

Organic compound distribution between nonionic surfactant solution and natural solids: Applicability of a solution property parameter

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Abstract

A solution property parameter φ was defined to examine the distribution characteristics of organic compounds between the solids and four nonionic surfactant solutions. The studied compounds consisted of BTEX (benzene, toluene, ethylbenzene, and *p*-xylene) and chlorinated pesticides (lindane, α -BHC, and heptachlor epoxide), which span several orders of magnitude in terms of water solubility (S_w). The solid samples were composed of a very low organic matter clay (Ca-montmorillonite), and a high organic matter natural soil (Shamou Mountain soil). The surfactants tested included two alkyl chain surfactants and two containing aromatic group surfactants with added concentrations both below and above their critical micelle concentration (CMC). By observing the K_{om} or K_{sf} variation, the result indicates, besides the S_w of the organic compounds, the distribution coefficient is regarded as a function of the soil organic matter (SOM) constituents, and the chemical structure of the organic compounds. Also, it can be found the greater φ values represent the higher releasing ratios of the organic compounds from the contaminated soil to groundwater. For the relatively higher S_w compounds, such as BTEX, all of the φ values are close to 1. The φ values for the relatively lower S_w compounds are far greater than 1, and increase with the increasing affinity of the compounds to the surfactants.

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1. Introduction

The problem of soil and groundwater pollution has become an increasingly important issue in recent years. Surfactants offer a potential means for remedying contaminated soils or sediments via a pump-and-treat or soil/sediment-washing operations because the presence of surfactants in the solution can enhance the apparent solubilities of the compounds, more effective by washing organic compounds away from the contaminated soil [1–7]. Aside from this above-mentioned application, surfactants in a soil–groundwater system may increase the SOM content, which organic compounds can increasingly partition to or enhance the organic compound S_w , which can cause the organic compounds to be released into the groundwater [8–10]. The mechanisms with regard to the surfactant adsorption on soils have already been widely discussed. Ionic surfactant adsorption on solids is strikingly affected by electrostatic forces [11,12].

Nonionic surfactant adsorption is mainly correlated with the properties of the soil mineral phase [13–15]. In addition, the amount of organic compounds released to the surfactant solution depends on the compound S_w and the surfactant polarity [16].

When soils are water-saturated, the predominated nonionic organic compound sorption is partitioning into the SOM because water suppresses the compound adsorption on mineral matter. The distribution coefficients (K_d) of organic compounds between the solid and the solution may be expressed by a linear relation [17].

$$x/m = K_d C \quad (1)$$

where x is the compound uptake on the solid (mg), m the weight of the solid (kg) and C is the equilibrium compound concentration in the solution (mg/L). The K_d values of the selected compounds increase as the organic matter fraction (f_{om}) of the solid increases, furthermore for a specific soil they decrease as the S_w of the organic compound increases. A more useful compound distribution coefficient would be when the K_d for a soil

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is normalized to the corresponding soil organic carbon fraction f_{oc} or soil organic matter fraction f_{om} , i.e. [18]

$$K_{oc} = K_d/f_{oc} \quad (2)$$

$$K_{om} = K_d/f_{om} \quad (3)$$

with

$$K_{oc} = 1.742K_{om} \quad (4)$$

Although the SOM contents vary with the collection sites, the normalized value, K_{oc} or K_{om} , for an organic compound is similar [18]. However, some research has revealed that the polycyclic aromatic hydrocarbon compounds (PAHs) in sediments have relatively higher K_{oc} values than those in other natural soils [19–21]. The reason for this is ascribed to the presence of a greater proportion of polycyclic aromatic group compounds in the organic matter of the sediments, which enhances the affinity of the PAHs to the organic matter. However, it is difficult to conclude the above result due to the complex SOM constituents. When the organic matter consists of the sorbed surfactant, the structure and polarity of the surfactant has been known, and thus the effects of the SOM constituents on the distribution coefficient of a given compound can be realized. For a nonionic organic compound in a surfactant–soil–water system, the linear relation mentioned above in Eq. (1) can be rewritten as [8,10,22]

$$x/m = K_d^*C \quad (5)$$

where K_d^* is the distribution coefficient of the compound in the surfactant–soil–water system. The observed K_d^* is significantly affected by the characteristics of the soil, the surfactants and the compounds [16,23–27]. With a very low SOM (≈ 0) soil, the sorbed surfactant is regarded as the sole SOM. Thus K_d^* in Eq. (5) is directly expressed as follows:

$$K_d^* = f_{sf}K_{sf} \quad (6)$$

where f_{sf} is the sorption fraction of the surfactant with respect to the soil and K_{sf} is the distribution coefficient of the organic compound between the sorbed surfactant and the solution. The characteristics of f_{sf} have already been stated in the literature [8,28–30]. The magnitude of K_{sf} is not a direct function of f_{sf} , but is primarily correlated with the properties of the sorbed surfactants and the compounds. On the other hand, for a natural soil, although surfactant adsorption on the soil surface can enhance the SOM, the physico-chemical properties of the sorbed surfactants relative to those of the natural SOM have quite obvious diversity. A more detailed equation would be

