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SORPTION OF NONIONIC ORGANIC COMPOUNDS BY ANTHROPOGENIC ORGANIC PHASES IN SOIL-WATER SYSTEMS

By

Shaobai Sun

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

SORPTION OF NONIONIC ORGANIC COMPOUNDS BY ANTHROPOGENIC ORGANIC PHASES IN SOIL-WATER SYSTEMS

By

Shaobai Sun

The role of residual petroleum or PCB oils (commercial Aroclor) present in soils in sorptive uptake of nonionic organic compounds (NOCs) from water has been studied and compared with the role of the natural soil organic matter (SOM). The NOCs involved in this study were pentachlorophenol, toluene, and 2-chlorobiphenyl. Both residual petroleum and PCB oils functioned as highly effective partitioning media for NOCs. The former is approximately as effective as octanol which is about 10 times more effective than the natural SOM for pentachlorophenol and toluene; the latter is approximately 67 times more effective than the natural SOM and about 3.5 times more effective than octanol for 2-chlorobiphenyl.

The effects of petroleum sulfonate-oils surfactants (commercial Petronates) on sorption of naphthalene, phenanthrene, and 2,2',4,4',5,5'-hexachlorobiphenyl in soil-water systems has been investigated. In the range of Petronate equilibrium aqueous concentrations from 0 to 170 mg l⁻¹, a slight increase of the soil-water distribution coefficient (K) for naphthalene, a moderate decrease of K for phenanthrene, and a large decrease (more than 200-fold) of K for 2,2',4,4',5,5'-hexachlorobiphenyl were observed. The degree of the decrease of K inversely corresponded to the water solubilities of these compounds. We have developed two models that can predict accurately the apparent soil-water distribution coefficients of NOCs in soil-Petronate-water systems, by simply knowing the Petronate sorption isotherm and couple of well-documented or easily estimated constants.

A two-domain mass transfer model has been mathematically developed for the study of desorption of NOCs from soil into water. This model attempts to interpret the data from gas-purge experiments, and obtain some important kinetic parameters, such as the mass transfer (desorption) rate constant (k_d). The conceptualization and mathematical derivation of this model can be easily employed for the sorption-retarded chemical or biological reactions in soil-water systems.

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Literature Review and Research Objectives

It is well known that the sorption and desorption of a chemical by soils and sediments in soil-water systems will influence transport and transformation of that chemical in the environment. Knowledge of the thermodynamic and kinetic aspects of the sorption and desorption of chemicals in soil-water systems, and the factors that affect these processes is essential in understanding and predicting the fate of contaminants in the real world, and provides a basis for the design of highly efficient remediation technologies for contaminated soils.

[1] Sorption of Nonionic Organic Compounds by Natural Soil Organic Matter in Soil-Water Systems

The isothermal uptake of chemicals by soils and sediments from water can be described by many models, such as the most popular Langmuir and Freundlich equations. It has been demonstrated that the uptake of nonionic organic compounds (NOCs) in soilwater systems usually displays linear isotherms, which can be fitted in a Freundlich model with the exponential parameter (n) equal to one:

$$C_s = K(C_e)^n \stackrel{n=1}{\Rightarrow} KC_e \tag{1-1}$$

where C_s and C_e are the solute equilibrium concentrations in the soil and aqueous phases, respectively, K is the distribution coefficient, and n is a constant accounting for the isotherm curvature. In the following discussion, several terms are used that need to be defined specifically:

- Adsorption the condensation of chemical molecules or ions (sorbate) from solution onto a solid surface or interior pores of soil minerals or other soil components (sorbent) by physical or chemical interactions, such as van der Waals forces, hydrogen bonding, ion-pair formation, *etc*.
- Sorption the uptake of the solute by soils and sediments from water without a concern of the specific mechanisms.
- **Partitioning** a sorptive model (mechanism) in which the solute permeates (*i.e.*, dissolves into) the network of an organic phase by weak forces common to solution (*e.g.*, van der Waals forces and other hydrophobic forces).
- **Distribution** the overall allotments of the solute in the soil phase and the aqueous phase at steady state or equilibrium.

Since the middle 1960s, soil scientists have noticed that the extent of soil uptake for nonionic organic compounds (contaminants and pesticides) is closely related to the organic matter content of the soil (Bailey and White, 1964; Goring, 1967; Lambert, 1968; Hamaker and Thompson, 1972; Saltzman *et al.*, 1972; Browman and Chesters, 1977). Since then, the role of natural soil organic matter (SOM) in sorption of nonionic organic compounds (NOCs) in soil-water systems has been extensively studied and established. In 1979, Chiou *et al.* suggested that the transfer of NOCs from water to soil may be described in terms of solute partitioning into the SOM. In that study, experimentally determined SOM-water distribution coefficients (K_{om}) were obtained by dividing the slopes of the linear isotherms (*i.e.*, the soil-water distribution or sorption coefficient K) by the SOM content of soil. The SOM-water distribution coefficient K_{om} was highly correlated to the water solubility (S) of the solute and its octanol-water partition coefficient (K_{ow}). The data covered a wide range of S and K_{om} values: approximately 8.9×10^{6} times difference for S and 1.2×10^{4} times difference for K_{om} . Fifteen NOCs were evaluated ranging from the very poorly water soluble 2,2',4,4',5,5'-hexochlorobiphenyl to 1,2-dichloroethane which has comparatively high water solubility among common NOCs. The linear fit of log K_{om} to log S or log K_{ow} suggests a partitioning mechanism in which the NOC distributes itself between water and SOM, based on its solubility in each of these two phases. Hence sorption by SOM was viewed as a dissolution phenomena, not as a surface adsorptive mechanism (Chiou *et al.*, 1979).

Karickhoff *et al.* reported in 1979 that (a) the sorption of hydrophobic compounds (aromatic hydrocarbons and chlorinated hydrocarbons, with water solubilities from 500 parts per trillion to 1800 parts per million) by pond and river sediments exhibited linear isotherms over a broad range of aqueous-phase pollutant concentrations, (b) the partition coefficients were relatively independent of sediment concentrations and ionic strength in the suspensions, and (c) the partition coefficients were directly related to fractional organic carbon content (f_{OC} , w/w) for given particle size isolates in the different sediments. They comprehensively defined the concept of the OC-normalized partition coefficients, K_{OC} , (which is convertible to SOM-normalized K_{OM} and will be discussed in more detail later in this chapter) and demonstrated that although K_{OC} was dependent on the particle size, an apparent K_{OC} value over the whole sediment could be experimentally determined (Karickhoff *et al.*, 1979). Importantly, K_{OC} (or K_{OM}) values from different soil and sediments seem to converge on a single value, and hence K_{OC} (K_{OM}) becomes a unique physical constant of the particular NOC, as will be discussed in detail below. The role of soil minerals in the sorption of these NOCs was also found to be unimportant.

More experimental results and thermodynamic analyses (Chiou *et al.*, 1979, 1983; Karickhoff *et al.*, 1979; Karickhoff, 1981, 1984; Schellenberg *et al.*, 1984; Chiou, 1989a, 1989b) strongly support that the partitioning is the predominant mechanism accounting for the uptake of NOCs to soil from water. The partitioning process basically resembles a dissolution process of NOCs from a hydrophilic medium (*e.g.*, water as an extreme example) into a relatively hydrophobic medium (*e.g.*, SOM). Evidence for the partitioning theory can be summarized as follows:

- (a). The uptake of a NOC from water by soils exhibits linear isotherms which extend from zero aqueous concentration to the water solubility of the NOC.
- (b). The water solubility of a NOC is the primary factor that determines the distribution coefficient of the NOC in soil-water or sediment-water systems.
- (c). No competitive effect on the sorption of NOCs is observed in a multisolute system.
- (d). Low and constant sorption heat change (Δ H) accompanies the uptake process of NOC sorption from water by soils.

Adsorption of NOCs by soil minerals have been shown to be important when *dry* or *subsaturated* soils are used as adsorbents (Chiou *et al.*, 1985). However, adsorption models run into difficulty in attempting to interpret the sorption of NOCs in water-saturated soils. In water-saturated soils, due to either hydration of exchangeable cations or the preferential adsorption of water onto the mineral surfaces, the soil minerals are

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effectively deactivated as NOC adsorbent surfaces by a film of water which blocks the direct access of NOC molecules to the mineral surfaces. Therefore, the adsorption of NOCs by water-saturated soil minerals is suppressed by water, and hence the soil uptake consists mainly of solute partitioning into SOM (Chiou, 1989b). Figure 1-1 graphically illustrates the partitioning model.

Because in most soil-water systems the distribution coefficients, K, of NOCs are primarily determined by the SOM content of the soils, the apparent K values can be normalized for the fractional SOM contents, f_{om} (w/w), to define a new constant called *SOM-water partition coefficient*, K_{om} :

$$K_{om} = \frac{K}{f_{om}} \tag{1-2}$$



Figure 1-1. Conceptualization of the partitioning model.

It has been demonstrated that K_{om} values obtained for a given NOC on different soil converge to a relatively constant value such that K_{om} becomes a unique constant characteristic of the NOC (Karickhoff *et al.*, 1979; Karickhoff, 1981, 1984; Chiou, 1989a). The relative invariance of the K_{om} value suggests that the SOM content controls uptake of NOCs by soils, and that SOM from different soils behaves similarly as a partition medium for NOCs. The simple concept established here renders a simple way to predict the distribution coefficients of NOCs in soil-water systems. Knowing the K_{om} value and the fractional SOM content, f_{om} , the distribution (partition) coefficient, K, can be calculated:

$$K = K_{om} \times f_{om} \tag{1-3}$$

In laboratory, however, the SOM is usually measured as fractional organic carbon content, f_{OC} . Fortunately, substantial study on SOM has demonstrated that the statistical average of carbon content of the humic and fulvic materials is approximately 57.5% (Stevenson, 1982), and hence provided a simple way to convert f_{OC} to f_{Om} , and (as preferred) K_{Om} to K_{OC} :

$$f_{om} \approx 1.74 \times f_{oc}$$

$$K_{om} \approx \frac{K_{oc}}{1.74}$$
(1-4)

As mentioned earlier, the uptake of NOCs by soils from water is believed to be a mass transfer process (partitioning/dissolving) from the aqueous solution to a relatively hydrophobic medium (SOM). Thus, it is expected that a more hydrophobic NOC which has lower water solubility (S) and higher octanol-water partition coefficient (K_{OW}) should

show higher affinity in SOM phase and consequently have a greater K_{OM} value. As early as in 1960s, a linear relationship between the logarithms of the aqueous solubilities of organic liquids and their octanol-water partition coefficients was reported (Hansch *et al.*, 1968). In further investigation of the relationship among K_{OM} (K_{OC}), S, and K_{OW} , many empirical equations have been proposed to estimate the K_{OM} and K_{OC} values from S or K_{OW} (Chiou *et al.*, 1983; Karickhoff *et al.*, 1979; Schellenberg *et al.*, 1984). Several examples are shown here:

$$log K_{oc} = -0.54 log S + 0.44$$

$$log K_{oc} = 1.00 log K_{ow} - 0.21$$

$$log K_{om} = -0.729 log S + 0.001$$

$$log K_{om} = 0.904 log K_{ow} - 0.779$$

(1-5)

These simple linear equations provide a practical way to calculate the K_{om} or K_{oc} value for a given NOC, because S and K_{ow} values are usually more available in the literature. Once K_{om} is known or has been estimated, the NOC distribution coeffcient K in any soilwater systems can be estimated by knowing the SOM content of the soil (Equation 1-3). The K value defines the actual soil-water distribution of a NOC.

In some recent studies the significance of the quality of SOM in determining the sorptive behavior of SOM for NOCs has been reported. It appears that the efforts are currently focused on two major aspects: (a) the O/C, H/C and H/O ratios of the SOM (Grathwohl, 1990) and (b) the water or solvent content of the SOM (Rutherford and Chiou, 1992). However, these studies were done using soils (peat or muck) with very high SOM content (usually greater than 18% w/w). For the soil-water systems we have been working on (where the SOM content is below 3% in most of the cases) it does *not* appear to be necessary to modify the partitioning model for the SOM makeup. As a rule,

the K_{om} values do not vary by more than a factor of 2 to 3 among soils from different origins.

[2]. Surfactant Effect on Solubilities of Nonionic Organic Compounds in Water

Surfactants are surface active agents that can significantly reduce the free energy, ΔG , on the phase-boundary in a multi-phase system. A typical surfactant is an amphiphilic molecule which consists of a hydrophobic group (*e.g.*, long alkyl chain) and a hydrophilic group (*e.g.*, sulfonate, ammonium, hydroxyl, carbonyl, *etc.*). Commercial surfactants are available in any of the following forms: (a) neutral (*e.g.*, Triton X-100), cationic (*e.g.*, cetyltrimethylammonium bromide or CTAB), or anionic (*e.g.*, sodium dodecyl sulfate or SDS) compound, or (b) a mixture of a specific compound and other auxiliary components (*e.g.*, Petronates).

The thermodynamic properties of conventional surfactants in water solution, such as reduction of surface tension and formation of micelles, have been extensively studied and documented (Di Toro *et al.*, 1990; Porter, 1990; Jafvert, 1991; Jafvert and Heath, 1991). Generally, as shown in Figure 1-2, when the surfactant concentration is low in the solution, the surfactant molecules (monomers) predominantly concentrate and spread out on the surface, and hence greatly reduce the surface tension in a linear manner (line A-B). When a certain surfactant concentration is reached (point B), the surface is saturated with surfactant molecules, which then start forming micelles inside the bulk solution, and the reduction of surface tension levels off (line B-C). This characteristic concentration (B point) of a given surfactant in aqueous solution is called *critical micelle concentration*



Figure 1-2. Illustration of critical micelle concentration, CMC.

(CMC) of the surfactant.

The immense quantity of surfactants used in industrial and domestic applications renders certain environmental concerns: while some surfactants themselves could become potential contaminants in surface and ground water, surfactants generally are expected to alter the behavior of other organic contaminants in the environment. One extensively studied and environmentally important property of surfactants is their solubilizing effects on relatively water-insoluble chemicals. The water solubility enhancement of NOCs by surfactants may have both deleterious and beneficial impacts in the environment. For instance, it could accelerate the transport of NOCs from the top soil to the ground water. On the other hand, environmental remediation technologies such as soil-washing frequently employ surfactants for the solubilization of NOCs bound to soils. Perhaps in the future surfactants may be used to enhance bioavailability of contaminants to microbial degraders. With regard to the latter, however, the inhibition of phenanthrene

mineralization by some surfactants in soil-water systems, probably due to some kind of unfavorable micelle-membrane interactions on biodegraders, has been reported (Laha and Luthy, 1991). This will need to be overcome to successfully employ surfactants to enhance biodegradation rates.

