DCB	Sediment	51 <sup>a</sup>	Vrind et al.(2006)
1,4-DCB	Bentonite	10 - 25	Shu et al.(2010)
1,4-DCB	Sediment	48	Wu and Gschwend (1986)
1,3,5-TCB	Sediment	13.8	Present study
1,2,4-TCB	Sediment	13 <sup>a</sup>	Vrind et al. (2006)
TCBs	Soil	18 - 19	Paya-Perez et al. (1991)
1,3,5-TCB	Sediment	48	Schrap et al. (1994a)
1,2,4,5-TeCB	Sediment	14.3	Present study
1,2,3,4-TeCB	Sediment	48	Schrap et al. (1994a)
1,2,4,5-TeCB	Wastewater COC <sup>b</sup>	>12	McPhedran et al. (2013)
1,2,4,5-TeCB	Bentonite	10 - 25	Shu et al.(2010)
QCB	Sediment	12.1	Present study
QCB	Soil	18 - 19	Paya-Perez et al. (1991)
QCB	Sediment	48	Schrap et al.(1994a)
QCB	Wastewater COC <sup>b</sup>	>12	McPhedran et al. (2013)
QCB	Sediment	48	Wu and Gschwend (1986)
HCB	Sediment	6.7	Present study
HCB	Algal detritus	20 - 30	Koelmans et al. (1993)
HCB	Sediment	48	Schrap et al. (1994a)
HCB	Wastewater COC <sup>b</sup>	>12	McPhedran et al. (2013)

<sup>a</sup> 95% equilibrium, low energy adsorption; <sup>b</sup> colloidal organic carbon



**Table 3. QSAR of kinetics rate constants and times to establish equilibrium in the sediment-water system with physicochemical characteristics of chlorobenzenes.**

QSAR Plot		Equation	R <sup>2</sup>	Eq. No.
X-axis	Y-axis			
$\nu$	$\log k_1$	$\log k_1 = 0.0026 \nu + 0.87$	0.86	(23)
		$\log k_1 = -0.00005 \nu^2 + 0.017 \nu - 0.37$	0.98	(24)
$\nu$	$\log k_2$	$\log k_2 = -0.019 \nu + 2.31$	0.98	(25)
$\log S_w$	$\log k_1$	$\log k_1 = -0.054 \log S_w + 1.05$	0.82	(26)
		$\log k_1 = -0.017 (\log S_w)^2 - 0.24 \log S_w + 0.58$	0.99	(27)
$\log S_w$	$\log k_2$	$\log k_2 = 0.41 \log S_w + 1.008$	0.96	(28)
$\log K_{ow}$	$\log k_1$	$\log k_1 = 0.11 \log K_{ow} + 0.82$	0.94	(29)
		$\log k_1 = -0.049 (\log K_{ow})^2 + 0.55 \log K_{ow} - 0.13$	0.99	(30)
$\log K_{ow}$	$\log k_2$	$\log k_2 = -0.79 \log K_{ow} + 2.47$	0.93	(31)
		$\log k_2 = -0.32 (\log K_{ow})^2 + 2.01 \log K_{ow} - 3.59$	0.99	(32)
$\log k_1$	$\log K_{oc}$	$\log k_1 = 0.12 \log K_{oc} + 0.88$	0.84	(33)
		$\log k_1 = -0.088 (\log K_{oc})^2 + 0.79 \log K_{oc} - 0.37$	0.99	(34)
$\log k_2$	$\log K_{oc}$	$\log k_2 = -0.88 \log K_{oc} + 2.22$	0.99	(35)
		$\log k_2 = -0.76 \log K_{oc} + 0.83$	0.93	(36) <sup>a</sup>
$\log k_2$	$\log K_{ow}$	$\log k_2 = -0.79 \log K_{ow} + 2.47$	0.93	(37)
		$\log k_2 = -0.82 \log K_{ow} + 3.92$	0.91	(38) <sup>b</sup>

All QSAR plots are from present study, except with superscript symbols <sup>a</sup> McPhedran et al.(2013); <sup>b</sup> Legierse et al.(1998)

Molar volume ( $\nu$ ) Dannenfelser et al. (1991) DCB 137.8; TCB 158.7; TeCB 179.6; QCB 200.5, and HCB 221.4 ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )

Log  $K_{oc}$  from Djohan et al. (2005) DCB 2.90; TCB 3.45; TeCB 3.70; QCB 4.23, and HCB 4.8 ( $\text{L} \cdot \text{kg}^{-1}$ )

Log  $K_{ow}$  from Dannenfelser et al. (1991) DCB 3.44; TCB 4.17; TeCB 4.60; QCB 5.12, and HCB 5.41