$$K_d^* = f_{om}K_{om} + f_{sf}K_{sf} \quad (7)$$

The above-mentioned equation can differentiate the discrepancy between the SOM and the sorbed surfactant, but the force of the surfactants attracting the organic compounds into the solution might cause the bias in Eq. (7). The desorptions of organic compounds from various organic matter content soils using the nonionic surfactant solution have been studied [8,10]. The added surfactant concentration, the SOM content and the compound S_w

are the most important key points. The effects of these parameters on the apparent K_d^* need to be determined. With regard to the estimated K_d^* , a considerable equation has been presented as follows [31]:

$$K_d^* = K_d(1 + f_{sf}K_{sf}/K_d)/(1 + X_{mn}K_{mn} + X_{mc}K_{mc}) \quad (8)$$

where X_{mn} is the concentration of the surfactant as monomer in water (mass/mass, dimensionless), X_{mc} the concentration (dimensionless) of the surfactant as micelle in water, K_{mn} the partition-like coefficient of the solute between surfactant monomer and water (dimensionless), and K_{mc} is the partitioning coefficient between the aqueous micellar phase and water (dimensionless). The effects of the solubility enhancement on K_d^* have been incorporated in Eq. (8). For the characteristics of K_d^* in Eq. (8), the low S_w compounds in a given surfactant–soil–water system show the lower K_d^* values, resulting from the surfactant in the solution enhances the apparent S_w of the compounds [10,16]. However, it is difficult to estimate the effects of the surfactant on either solid or liquid phase because of the unknown parameters, such as K_{sf} , K_{mn} and K_{mc} . Therefore, a simply approach to quantitatively determine these effects need to be developed. In this study, we elucidate the characteristics of K_{sf} and furthermore establish a solubility property parameter that quantitatively describes the effects of surfactants on organic compounds released from contaminated soils to the groundwater.

To eliminate the influence of electrostatic forces in this study, four nonionic surfactants are used in the sorption experiments including TritonX-305 (TX-305) and TritonX-405 (TX-405) contained the aromatic ring and only alkyl chain $C_{12}E_5$ and $C_{12}E_9$. Differences in K_{sf} , resulting from differently structured surfactants, are elucidated so as to further understand the effects of the SOM constituents on the distribution coefficients. A very low SOM clay, Ca-montmorillonite, was used to obtain the K_{sf} values of the selected compounds relative to the surfactants. A high SOM soil, Shamou Mountain soil, was selected to confirm the variation in the solution property parameters of the different S_w compounds. The K_{om} characteristics of the different S_w compounds relative to the surfactant properties are discussed. A approach was established to obtain the solution property parameter. Currently organic compound desorption from the soil is frequently observed with a practical surfactant washing pilot, however the method (or parameter) developed in this study, the determination of the distribution coefficient, given the applied surfactant levels, should facilitate the evaluation of the potential impact of this and similar surfactants on the compound distribution behavior in natural water and/or at waste-disposal sites. The results can be applied to predict the amount of organic compounds that may be released from contaminated soil into the groundwater.

2. Experimental methods

2.1. Chemicals

The selected compounds, which have a wide range of S_w and K_{ow} , were the four BTEX compounds (benzene, toluene,

Table 1
Selected properties of BTEX and chlorinated pesticides at room temperature

Compound	MW	MP (°C)	log S_w^a (mol/L)	log K_{ow}^b
Benzene	78	5.5	−1.64	2.13
Toluene	90	−95	−2.25	2.69
Ethylbenzene	102	−95	−2.84	3.15
<i>p</i> -Xylene	102	13.2	−2.73	3.15
Lindane	291	113	−4.57	3.72
α -BHC	291	160	−5.16	3.72
HPOX	389	161	−6.29	4.97

MW: molecular weight, MP: melting point, S_w : water solubility (25 °C), K_{ow} : octanol–water partition coefficient (25 °C).

^a As cited in ref. [8].

^b Estimated from ref. [18].

Table 2
Selected properties of surfactants used in solubilization and partitioning experiments

Surfactants	Molecular formula	MW (g/mol)	CMC (mg/L)
C ₁₂ E ₅	C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₅ OH	406.6	25
C ₁₂ E ₉	C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₉ OH	582.6	44
TX-305	C ₈ H ₁₇ C ₆ H ₄ O(CH ₂ CH ₂ O) ₃₀ H	1526	1068
TX-405	C ₈ H ₁₇ C ₆ H ₄ O(CH ₂ CH ₂ O) ₄₀ H	1966	1592

ethylbenzene and *p*-xylene) and three pesticides α -BHC (hexachlorocyclohexane, α -isomer), lindane (hexachlorocyclohexane, β -isomer) and heptachlor epoxide (HPOX). The four BTEX compounds were supplied by the Aldrich Company, Milwaukee, WI. The three pesticides were obtained from the Riedel de Haën Company, Germany. All these compounds were of analytical grade or better and were used as received. The selected physico-chemical properties of the compounds are given in Table 1.

