

## Effect of soil organic carbon on sorption and desorption of perchloroethylene in soils

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**Abstract**—The objective of this study was to elucidate the sorption and desorption behaviors of PCE (Perchloroethylene,  $C_2Cl_4$ ) in seven soils with different organic carbon (OC) content. Sorption/desorption kinetic and serial dilution desorption experiments were conducted in batch slurries. The sorption distribution coefficient ( $K_d$ ) of PCE ranged from 0.60 to 4.66 L kg<sup>-1</sup>.  $K_d$  tended to increase as the soil OC increased, but  $K_{oc}$  tended to decrease, suggesting that adsorption into the mineral surface was not negligible in soils with low OC. Desorption kinetic data were analyzed by the two-site desorption model. The sorption/desorption of PCE was not reversible over short incubation times due to the presence of a non-desorbable site. The desorbable site fractions of PCE increased and non-desorbable site fractions decreased as the soil OC increased. It is suggested that partition of PCE into soil organic carbon is more reversible than adsorption on soil minerals.

Key words: Sorption, Desorption, Organic Carbon, Hysteresis, Perchloroethylene

### INTRODUCTION

Soils and groundwater are commonly contaminated by anthropogenic chemicals such as chlorinated solvents, aromatic hydrocarbons and pesticide as a result of the improper design of hazardous waste disposal facilities, accidental spills and agricultural activities. These organic contaminants are persistent and have slow transport rates in the subsurface. Many mechanisms such as advection, dispersion, diffusion, volatilization, sorption and desorption are related to the movement and fate of contaminants in the subsurface environment [1,2]. The slow release of organic contaminants from soil has been shown to reduce the effectiveness of many cleanup technologies. The transport, distribution and fate of hydrophobic organic chemicals in soils and groundwater are known to be dependent on characteristics of soils such as organic carbon content, pore size, soil texture, pH, etc [3-6].

Sorption often follows a two-phase pattern with an initially rapid sorption phase followed by a much slower sorption phase [7,8]. Similarly, desorption often follows a two-phase pattern, with a rapid phase followed by a much slower phase [9]. Studies have shown that increased contact time between chemicals and soil can decrease the availability of chemicals to the microorganisms responsible for biodegradation and the extractability of the chemicals from soil [6,9-12].

Several processes have been proposed to describe the sorption of an organic chemical to natural solids. The adsorption of organic chemicals into the mineral surface is generally believed to be a surface phenomenon that is non-linear and competitive, while sorption into organic matter is known to be a partitioning, linear and noncompetitive process [6]. Organic compounds are known to pene-

trate and bind at the expandable interlayer regions of 2 : 1 layer (two tetrahedral aluminosilicate sheets that sandwich an octahedral aluminosilicate sheet to form a layer of clay minerals) silicated clays of the smectite-vermiculite group. According to a study of the persistence of 1,2 dibromoethane used for soil fumigation by Steinberg et al. [13], the release of residual 1,2 dibromoethane was greatly enhanced by pulverization of the soil. The results suggested that the residual 1,2 dibromoethane is trapped in soil micropores other than the interlayers of expandable clays. However, the effect of soil organic matter on the desorption of sorbed organic chemicals has not been studied widely, and published information is scarce.

This study was conducted to investigate the effect of soil organic carbon content on desorbable fractions of sorbed organic chemicals. PCE (Perchloroethylene,  $C_2Cl_4$ ), which is a halogenated volatile organic compound that has strong toxicity against human health, was selected as a sorbate. PCE is known to resist to transformation over long periods of time in soil/water systems and to be dechlorinated biologically in anaerobic environments. The physical and chemical properties of PCE are shown in Table 1. Seven soils with different contents of organic carbons were used as sorbents, and batch experiments were conducted to evaluate the influence of organic carbon on the sorption and desorption.

**Table 1. Molecular properties of PCE**

Properties of sorbate	
Vapor pressure at 30 °C (kPa)	4.28
Density at 20 °C (g/ml)	1.632
Boiling point (°C)	121
Water solubility at 20 °C (mg/l)	150
Henry's law const. (atm m <sup>3</sup> /mol)	$2.59 \times 10^{-3}$
Octanol-water coeff. (log $K_{ow}$ )	2.60

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**Table 2. Physicochemical properties and taxonomy of soils**