The water solubility enhancement of NOCs by surfactants is mathematically described (Kile and Chiou, 1989) as:

$$\frac{S^*}{S} = 1 + X_{mn} K_{mn} + X_{mc} K_{mc}$$
(1-6)

where, S^{*} is the apparent solute solubility at the total stoichiometric surfactant concentration of X (= $X_{mn} + X_{mc}$), S is the intrinsic solute solubility in pure water, X_{mn} and X_{mc} are the fractional concentrations of surfactant as monomers and micelles, respectively, and K_{mn} and K_{mc} are the monomer/water and micelle-water partition coefficients of the solute, respectively. It has been demonstrated that Kmc is generally 2 to 3 orders of magnitude greater than K_{mn}, showing that the surfactant micelles have much greater capability to enhance the water solubility than surfactant monomers. Thus, for conventional surfactants, the formation of micelles appears to be a critical point (Figure 1-2), above which the water solubility enhancement of NOCs can be significantly observed (Kile and Chiou, 1989; Chiou et al., 1991; Edwards et al., 1991). The importance of CMC in water solubility enhancement may be accounted for by two possible mechanisms: (a) at CMC the surface tension is greatly reduced and the solute movement across the phase boundary may be accelerated, and (b) micelles serve as an effective partition and hosting medium for NOCs. The CMC for conventional neutral, cationic and anionic surfactants typically lies in a range of 100 to greater than 1000 mg l⁻¹ (Kile and Chiou, 1989). After examining the partition of 13 NOCs and molecular oxygen in a

dodecylsulfate-water system, Jafvert (1991) proposed an empirical equation that can be employed to estimate (on a mole fraction basis) K_{mc} of a given NOC by knowing its K_{ow} value:

$$\log K_{mc} = 1.04 \log K_{ow} - 0.126 \tag{1-7}$$

The water solubility enhancement is usually inversely proportional to the intrinsic water solubility (S), that is, the smaller the S is, the greater the enhancement will be. Sometimes the water solubility enhancement of NOCs that have very small S can be dramatic. For instance, Kile and Chiou (1989) reported that the apparent water solubility of 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane (DDT, S = 5.5 μ g l⁻¹ at 25 °C) was boosted to over 1000 μ g l⁻¹ at a surfactant (TX100) concentration of 300 mg l⁻¹. 1,2,3-trichlorobenzene (TCB), which has a much higher water solubility (S = 18 mg l⁻¹ at 25 °C) exhibited an apparent water solubility of 35 mg l⁻¹ at the same TX100 concentration, corresponding to only a 2-fold increase.

When a surfactant is added to a soil-water system, it is expected that the surfactant itself will have an equilibrium distribution between the aqueous phase and the soil phase. Some nonionic surfactants (*e.g.*, Igepal, CA-720, Tergitol NP-10, Triton X-100, Brij 30) are demonstrated to have Freundlich type of sorption isotherms (Equation 1-1) with K ranging from 1.1 to 6.2×10^7 and n ranging 0.56 to 2.1 (Liu *et al.*, 1992).

Although most of the conventional surfactants have a clear CMC, there are some surfactants that do not possess a characteristic CMC. For instance, petroleum sulfonateoil surfactants (PSO, or commercially called Petronates) do not exhibit a distinct CMC, and the extent of NOC solubility enhancement is linearly proportional to the Petronate concentration, starting from nearly zero to 150 mg l^{-1} for DDT and to 500 mg l^{-1} for TCB (Kile and Chiou, 1990). Unlike conventional surfactants, Petronates are mixtures of petroleum sulfonated hydrocarbons and free mineral oils, which form a stable emulsion in aqueous solution and thus behave much like a bulk phase in concentrating NOCs. Another promising property of Petronates is that they seem to exhibit relatively low toxicity regarding the bioactivity of naphthalene and phenanthrene degraders in aqueous solution (according to some unpublished work done by D.P. Breakwell in S.A. Boyd's laboratories, 1992).

[3]. Models of Sorption-Desorption Kinetics of Nonionic Organic Compounds in Soil-Water systems

In more than two decades, the thermodynamics of sorption of NOCs in soil-water and sediment-water systems has been studied extensively and amply documented (see the review in Section [1] of this chapter). On the other hand, due to the theoretical complication and experimental difficulty, sorption kinetics have not been investigated in a sufficient manner until this decade. In recent years, however, this field has attracted more and more attention and interest, and numerous research papers have been published (Rao *et al.*, 1979, 1980; Karickhoff, 1980; Karickhoff and Morris, 1985; Wu and Gschwend, 1986; Steinberg *et al.*, 1987; Lee *et al.*, 1988; Brusseau *et al.*, 1989, 1991; Pignatello, 1989; Shorten *et al.*, 1990; Ball and Roberts, 1991a, 1991b).

An important property of many sorption-desorption equilibria is that the uptake and release of NOCs in a soil-water system appear not to follow the same pathway. In other words, the sorption isotherm and the desorption isotherm do not overlap, as illustrated in Figure 1-3. This is known as *nonsingularity* (or, in some literature,

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Figure 1-3. Nonsingularity of sorption-desorption isotherms.

hysteresis) of sorption-desorption equilibria. An ideal NOC-soil-water system at true equilibrium will yield a characteristic distribution coefficient (*i.e.*, the slope of the isotherm) that is constant no matter whether the equilibrium is approached from a sorptive (uptake) or desorptive (release) direction (Pignatello, 1989). However, actual distribution coefficients in the sorptive direction seem to be smaller than those in the desorptive direction in real situations, which suggests the reality of slow desorption of NOCs in soilwater systems. Studies show that even at the sorptive direction a considerable time period (days and months) is needed to establish true equilibrium in some cases (Ball and Roberts, 1991a; Liu *et al.*, 1992). The slow sorption-desorption processes have a great impact on the transport and transformation of NOCs in the soil and aquatic environments, and usually become the key steps that limit the rate of the chemical and biological transformation reactions (which generally require much less time, *e.g.*, hours and days) to reach equilibrium or steady state (Rijnaarts *et al.*, 1990; Brusseau *et al.*, 1991; Scow and Hutson, 1991). Mathematically modeling sorption-desorption processes has been one of the most active field for many years. Universally, all the sorption-desorption models contain temporal and concentration variables. However, mathematical approaches and requirement of spatial parameters are different from model to model. At present, these models can be divided into two general categories.

- (a). Diffusion models emphasize solute diffusion processes (inside bulk solution, SOM network and/or mineral micropores), in which many spatial (e.g., average radius of soil particles, porosity, tortuosity) parameters are critical and necessary (Wu and Gschwend, 1986; Steinberg et al., 1987). Fick's laws (first and second) are the basis for derivation of the system equation (Crank, 1975). These models treat the sorption-desorption processes from a microscopic point of view, and hence require a lot of microstructural information of the systems, which sometimes are difficult to measure or estimate.
- (b). Overall mass transfer models view the sorption-desorption processes on a macroscopic scale. That is, these models provide information about the fractional amount of solute that travels across the phase boundary at a given time (*i.e.*, mass transfer rate), without a detailed concern that how the transfer is made (Karickhoff and Morris, 1984; Brusseau *et al.*, 1990; Rijnaarts *et al.*, 1990). The solute mass balance serves as the start point in the modeling procedure. This type of models is relatively simple, and usually requires fewer system parameters and structural details.

Frequently used laboratory experiments for the study of sorption-desorption kinetics include: (a) the batch method, which is simple but measures the solute concentration only in a periodical way (Steinberg *et al.*, 1987; Rijnaarts *et al.*, 1990; Ball and Roberts, 1991); (b) the gas-purging method, which monitors the system continuously but is only good for volatile compounds (Karickhoff, 1980; Wu and Gschwend, 1986;

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Brusseau et al., 1990); and (c) the miscible-displacement (column flow) method, which simulates the field situation best but requires a relatively large amount of sorbent (Lee et al., 1988; Brusseau et al., 1990).

In this dissertation we will focus on an overall mass transfer model, which is specially developed for gas-purge methodology.

[4]. Research Objectives

Research Objective #1 To investigate the individual roles of anthropogenic organic phases (AOPs) and the natural soil organic matter in the sorption of nonionic organic compounds in soil-water systems. Several soils heavily contaminated with residual petroleum and PCB oils (commercial Aroclor) from actual field sites will serve as the sorbents. The effectiveness of the anthropogenic organic phases as partitioning media for NOCs will be evaluated and compared with that of natural soil organic matter. Theoretical prediction of the distribution coefficients in the multi-phase systems will be examined for the agreement with actually measured values. Finally, an approach to experimentally obtain the AOP-water partition coefficients, including mathematical derivation and laboratory techniques will be developed.

[Chapters 2 and 3]

Research Objective #2 To study the effect of surfactants on the sorption of naphthalene, phenanthrene, and PCB congeners in Oshtemo(B)-water system. Due to their unique properties described previously, especially their ability to enhance the apparent solubilities of NOCs, petroleum sulfonate-oil surfactants (PSOs, *e.g.*, commercial

Petronates) will be used in this work. First, the sorption of PSOs onto the soil from water will be examined. Then, the sorption of NOCs in the soil-PSO-water systems, in terms of the apparent soil-water distribution coefficients (K^*), will be measured and analyzed. Models that can accurately predict the K^* values will be developed.

[Chapter 4]

Research Objective #3 To develop the analytical solution of an overall mass transfer model of the sorption-desorption of NOCs in soil-water systems. This work will be primarily based on the conceptualization of two-domain models which have been successfully used in many sorption-desorption kinetics studies (see Introduction of Chapter 5). In coordination with other colleagues' current research, this model will be able to directly interpret experimental data obtained using the gas-purge method. Application of this model will be demonstrated using actually measured gas-purging data. [Chapter 5]

Residual Petroleum and Polychlorobiphenyl Oils as Sorptive Phases for Organic Contaminants in Soils

[1] Introduction

The natural organic matter fraction of soils and sediments controls the sorptive uptake of nonionic organic contaminants (NOCs) and pesticides from water (Chiou *et al.*, 1979, 1983; Karickhoff *et al.*, 1979). Mechanistically, SOM appears to function as a partition medium for the dissolution of NOCs (Chiou *et al.*, 1979, 1983). The uptake of NOCs by soils and sediments can be described by a simple linear equation of the form:

$$C_s = KC_e \tag{2-1}$$

where C_s is the solute concentration in soil, C_e is the equilibrium solute concentration in water, and K is the soil-water distribution coefficient. K can be normalized for the fractional organic matter content of soil (f_{om}) to define a new constant K_{om} :

$$K_{om} = \frac{K}{f_{om}} \tag{2-1}$$

It has been demonstrated that Kom values obtained for a compound on different soils

converge to a relatively constant value such that K_{om} becomes a unique constant characteristic of the compound (Chiou, 1989). The relative invariance of the NOC K_{om} value demonstrates that the organic matter fraction controls uptake of NOCs by soils, and that organic matter from different soils behaves similarly as a partition medium for NOCs.

The established relationship between organic matter content and sorption of NOCs has greatly simplified the predictions of sorption of NOCs by soils and sediments. Once K_{om} is known for a NOC, the K value on any soil or sediment can be estimated simply by knowing f_{om} . Fate and transport models now routinely use K_{om} values to assess the leaching potential of organic contaminants and pesticides.

In this study, the role of residual petroleum as a highly effective sorptive phase for NOCs in soil-water systems was evaluated and compared to that of the natural SOM. A case in which the PCB oils appear to function as an even more effective partitioning medium for NOCs was also introduced. The soil-water distribution coefficients of pentachlorophenol (PCP), toluene, and 2-chlorobiphenyl (2-CB) in actual field soils contaminated with such anthropogenic organic phases (AOPs) are presented here. The results show that both the natural SOM and residual petroleum components of these soils act as partition media for organic solutes, with the latter being approximately 10 times more effective as a sorptive phase.

[2] Materials and Methods

Soils. Four soils and one soil particle-size fraction were used in the study. Two soils, designated MG and UP, are from the actual wood-preserving sites in Minnesota and

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Michigan, respectively, and are contaminated with PCP. The MG silt + clay sample (designated MG-SC) was obtained by allowing the sand-size particles to settle out of a an aqueous slurry for one minute and then filtered. The soil denoted PP is contaminated with Aroclor 1254 as a result of a transformer spill as a Minnesota power plant. The Capac soil is an uncontaminated subsurface soil (B_t horizon) with a high clay content. All the soils and soil particle-size fraction were air-dried before use.

Soil Properties. The soil properties were measured using the well-established methods.

- (a). The native PCP content soil was determined as described previously (Mikesell and Boyd, 1988). A certain amount of the soil (depending on its native PCP concentration) was extracted with methylene chloride in a Soxhlet apparatus for 20 hours. The methylene chloride solution then was back-extracted with 0.1 M KCO₃ (pH = 12) twice. The two parts of KCO₃ extract were mixed and brought to an appropriate volume, and analyzed by high-performance liquid chromatography (Waters, Milford, MA) to determine the PCP concentration.
- (b). The PCB-oil content was measured using the method described previously (Quensen et al., 1988). The soil was extracted with a mixture of hexane and acetone (9:1 v/v) in a Soxhlet apparatus for 24 hours, and then was treated using a routine clean-up procedure. The quantitative congener analysis was performed using an HP 5890A gas chromatography (Hewlett Packard, Avondale, PA) with an electron capture detector.
- (c). The oil/grease content was determined by mixing 20 g of air-dried soil (acidified to pH 2 with concentrated HCl) and 10 g of MgSO₄. The sample was extracted with 200 ml of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon) in a Soxhlet apparatus for 20 hours. The extract was backextracted twice with 0.1 M KCO₃ (pH = 12) to remove the native PCP. Then the organic extract was filtered, dried with anhydrous MgSO₄, and

evaporated. The oil/grease remaining was determined gravimetrically.

- (d). A 1:2 soil-water mixture was used for pH determination. The pH value of the soil solution was read to the third place after the decimal point on a high-precision pH meter.
- (e). The organic carbon content (OC %) was determined by measuring CO₂ released from combustion. The analysis was done by Huffman Laboratories, Inc., Golden, CO. The sample was previously extracted with methylene chloride to remove PCP or PCBs and oil/grease.
- (f). The soil particle-size analysis was by the Michigan State University Soil Testing Laboratory, East Lansing, MI.