2.2. Surfactants

The molecular structures, molecular weights and CMCs of the selected surfactants are given in Table 2. The alkyl surfactants, C₁₂E₅ and C₁₂E₉, had a purity of >98%. The Triton series of surfactants supplied by the Riedel de Haën Company were mixtures, with an indicated average ethylene oxide (EO) chain numbers of 30 for TX-305 and 40 for TX-405. The sorption capacities of the surfactants on the tested solids as a function of surfactant concentration were determined by adding 0.1 g (for alkyl chain surfactants) or 1.0 g (for Triton series surfactants) of the solid samples to 20 mL of deionized water in Corex centrifuge tubes. The concentration of each surfactant added covered a large range from below to above the nominal CMC of the surfactant in deionized water. The suspensions were equilibrated in a reciprocating shaker for 48 h at 25 °C. The solution

Table 3
Properties of studied solid samples

Solid	Clay (%)	SA (m ² /g)	f_{om} (%)	pH	CEC (mequiv./100 g)
Ca-montmorillonite	>99	76.0	0.30	8.03	120
Shamou Mountain soil	8	57.2	27.3	5.21	53.9

SA: BET-(N₂) surface area, f_{om} : fraction of organic matter in solid and CEC: cation exchange capacity.

and solid phase were separated by centrifugation at 8000 rpm (7649 × g) for 30 min in a Sorvall RC-5C centrifuge. A 1 mL aliquot sample of the supernatant was removed and analyzed for the Triton series surfactant by UV at wavelength of 275 nm; no major changes in UV spectral pattern of the two Triton surfactants were observed after equilibration for the solid samples. Since only the surfactant's aromatic component can be measured at a UV wavelength of 275 nm, the amounts of alkyl chain surfactants sorbed were determined by a TOC Analyzer (O. I. Analytical Corporation). The amounts of surfactants sorbed could be simply computed by the difference between the initial and final surfactant concentration in the solution. Although the dissolved organic matter could release from the SOM to the surfactant solutions which affect the above-mentioned analysis result, the significant influence do not be found in this study. The obtained result is therefore considered as the effective data.

2.3. Pretreatment and soil properties

A natural soil and a clay were selected for the sorption mediums. The Ca-montmorillonite purchased from Source clay Minerals Repository in University of Missouri–Columbia, designated as Ca-Mon, could be used directly and did not need to be pretreated further. A natural organic-rich top soil from Shamao Mountain designated as SM, in Taipei County, Taiwan, was used. Before all of the sorption experiments, the natural soil samples were air-dried and then sieved to obtain particles of less than 2.0 mm. For surface area determination, the soil and clay samples were outgassed at 135 °C prior to the measurement. The surface areas (SAs) were determined using a Brunauer–Emmett–Teller (BET) plot of the nitrogen adsorption data taken at the temperature of liquid nitrogen using a Quantasorb Jr. sorption apparatus, with helium as the carrier gas. The dry SAs and other properties of the solid samples are given in Table 3.

2.4. Analytical conditions of organic compounds

The initial surfactant concentrations were set to be below and above the nominal CMC in deionized water. 0.1–1.0 g samples of the tested solids, determined by adding varying quantities of a given test compound, were mixed with 20 mL of the above-mentioned surfactant solution in a Corex glass tubes. The target compound concentrations, about 30–70% S_w in the surfactant–soil mixture solution, were then added into the tubes. For convenience of analysis, the high S_w BTEX and low S_w pesticides were treated individually.

The BTEX compounds were added directly as neat liquids using a Hamilton microliter syringe. The pesticides were added

as stock solutions in methanol. It was assumed that the small amount of methanol in the water solution (<2%) would have an insignificant effect on the distribution of the tested compound, as has been found in similar studies on the organic compound sorption on soils. After the above process, the tubes were closed with Teflon foil-lined screw caps and equilibrated for 48 h in a reciprocating shaker. The resultant slurries were then centrifuged for 30 min at 8000 rpm to separate the solution and solid phases. Aliquot samples of the solution phase (1 mL) were then transferred into glass vials containing 2 mL of carbon disulfide (for BTEX solutes) or of hexane (for lindane, α -BHC, and HPOX). These vials were sealed with Teflon foil-lined screw caps and shaken for 3 h on a reciprocating shaker. The extracts were injected into a GC to obtain equilibrium concentrations of the selected compounds under various added surfactant concentrations. According to Eqs. (1) and (5), the distribution coefficients (K_d or K_d^*) of the compounds in the system were determined by a linear regression.