Soils	pH (1 : 5)	OC (%)	Sand (%)	Silt (%)	Clay (%)	Taxonomy
Hanam	7.3	0.18	96	3	1	Sand
Donggu	6.3	0.34	60	20	20	Sand clayloam
Busudong	5.9	1.02	56	25	19	Sand clayloam
Kigae	6.1	1.08	23	36	41	Clayloam
Yangdong	5.9	1.70	69	21	10	Sandy loam
Bugku	6.6	2.83	67	18	15	Sand clayloam
Kwasuwon	5.2	2.92	53	23	24	Sand clayloam

## METHODS AND MATERIALS

### 1. Soils

Soils were obtained from seven sites at Gwangju in Korea. Surface soils (0–15 cm) were sampled after the removal of weeds and leaves. The soil samples were air-dried and passed through a 2 mm sieve prior to use. The properties and taxonomy of the soils are presented in Table 2. The organic carbon content of the soils, which was measured using TOC instrument (TOC-VCPH, Shimadzu), ranged from 0.18 to 2.92%.

### 2. Experimental Methods

In the sorption experiments, nine 4.5 ml glass vials containing 4.2 ml of sterile 20 mM phosphate buffer (PB, pH 7.0) and 0.4 g of sterile soil were prepared for each soil. An aliquot of  $^{14}\text{C}$  PCE stock (in methanol) was spiked into each vial to give an appropriate initial aqueous concentration ranging from 0 to 5,000  $\mu\text{g L}^{-1}$ . Vials were mixed at 150 rpm for two days in the dark and centrifuged for 10 min at 3,000 rpm. The radioactivity of the chemical in the supernatant was then determined by LSC (liquid scintillation counting). Sorbed concentrations were calculated based on the difference between the initial and final liquid phase concentrations. Linear regression was used to compute the slope of the sorption isotherm from a plot of the sorbed amount ( $\mu\text{g kg}^{-1}$ ,  $S$ ) versus the concentration in solution ( $\mu\text{g L}^{-1}$ ,  $C$ ).

The linear sorption equation model is a commonly used approach for describing the distribution of a substance between soil and solution. The linear equation is expressed as

$$S = K_d C \quad (1)$$

where  $S$  is the amount of solute retained by the soil ( $\mu\text{g kg}^{-1}$ ),  $C$  is the solution concentration ( $\mu\text{g L}^{-1}$ ), and  $K_d$  ( $\text{L kg}^{-1}$ ) is the distribution coefficient.

Desorption experiments were conducted by following the sorption equilibrium. After the sorption equilibrium was reached, the supernatant was decanted to the greatest extent possible, and the amount of residual water was determined gravimetrically. Desorption was initiated by adding PCE free PB solution to make up the original volume. Next, the vials were mixed at 150 rpm again, and then removed periodically and the liquid phase was sampled for analysis. In addition, successive desorption experiments were conducted. In each desorption step, a portion of the supernatant was replaced with sterile PB to induce further chemical desorption.

In the desorption study, a two-site desorption model was used to analyze desorption data, assuming that the soil sorbent was composed of desorbable and non-desorbable sites. This model was modified

from a three-site desorption model that included equilibrium and non-equilibrium sites as desorbable sites [12,14,15]. In the two-site model, non-desorbable sites are described by:

$$S_{nd} = f_{nd} K_d C_e \quad \text{non-desorbable site} \quad (2)$$

while the release from desorbable sites follows the first-order expression:

$$dS_d/dt = \alpha [f_d K_d C - S_d] \quad (3)$$

where,  $S_{nd}$  and  $S_d$  ( $\mu\text{g kg}^{-1}$ ) are the sorbed concentrations in non-desorbable sites and desorbable sites, respectively,  $C$  ( $\mu\text{g L}^{-1}$ ) is the liquid-phase concentration,  $t$  is the desorption time (min), and  $\alpha$  ( $\text{min}^{-1}$ ) is the first-order desorption rate coefficient for the desorption site. In addition,  $f_d$  and  $f_{nd}$  are the desorption site and non-desorption site fraction, respectively.  $K_d$  is calculated from the sorption isotherm and  $f_{nd}$  is determined based on the plateau of the desorption rate profile, while  $f_d$  and  $\alpha$  are estimated by non-linear regression analysis of the desorption data, with the constraint that the sum of the site fractions is one.

## RESULTS AND DISCUSSION

### 1. Sorption

The sorption isotherms of PCE in soils are shown in Fig. 1. The concentrations of chemicals sorbed to the soil ( $S$ ) were plotted against the equilibrium aqueous concentration ( $C$ ) to determine the distribution coefficient. The PCE sorption isotherm was linear, with  $R^2$  values ranging from 0.93 to 0.95 over the concentration range employed in this study. The Freundlich equation ( $S = K_F C^{1/n}$ ) was used to evaluate the sorption linearity and  $n$  (a constant characterizing sorption isotherm curvature) values ranged from 1.04 to 1.17, resulting in linear sorption.