Log  $S_w$  from Dannenfelser et al. (1991) DCB -3.32; TCB -4.54; TeCB -5.34; QCB -5.74, and HCB -7.52 ( $\text{mol} \cdot \text{L}^{-1}$ )

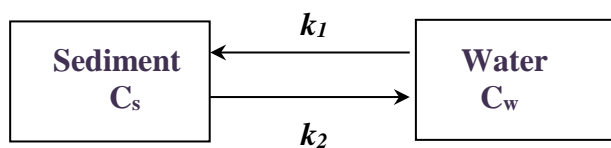


Figure 1. Single compartment model of partition kinetics of chlorobenzenes in the sediment-water system,  $k_1$  and  $k_2$  are adsorption and desorption rate constants, respectively.

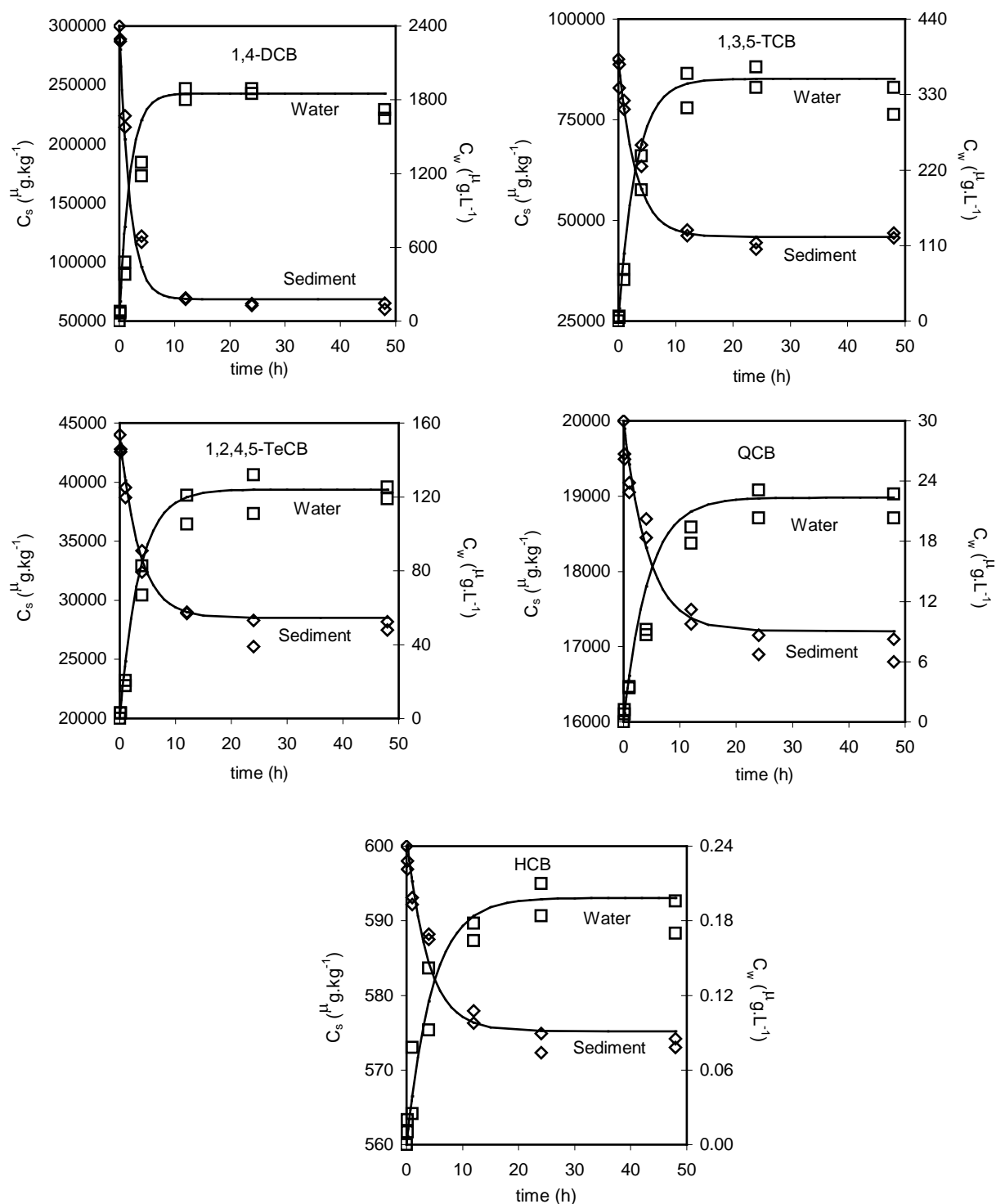


Figure 2. Comparison of the concentrations of chlorobenzenes in sediment and water obtained in the partition kinetics experiments to those estimated by the first-order kinetics model. Diamonds and squares refer to the experimental concentrations in sediment and water, respectively. Lines refer to the concentrations estimated by the model.