The GC analysis was performed on a Model 5890A Hewlett Packard gas chromatograph equipped with either a flame ionization detector (for the BTEX compounds) or an electron capture detector (for lindane, α -BHC, and HPOX). A 5% sp-1200/1.5% Bentonite 34 on 100/120 Supelcoport packed steel column (1.8 m \times 3.2 mm i.d.) was used for the separation of the BTEX compounds; a 1.5% sp-2250/1.95% sp-2401 on 100/120 Supelcoport packed glass column (2.4 m \times 6.4 mm i.d.) was used for the separation of the pesticides. Each experiment was duplicated and the data was averaged. If the bias of the repeated experiments exceeded 15%, triplicate repetitions were made. Blank experiments, without solid, were performed for the tested compounds for each batch experiment; the recoveries ranged from 90 to 95%. The measured equilibrium concentrations were not adjusted for the recoveries.

3. Results and discussion

In this study, a clay and natural soil listed in Table 3 are used to elucidate distribution characteristics of organic compounds in a surfactant–soil–water system. The clay, Ca-Mon, acted as the reference material to obtain the K_{sf} at selected compounds partitioned to the sorbed surfactants because the effects of the natural SOM on organic compounds partitioning to Ca-Mon could be neglected. The natural soil, SM was selected because of its higher SOM content. When the data for SM fit the expectations, the obtained results could also be applied to other soils with a relatively lower SOM content. Generally, the exhibited sorption isotherms of the nonionic surfactants on soils are the “L-type” curves and the surfactant uptake reaches a plateau at equilibrium concentration (C_e) around 1–2 times the nominal CMC in pure water [8,10,13,15,30]. To more conveniently estimate f_{sf} and K_{sf} , changes in the f_{sf} values of the different added surfactant concentrations (X) sorbed on Ca-Mon and SM are illustrated in Figs. 1 and 2, respectively. All show the “L-type” curves with maximum uptake at X about 1–2 times the CMC. This indicates that there was competition of the adsorptive sites for a given surfactant relative to the selected solids. Due to the very low SOM content of Ca-Mon, the major mech-

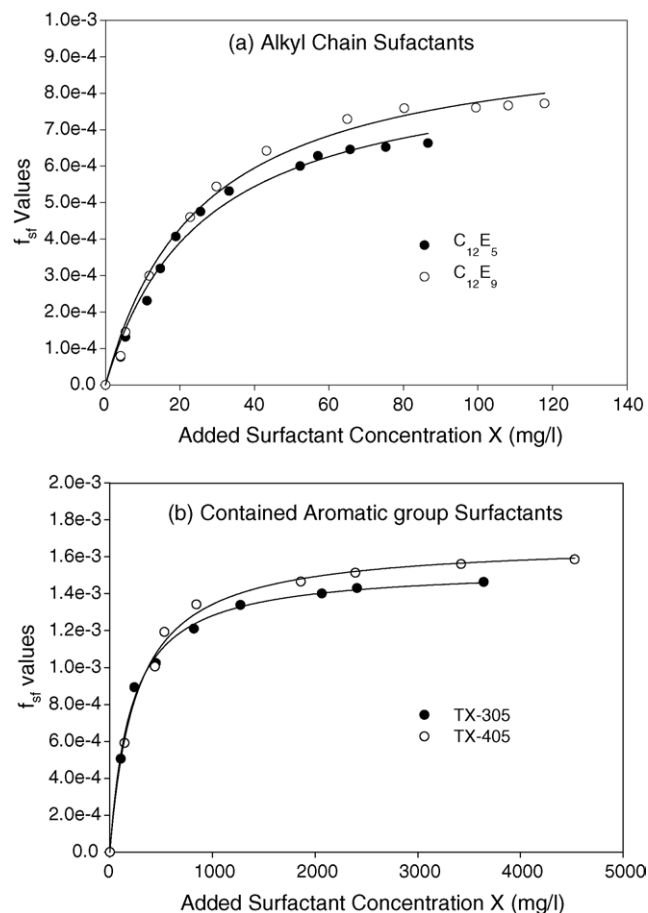


Fig. 1. The relationship between the added surfactant concentration (X) and the uptake (f_{sf}) on Ca-montmorillonite.

anism of the surfactant uptake is adsorption that is easily to be understood. For the SM with the higher SOM content, the above-mentioned result indicates the effects of the surfactant partitioning to the SOM can be neglected in the experiments. On the other hand, the polarity of the surfactant, i.e. the EO chain numbers, is regarded as a dominator factor in determining the adsorption capacity. As expected, the limiting monolayer adsorption capacity of the surfactants, for Ca-Mon and SM, is closely related to the EO chain numbers, in the following order: TX-405 > TX-305 > C₁₂E₉ > C₁₂E₅. The results indicate the opposite order with respect to the literature [12,13]. A major difference for this is the micromole per gram is generally applied in the literature to express surfactant uptake unit for soils. On the basis of the adsorptive surfactant mass, the higher EO chain number surfactants have a more significant affinity with the soil's mineral phase surface which causes the higher surfactant uptake. Also, it should be noted if the surfactants possess the obviously different homologs, the obtained result might have some bias. To compare Ca-Mon with SM, the Ca-Mon has a relatively higher surface area, resulting in the higher monolayer adsorption capacity for the surfactants. The results further demonstrate that the mechanism of the selected surfactant uptake on the solids is adsorption. In other words, Eq. (7) can be confirmed, regardless of the influence of the surfactants in liquid phase.