The sorption distribution coefficient ( $K_d$ ) and organic carbon normalized distribution coefficient ( $K_{oc}$ ) are presented in Table 3. The  $K_{oc}$  of PCE was obtained by normalization of the slope of the isotherm ( $K_d$ ) against the soil organic carbon fraction ( $f_{oc}$ ).  $K_d$  ranged from 0.60 to 4.94  $\text{L kg}^{-1}$ .

$K_d$  values are dependent on characteristics of the chemical and soils. Studies have shown that the soil organic matter acts primarily as a partition medium and that mineral matter acts as an adsorption sorbent in the sorption of nonpolar organic compounds [4,16–18].

The  $K_{oc}$  of compounds is correlated with their solubilities in water ( $S_w$ ) and octanol-water distribution coefficients ( $K_{ow}$ ). The correlation equation between  $K_{oc}$  and  $K_{ow}$  was reported by Chiou et al. [19] for relatively nonpolar compounds:

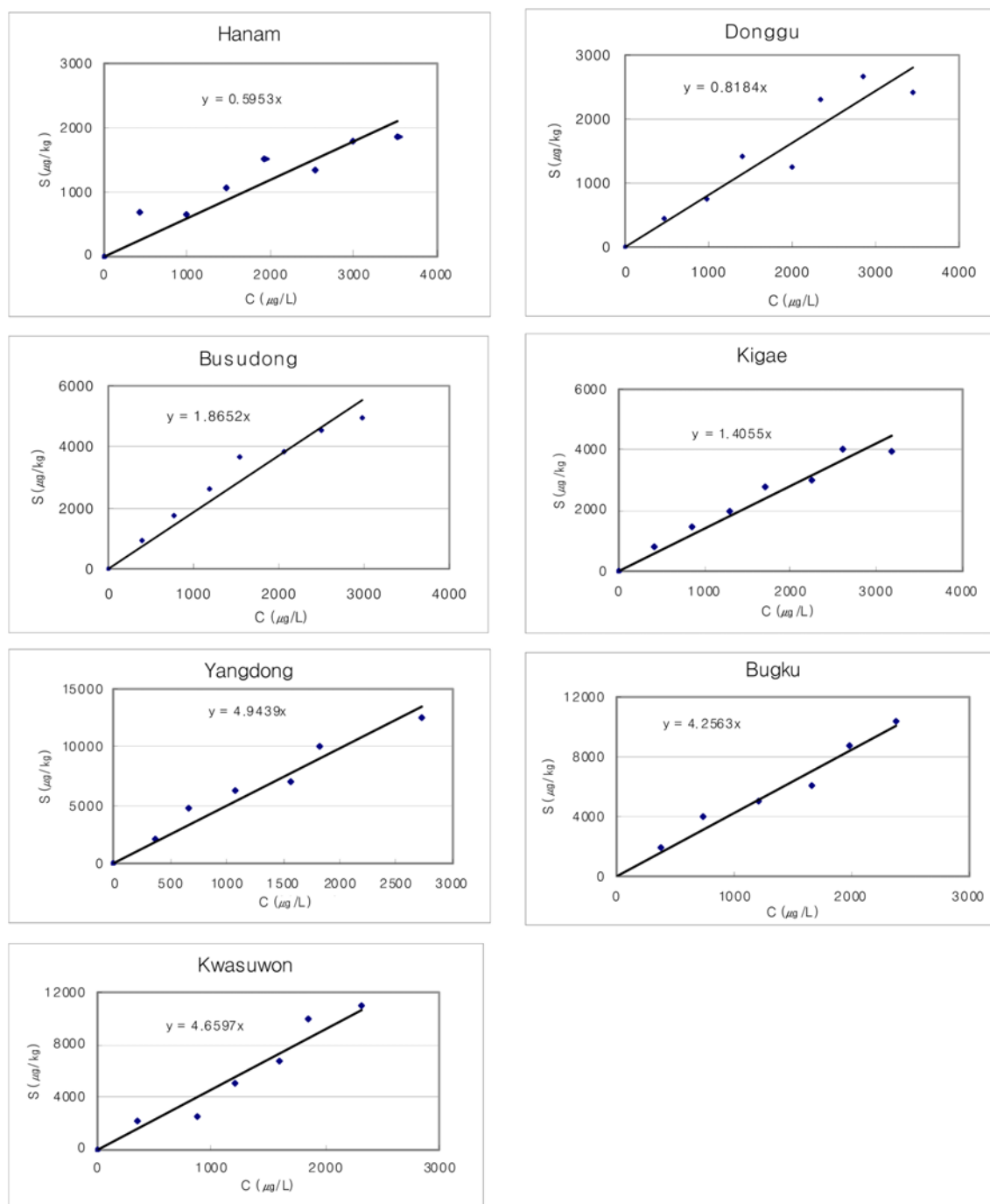


Fig. 1. Sorption isotherms of PCE in seven soils.

Table 3.  $K_d$  and  $K_{oc}$  of PCE in seven soils

Soils	$K_d$ (L kg <sup>-1</sup> )	$K_{oc}$ (L kg <sup>-1</sup> )
Hanam	0.60	333.3
Donggu	0.82	238.2
Busudong	1.87	183.3
Kigae	1.41	130.6
Yangdong	4.94	290.6
Bugku	4.26	150.5
Kwasuwon	4.66	159.6

$$\log K_{oc} = 0.904 \log K_{ow} - 0.779 \quad (4)$$

The  $K_{oc}$  for PCE predicted by the above equation is 37. This relationship assumes that the dominant sorbate-sorbent interaction is hydrophobic partitioning of sorbate into the soil organic carbon. The other reported correlation equation between  $K_{oc}$  and  $S_w$  is [20]:

$$\log K_{oc} = -0.557 \log S_w + 4.277 \quad (5)$$

The  $K_{oc}$  for PCE predicted by this equation is 427.

The estimated  $K_{oc}$  values observed in this study ranged from 130.6

to 333.3, which was between the values predicted by the two aforementioned equations (Table 3). The  $K_{oc}$  values tended to increase as the  $f_{oc}$  values decreased, suggesting that adsorption into the mineral surface or micropores in addition to partitioning into soil OC is not negligible in soils with low  $f_{oc}$ . Pore filling and capillary condensation in soils with low OC and partitioning into soil organic matter in soils with high OC have been reported as the major sorption processes [21].