Sorption Isotherms. The MG, MG-SC, PP, and UP isotherms were obtained by using ¹⁴C-labeled PCP, toluene, or 2-CB (all from Sigma Chemical Co., St. Louis, MO) and the concentration plotted (Figure 2-1) are for the ¹⁴C compound. The Capac isotherm was obtained by adding 5 μl of a methanol solution of ¹⁴C PCP and different volumes of nonlabeled PCP solution to soil. All the isotherms were measured using the standard batch equilibration technique. 2 to 10 g of air-dried soil was mixed with 20 ml of distilled water, and various amounts of ¹⁴C-labeled PCP, toluene or 2-CB in screw-top glass centrifuge tubes that were closed with aluminum foil lined caps. After being continuously shaken for 24 hours at 22 °C, the samples were centrifuged at a relative centrifugal force (RCF) of approximately 7500 for 20 minutes. The solute concentration in the aqueous phase (supernatant) was measured by liquid scintillation counting (Packard 1500 TRI-CARB Liquid Scintillation Analyzer, Downers Grove, IL). A recovery test was conducted separately, and the average recovery was great than 96 %.

[3] Results and Discussion

Table 2-1 lists the chemical structure, molecular weight, log K_{om} , and log K_{ow} of the solutes used in this study. Table 2-2 summaries the soil properties. Table 2-3 shows the measured solute equilibrium concentrations in the aqueous phase, C_e , and in the soil phase (calculated by difference), C_s . The data in Table 2-3 were plotted as C_s against C_e (*i.e.*, the isotherms, shown in Figure 2-1) to determine the soil-water distribution coefficient, K.

In studies of PCP sorption by PCP-contaminated soils from former woodpreserving sites we observed that the measured PCP distribution coefficients were much higher than the values predicted in the conventional manner from the K_{om} of PCP and the SOM content. PCP-contaminated soils are numerous, with over 500 sites in the United States alone (Cirelli, 1978), and these soils typically contain residual petroleum that was used as a carrier of PCP. Many contaminated soils and sediments contain residual oil/grease due to the widespread transport, use, and disposal of petroleum products. Terrestrial petroleum pollution has been estimated at 1.7 - 8.8 million metric tons per annum. Although petroleum biodegradation does occur, it is often far from quantitative, leaving a residual petroleum component. (Bartha, 1986).

For the sorption of organic contaminants by soils containing residual petroleum, we hypothesized that these soils may be treated as a three-component system consisting of (a) an inert mineral phase, (b) a sorptive natural SOM phase, and (c) a highly sorptive residual petroleum phase. The potential effectiveness of the two sorptive phases can be evaluated by comparing the SOM partition coefficient, K_{om} , to the oil-water partition coefficient, K_{oil} . The K_{oil} should be approximately equal to the octanol-water coefficient, K_{ow} , because both octanol and oil are bulk-phase hydrocarbon media. Comparing K_{om}

 Table 2-1.
 Solute properties.

	Structure	MW	log Kom	log Kow	log Ka
Pentachlorophenol (PCP)		266.34	4.27 a	5.24 a	4.75 a
Toluene	CH ³	94.11	1.94 b	2.69 b	-
2-Chlorobiphenyl (2-CB)		188.66	3.23 b	4.51 b	-

a Schellenberg et al, 1984. b Chiou, 1989.

	MG	MG-SC	UP	PP	Сарас
OC, %	1.81	12.51	0.29	1.25	0.40
OM, %	3.15	21.79	0.51	2.18	0.70
Oil/Grease, %	0.97	7.60	0.24	0	0
PCP, %	0.074	0.247	0.062	0	0
PCB, %	0	0	0	0.730	0
рН	7.581	7.353	5.617	8.750	6.668
Sand (0.05-2.0 mm)	90.3	0.7	96.8	47.0	25.0
Silt (0.002-0.05 mm)	4.9	33.4	2.5	45.0	45.0
Clay (<0.002 mm)	4.8	65.9	0.7	8.0	30.0

Table 2-2. Properties of the four soils and a soil particle-size fraction used in this study.

PCP	/MG	PCP /	MG-SC	PCP / UP		PCP / Capac	
Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg
0.067	0.386	0.0200	0.850	0.0142	0.847	1.189	3.208
0.141	0.758	0.0401	1.697	0.0197	1.711	2.102	4.983
0.202	1.154	0.0612	2.534	0.0395	2.547	2.948	6.891
0.279	1.521	0.0813	3.382	0.0444	3.412	3.965	8.458
0.335	1.928	0.0966	4.285	0.0498	4.276	5.087	9.814
0.498	2.902	0.1493	6.377	0.0776	6.409	7.533	13.921
0.660	3.876	0.1980	8.515	0.1263	8.499	10.109	17.770
Toluer	Toluene / MG		Toluene / PP		2-CB / PP		
Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg		
0.0024	0.0117	0.0044	0.0243	0.0023	1.214		
0.0046	0.0239	0.0084	0.0494	0.0041	2.432		
0.0070	0.0356	0.0131	0.0731	0.0054	3.654		
0.0088	0.0486	-	-	0.0070	4.875		
0.0112	0.0604	•	-	0.0093	6.088		
0.0124	0.0744	-	-	0.0129	9.142		
0.0156	0.0845	-	-	0.0168	12.192		

Table 2-3. Measured solute equilibrium concentrations in the aqueous phase (C_e) and soil phase (C_s) of the seven systems (expressed as Solute / Soil) studied.



Figure 2-1. Sorption isotherms of PCP, toluene, and 2-CB on the MG, UP and PP soils and MG-SC soil particle-size fraction.
(18900) and K_{oil} ($K_{ow} = 174000$) for PCP (Schellenberg *et al.*, 1984) suggests that the oil phase could be as much as 10 times more effective than the natural SOM as a partitioning medium for organic contaminants.

To test this hypothesis, four soils and a soil particle-size fraction were evaluated for the sorption of PCP (Table 2-4). Each sample was analyzed for native PCP concentration, natural SOM content, oil/grease content, pH, and particle size distribution.

Soil	Compound	Distribution Coefficient	
		Measured	Predicted (a)
MG	PCP	5.79	3.36
MG-SC	PCP	42.88	43.09
UP	PCP	72.84	61.29
Сарас	РСР	1.57	1.52
MG	Toluene	5.52	7.5
PP	Toluene	5.66	5.47
PP	2-CB	702	273

Table 2-4. Measured and predicted soil-water distribution coefficients of PCP, toluene, and 2-CB in soils containing residual petroleum or PCB oils.

(a). Predicted value form Equation 2-3, assuming $K_{oil} = K_{ow}$.

Table 2-4 shows that the MG and UP soils each have high PCP contamination and a significant oil/grease component. The MG-SC sample shows that the oil/grease component, and PCP, are associated primarily with the silt and clay fraction. The pristine Capac soil has no PCP contamination and no oil/grease component.

For the soils shown in Table 2-4 that have an oil/grease component, the predicted soil-water distribution coefficient of a given NOC, K, was expressed as:

$$K = f_{om}K_{om} + f_{oil}K_{oil}$$

= $f_{om}K_{om} + f_{oil}K_{ow}$ (2-3)

where f_{Om} and f_{Oil} are the fractional content of the natural SOM and oil/grease phase, and K_{Om} , K_{Oil} and K_{Ow} are SOM-water, oil/grease-water and octanol-water partition coefficients, respectively. In this model, both natural SOM and the oil/grease component are acting as sorptive phases for the NOC as defined by the K_{Om} and K_{Oil} values. For a partially ionized compound like PCP, the actual overall distribution coefficient, D, can be estimated at any soil pH by using the equation:

$$D = QK = K \frac{1}{1 + \frac{K_a}{[H^+]}}$$
(2-4)

where K is the soil-water distribution coefficient of the nonionized PCP (Equation 2-3), Q is the fraction of the PCP present in the nonionized form, K_a is the dissociation coefficient of the solute (for PCP, log $K_a = 4.72$), and [H⁺] is the concentration of hydrogen ion (Schellenberg *et al.*, 1984). By use of this approach, the D values (Table 2-4) were predicted for each soil from the pK_a, K_{om}, and K_{ow} values of PCP and the measured SOM content, oil/grease content, and pH (Table 2-2).

To substantiate that the residual petroleum (oil/grease) component was acting as a sorptive phase for PCP, PCP sorption isotherms were measured by using the contaminated soils and, for comparison, the uncontaminated Capac soil. The sorption isotherms shown in Figure 2-1 for the contaminated soils were obtained by adding ¹⁴C-PCP at various

concentrations to soil-water mixtures and then measuring ¹⁴C-PCP in the aqueous phase at equilibrium. The sorption isotherms obtained were highly linear for all samples (Figure 2-1), as observed previously for chlorophenol sorption by soils and sediments ((Schellenberg et al., 1984; Lagas, 1988). Because the PCP sorption isotherms are linear, the measured distribution of ¹⁴C-PCP represents the overall PCP distribution in the contaminated soils. The experimentally determined values of soil-water distribution coefficients D for PCP are given in Table 2-4, which shows excellent agreement in all cases between the predicted and measured distribution coefficients. A graphical comparison of the measured and predicted (using Equation 2-3) K (D) values is presented in Figure 2-2. For the Capac soil, where no oil/grease phase is present, only the natural SOM is functioning as a sorptive phase for PCP and the distribution coefficient is accurately predicted from the SOM content. For the contaminated soils, consideration of both the oil/grease and SOM components is required to accurately predict the PCP distribution coefficient. The similarity of the measured D values to those predicted by using $K_{oil} = K_{ow}$ shows that the oil/grease component was approximately 10 times more effective than natural SOM as a sorptive phase for PCP. Similar results were obtained for the sorption of toluene by the MG soil (Figure 2-1 and Table 2-4). Thus, these results are directly applicable to other organic contaminants (e.g., benzene, toluene, and xylene) found in soils and sediments where residual petroleum is present.

The sorptive behavior of residual PCB oil (commercial Aroclor) in a PCBcontaminated soil was evaluated by using the soil denoted PP (Table 2-4). To obtain the predicted K values, the PCB oil-water partition coefficient was again estimated as being approximately equal to K_{OW} (Table 2-2). This assumption appears valid for toluene where the measured sorption coefficient (Table 2-4), obtained from the slope of the linear isotherm (Figure 2-1), was in excellent agreement with the predicted value. However, for 2-chlorobiphenyl, use of K_{OW} to approximate the PCB oil-water partition coefficient

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Figure 2-2. Graphical comparison of measured and predicted soil-water distribution coefficients (K) of PCP, toluene and 2-CB on the MG, UP, PP and Capac soils and MG-SC soil particle-size fraction.

underestimated the observed K (Figure 2-1 and Table 2-4). The measured K value for 2-CB corresponds to a log K_{oil} value of about 5 (log $K_{OW} = 4.51$) and this is entirely reasonable because 2-CB would be expected to form a more nearly ideal solution in PCB oil than in octanol, making $K_{oil} > K_{OW}$. In fact, a plot of log K_{OW} versus water solubility for various organic compounds shows that 2-CB falls below the ideal line by approximate 0.7 log unit (Chiou and Schmedding, 1982). Thus, the sorptive behavior of residual PCB oils appears similar in nature to that of residual petroleum. However, in the case of sorption of individual PCB congeners by residual PCB oils, nearly ideal solution behavior is observed and K_{oil} will be greater than Kow; the magnitude of this difference will increase for the more heavily chlorinated PCB congeners (Chiou and Schmedding, 1982). The resulting effect of residual PCB oils on the soil-water distribution coefficient is dramatic; the K value predicted in the conventional manner, where only SOM is acting as a sorptive phase, is about 37, whereas the observed value is 702. More extensive study on the sorption of PCB congeners by residual PCB oils is presented in Chapter 3.

These results demonstrate that residual petroleum and PCB oils present in soil act as highly effective partition media for NOCs. The presence of these highly sorptive anthropogenic organic phases in soils and sediments will significantly increase the immobilization of organic contaminants and thus strongly influence their environmental fate and behavior. The observed soil-water distribution coefficient of organic contaminants were accurately predicted from the SOM content, the oil/grease content (expressed as oil/grease or PCB content), and the solute K_{OM} and K_{OW} values. The magnitude of the oil-water partition coefficient makes the residual oil/grease phase a significant sink for organic contaminants in these systems. For accurate prediction of soilwater distribution coefficients in such soils and sediments, the oil components, along with the natural SOM component, must be measured and accounted for individually. The limited effectiveness of soil washing and pump and treat technologies (Bouchard *et al.*, 1989; Mackay and Cherry, 1989) for remediating soils contaminated by petroleum spills and PCBs may be related in part to the sorptive behavior of residual oil components as described here.

Chapter 3

Sorption of Polychlorobiphenyl (PCB) Congeners by Residual PCB-Oil Phases in Soils

[1] Introduction

The predominant role of the organic matter of soils and sediments in sorption of nonionic organic contaminants (NOCs) from water has been extensively studied and well-documented. Partitioning of NOCs into soil organic matter (SOM) is believed to be the primary mechanism accounting for their sorptive uptake in soil-water systems (Chiou *et al.*, 1979, 1983; Karickhoff *et al.*, 1979). The partitioning process can be described by a linear equation:

$$C_s = KC_e \tag{3-1}$$

where C_s is the NOC uptake per unit mass of soil, C_e is the NOC equilibrium concentration in the aqueous phase, and K is the soil-water distribution (sorption) coefficient, which is the ratio of the NOC concentration in soil to its equilibrium concentration in water contacting the soil.

Because of the controlling importance of the natural SOM, for any given NOC, the apparent soil-water distribution coefficient can be normalized for the natural SOM fraction of soil to give a characteristic constant K_{om} (Chiou, 1989):

$$K_{om} = \frac{K}{f_{om}} \tag{3-2}$$

where f_{om} is the fractional SOM content of the soil on a mass basis. The SOM normalized partition coefficient (K_{om}) remains relatively constant among soils indicating that the solvency of natural SOM is similar for different soils. The K_{om} value can be used to predict the uptake of NOCs in soil, as long as the SOM content is known:

$$K = f_{om} K_{om} \tag{3-3}$$

The values of K_{om} and f_{om} are widely used to predict the leaching potential of pesticides and NOCs in soils and subsoils.