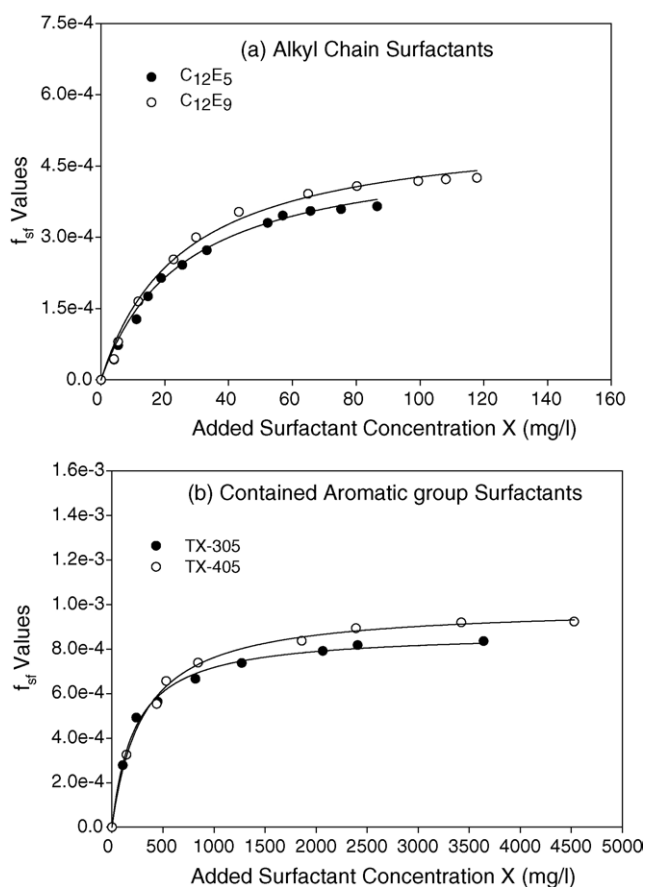


Fig. 2. The relationship between the added surfactant concentration (X) and the uptake (f_{sf}) on Shamou Mountain soil.

Both K_{oc} and K_{om} are frequently used to evaluate the characteristics of the organic compounds partitioning to the SOM. In this study, two Triton series surfactants are composed of the different EO chain number surfactants. The surfactant uptake on the solids varies with the different EO chain number, leading to the uncertain organic carbon fraction (f_{oc}). Accordingly, the K_{om} is a better parameter which is used to explain difference in the organic compound distributions between the solids and the surfactant solutions. As mentioned earlier in Eq. (6), the K_{om} obtained from the surfactant sorbed on Ca-Mon can be replaced with the K_{sf} while the sorbed surfactant is the sole organic matter source. The identical SOM constituents purified with a given

surfactant can clarify K_{oc} or K_{om} bias for the natural solids. As a result, the K_{sf} values of the target compounds relative to the tested surfactants need to be determined before applicability of different S_w organic compounds in Eq. (7) is considered. It was well known that the K_{sf} value is a function of the compound S_w and the surfactant properties such as their polarity and chemical structure. The average K_{sf} values as well as standard deviation of the target compounds with respect to the tested surfactants at three added concentrations are presented in Table 4. The striking features are as follows: (i) according to the observed standard deviation, there is a similar K_{sf} value for a given compound associated with a specific surfactant. Also, the relative standard deviation values of the selected compounds increase as the S_w value decreases; (ii) the K_{sf} values of the compounds relative to a given surfactant roughly increased as the compound S_w decreased. However, there are some differences in the K_{sf} values for the different surfactants; (iii) for the selected surfactants, the K_{sf} values of the aromatic compounds have the order: $C_{12}E_5 > TX-305 > TX-405 > C_{12}E_9$. This is not related to the EO chain numbers, but those of the pesticides are inversely proportional to surfactant EO numbers; (iv) the K_{sf} values of the higher S_w aromatic compounds are similar to estimations from the literature. The K_{sf} values of the relatively lower S_w compounds are significantly different from those in the literature, especially for HPOX.