Many studies have investigated the effects of soil organic carbon content on chemical partitioning in soils [4,22]. Karickhoff et al. [4] found that the distribution coefficients ( $K_d$ ) of hydrophobic compounds were directly related to the soil organic carbon content. While the fundamental phenomena governing the strong sorption of organic chemicals to geosorbents are unknown, the prevailing theory is that such sequestration occurs via interactions with different types of sorbent organic matter. As discussed by Gillette et al. [22], these organic matter components may take different forms, both amorphous and ordered, which makes differentiation of the specific roles of sorbent components extremely difficult and a priori predictions virtually impossible. It has been shown that binding and sorption processes are affected by the nature of the humic material. Organic matter in soils and sediments is commonly pictured as a three-dimensional network of polymer chains, with a relatively open, flexible structure perforated with voids. Within such a structure, the diffusive mass transfer of sorbate into the interior of organic matter is conceptually viable [17]. As reported by Chiou et al. [23], the nonlinear sorption of nonpolar solutes on soils results from adsorption onto a small amount of high-surface-area carbonaceous materials (HSACM), such as a charcoal-like substances or soot. The geosorbents containing HSACM show increased amounts of microporosity, which increases the sorption capacities of organic contaminants.

## 2. Desorption

The single dilution desorption of PCE in seven soils is presented in Fig. 2. As seen in the profile, apparent desorption equilibrium was approached rapidly within 1 hr. The desorption of PCE followed a biphasic pattern, rapid desorption within 1 hr and a slow desorption after 1 hr. Similarly, the desorption equilibrium of TCE from different soils was reportedly reached within 1 hr in other studies [1,2]. Pavlostathis and Jagal [2] reported that approximately 27% of the TCE in soil resisted desorption and the sorption was not reversible after a few days of sorption equilibrium. Thus, even short incubation times between chemicals and soils can limit desorption.