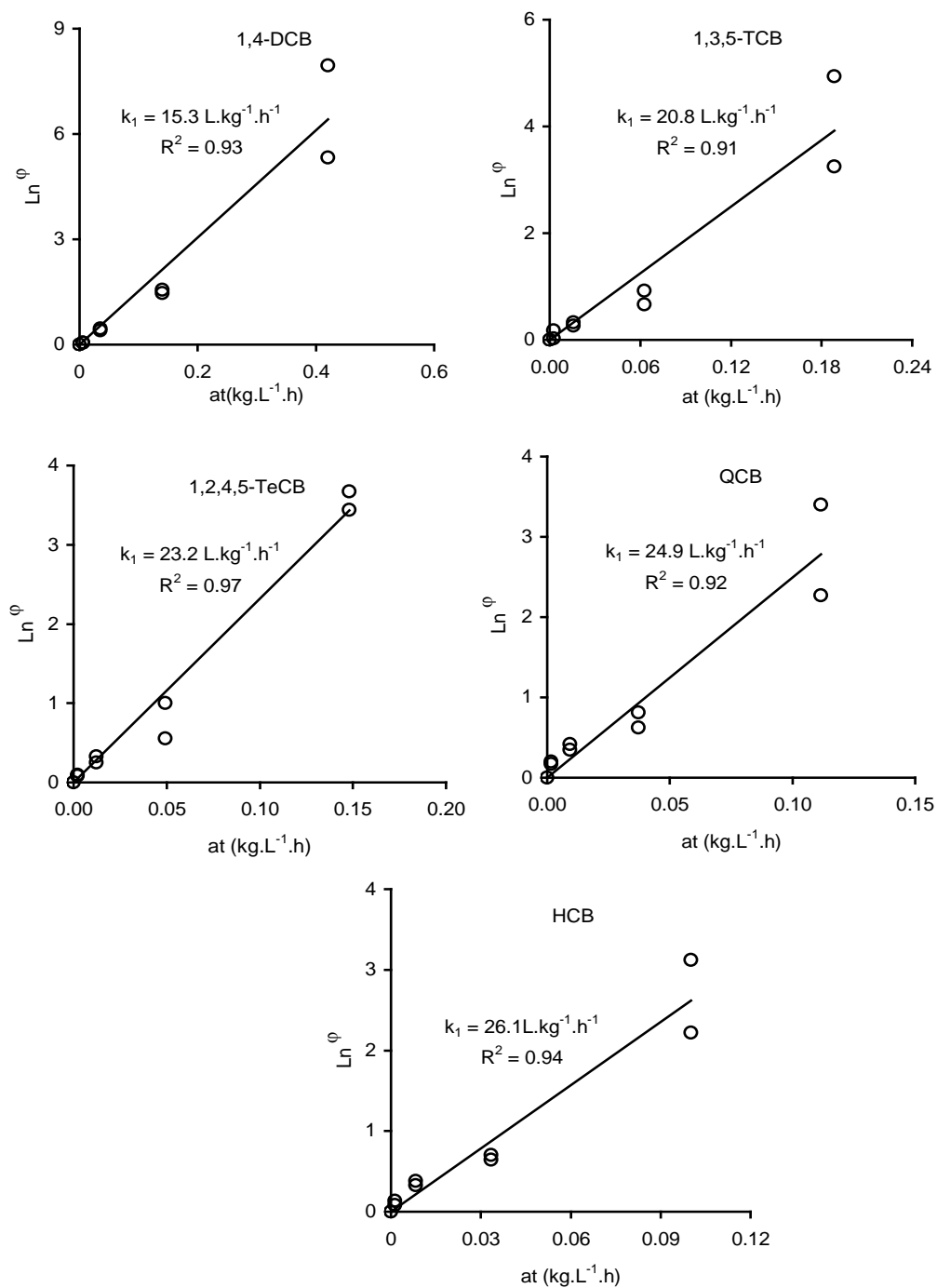


Figure 3. Linear regression plots of  $\ln \phi$  versus ( $at$ ) of chlorobenzenes. The slopes ( $k_1$ ) (L.kg<sup>-1</sup>.h<sup>-1</sup>) are the adsorption rate constants of chlorobenzenes in the sediment-water system as described in Eq. (12) in the text.