Contaminated soils may possess a considerable amount of anthropogenic organic materials, such as petroleum and PCB oils (commercial Aroclors) that may affect the sorption of NOCs. In such soils, the K values predicted in the conventional manner using only K_{om} and f_{om} (*i.e.*, Equation 3-3) were found to underestimate severely the actual soil-water distribution coefficients. We previously demonstrated in Chapter 2 that, for pentachlorophenol (PCP) and toluene, a residual petroleum phase in soil acted as a powerful partitioning medium for removing NOCs from water. This anthropogenic sorptive phase was about 10 times more effective per unit mass than the natural soil organic matter. Even more effective partitioning of 2-chlorobiphenyl into a residual PCB oil fraction of soil was also observed.

Including the contribution of residual petroleum phase to the overall uptake of NOCs, the following equation was used in Chapter 2 to estimate the K value:

$$K = f_{om}K_{om} + f_{oil}K_{oil}$$
(3-4)

where f_{oil} is the residual petroleum fraction of soil, and K_{oil} is the oil-water partition coefficient; the term $f_{oil}K_{oil}$ represents the sorptive uptake of NOCs by the residual petroleum phase and the term $f_{om}K_{om}$ the sorption by natural SOM. A similar equation can be used to predict the sorption of NOCs in PCB-oil contaminated soils. Unfortunately, K_{oil} values are generally not available for most NOCs. Because the solvency of petroleum should be similar to that of other hydrocarbon media such as octanol, the more accessible octanol-water partitioning coefficient, K_{ow} , was shown to serve as a reasonable substitute for K_{oil} . Thus, by simply assuming that $K_{oil} = K_{ow}$ Equation 3-4 becomes:

$$K = f_{om}K_{om} + f_{oil}K_{ow}$$
(3-5)

Equation 3-5 successfully predicted the sorptive behavior of petroleum contaminated soils for a variety of NOCs. However, this equation underestimated the sorption of 2-chlorobiphenyl by soils containing a residual PCB-oil phase derived from a commercial Aroclor.

In this study, the sorptive uptake of 2-chlorobiphenyl by four PCB-oil contaminated soils was evaluated. The soils studied were from two different locations possessing different PCB oil amounts, ranging from 2170 mg/kg (ppm) to 7670 mg/kg, *i.e.*, 0.217% to 0.767%. The objective of this study was to define quantitatively the role of residual PCB-oil phases in the sorption of a representative PCB congener. The sorption coefficients of the contaminated soil, and of the same soil after being extracted to remove the residual PCB oil phase were measured and compared to the predicted

partitioning coefficients from Equations 3-3 and 3-5. These data were used to obtain a PCB-oil normalized partitioning coefficient, K_{pCb} , which should allow more accurate prediction of overall soil-water distribution coefficients for individual PCB congeners in PCB oil contaminated soils and sediments. The K_{pCb} value reported here demonstrates that, for 2-chlorobiphenyl, the residual PCB-oil phase in soils is a partitioning medium approximately 67 times more effective per unit mass than natural soil organic matter, and about 3.5 times more effective than octanol (K_{OW}).

[2] Materials and Methods

Soils and Their Properties. Four heavily PCB-oil contaminated soils were used in this study. Three of the soils, denoted PCB-I, PCB-II, and PCB-III, were sampled from different locations within the same general area. These soils are contaminated with Aroclor 1254 as a result of a transformer oil spill at a Minnesota power plant. The PCBoil levels of these three soils range from 2.17 g/kg (2170 ppm) to 7.67 g/kg (7670 ppm). The Oakland soil is from a different site. This soil is contaminated with Aroclor 1260 at a level of 3.79 g/kg (3790 ppm). The PCB-oil contents of the soils were determined using the method reported by Quensen *et al.* (1988). The soil was extracted with a mixture of hexane and acetone (9:1, v/v) for 24 hours, and then the extract was treated using a routine clean-up procedure. A quantitative congener analysis was performed using an HIP 5890A gas chromatograph with an electron capture detector. To obtain the sorption isotherms of PCB-oil free soils, the soils were extracted with a mixture of hexane and acetone (9:1, v/v). This extracting treatment is highly selective for PCB oils, and only 2% to 6% of the total amount of natural soil organic matter would be removed (Stevenson, 1982). The natural organic carbon contents of the soils were determined by measuring CO_2 released from combustion (Huffmann Laboratories, Inc, Golden, CO). Before the measurement, the soil was extracted with a mixture of hexane and acetone (9:1, v/v) to remove the residual PCB oils. Organic carbon content (OC) multiplied by 1.74 (Equation 1-4 in Chapter 1) equals organic matter content (OM). PCB-I, PCB-II, and PCB-III soils have approximately identical natural organic matter content: 20.0, 16.4, and 16.2 g/kg (*i.e.*, 20000, 16400, and 16200 ppm), respectively; and the Oakland soil has 2.10 g/kg (*i.e.*, 2100 ppm) of natural organic matter.

Particle-size analysis of the soils was done by the Michigan State University Soil Testing Laboratory. The sand (0.05 - 2.0 mm), silt (0.002 - 0.05 mm), and clay (< 0.002 mm) contents of PCB-I, PCB-II, PCB-III, and Oakland soils are listed in Table 3-1.

Sorption Isotherms. The isotherms of 2-chlorobiphenyl on the soils were obtained by using ring labeled ¹⁴C-2-chlorobiphenyl (specific activity of 4.92 mCi/mmol) from Sigma Chemical Company, St. Louis, MO. Standard batch sorption experiments were carried out by mixing 1.00 g of soil, 25.0 ml of distilled water, and various amounts of ¹⁴C-2-chlorobiphenyl (dissolved in acetone) ranging from 2 μ g to 50 μ g. The samples were prepared in screw-top 25 ml Corex centrifuge tubes, and shaken for 20 hours at 22 °C. After being centrifuged at a relative centrifugal force of approximately 7500 (RCF) for 20 minutes., the supernatant of each sample was analyzed on a Packard 1500 TRI-CARB Liquid Scintillation Analyzer to determine the equilibrium concentration of ¹⁴C-2-chlorobiphenyl in the aqueous phase.

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[3] Results and Discussions

Table 3-1 lists the natural organic matter content, the residual PCB-oil content and the soil particle size distribution of the soils, as well as the molecular weight, log K_{OM} and log K_{OW} of 2-chlorobiphenyl. Table 3-2 presents the measured solute equilibrium concentrations in the aqueous phase, C_e, and soil phase, C_s, of the studied systems. Table 3-3 summarizes the measured soil-water distribution (partition) coefficients of 2-CB, and as well the predicted values based on the fractional SOM content only (Equation 3-3) and on both the fractional SOM content and PCB-oil content (Equation 3-5) of the soils used in this study. Figure 3-1 shows the sorption isotherms of ¹⁴C-labeled 2-CB on four PCBoil contaminated soils before and after extraction to remove the PCB oils. The slopes of these isotherms correspond the distribution coefficients of 2-CB. Figure 3-2 graphically compares the measured and predicted K values in Table 3-3.

Soil						
	РСВ-І	PCB-II	PCB-III	Oakland		
Natural SOM, g/kg	20.0	16.4	16.2	2.1		
Residual PCB Oil, g/kg	2.17	7.36	7.67	3.79		
Sand, %	47	47	47	34		
Silt, %	45	45	45	48		
Caly, %	8	8	8	18		
	2-Chioro	biphenyl				
Molecular Weight	188.7					
log Kom	3.23 *					
log Kow		4.5	51 *			

Table 3-1. Properties of the four soils and 2-chlorobiphenyl.

Chiou, 1989.

PC)B-I	PC	:B-II	PCB-III		Oakland	
Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/i	Cs, mg/kg
0.0080	1.177	0.0022	1.238	0.0064	4.177	0.0074	2.273
0.0161	2.354	0.0037	2.482	0.0087	6.290	0.0150	4.543
0.0224	3.548	0.0054	3.725	0.0124	6.364	0.0227	6.808
0.0331	4.698	0.0071	4.967	0.0151	10.465	0.0288	9.115
0.0381	5.906	0.0096	6.202	0.0221	15.712	0.0371	11.364
0.0550	8.879	0.0129	9.317	0.0276	20.997	0.0546	17.073
0.0747	11.826	0.0170	12.426	0.0344	26.247	0.0717	22.792
Extracte	ed PCB-I	Extracted PCB-II		Extracted PCB-III		Extracted	l Oakland
Ce, mg/i	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg	Ce, mg/l	Cs, mg/kg
0.0252	1.542	0.0260	1.522	0.0203	1.013	0.0548	0.753
0.0558	2.952	0.0516	3.055	0.0403	2.035	0.1115	1.458
0.0858	4.373	0.0810	4.493	0.0612	3.035	0.1843	1.761
0.1138	5.846	0.1134	5.857	0.0929	3.762	0.2334	2.658
0.1437	7.272	0.1381	7.411	0.1113	4.824	0.3030	3.038
0.2281	10.594	0.2167	10.877	0.1781	6.956	0.4578	4.475
0.3131	13.898	0.3009	14.203	0.2372	9.279	0.6329	5.398

Table 3-2. Measured equilibrium concentrations of 2-CB in the aqueous phase (C_e) and in the soil phase $(C_s, calculated by difference)$ of the eight systems studied.



Figure 3-1. Sorption isotherms of 2-CB from water by four soils before and after extraction to remove residual PCB oils (commercial Aroclor).



Figure 3-2. Graphical comparison of measured and predicted soil-water distribution coefficients (K) of 2-CB on four soils before and after extraction to remove residual PCB oils (commercial Aroclor).

The data in Figure 3-2 show that for the non-extracted soils, the measured partition coefficients (ranging from 162 to 788) were much greater than the predicted K values calculated in the conventional manner using Equation 3-3 (ranging from 3.55 to 34.0) in which only natural soil organic matter is considered as a sorptive phase. The K values predicted using Equation 3-5 (ranging from 104 to 276), which considers both soil organic matter and residual PCB-oil phases, and which sets Kpcb equal to Kow, were also significantly lower than the measured K values. After extracting the PCB-I, PCB-II, PCB-III, and Oakland soils to remove residual PCB-oils, however, the measured K values (43.0, 46.0, 37.0, and 8.15, respectively) all decreased dramatically to nearly the same level as those predicted only using for and Kom, i.e., Equation 3-3 (34.0, 27.8, 27.5, and 3.55, respectively). It is noteworthy that before extraction to remove residual PCB oils the PCB-I, PCB-II, and PCB-III soils exhibited the measured K values of 162, 747, and 788, respectively, which roughly paralleled the difference in PCB-oil contents of the three soils (0.217%, 0.736% and 0.767%, respectively). However, after extraction these three soils, which have nearly identical natural soil organic matter contents, gave approximately identical K values (43.0, 46.0, and 37.0, respectively) for sorption of 2-chlorobiphenyl.

The data described above demonstrate that the residual PCB-oil fractions of the

	PCB-I	PCB-II	PCB-III	Oakland
Measured K	162	747	788	319
Predicted K	104	266	276	126
	Extracted PCB-I	Extracted PCB-II	Extracted PCB-III	Extracted Oakland
Measured K	43.0	46.0	37.0	8.2
Predicted K	34.0	27.8	27.5	3.6

Table 3-3. Summary of measured and predicted soil-water distribution coefficients (K) of 2-CB on four PCB-oil contaminated soils before and after extraction to remove residual PCB oils.

soils heavily contaminated with commercial Aroclors play a predominant role in the sorptive behavior of 2-chlorobiphenyl. The residual PCB-oil phase in these soils functions as a highly effective partitioning medium for 2-chlorobiphenyl, being much more effective per unit mass than natural soil organic matter, and also more effective than octanol. Thus, the prediction of a sorption coefficient, K, of 2-chlorobiphenyl for such soils using K_{Om} , f_{Om} , K_{OW} and f_{pcb} (Equation 3-5) results in a significant underestimation. A qualitative explanation could be made based on the concept of the solvency of the natural and anthropogenic organic phases. Because partitioning is mechanistically a process of dissolution, the structural similarity between 2-chlorobiphenyl and PCB oils (which are mixtures of PCB congeners) suggests that 2-chlorobiphenyl would be more soluble in a residual PCB oil phase than in the natural soil organic matter or octanol.

The data presented in Figure 3-2 appear to show that the degree of underestimation of K using Equation 3-5 is directly proportional to the PCB-oil content of soil. To confirm this point from a quantitative view, a correlation analysis can be made by plotting the magnitude of the underestimation of K, *i.e.*, $U_k = K$ (measured) - K (predicted from Equation 3-2), against the residual PCB-oil content (%) of soil (Figure 3-3). The excellent correlation ($r^2 > 0.9999$) shows that the PCB-oil fraction of soil can account entirely for the underestimation of K. Thus, an empirical equation describing the relation of the degree of underestimation of K and the PCB-oil content (%) of soil can be derived through linear regression:

$$U_k = 820 \times PCB \% - 120 \tag{3-6}$$

where U_k is the underestimation of K, *i.e.*, measured K - predicted K (by Equation 3-5). This correlation can be used to correct Equation 3-5 to give a better prediction:

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Figure 3-3. Correlation between residual PCB-oil content (%) and underestimation of soil-water distribution coefficient (K) of 2-CB resulting from the use of K_{OW} of 2-CB to quantitate the partition of 2-CB into residual PCB-oil phase.

$$K = f_{om}K_{om} + f_{pcb}K_{ow} + U_k \tag{3-7}$$

Equation 3-7 is expected to be valid only if the residual PCB-oil content falls within the range of our studied soils, *i.e.*, approximately from 0.2 % to 0.8 %.

An even better way to make an accurate prediction of the sorptive uptake of 2chlorobiphenyl by PCB-oil contaminated soils should utilize its true partition coefficient normalized for the PCB-oil fraction, K_{pCb} , rather than utilizing Kow. In order to obtain the empirical K_{pCb} of 2-chlorobiphenyl we defined a multi-phase soil as a soil possessing several lipophilic phases (such as natural soil organic matter, residual petroleum, residual PCB oils) that are strongly associated with the soil. If a lipophilic phase is present above a critical level in soil (*e.g.*, greater than 0.1 %), it may function as an independent sorptive (partitioning) phase. The uptake of NOCs from water by soil minerals is negligible due to the preferential adsorption of water onto the mineral surface. Thus, the mineral phase need not to be considered as an effective sorptive component in these systems (Chapter 1).