It has been well documented that sorption and desorption of many organic compounds follow a biphasic pattern, with an initial rapid phase followed by a prolonged slower phase. Such slow phase processes could have important effects on the fate of chemicals, reducing the effective movement of a solute and increasing the time re-

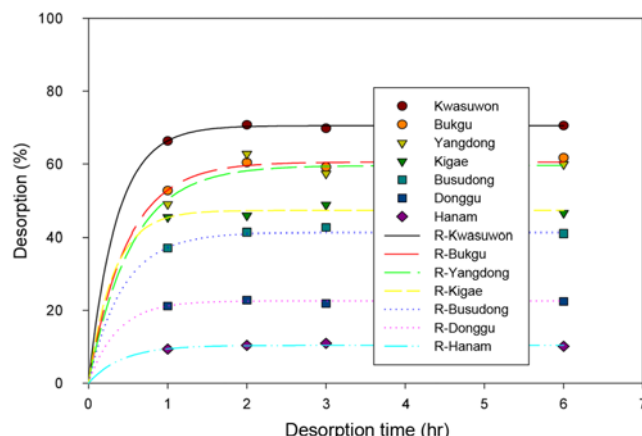


Fig. 2. Desorption data and regression obtained using a two-site desorption model of PCE in seven soils.

quired to flush a contaminated aquifer [24-26].

The slow release of the residual fraction was attributed to molecular diffusion from remote sites in the soil organic matter matrix [27]. The non-equilibrium of desorption is the result of rate-limited mass transfer of sorbate from the interior matrix of soils into the exterior surface. Such diffusional mass transfer is a function of three factors, the diffusivity of the diffusion species, the resistance to diffusion associated with the sorbent matrix, and the diffusion path length [17].

The two-site desorption model was used to fit desorption data and evaluate desorption parameters and the site fraction (Table 4). The results revealed that PCE was desorbed in two types, indicating the presence of a desorbable site and a non-desorbable site. Apparent desorption equilibrium was approached within approximately 1 hr for all combinations of soils and PCE. The model fit the experimental data, with  $R^2$  values ranging from 0.37 to 0.92. The fraction of desorbable (sum of equilibrium and non-equilibrium) sites tended to increase as the soil OC content increased, ranging from 0.085 to 0.570, suggesting that sorption into soils with high OC is more reversible. The non-desorbable site fraction increased as the OC decreased, suggesting that higher hysteresis in sorption/desorption process occur in soils with low OC.

Six consecutive dilution desorption experiments were conducted and desorption hysteresis was observed (Fig. 3). The existence of non-desorbable sites was observed in these experiments, demonstrating that desorption isotherms lie significantly above the sorption line in Fig. 3. The non-desorbable site fraction decreased as the OC content increased, and the evaluated fraction was similar to the estimated value obtained from the three site desorption model for desorption experiments, ranging from 0.915 to 0.430. Sorption

Table 4. Each site fraction and desorption rate coefficients of PCE in soils

	Hanam	Donggu	Busudong	Kigae	Yangdong	Bugku	Kwasuwon
$f_d$	0.085	0.181	0.322	0.388	0.439	0.432	0.570
$f_{nd}$	0.915	0.819	0.678	0.612	0.561	0.568	0.430
$\alpha$ (hr <sup>-1</sup> )	0.039	0.044	0.033	0.046	0.022	0.024	0.032
$R^2$	0.579	0.615	0.774	0.373	0.711	0.921	0.944