The above results can be understood on the basis of the distribution characteristics of the organic compounds in the surfactant–soil–water system. It has been mentioned earlier that the K_{om} values of an aromatic compound relative to the various soils or sediments have the obvious bias. The result of the quite similar K_{sf} value under the different added surfactant concentrations indicates that the K_{om} value of a given compound approaches a constant if the SOM constituent is identical. However, a small K_{sf} (or K_{om}) bias is found for sorbed surfactants with the different polarity and the chemical structure, further demonstrating the properties of the surfactants will affect the distribution of the organic compounds between the surfactant solution and the solids. For the higher standard deviation on the low S_w compounds, the major factor that influence their K_d^* values is the solution properties as shown in previous investigation [8,10,16,31]. A possible reason for the higher standard deviation is that the surfactants form micelles in the solution, offering a better hydrophobic environment in the solution to reduce the K_{sf} values.

Table 4
Average K_{sf} (standard deviation) values of the target compounds for the selected surfactants on Ca-Mon

	$C_{12}E_5^a$	$C_{12}E_9^a$	TX-305 ^a	TX-405 ^a	Estimation ^b
Benzene	24.0 (1.74)	17.6 (1.54)	22.4 (1.11)	20.3 (0.92)	15.8
Toluene	36.6 (2.60)	30.9 (3.52)	34.1 (1.98)	32.5 (1.25)	44.7
Ethylbenzene	78.5 (4.29)	60.6 (2.32)	73.5 (2.62)	63.5 (2.79)	118
<i>p</i> -Xylene	87.5 (4.44)	67.9 (4.13)	80.1 (5.04)	70.6 (3.17)	98.0
Lindane	1675 (238)	1403 (203)	899 (168)	695 (143)	3746
α -BHC	4277 (691)	3684 (628)	2755 (411)	2080 (388)	10085
HPOX	6958 (1042)	5163 (836)	3637 (582)	2890 (536)	67214

^a The respectively added concentrations (mg/L) for $C_{12}E_5$ are 10, 31.9 and 85.1; for $C_{12}E_9$ are 10, 47.5 and 166.4; for TX-305 are 500, 1000, and 2000; for TX-405 they are 600, 1500, and 3000.

^b $\log K_{om} = 0.729 \log S_w + 0.01$; S_w : mol/L [18].

Over the last decade, S_w of the organic compounds has come to be regarded as the main parameter influencing organic compound partitioning to the SOM. This is because the partitioning behavior is controlled by the affinity of organic compounds to the SOM. SOM is classified as a very low polarity medium, and thus a compound with a relatively lower S_w (or higher K_{ow}) generates a higher normalized partitioning coefficient K_{om} . According to the standpoint, when the surfactant sorbed to be the enhanced SOM has a higher affinity with the organic compounds, and then higher K_{sf} values should be expected. In theory, a low polarity organic compound relative to the sorbed surfactant with the higher EO chain numbers can generate lower K_{sf} values because EO chain numbers can represent the quantified surfactant polarity in this study. Similarly, the K_{sf} values of the various compounds for a given surfactant are closely inversely proportional to the compound's S_w . However, the partial results that do not correspond to the above characteristics indicate existence of other parameters dominates organic compound distribution. The discrepancy might be a result of other parameters competes with the compound's S_w . The differences in chemical structure between the compounds and the surfactants are considered to be an important factor [22]. The functional groups of aromatic and aliphatic chemicals play a key role in dictating their partitioning behavior [22,32]. Generally, aromatic compounds with instable π bonds are more polarizable, thus promoting molecular attractions by the induced dipole-induced dipole force [33]. The obtained K_{sf} values for aromatic compounds relative to the selected surfactants are regarded as a function of two parameters, including compound S_w and the π - π election interactions between the planar structures. For a selected pesticide without the aromatic group, the order of the K_{sf} values is reasonably related to the surfactant EO numbers. The results demonstrate that the affinity of compounds to the natural SOM can be determined based on their chemical structures and S_w . The traditional explanation for organic compounds partitioning to the SOM only focuses on the S_w values of the compounds. To simulate the SOM by sorbed surfactants, the effects of the chemical structures of the certain SOM constituents on organic compounds partitioning to the SOM can be confirmed.

Although sorbed surfactants can be thought of enhanced SOM, this surfactant differs from the natural SOM, which possesses a quite low polarity. This leads the estimated K_{om} values of the organic compounds in the natural SOM–water system to be higher than the K_{sf} values in the simulated SOM–water system. The difference for the various S_w compounds also increases as S_w decreases. According to previous investigation, the K_d^* value of a high S_w compound in the surfactant–soil–water system is determined via the SOM properties, but that of a low S_w compound is significantly affected by the solution properties [8,16]. The estimated K_{om} values for the relatively higher S_w BTEX are slightly higher than the K_{sf} values. This can be attributed to be different properties between the natural SOM and the sorbed surfactants. With the low S_w pesticides, the surfactants in the solution might enhance the compound solubility, increasing the amount of pesticide released from the solid into the solution. More obvious released amounts can be found when the surfactants form micelles in the solution, offering a better hydrophobic

environment. On the basis of S_w enhancement theory, the lower S_w organic compound indicates a more significant amount of S_w enhancement in the surfactant solution [34]. As expected, the three pesticides in the surfactant solutions can lead to the reduction of pesticides uptake into the sorbed surfactants. In particular for the less water-soluble compounds in a surfactant–soil–water system, the solution's properties lead to a greater difference in the K_{sf} values from the estimated values. As a result, for a relatively lower S_w compound, such as HPOX, there is a dramatic increase in the K_{sf} value.