For any multi-phase soil system, the contributions of all sorptive phases (partitioning media) to the overall uptake of a NOC are additive, that is, the overall distribution coefficient, K, is a sum of the products of normalized partitioning coefficient for a specific phase, K_m , and the fractional quantity of this phase, f_m :

$$K = \sum f_m K_m \tag{3-8}$$

This is a generalized version of Equation 3-4. In addition, we assumed that K_m is (as analogy to the case of K_{om} , see Chapter 1) a characteristic constant of the sorptive phase, m, and the chosen NOC, regardless of the soils used .

To evaluate the normalized K value for a specific chosen phase, say, phase x, the term including K_x , *i.e.*, $f_x K_x$, must be isolated on the right side of Equation 3-8 to give a form ready for linear regression:

$$K - \sum_{m \neq x} f_m K_m = f_x K_x \tag{3-9}$$

Equation 3-9 indicates that a plot of the experimental data as $K - \sum_{m \neq x} f_m K_m$ against f_X should yield a straight line (through linear regression) with a slope equal to K_X .

Each of the four soils used in this study has been treated as a system of two partitioning media responsible for the uptake of 2-chlorobiphenyl from water: (a) the natural organic matter, and (b) the residual PCB-oil contaminant (commercial Aroclors); thus Equation 3-8 is reduced to:

$$K = f_{om}K_{om} + f_{pcb}K_{pcb}$$
(3-10)

here K_{pcb} is the PCB-oil normalized partition coefficient to be evaluated. This equation can be rearranged to isolate $f_{pcb}K_{pcb}$ term on the right side ($f_{om}K_{om}$ would not stay constant for experimental data involving different kinds of soils):

$$K - f_{om}K_{om} = f_{pcb}K_{pcb}$$
(3-11)

The $f_{om}K_{om}$ term can be evaluated using either of two methods: (a) utilizing the published K_{om} value of 2-chlorobiphenyl (Chiou, 1989) and the measured natural organic

matter content of soil, or, (b) employing the measured K value of the extracted soil, denoted K^{ex}. Because the PCB oil phase is completely removed from the soil by extraction, only the contribution of the natural soil organic matter to the uptake of 2chlorobiphenyl is included in the measured K^{ex} using extracted soil, and thus we can assume that $f_{Om}K_{Om}$ is equal to K^{ex}. The latter method is particularly convenient in the situation when the K_{Om} value for the chosen congener is not available. Thus, substituting K^{ex} value for $f_{Om}K_{Om}$ would change Equation 3-11 into:

$$K - K^{ex} = f_{pcb} K_{pcb} \tag{3-12}$$

Both (K - $f_{om}K_{om}$) and (K - K^{ex}) were plotted against f_{pcb} , as shown in Figure 3-4. Excellent linear correlations were observed for both lines ($r^2 > 0.999$), and a K_{pcb} value of 114000 was derived from the slopes. In comparison with K_{om} and K_{ow} values of 2-chlorobiphenyl (1700 and 32400, respectively), the K_{pcb} reported here indicates that the residual PCB-oil phase in soil functions as a partitioning medium approximately 67 times more effective per unit mass than natural soil organic matter, and about 3.5 times more effective than octanol.

Figure 3-4 also suggests a "threshold effect" for the contribution of the PCB-oil fraction of soil to the uptake of 2-chlorobiphenyl. When extrapolated, the two lines intercept the PCB-oil fraction axis at a value of about 0.001 (0.1%), suggesting that this may be the minimum level of PCB oil necessary for it to function as a separate partitioning phase. Theoretically, the two lines should pass through the origin since Equations 3-11 and 3-12 do not have a constant term. The existence of a "threshold effect" suggests that, when the PCB oil content in soil reaches a critical level, the discrete PCB solute molecules start forming a separate anthropogenic sorptive phase that is highly effective in removing



Figure 3-4. Contribution of PCB-oil phase to soil-water distribution coefficient (K) of 2-CB as a function of the fractional PCB-oil content (w/w) in soil. The squares and solid line are plotted for Equation 3-11, and the triangles and dotted line for Equation 3-12.

individual PCB congeners from aqueous solution. For example, the PCB mixture may form a separate phase when the solubility of liquid PCB in soil organic matter is exceeded. The soils used in this study had an average organic matter content of about 1.5%, and thus the estimated solubility of the liquid PCB mixture in soil organic matter is about 6% to 7% (w/w), based on a threshold value of 0.1% PCB oil in soil (w/w). This estimation is in agreement with the calculated solubility of relatively non-polar organic liquids in soil organic matter (Chiou *et al.*, 1988). Thus, the threshold value for a soil may be related to the soil organic matter content and the solubility of the anthropogenic organic substance in soil organic matter. When the threshold is exceeded, the resultant residual PCB-oil phase will play a predominant role in determining the soil-water distribution of PCB congeners because of its greater effectiveness as a partitioning medium, *i.e.*, K_{pcb} is much greater than K_{om} .

Sorption of Nonionic Organic Compounds in Soil-Surfactant-Water Systems

[1] Introduction

The apparent water solubilities of nonionic organic contaminants (NOCs) can be substantially increased in the presence of conventional nonionic (*e.g.*, Triton, Brij), cationic (*e.g.*, cetyltrimethylammonium bromide), and anionic (*e.g.*, sodium dodecyl sulfate) surfactants (Kile and Chiou, 1989; Edwards *et al.*, 1991; Jafvert 1991). The extent of solubility enhancement was observed to be much greater above the critical micelle concentration (CMC) of these surfactants than below it. Solubility enhancement was attributed to partitioning of NOCs into surfactant micelles which behaved as a microscopic pseudo-solvent phase that is compositionally similar to a bulk solvent phase. The solute solubility enhancement by micelle-forming surfactants was mathematically described (Kile and Chiou, 1989) as:

$$\frac{S^{*}}{S} = 1 + X_{mn} K_{mn} + X_{mc} K_{mc}$$
(4-1)

where, S^* is the apparent solute solubility at the total stoichiometric surfactant concentration of X, S is the intrinsic solute solubility in pure water, X_{mn} and X_{mc} are the fractional concentrations of surfactant as monomers and micelles, respectively, and K_{mn} and K_{mc} are the surfactant monomer-water and surfactant micelle-water partition coefficients of the solute, respectively. The micelle-water partition coefficients (K_{mc}) were similar to the corresponding octanol-water partition coefficients (K_{OW}). Solubility enhancement below the CMC was greater for nonionic surfactants than for ionic surfactants. In general, however, K_{mn} values were at least 1.5 to 2 log unit less than K_{mc} values, demonstrating that surfactant micelles were far more effective than surfactant monomers in enhancing solubility. The extent of solubility enhancement of a very poorly water soluble compound (*e.g.*, *p*, *p'*-DDT, $S = 5.5 \ \mu g \ l^{-1}$) was much greater than a relatively more water soluble compound (*e.g.*, 1,2,3-trichlorobenzene, $S = 18 \ m g \ l^{-1}$). The apparent solubility of *p*, *p'*-DDT was increased from 5.5 $\ \mu g \ l^{-1}$ in the absence of surfactant to 1300 $\ \mu g \ l^{-1}$ at a Triton TX-100 concentration of 300 mg $\ l^{-1}$ (Kile and Chiou, 1989). The water solubility enhancement of *p*, *p'*-DDT above the CMC was linearly related to the surfactant concentration.

An alternative to conventional surfactants are the petroleum sulfonate-oil surfactants (PSO, or Petronates as a commercial name), which also result in substantial solubility enhancement of NOCs (Kile *et al.*, 1990). The Petronates are mixtures of petroleum sulfonates (Figure 4-1) and free mineral oils. Properties that distinguish these surfactants from conventional homogeneous surfactants are that (1) they form stable



Figure 4-1. The chemical structure of petroleum sulfonates (Porter, 1990).

emulsions instead of micelles in aqueous solution, and (2) they do not have a distinct CMC. Importantly, they enhance the water solubility of NOCs in a linear manner proportional to the PSO concentration from nearly zero to hundreds of mg l⁻¹ (Kile *et al.*, 1990). In this sense they are distinct from conventional homogeneous surfactants which only manifest substantial solubility enhancement above their CMC.

The linear solubility enhancement effects of Petronates were expressed by Kile et al. (1990) as:

$$\frac{S^*}{S} = 1 + X_{em} K_{em} \tag{4-2}$$

where S^* and S are the apparent and intrinsic solute solubilities, respectively, X_{em} is the PSO emulsion concentration on a water-free basis, and K_{em} is the emulsion-water partition coefficient of the solute. Generally, the K_{em} value of a PSO was found to be greater than or equal to the K_{mc} value of conventional surfactants (Kile and Chiou, 1989). The absence of a certain CMC and linear solubility enhancement starting at nearly zero PSO concentration give Petronates the certain potential advantages over conventional surfactants, one of which is that Petronates appear to be much more effective at low concentrations (sub-CMC, *e.g.*, lower than 100 mg l⁻¹) for enhancing solubility. In addition, because they do not form micelles, Petronates may have greater biocompatibility with biodegradative bacteria, and hence be useful in biorestoration schemes where low solubility may limit biodegradation of target NOCs. Deleterious micelle-membrane interactions between the conventional surfactants and the phenanthrene degrading bacteria have been reported recently (Laha and Luthy, 1991), thwarting efforts to use surfactants to enhance the bioavailability of phenanthrene in soil. Hence, Petronates may be useful in the development of biorestoration technologies for contaminated soils. The purpose of this study was to quantitatively assess the effect of Petronate surfactants on the soil-water distribution of several NOCs. Although the effect of Petronates on contaminant solubility in surfactant-water systems has been established (Kile *et al.*, 1990), a soil-surfactant-water system is more complicated than a surfactant-water system, based on the following considerations:

- (a). The solute will partition into the natural soil organic matter (SOM) from water and exhibit an intrinsic distribution coefficient, K.
- (b). PSO itself may be sorbed by soil in a linear or nonlinear manner and establish an equilibrium distribution pattern.
- (c). The sorbed PSO itself may act as a partition phase and compete with the natural SOM for NOCs.
- (d). The PSO left in the bulk solution forms emulsion that will enhance the solute solubility in the aqueous phase.

These factors would change the intrinsic distribution of NOCs in soil-water systems with addition of the surfactant, and hence render an apparent distribution coefficient, K^* , which may be substantially different from the intrinsic K. However, depending on the net effect of mechanisms (c) and (d), it is unclear *a priori* whether there will be an increase or decrease of the K value.

The objective of this study was to quantitatively assess the sorption of NOCs in a soil-surfactant-water system. Our results show only a slight increase in the soil-water distribution coefficient for naphthalene, a moderate decrease for phenanthrene (from 13.3 to approximately 6), and a dramatic decrease for 2,2',4,4',5,5'-hexachlorobiphenyl (from

478 to approximately 2.5) in the presence of Petronates at an equilibrium aqueous concentration below 170 mg l⁻¹. A method for predicting the apparent soil-water distribution coefficients of NOCs in the soil-surfactant-water systems, using only a few of measured or estimated parameters, is presented.

[2] Materials and Methods

Commercial Petronates and Their Properties. The Petronates used in this study were purchased from Witco Chemical Corp., New York, New York. The commercial Petronates are mixtures which contain petroleum sulfonates (greater than 60 %) and free mineral oils. Table 4-1 summarizes the composition of Petronates L, HL, and CR, which differ primarily in the apparent molecular weight.

Solutes. Naphthalene, phenanthrene, and 2,2',4,4',5,5'-hexachlorobiphenyl (2,2',4,4',5,5'-PCB) were studied. They represent a series of decreasing water solubilities in the order listed here. Table 4-2 lists the chemical structures, molecular weights, water solubilities, log K_{om} and log K_{ow} values of these three compounds. ¹⁴C-Labeled compounds (Sigma Chemical Co., St. Louis, MO.), which had radiochemical purities of greater than 99 %, were used.

The Soil. The sorbent used in the study was an Oshtemo soil (B horizon), which contains 0.10 % organic carbon (*ca.* 0.17 % SOM), 89 % sand, 5 % silt, and 6 % clay. It was air-dried and sieved (< 2 mm) before use.

Sorption of Petronates. A study on the sorption of the three Petronates onto the

	Petronate L	Petronate HL	Petronate CR
Sulfonate, %	61 – 63	61 – 63	61 63
Water, %	4 5	4 5	4 5
Mineral Oil, %	33.0	32.5	32.5
Inorganic Salts %	0.5	0.5	0.5
Molecular Weight	415 430	440 470	490 510

 Table 4-1. Composition and properties of commercial Petronates (data from Witco Chemical Co., New York, New York).

Table 4-2. P	Properties of 2,2',4,4	',5,5'-hexachlorob	iphenyl (2,2',4,	4',5,5'-PCB),	phenanthrene,	and naphthalene.
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	Structure	MW	S, mg/l	log Kom	log Kow
2,2',4,4',5,5'-PCB		360.88	0.001 a	5.84 a	6.90 a
Phenanthrene		178.22	1.6 b	3.48 c	4.46 b
Naphthalene	$\bigcirc \bigcirc$	128.12	31.7 d	2.50 c	3.45 b

a Sklarew and Girvin, 1987.

b Verschueren, 1983.

c Abdul et al, 1987.

d May et al, 1978.

Oshtemo B-horizon soil from water was conducted using a batch equilibrium method. Samples were prepared by mixing the soil (1.00 g), an aqueous Petronate solution(500 mg l^{-1}) and distilled water in 25-ml centrifuge tubes to obtain 7 to 9 different initial Petronate concentrations between 0 and 200 mg l^{-1} . The total solution volume for each sample is 25.0 ml. The samples were shaken for 24 hours at 22 °C and then centrifuged at a relative centrifugal force (RCF) of approximately 7500 × g for 20 minutes. The supernatant of each sample was diluted with water at a 5:1 ratio, and then analyzed using a Perkin Elmer 320 spectrophotometer (Norwalk, CT) to determine the Petronate concentration in the aqueous phase. The wavelengths used were 198.5, 200.0, and 203.0 nm for Petronate L, HL, and CR, respectively.