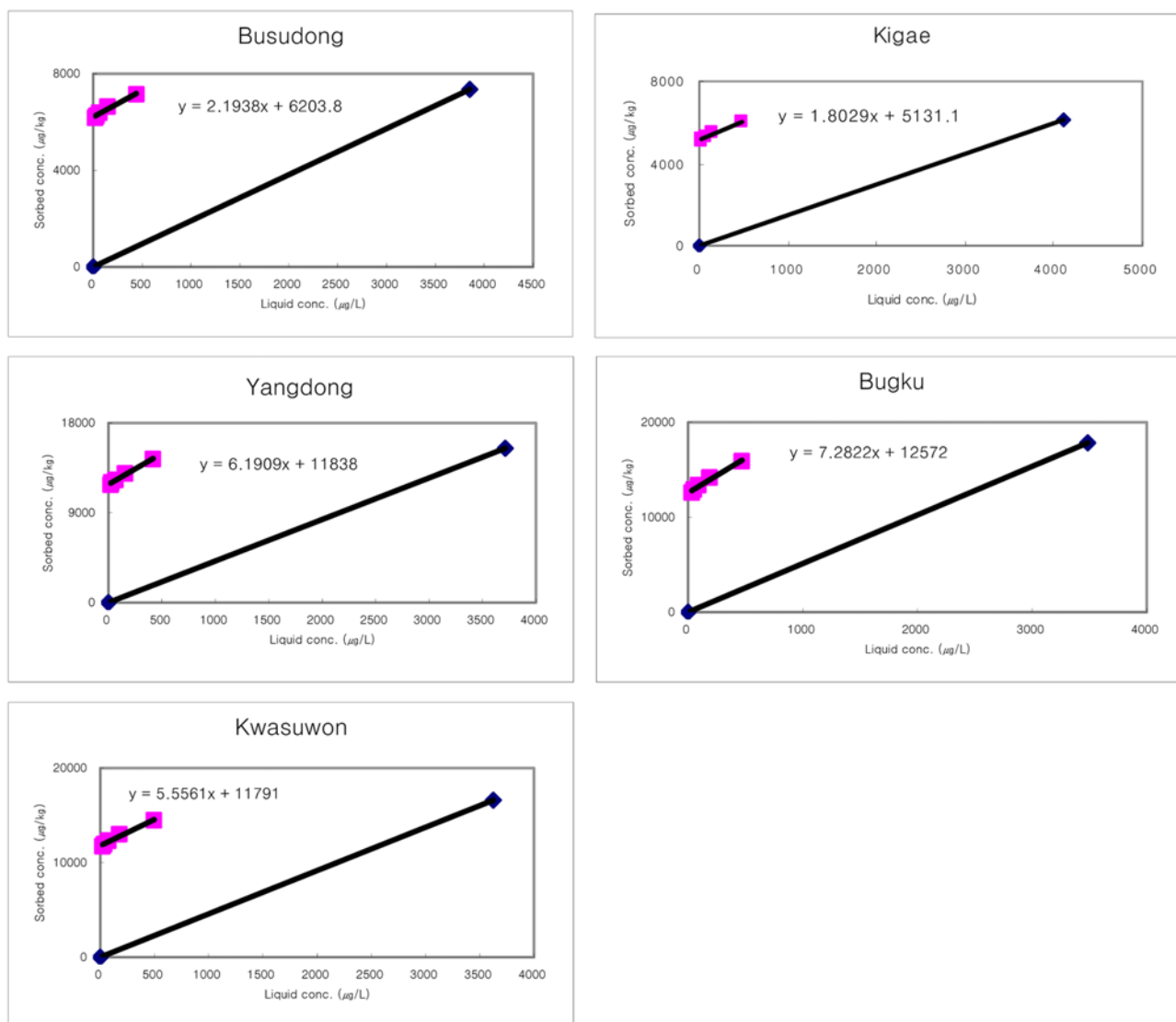


Fig. 3. Series dilution desorption of PCE in five soils.

and desorption could be clearly described as irreversible processes in this study.

Hysteresis is not consistent with classical equilibrium models that assume sorption processes to be completely reversible [24,25,28]. The hysteresis of sorption and desorption has been explained variously as the result of (i) irreversible chemical binding or sequestration of solute to certain components of soil aggregates, such as soil organic matter; (ii) entrapment of sorbed molecules in meso- and microporous structures within inorganic components of soil aggregate; and (iii) entrapment of sorbed molecules in SOM matrices. The observation of a high non-desorbable site fraction in soils with low OC may be explained by entrapment of PCE in mineral porous structures because estimated  $K_{oc}$  values of PCE are higher in soils with low OC than those with high OC, suggesting that the sorption onto the mineral surface and pores is not negligible. The observation of a low non-desorbable site fraction in soils with high OC suggests that sorption of PCE into soil organic matter is more reversible than sorption into soil minerals. The entrapment fraction of PCE in SOM was not as high as in the soil minerals in this study.

## CONCLUSION

The sorption distribution coefficient ( $K_d$ ) of PCE ranged from 0.60 to 4.66  $\text{L kg}^{-1}$  and the isotherm plots were nearly linear, with  $R^2$  values ranging from 0.93 to 0.95.  $K_d$  tended to increase as the soil OC increases, but  $K_{oc}$  tended to decrease, suggesting that adsorption on the mineral surface is not negligible in soils with low OC. Sorption/desorption of PCE was not completely reversible for even short incubation times due to the presence of irreversible and slowly desorbing sites. The desorbable and non-desorbable site fractions and desorption rate coefficients of PCE for all soils were enumerated from desorption data. Non-desorbable sites and sorption hysteresis were also observed and demonstrated by serial dilution desorption experiments. Additionally, non-desorbable sites and sorption hysteresis were observed and demonstrated by serial dilution desorption experiments. The desorbable site fractions of PCE increased and non-desorbable site fractions decreased as the soil OC increased. It is suggested that partition of PCE into soil organic carbon is more reversible than adsorption on soil minerals.

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