In the previous descriptions, it can be found that the characteristics of the sorbed surfactant and the natural SOM are different. Although effects of the surfactants in soil–water system on the organic compound distribution have been discussed in the literature, the obtained result cannot differentiate the effects of surfactants from solid phase or liquid phase. In Eq. (8), the characteristics of the K_d^* value for a natural soil can be obtained from the distribution change of the organic compounds between the solid and solution. However, too many unknown parameters lead to difficultly quantified the effects the surfactants on the K_d^* values. Thus, we develop a simply approach to examine the result. The SM with the high natural SOM soil was selected as target. A solution property parameter ϕ for surfactant attracting organic compounds released into solution is defined as follows:

$$\begin{aligned}\phi &= K_{d(\text{estimated})}^*/K_{d(\text{apparent})}^* \\ &= (K_{sf}f_{sf} + K_{om}f_{om})/K_{d(\text{experiment})}^*\end{aligned}\quad (9)$$

where $K_{d(\text{apparent})}^*$ is the apparent distribution coefficient of the organic compound between the solid and the surfactant solution, that is, $K_{d(\text{experiment})}^*$ is obtained via the experiments. The $K_{d(\text{estimated})}^*$ values are calculated according to Eq. (7). The ϕ values represent the releasing ratios of the organic compounds into the solutions because surfactants attract organic compounds. Significantly, the ϕ value is close to 1 can represent the negligible influence on the solution properties. Before the ϕ values are obtained, the term $K_{om}f_{om}$ (i.e. K_d) for the natural SOM needs to be determined. The K_d and K_{om} values of the selected organic compounds for the relatively higher SOM soil, SM, without the surfactants are given in Table 5. The obtained K_{om} values can be compared with the K_{sf} values in Table 4. It can be found the K_{om} values of the relatively high S_w BTEX compounds are more consistent with the K_{sf} values obtained from the sorbed surfactant and with K_{om} values estimated according to the literature. However, the low S_w pesticides indicate the lower K_{om}

Table 5
 K_d and K_{om} values of the selected compounds partition in SM with the high SOM ($f_{om} = 0.273$)

	K_d	K_{om}
Benzene	5.52	20.2
Toluene	10.5	38.5
Ethylbenzene	24.8	90.8
<i>p</i> -Xylene	25.2	92.3
Lindane	488	1788
α -BHC	1460	5348
HPOX	5450	19963

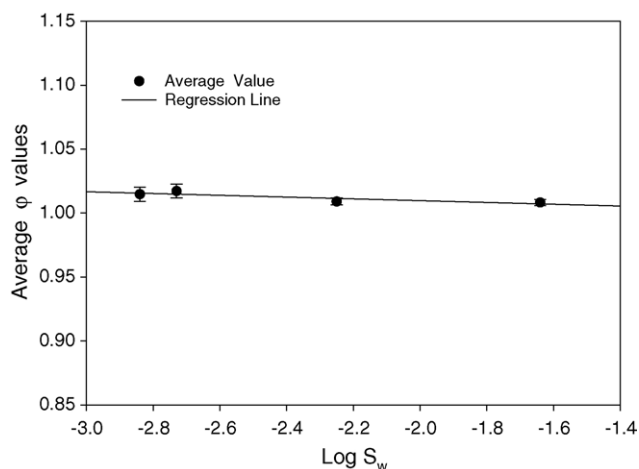


Fig. 3. The average ϕ values and standard deviation of the relatively higher S_w BTEX in the selected surfactant–soil–water system.

values than those estimated from literature and the higher K_{om} values than K_{sf} values in Table 4. There are two interpretations for the above difference. The first is the SOM constituent diversity. Besides the difference in the natural SOM constituent, the sorbed surfactants have a practical polarity difference with the natural SOM. The second is the S_w estimation error. Precise S_w values for low S_w compounds are often difficult to be obtained.

Since S_w is a very important factor for determining ϕ values, the higher S_w BTEX and the three lower S_w pesticides need to be described separately. In Table 4, the presence of surfactants in the system does not make obvious diversity for the K_{sf} values of BTEX. Therefore, we plot the average ϕ values of BTEX in the four surfactants solution with the identical concentrations in Table 4 against their S_w in Fig. 3. As expected, all of the ϕ values of the selected compounds are close to 1 and the standard deviation values are low. In addition, the linear regression line indicates that all of the ϕ values have a low sensitivity on S_w . The relatively higher S_w compounds, such as BTEX, indicate a low trend of released to the surfactant solution to cause small changes in ϕ values. Moreover, most of the surfactants in the soil–water system do not influence the distribution coefficient (K_d) of these organic compounds.