Sorption of Solutes in Soil-Petronates-Water Systems. Sorption coefficients of naphthalene, phenanthrene, and 2,2',4,4',5,5'-PCB in the presence of various concentrations of Petronates was evaluated. Apparent soil-water distribution coefficients were obtained from sorption isotherms, which were measured using ¹⁴C-labeled naphthalene, phenanthrene, and 2,2',4,4',5,5'-PCB. A batch equilibrium method was employed. For each sample, the total solution volume (25.0 ml) and the amount of soil added (1.00 g) were fixed. At a chosen initial Petronate concentration, a set of samples was prepared, containing various amounts of the solute, ranging from zero to near its saturated concentration. The initial Petronate concentrations ranged from zero to 200 mg l^{-1} , with intervals of no more than 40 mg l^{-1} . The corresponding equilibrium concentrations were calculated based on the Freundlich coefficients (K and n) of Petronate sorption isotherms. The samples were shaken for 24 hours at 22 °C, and then centrifuged at a RCF of approximately $7500 \times g$ for 20 minutes. 1.00 ml of the supernatant of each sample was mixed with scintillation cocktail (15 ml), and then counted on a Packard 1500 TRI-CARB liquid scintillation analyzer (Downers Grove, IL) to determine the equilibrium concentration of the solute. Separate tests were conducted in which the supernatant and

soil extract (hexane as the solvent) were analyzed to evaluate the total solute recovery. The results showed that the solute recovery was greater than 95 % for all three compounds.

[3] Results and Discussion

The sorption isotherms, representing Petronate sorption onto soil, are illustrated in Figure 4-2. The sorption of the Petronates by soil can be described by the Freundlich equation:

$$C_s = K(C_e)^n \tag{4-3}$$

where, C_s and C_e are the solute concentrations in the soil phase (mg kg⁻¹) and the solution phase (mg l⁻¹), respectively, K is the Freundlich sorption coefficient, and n is a characteristic constant of the system that describes the curvature of the isotherm. The measured Petronate equilibrium concentrations in the aqueous phase (C_e) and the soil phase (C_s), as well as the Freundlich coefficients (K and n) of the isotherms, are listed in Table 4-3, in comparison with the data for some nonionic surfactants (Liu *et al.*, 1992). Because the isotherms were obtained using UV spectrometry, they may reflect the apparent sorption of the UV-detectable component(s) in the Petronate. However, the major component of the Petronates (alkyl-aryl sulfonates, which account for more than 60 %) is UV-detectable and hence may serve as a good reference for the overall sorption onto the soil. The nonlinearity of the isotherms for the sorption of Petronates by the Oshtemo (B) is similar to that observed by Liu *et al.* (1992) for nonionic alkylphenol ethoxylate surfactants. 4-3. Measured Petronate equilibrium concentrations in the aqueous phase (C_e) and in the soil phase (C_s). Also presented is the comparison of the Freundlich coefficients of Petronate sorption in the studied soil-water system with published values of three nonionic surfactant (data from Liu *et al*, 1992).

	Equilibrium Concentrations						
Petro	nate L	Petror	ate HL	Petron	Petronate CR		
Ce, mg/l	Cs, mg/kg	Ce, mg/i	Cs, mg/kg	Ce, mg/l	Cs, mg/kg		
3.5	11.5	10.2	144.9	9.6	160.6		
4.2	95.0	21.9	251.8	21.1	272.5		
24.1	197.0	32.5	381.1	31.6	408.8		
36.1	297.2	42.7	533.0	43.2	519.5		
64.4	389.2	72.9	677.8	71.4	713.8		
99.2	520.7	116.5	838.5	112.8	930.2		
133.6	659.2	158.9	1028.1	156.0	1100.0		
171.1	722.2	-	-	-	-		
		Freundlich	Coefficients				
Petro	nate L	Petron	ate HL	e HL Petronate CR			
К	n	K	n	K	n		
27.3	0.643	44.4	0.623	44.1	0.642		
Igepal CA-720		Tergitol	NP-100	Triton X-100			
К	n	K	n	К	n		
1.14	0.559	2.57	0.599	7.24	0.746		



Figure 4-2. Sorption isotherms of Petronates onto Oshtemo (B) soil from water.

At sorption equilibrium, if no surfactant is added into the system, the distribution of a NOC between the solution and soil is mainly determined by the different solubilities of the NOC in water and in the natural SOM phase (Chiou *et al.*, 1979; 1983). However, when a surfactant is present in the soil-water system, two processes that may affect the distribution of the NOC can occur: (1) the formation of micelles in the aqueous phase will enhance the water solubility of the NOC as described by Kile and Chiou (1990) for surfactant-water systems, and (2) the surfactant sorbed on the soil may actually increase the sorption of NOCs. With regard to the latter, when the amount of sorbed surfactant reaches a certain level, the soil-associated Petronate may function as a partitioning medium for NOCs. This is analogous to residual petroleum or commercial PCB oil-phases present in contaminated soils, which act as a sorptive phase for NOCs (Chapter 2 and 3). Thus a change of the intrinsic soil-water distribution coefficient is expected, however it is unclear *a priori* whether it will be positive or negative.

Some typical sorption isotherms for phenanthrene and 2,2',4,4',5,5'-PCB in soilwater-Petronate systems are shown in Figure 4-3. The sorption of naphthalene, phenanthrene and 2,2',4,4',5,5'-PCB in the Oshtemo (B) soil-water system, with or without the presence of the Petronate, is characterized by highly linear isotherms ($r^2 > 0.99$). This suggests that the uptake in this system involves predominantly a partitioning mechanism (Chiou *et al.*, 1979; Karickhoff *et al.*, 1979). When no Petronate was added, the soil-water distribution coefficients (K, corresponding to the slope of the linear isotherms) for naphthalene, phenanthrene, and 2,2',4,4',5,5'-PCB were 1.50, 13.3, and 478, respectively, in inverse order of their solubilities, as expected. As clearly shown in Figure 4-3, the sorption of phenanthrene and especially 2,2',4,4',5,5'-PCB is diminished substantially when Petronates are added to the soil-water system.



Figure 4-3. Examples of sorption isotherms of phenanthrene and 2,2',4,4',5,5'-PCB in the soil-water system with or without Petronate L added.

Table 4-4 lists the apparent soil-water distribution coefficients (K^*) of naphthalene, phenanthrene, and 2,2',4,4',5,5'-PCB at different levels of added Petronate. In a range of 0 to 200 mg l⁻¹ of Petronate L added, the K^{*} of naphthalene, which has the highest S (31.7 mg l⁻¹) of the three solutes tested, shows no significant change. In the case of 2,2',4,4',5,5'-PCB which has the lowest S (0.001 mg l⁻¹), a 202-fold decrease of the K^{*} (*i.e.*, from 478 to 2.36) was observed. For phenanthrene which has an intermediate S of 1.6 mg l⁻¹, the K^{*} was reduced by a factor of 2 (*i.e.*, from 13.3 to 6.02). The CMC requirement was not observed in these systems, which is in agreement with the conclusion of the previous report (Kile *et al.*, 1990). That is, a substantial decrease in sorption coefficient was observed even at the lowest Petronate equilibrium concentrations. This is one of the unique properties of the Petronate surfactants that makes them potentially useful for environmental remediation technologies (*e.g.*, increasing bioavailability). It is particularly noticeable for the 2,2',4,4',5,5'-PCB case where K^{*} dropped from 478 to 8.01 (a 60-fold decrease) when the equilibrium concentration of Petronate L in solution was only approximately 30 mg l⁻¹.

Figure 4-4 plots the measured K^* values as a function of the equilibrium aqueous concentration of Petronates (mg l⁻¹) in the system. In the cases of phenanthrene and 2,2',4,4',5,5'-PCB, the K^* values decrease in a similar pattern, which shows an initial decrease in K^* at low Petronate equilibrium concentrations followed by a more gradual drop at higher Petronate equilibrium concentrations. The error bars plotted with phenanthrene K^* values suggest that the K^* change patterns in different Petronate systems are somewhat different but not practically different. For naphthalene, a slight increase is observed in the Petronate concentration range tested. It is demonstrated clearly in Figure 4-4 that the decrease of K^* values is a function of the intrinsic water solubility (S) of the solute.

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	Petronate Added, mg/l							
	0	10	20	40	80	120	160	200
	Calculated Equilibrium Aqueous Concentration of Petronate, mg/l							
Petronate L	0.00	6.40	14.03	30.23	64.14	99.03	134.48	170.29
Petronate HL	0.00	5.10	11.75	26.36	57.77	90.58	124.19	158.33
Petronate CR	0.00	5.03	11.53	25.79	56.49	88.61	121.55	155.05
K* of Naphthalene								
Petronate L	1.50	-	-	1.54	1.73	2.08	2.07	2.01
K* of Phenanthrene								
Petronate L	13.3	-	-	11.5	9.36	8.05	6.24	6.02
Petronate HL	13.3	-	-	12.6	10.8	9.29	7.34	6.88
Petronate CR	13.3	-	-	12.7	9.38	7.78	6.87	5.98
K* of 2,2'4,4',5,5,'-PCB								
Petronate L	478	28.3	15.1	8.01	4.93	3.71	2.70	2.36
Petronate HL	478	27.7	13.9	7.50	4.96	3.76	2.43	2.28
Petronate CR	478	23.5	13.8	9.20	5.06	3.36	3.01	2.86

Table 4-4. Measured apparent soil-water distribution coefficients (K^{*}) of naphthalene, phenanthrene, and 2,2',4,4',5,5'-PCB at different Petronate equilibrium concentrations.



Figure 4-4. Apparent soil-water distribution coefficients (K^{*}) of naphthalene, phenanthrene, and 2,2',4,4',5,5'-PCB in soil-Petronate-water systems.

We attempted to develop a predictive model to describe the NOC sorptive processes involved in a soil-surfactant-water system. The conceptualization of this model is described as follows:

- (a). The distribution of PSO in the system is described by the PSO sorption isotherm. Due to its huge size, PSO molecules may be unable to permeate the SOM network, and thus exhibit some kind of surface adsorption and nonlinear isotherm.
- (b). In the solution phase, the equilibrium concentration of a NOC is greatly affected by the PSO emulsion and described by Equation 3-2, in which K_{em} is defined as the partition coefficient of NOCs between the emulsified PSO and water, and X_{em} is the fractional concentration of water-free PSO emulsion in solution (Kile *et al.*, 1990).
- (c). The amount of sorbed PSO is from 0.009% to 0.1 % (relative to soil mass) while the added PSO ranges from 20 to 200 mg l⁻¹. We assume that, in addition of the natural SOM, the sorbed PSO adds a positive contribution to the uptake of NOCs from water. This case may resemble the PSO emulsion formed in the solution phase. Thus, a variable X_{pSO} can be defined which is equal to the mass of sorbed PSO divided by mass of the natural SOM. This definition of X_{pSO} also implies that, if no surfactant added, the natural SOM in soil plays a predominant role in the uptake of NOCs by soils, and hence the effect of sorbed PSO is added to the natural SOM phase.
- (d). The positive effect of sorbed PSO on uptake of NOCs by soil can be characterized by a sorbed PSO-SOM partition coefficient, K_{pso}, which should be maximally equal to K_{em} divided by K_{om}:

$$K_{pso} \le \frac{K_{em}}{K_{om}} \tag{4-4}$$

where Kom is the partition coefficient of NOCs between the natural SOM

and water.

(e). The apparent soil-water distribution coefficient of a NOC (K*) in a soil-PSO-water system should be determined by the intrinsic soil-water distribution coefficient (K) in the PSO-free system, as well as the overall effect of the PSO emulsion in solution (which attempts to decrease K) and the soil-sorbed PSO (which attempts to increase K).

Therefore, the apparent distribution coefficient of a given NOC in a soil-PSO-water system may be predicted by:

$$K^{*} = \frac{C_{s}^{*}}{C_{e}^{*}} = \frac{C_{s}(1 + X_{pso}K_{pso})}{C_{e}(1 + X_{em}K_{em})} = K\frac{1 + X_{pso}K_{pso}}{1 + X_{em}K_{em}}$$
(4-5)

where C_s^* and C_s are the solute equilibrium concentrations in the soil phase with and without a PSO in the system, respectively, C_e^* and C_e are the solute equilibrium concentrations in the aqueous phase with and without a PSO in the system, respectively. Here, the numerator of Equation 4-5 accounts for the effect of the sorbed PSO which attempts to increase the K^{*} value, and the denominator accounts for the contribution of the aqueous-phase PSO emulsion which attempts to decrease the K^{*} value.

In a system where the sorption of PSOs onto the soil is weak enough to make X_{pso} negligible, or $X_{pso}K_{pso}$ is much smaller than $X_{em}K_{em}$ (e.g., K_{em} is several orders of magnitute greater than K_{pso}), Equation 4-5 can be reduced to a simpler model:

$$K^{*} = K \frac{1}{1 + X_{em} K_{em}}$$
(4-6)

Unfortunately, the K_{pso} and K_{em} values are not available for most of the environmentally relevant NOCs. However, there are several approaches to estimate the K_{em} and K_{pso} values in our study.

(a). Knowing the octanol-water partition coefficient (K_{OW}) of the NOC, its micelle-water partition coefficient (K_{mc}) can be estimated by empirical equations. For instance, Jafvert (1991) proposed the following equation:

$$\log K_{mc} = 1.04 \log K_{ow} - 0.126 \tag{4-7}$$

Then, K_{em} is assumed to be approximately equal to K_{mc} . In this way, the log K_{em} values for phenanthrene and 2,2',4,4',5,5'-PCB are 4.51 and 7.05, respectively. Actually, some kind of correlation between K_{ow} and K_{em} may be found, if sufficient experimental data are available.

- (b). Because the water solubilities of DDT and 2,2',4,4',5,5'-PCB fall in the same order of magnitude (*i.e.*, 5.5 and 1.0 μg l⁻¹, respectively), we can assume that they have approximately the same log K_{em}, *i.e.*, 6.32 (Kile *et al.*, 1990).
- (c). For the "real situation" values, the measured K* values (Table 4-4 and Figure 4-4) can be analyzed by least-square curve-fitting, using either of the two models (Equations 4-5 or 4-6) to obtain the best fitted K_{em} (and K_{pso}) values. Here, X_{em} and X_{pso} can be evaluated from the initial or equilibrium concentrations of the PSO using the Freundlich coefficients (K and n in Table 4-3) which describe the sorption of PSO by soil. Thus, the curve-fitting can be done setting the equilibrium aqueous concentration of PSO as the independent variable, and the apparent soil-water distribution coefficient (K*) of the solute as the dependent variable.

In the absence of experimental data for curve-fitting, K_{pso} can be estimated by Equation 4-4, utilizing K_{om} of the given NOC (Table 4-2) and known or estimated K_{em} .

The log K_{em} and K_{pso} values obtained using these three methods are listed and compared in Table 4-5. Regardless of the methods used, the log K_{em} values in Table 4-5 are satisfactorily consistent for a given compound. The K_{em} values of 2,2',4,4',5,5'-PCB from method (c) are greater than those from method (b), which agrees with the fact that the water solubility of 2,2',4,4',5,5'-PCB is about 5 times smaller than that of DDT (*i.e.*, 5.5 and 1.0 μ g l⁻¹, respectively).

Table 5. Comparison of the log K_{em} and K_{pso} values of phenanthrene and 2,2',4,4',5,5'-PCB obtained using methods (a), (b), and (c). For method (c), log K_{em} is evaluated using both Equations 4-5 and 4-6 (in square brackets).

Solute	Solute Phenanthrene		2,2',4,4',5,5'-PCB			
Method	(a)	(c)	(a)	(b)	(c)	
log Kem						
Petronate L	4.51	4.51 [3.84]	7.05	6.32	6.48 [6.37]	
Petronate HL	4.51	4.54 [3.72]	7.05	6.32	6.62 [6.48]	
Petronate CR	4.51	[3.86]	7.05	6.32	6.79 [6.54]	
Крѕо						
Petronate L	10.7 *	2.79	16.2*	3.02 *	2.40	
Petronate HL	10.7 *	2.43	16.2 *	3.02 *	2.25	
Petronate CR	10.7 *	•	16.2*	3.02 *	4.82	

Estimated using Equation 4-4.

The K_{pSO} values in Table 4-5 appear to be several orders of magnitude smaller than K_{em} , and very similar for both phenanthrene and 2,2',4,4',5,5'-PCB. In fact, K_{pSO} defined in the model (Equation 4-5) is a measurement of the relative affinities of the sorbed PSO phase and the natural SOM phase for the sorbed solute; whereas K_{em} is a measurement of the relative affinities of the PSO emulsion phase and water for the solute

in the aqueous phase. Water is a poor solvent phase for phenanthrene and 2,2',4,4',5,5'-PCB, but PSO emulsion provides an excellent microscopic pseudo-solvent phase for these solutes. Therefore, the Kem value can be very large for many NOCs, inversely related to their water solubilities. The comparatively smaller values of K_{DSO} suggest that both the natural SOM and sorbed PSOs function similarly as sorptive phases for NOCs. There is a degree of structural similarity between the basic aromatic structure of humic materials and PSO. The measured K_{pso} (method c, Table 4-5) for both phenanthrene and 2,2',4,4',5,5'-PCB were between 2 and 3 (5 in one case), and were smaller than those estimated using Equation 4-4. This suggests that the sorbed PSO is not as effective as the PSO emulsion in solution as a partition phase for NOCs, but is somewhat more effective than the natural SOM. Also, the sorbed PSO is not as effective as the residual petroleum and PCB oils, which have been shown to form separate partition phases that are about 10 times more effective than the natural SOM (Chapters 2 and 3). This may result from the fact that the sorbed PSO is present in our experiments ranging approximately from 0.009 % to 0.1 % of the soil mass. Our earlier study of the sorptive behavior of residual PCB oils in soil suggested a threshold level of about 0.1 % (w/w) relative to the soil mass to form a sorptive phase for NOCs that was nearly as effective as a bulk phase organic solvent (Chapter 3).

The similarity of K_{pso} for phenanthrene and 2,2',4,4',5,5'-PCB may be explained by the fact that both K_{em} and K_{om} are linearly related to K_{OW} (Karickhoff *et al.*, 1979; Chiou *et al.*, 1983; Schellenberg *et al.*, 1984; Jafvert, 1991). Thus, K_{pso} which is equal to or smaller than the ratio of K_{em} to K_{Om} (Equation 4-4) would fall in a narrow range, although K_{OW} and K_{Om} themselves may change substantially from compound to compound.

Figure 4-5 attempts to evaluate the two models (Equations 4-5 and 4-6) for their

capability to predict soil-water distribution coefficient of NOCs in soil-PSO-water systems. In Figure 4-5, the predicted curves (solid lines for Equation 4-5 and dotted lines for Equation 4-6) are compared with the measured K^* values of phenanthrene (squares) and 2,2',4,4',5,5'-PCB (triangles) in the soil-Petronate-water systems. The curves predicted by Equation 4-5 use the Kem and Kpso obtained by best fitting Equation 4-5 itself, and the curves predicted by Equation 4-6 use the Kem obtained by best fitting Equation 4-6 itself (Table 4-5). Thus, Figure 4-5 demonstrates that how well the two models fit in the actually measured K^* data, *i.e.*, how well they may predict K^* values. Generally, both models give satisfactory prediction curves. For phenanthrene, the two models make nearly identical predictions of K^{*} (the sum of squared residues are 0.83 and 0.87, respectively). It is noticeable that at very low PSO equilibrium concentration in solution (*i.e.*, below about 10 mg l^{-1}), Equation 4-5 predicted a peculiar increase of K^{*} of phenanthrene, because X_{DSO}K_{DSO} is greater than X_{em}K_{em} in this PSO concentration range. However, this was not confirmed experimentally. In the case of 2,2',4,4',5,5'-PCB, Equation 4-5 appears to make more accurate prediction of K^{*} (the sum of squared residues is 0.50) than Equation 4-6 does (the sum of squared residues is 3.73), especially at higher PSO equilibrium concentration in solution (*i.e.*, above 20 mg l^{-1}). This results because Equation 4-6 neglects the role of sorbed PSO (i.e., the XpsoKpso term in Equation 4-5), which functions to increase K^* .

To test the predictive capability of Equation 4-5, we can generate a theoretical curve for naphthalene in the soil-Petronate L-water system as follows. Due to their close water solubilities, *i.e.*, 31.7 mg l⁻¹ for naphthalene (Table 4-2) and 18 mg l⁻¹ for 1,2,3-trichlorobenzene (Kile *et al.*, 1990), the log K_{em} value of naphthalene is assumed to be equivalent to that of 1,2,3-trichlorobenzene, *i.e.*, 3.94 (Kile *et al.*, 1990). The K_{pso} value of naphthalene is estimated as the average K_{pso} in Table 4-5 for Petronates L and HL, *i.e.*, 2.47. The predicted curve is plotted in Figure 4-5 (thick line), as well the actually

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Figure 4-5. Comparison of predicted K* curves of phenanthrene and 2,2',4,4',5,5'-PCB using Equation 4-5 (solid lines) and Equation 4-6 (dotted lines) with actually measured K* values (squares = phenanthrene, triangles = 2,2',4,4',5,5'-PCB). Predicted (thick line) and measured (circles) K* of naphthalene are plotted as a test of the model (Equation 4-5).

measured apparent soil-water distribution coefficients of naphthalene (Table 4-4) in this system (circles). Obviously, the model works very well here, and even shows the slight increase of K^* in the PSO concentration range studied.

In conclusion, these two models (*i.e.*, Equations 4-5 and 4-6) may be used to predict the apparent soil-water distribution coefficients of NOCs in soil-PSO-water system, by knowing the intrinsic K value of the solute, the soil-water distribution of the PSO, and K_{em} (and K_{pSO}) of the solute. The intrinsic K can be estimated using the K_{Om} value of the solute and the SOM content. The K_{em} value can be estimated from K_{OW} , and K_{pSO} can either be estimated from K_{em} and K_{Om} (Equation 4-4) or obtained from experimental data for a particular soil-surfactant-water system (*e.g.*, for soil-PSO-water systems, $K_{pSO} \approx 2.5$). The surfactant equilibrium concentrations in soil and water are obtained from its sorption isotherms. Thus, by simply measuring the surfactant sorption isotherm for a particular soil, accurate predictions of the soil-water distribution coefficients of a solute at different surfactant concentrations can be obtained.

A Mathematical Solution for Two-Domain Model of Desorption Kinetics in Gas-Purging Systems

[1] Introduction

The two-domain mass transfer model of desorption kinetics divides the sorbent phase into two domains: (a) a "labile" domain, S1, in which the solutes have direct access to and are at instantaneous equilibrium with the aqueous phase; (b) a "nonlabile" domain, S2, in which the solutes do not have direct access to the aqueous phase, and slow solute mass transfer processes bidirectionally occur in between the two domains obeying the first-order kinetics (Karickhoff and Morris, 1984). Although the two-domain models generally do not include the microscopic mechanisms involved in the slow mass transfer, it is believed that the labile domain consists of the external surface fractions of the SOM and the interlayer micropores of the clay minerals, where the retarded intraorganic matter and intraparticle diffusion of solutes takes place at a very slow rate (Brusseau et al., 1991).

The conceptualization of a two-domain model is illustrated in Figure 5-1. All the definitions of the variables and parameters used in this chapter are listed in Section [3].



Figure 5-1. The two-domain model for desorption kinetics study.

Four most important parameters, which are not controllable experimentally, in this model are defined as follows:

(a). K: the equilibrium sorption coefficient of the solute between the aqueous phase and sorbent phase:

$$K = \frac{C_s^E}{C_s^E}$$
(5-1)

(b). \$\phi\$: the fractional solute concentration in the S1 domain relative to the overall solute concentration in the sorbent phase:

$$\phi = \frac{C_{s1}}{C_s} = \frac{C_{s1}}{C_{s1} + C_{s2}}$$
(5-2)

This definition also give the following relationship:

1

$$C_{s1} = \phi K C_a \tag{5-3}$$

(c). k_s and k_d : the first-order mass transfer rate constants at the sorption direction and at the desorption direction, respectively:

$$\frac{dC_{s2}}{dt} = k_s C_{s1} - k_d C_{s2}$$
(5-4)

Under the closed and equilibrated condition, Equations (5-2) and (5-4) produce an important relation among ϕ , k_s and k_d :

$$\frac{dC_{s2}^E}{dt} = k_s C_{s1}^E - k_d C_{s2}^E$$
$$= k_s \phi C_s^E - k_d (1 - \phi) C_s^E = 0$$
$$\phi k_s = (1 - \phi) k_d$$
(5-5)

However, because ϕ , k_s and k_d are all constants, $\phi k_s = (1-\phi)k_d$ becomes universally true under *any*, not just closed and equilibrated, conditions.

[2] Conceptualization of Two-Domain Model for Desorption Kinetics Study Using Gas-Purging Method

Gas-purging is a convenient and continuously monitoring laboratory method especially suitable for the sorption-desorption kinetics study of volatile compounds in soilwater systems. The methodology of the gas-purging experiment is well-documented (Karickhoff *et al.*, 1984; Wu and Gschwend, 1986; Brusseau *et al.*, 1990). Thus, only an outline is given here, without technical details. Before the sample container is connected to a switchable tubing system, the solute, sorbent and water are mixed and shaken for a sufficient time period allowing the sorption equilibrium or at least steady state to be reached. First, the whole system is closed, and the air is pumped circulating through all the phases (gas, aqueous and sorbent) at a constant flow rate until the sorption equilibrium in the entire system is established. Then, the tubing is switched to open: fresh air being sucked in on one end, pumped through the sample container, and finally purged out on the other end. The solute concentration in the gas phase is continuously measured and recorded right before the air-outlet. Typically, a decay curve of the solute concentration in the gas phase is obtained.

The data interpretation is based on the well-known Henry's law which states that in a closed and equilibrated solution-air system, the solute vapor concentration *above* the diluted solution is linearly proportional to the solute aqueous concentration *in* the solution:

$$C_g^E = K_h C_a^E \tag{5-6}$$

The volatilization equilibrium generally is a very fast process, and hence is assumed to be instantaneous in the gas-purging method and modeling. Figure 5-2 illustrates the



Figure 5-2. The two-domain model for desorption kinetics study using gas-purging method.

conceptualization of the gas-purging two-domain model.

Although their physical meaning seems to be vague at this moment, three abstract volumes (which will later naturally find their places in the system equations) can be defined in this system:

$$R_{t} = \frac{WK}{K_{h}} + \frac{V_{a}}{K_{h}} + V_{g}$$

$$R_{h} = \frac{V_{a}}{K_{h}} + V_{g}$$

$$R_{i} = \frac{\phi WK}{K_{h}} + \frac{V_{a}}{K_{h}} + V_{g}$$
(5-7)

where R_t is the total "system volume" normalized to the gas phase, R_h is the "volume" to which Henry's Law applies, including the gas and aqueous phases, normalized for the gas phase, and R_i is the "volume" in which the solution is under instantaneous equilibration, including the gas and aqueous phase and S1 domain, normalized for the gas phase. All other parameters used in Equation 5-7 are defined below.

[3] Variables, Parameters, and Assumptions

This section summarizes the symbol, definition and dimension (in square brackets, if any) of all the variables and parameters used in this chapter, as well as the assumptions made for the system to simplify the modeling procedure.

Variables.

Μ	Total solute mass in the system, [M].
Λ	Fractional solute mass remaining in the system at time t.
П	Fractional solute mass purged away from the system at time t.
M _{sl}	Solute mass in the S1 domain, [M].
M _{s2}	Solute mass in the S2 domain, [M].
Ma	Solute mass in the aqueous phase, [M].
Mg	Solute mass in the gas phase, [M].
C _s	Overall solute mass in the sorbent phase, [M].
C _{sl}	Solute concentration in the S1 domain, $[M(solute)M(domain)^{-3}]$.
C _{sl} E	Equilibrium solute concentration in the S1 domain, [M(solute)M(domain) ⁻³].
C _{s2}	Solute concentration in the S2 domain, [M(solute)M(domain) ⁻³].
C _{s2} E	Equilibrium solute concentration in the S1 domain, $[M(solute)M(domain)^{-3}]$.
Ca	Solute concentration in the aqueous phase, [ML-3].
C _a E	Equilibrium solute concentration in the aqueous phase, [ML-3].
Cg	Solute concentration in the gas phase, [ML-3].
$\tilde{C_g^E}$	Equilibrium solute concentration in the gas phase, [ML-3].
t	Time, [T].

Parameters.

м 0	Initial solute mass, [M].
C_g^0	Initial solute concentration in the gas phase, [ML-3].
К	Overall sorption coefficient of the solute between the aqueous phase and sorbent phase, $[M^{-1}L^3]$.
k _s	First-order mass transfer rate constant at sorption direction, [T ⁻¹].
k _d	First-order mass transfer rate constant at desorption direction, [T ⁻¹].
W	Sorbent mass, [M].
Va	Aqueous phase volume, [L ³].
Vg	Gas phase volume, [L ³].

F Gas-purging flow rate, $[L^3T^{-1}]$.

- φ Fractional solute concentration in the S1 domain relative to the overall solute concentration in the sorbent phase.
- R_t Abstract total system volume normalized for the gas phase, $[L^3]$.
- R_h Abstract volume to which Henry's law applies, including the aqueous and gas phases, normalized for the gas phase, [L³].
- R_i Abstract volume in which the solute is under instantaneous equilibration, including the aqueous and gas phases and S1 domain, normalized for the gas phase, [L³].
- P Compound parameter, [T⁻¹].
- Q Compound parameter, [T⁻²].
- L1, L2 Combined parameter, [T⁻¹].

Assumptions.

- (A). The solute concentration is spatially homogeneous in its residing phase or domain, and only depends on the time variable.
- (B). All the parameters $(e.g., \phi, K, V, etc.)$ remain constant in the system.
- (C). The solute mass transfer across the solution-vapor boundary requires no time (instantaneous equilibration). This changes Equation 5-6 into:

$$C_g = K_h C_a \tag{5-8}$$

- (D). The solute mass transfer across the solution-S1 domain boundary requires no time (instantaneous equilibration).
- (E). The solute mass transfer across the S1 domain-S2 domain boundary obeys the first-order kinetics (Equation 5-4).
- (F). The entire system is under an isothermal condition.

[3] Mathematical Derivation of the System Equations

Solute Mass Balances. The two-domain model developed in this chapter takes the total solute mass remaining in the system at time t as the dependent variable, and time t as the independent variable. Traditionally, the fractional solute mass (dimensionless) relative to its initial mass added to the system, M/M^0 , is often treated as the dependent variable in data interpretation.

The overall mass balance of the solute in the entire system can be expressed as:

$$M = M_{s} + M_{a} + M_{g}$$

$$= W(C_{s1} + C_{s2}) + V_{a}C_{a} + V_{g}C_{g}$$
(5-9)

During the gas-purging process, the solute mass purged away from the system is $-FC_g$. Thus, the change of solute mass with time in the system is:

$$\frac{dM}{dt} = \frac{dM_{s1}}{dt} + \frac{dM_{s2}}{dt} + \frac{dM_a}{dt} + \frac{dM_g}{dt}$$
$$= W\left(\frac{dC_{s1}}{dt} + \frac{dC_{s2}}{dt}\right) + \frac{dC_a}{dt} + \frac{dC_g}{dt}$$
$$= -FC_g$$
(5-10)

Now, we can establish the solute mass change related to each individual phase and domain (*i.e.*, each term in Equation 5-10), in terms of the solute concentration change in the gas phase.

(a). The gas phase:

$$\frac{dM_g}{dt} = V_g \frac{dC_g}{dt}$$
(5-11)

(b). The aqueous phase, according to Equation 5-8:

$$\frac{dM_a}{dt} = V_a \frac{dC_a}{dt} = \frac{V_a}{K_h} \frac{dC_g}{dt}$$
(5-12)

(c). The S1 domain, according to Equations 5-3 and 5-8:

$$\frac{dM_{s1}}{dt} = W \frac{d(C_{s1})}{dt} = \frac{\phi WK}{K_h} \frac{dC_g}{dt}$$
(5-13)

(d). The S2 domain, according to Equations 5-4 and 5-5:

$$\frac{dM_{s2}}{dt} = W \frac{dC_{s2}}{dt} = W(k_s C_{s1} - k_d C_{s2})$$

$$= k_d \left[\frac{(1-\phi)WK}{K_h} C_g - WC_{s2} \right]$$
(5-14)

To obtain the WC_{s2} , we can employ the total solute mass balance (Equation 5-9) and Equations 5-11. 5-12 and 5-13:

$$WC_{s2} = M - (WC_{s1} + V_a C_a + V_g C_g)$$

=
$$M - \left(\frac{\phi WK}{K_h} + \frac{V_a}{K_h} + V_g\right)C_g$$
 (5-15)

Putting Equation 5-15 into Equation 5-14, we have:

$$\frac{dM_{s2}}{dt} = \left\{ \left[\frac{(1-\phi)WK}{K_h} + \frac{\phi WK}{K_h} + \frac{V_a}{K_h} + V_g \right] C_g - M \right\} k_d$$
$$= \left[\left(\frac{WK}{K_h} + \frac{V_a}{K_a} + V_g \right) C_g - M \right] k_d$$
(5-16)

Finally, according to the definition of R_t (Equation 5-7):

$$\frac{dM_{s2}}{dt} = (R_t C_g - M)k_d \tag{5-17}$$

Placing Equations 5-11, 5-12, 5-13 and 5-17 in Equation 5-10, and noticing the definition of R_i (Equation 5-7), we obtain the differential equation that describes the change of solute mass with time in the system:

$$(R_t C_g - M)k_d + \left(\frac{\phi WK}{K_h} + \frac{V_a}{K_h} + V_g\right)\frac{dC_g}{dt} = -FC_g$$

$$(R_t C_g - M)k_d + R_f \frac{dC_g}{dt} = -FC_g$$

$$R_f \frac{dC_g}{dt} + (R_t k_d + F)C_g - k_d M = 0$$
(5-18)

Also notice:

$$\frac{dM}{dt} = -FC_g$$

$$C_g = -\frac{1}{F}\frac{dM}{dt} \text{ and } \frac{dC_g}{dt} = -\frac{1}{F}\frac{d^2M}{dt^2}$$
(5-19)

Thus, Equation 5-18 becomes:

$$R_i \frac{d^2 M}{dt^2} + (R_t k_d + F) \frac{dM}{dt} + F k_d M = 0$$
(5-20)

Here we define that:

$$P = \frac{R_t k_d + F}{R_i} \quad \text{and} \quad Q = \frac{Fk_d}{R_i} \tag{5-21}$$

Therefore,

$$\frac{d^2M}{dt^2} + P\frac{dM}{dt} + QM = 0$$
(5-22)

Equation 5-22 is the system differential equation. It is a second-order, linear, constant coefficient differential equation that can be analytically solved (Jeffrey, 1989).

Analytical Solution of Equation 5-22. The characteristic equation of this type of differential equation is:

$$L^2 + PL + Q = 0 (5-23)$$

which has two roots:

$$L_1 = \frac{-P + \sqrt{P^2 - 4Q}}{2}$$
 and $L_2 = \frac{-P - \sqrt{P^2 - 4Q}}{2}$ (5-24)

Thus, the general solution of Equation 5-22 is

$$M = Ae^{L_1 t} + Be^{L_2 t} (5-25)$$

where, A and B are two constants that can be determined by two initial conditions of the system. First, we differentiate Equation 5-25 to give:

$$\frac{dM}{dt} = L_1 A e^{L_1 t} + L_2 A e^{L_2 t}$$
(5-26)

Because the system is closed and pre-equilibrated before the purging, right at the time when the purging starts (t = 0), the two initial conditions of the system are:

(a).
$$t = 0 \implies M = M^0$$

(b). $t = 0 \implies \frac{dM}{dt} = -FC_g^0$
(5-27)

Condition (b) can be related to M^0 :

$$M^{0} = WC_{s}^{0} + V_{a}C_{a}^{0} + V_{g}C_{g}^{0}$$

$$= \left(\frac{WK}{K_{h}} + \frac{V_{a}}{K_{h}} + V_{g}\right)C_{g}^{0} = R_{t}C_{g}^{0}$$

$$t = 0 \implies \frac{dM}{dt} = -\frac{FM^{0}}{R_{t}}$$
(5-28)

Applying the two initial system conditions to Equation 5-25, we obtain two simultaneous equations:

$$A + B = M^0$$
 and $L_1 A + L_2 B = -\frac{FM^0}{R_t}$ (5-29)

which give:

$$A = -\frac{L_2 + \frac{F}{R_t}}{L_1 - L_2} M^0 \quad \text{and} \quad B = \frac{L_1 + \frac{F}{R_t}}{L_1 - L_2} M^0$$
(5-30)

Therefore, the analytical solution for the system differential equation (Equation 5-22) is:

.

$$M = M^{0} \left(-\frac{L_{2} + \frac{F}{R_{t}}}{L_{1} - L_{2}} e^{L_{1}t} + \frac{L_{1} + \frac{F}{R_{t}}}{L_{1} - L_{2}} e^{L_{2}t} \right)$$
(5-31)

The experimentally measured gas-purging data usually are plot as the fractional solute mass remaining in (Λ) or purged away from (Π) the system against time (t), and hence Equation 5-31 should be normalized by defining two dimensionless variables:

$$\Lambda = \frac{M}{M^0}$$
(5-32)
$$\Pi = 1 - \frac{M}{M^0}$$

Thus,

$$\Lambda = -\frac{L_2 + \frac{F}{R_t}}{L_1 - L_2} e^{L_1 t} + \frac{L_1 + \frac{F}{R_t}}{L_1 - L_2} e^{L_2 t}$$
(5-33)

$$\Pi = 1 + \frac{L_2 + \frac{F}{R_t}}{L_1 - L_2} e^{L_1 t} - \frac{L_1 + \frac{F}{R_t}}{L_1 - L_2} e^{L_2 t}$$
(5-34)

From equation group 5-24, we know that both L_1 and L_2 should be *negative*, and L_2 is more negative (with a greater absolute value). This suggests that the two exponential terms in Equation 5-31, 5-33 or 5-34 exhibit a decay of the solute concentration in the gas phase. Thus, Λ will change from 1 to 0 and Π will change from 0 to 1, if t changes from 0 to infinity.

Equations 5-31, 5-33 and 5-34 are system equations. They complete our modeling procedure. These equations can be used to analyze and interpret gas-purging data measured in laboratory. In most of the cases, the unknown values to be investigated are ϕ and k_d, which can be obtained by best curve-fitting using these equations. An example application of this model will be discussed later, using actually measured gaspurging data.

[5] Special Scenarios

The system equations can be used in some special scenarios that which have practical importance. For instance, Henry's Law constant, K_h, may be determined by using sorbent-free samples in the gas-purging system.

Sorbent-free. Because no sorbent is added to the system, W is equal to 0, and all the terms containing ϕ and k_d can be deleted. This makes the following substitutions in the derivation:

- (a). $R_t = R_h, R_i = R_h$ (Equation 5-7).
- (b). $P = F/R_h$ and Q = 0 (Equation 5-21).
- (c). $L_1 = 0$ and $L_2 = -F/R_h$ (Equation 5-24).
- (d). A = 0 and $B = M^0$ (Equation 5-30).

Therefore,

$$M = M^{0}e^{-\frac{F}{R_{h}}t}$$

$$\Lambda = e^{-\frac{F}{R_{h}}t}$$

$$\Pi = 1 - e^{-\frac{F}{R_{h}}t}$$
(5-35)

As mentioned above, these equations can be employed to determine R_h and then K_h , through curve-fitting or linearization (logarithmically) of the gas-purging data.

 $\phi = 0$. The following substitutions can be made:

(a). R_i = R_h (Equation 5-7).
(b). P = (R_t + F)/R_h and Q = Fk_d/R_h (Equation 5-21).

The system equations in this case have the same appearance as Equations 5-31, 5-33 and 5-34, but L_1 and L_2 have different insides. In fact, this scenario is equivalent to a one-

domain desorption model in which the mass transfer across the sorbent-solution boundary is no longer instantaneous but follows the first-order kinetics (rate-limiting process).

Other than gas-purging. The modeling conceptualization and mathematical derivation describe here can be easily adopted to other systems. For instance, a system in which a desorption-retarded chemical or biological reaction (first-order) occurs in the solution phase can be modeled with two modifications: (a) the gas phase does not exist, and (b) the depletion term in Equation 5-10, *i.e.*, $-FC_g$ is substituted by $-kC_a$ (k is the reaction rate constant).

[6] An Application of the Two-Domain Model

This example system employed toluene as the solute and MG soil (Chapter 2) as the sorbent. A soil-free sample was used to evaluate the Henry's Law constant. Table 5-1 lists the time-response data actually recorded using a gas-purging apparatus similar to the one described by Brusseau *et al.* (1990), as well as the calculated fractional mass purged, II, (*i.e.*, the cumulative area at time t divided by the total area under the decay curve). Table 5-2 summarizes the system parameters, and the curve-fitted ϕ and k_d values. A plot of the experimental data and the model-generated curve (II) against time (t) is shown in Figure 5-1, which shows that the measured data successfully fit in the two-domain model. Our best curve-fitted k_d value (0.054 min⁻¹ or 3.2 hour⁻¹) falls in the range of the k_d values of trichloroethene and benzene (from 1.32 to 17.1 hour⁻¹) reported by Brusseau *et al.* (1990), using soils with 0.39 to 18.0 % soil organic carbon (OC). More application of this two-domain model will be carried out in other study currently being conducted in our laboratories.

	No Soil		MG Soil			
Time (min)	Detector Response	Fractional Purged Mass	Time (min)	Detector Response	Fractional Purged Mass	
0	68.60	0.0000	0	63.40	0.0000	
1	43.00	0.1414	1	41.20	0.1326	
2	36.80	0.2424	2	34.75	0.2288	
4	29.15	0.4095	3	29.90	0.3108	
6	22.20	0.5396	4	26.35	0.3821	
8	17.70	0.6407	6	20.90	0.5019	
10	14.05	0.7211	8	16.40	0.5964	
12	10.95	0.7844	10	13.10	0.6712	
16	6.50	0.8728	12	10.50	0.7310	
20	3.90	0.9255	16	7.10	0.8203	
24	2.45	0.9577	20	4.75	0.8803	
28	1.40	0.9772	24	2.95	0.9194	
32	0.80	0.9883	28	1.85	0.9437	
36	0.45	0.9947	32	1.20	0.9592	
40	0.20	0.9980	36	0.90	0.9698	
44	0.10	0.9995	40	0.70	0.9779	
48	0.00	1.0000	44	0.55	0.9843	
-	-	-	52	0.30	0.9929	
•	•	•	60	0.15	0.9975	
-	-	-	68	0.05	0.9995	
-	-	•	76	0.00	1.0000	

Table 5-1. Actually measured gas-purge data of toluene from pure water system and MG soil-water system.

	No Soil	MG Soil		
Experimental Parameter				
Vg, ml	96.1	96.1		
Va, mi	200	200		
W, g	-	5		
К	•	5.52		
F, ml/min	144.30	143.90		
Curve-Fitting Result				
Kh	0.198	•		
kd	-	0.054		
ф	•	0.648		

Table 5-2. The experimental parameters for the gas-purge studyof desorption of toluene from MG soil. Also listed are thebest curve-fitting results.



Figure 5-3. Plot of the fractional toluene mass purged against time.

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