Although surfactants in the solution can attract the low S_w organic compounds into the solution has been discussed in the literature, the ϕ values offer a good reference to quantify the data. Fig. 4 illustrates the ϕ values of three pesticides related to their S_w for the lowest and highest added surfactant concentration (X) of the four selected surfactants in Table 4. The X values include below and above CMCs of the selected surfactant. The ϕ values obviously increase with the decreasing S_w and with the decreasing EO chain numbers of the surfactants, which correspond with the solubility enhancement concept. For the $X < CMC$ condition, the maximum ϕ value reach to about 1.5 that reflects the relatively low concentration surfactant in the soil–water system has already generated a comparable effect. The ϕ values of the lowest S_w compound HPOX ($\log S_w = -6.29$ mol/L) for $C_{12}E_5$ and $C_{12}E_9$ under $X > CMC$

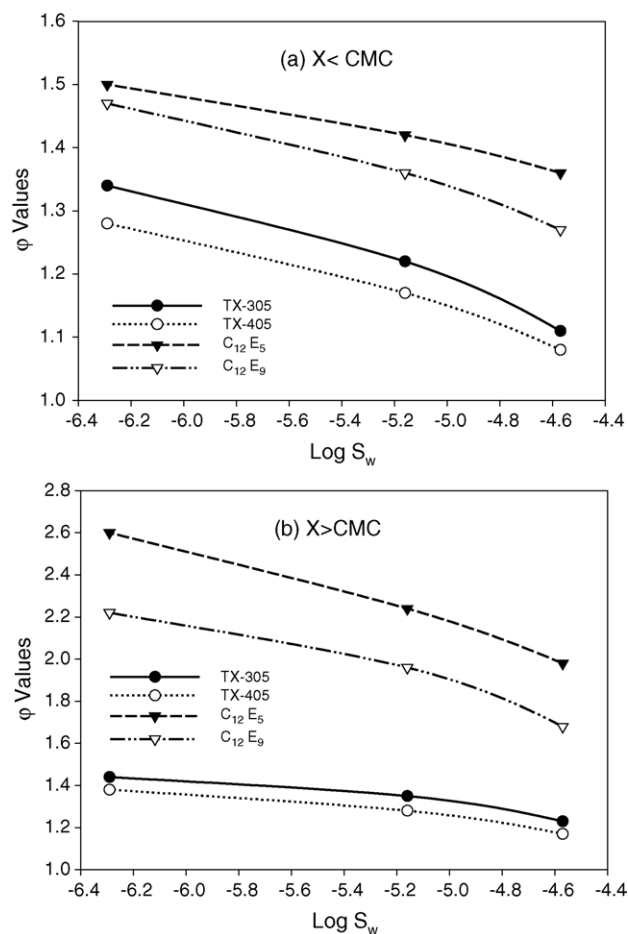


Fig. 4. The ϕ values of the relatively lower S_w pesticides on Shamou Mountain soil for the added surfactant concentrations (X) below and above their CMC.

condition is far higher than those under $X < CMC$. It is known that $C_{12}E_5$ and $C_{12}E_9$ have the lower CMC values. In the other words, these kinds of surfactants easily reach to the CMC in a soil–water system to attract the low S_w organic compounds partitioning into the solution. With a view of soil remediation by surfactant washing, these surfactants are capable of effectively remedying the soils contaminated by the low S_w compounds. If the partitioning of organic compounds between soil and groundwater is taken into account, the presence of these surfactants in soil–groundwater system leads to organic compounds release from the contaminated soil to the groundwater, which generates a possible impact on human being. As for TX-305 and TX-405, two possible reasons cause only little difference in the ϕ values of the given organic compounds. One is that surfactants with the relatively higher EO chain numbers have a poor solubility enhancement effect, and the other is that surfactants have not formed micelles in the solution. The presence of high concentrations of these surfactants in the soil–water system can form micelles. However, it is difficult for the above surfactants up to CMCs to be found in a real environment. Thus, the presence of these surfactants does not significantly influence the distribution coefficients K_d^* of the organic compounds.

4. Conclusions

Usually studies over the past few years regarding the distribution coefficients of organic compounds in the surfactant–soil–water system have focused on surfactant adsorption on the soils which enhance the SOM. Although sorbed surfactants can be thought of as enhanced organic matter, the properties of the natural SOM and sorbed surfactants still need to be discussed separately due to the obvious polarity variation. As the SOM is purified by the sorbed surfactant, the effects of the SOM constituents on the distribution characteristics of the organic compounds can be understood according to variation in the chemical structure. In order to precisely delineate the effects of the surfactants in the solution on the distribution coefficients, we need to present the solution property parameter φ . The obtained φ values can be applied during the surfactant washing of contaminated soil or the study of organic compound partitioning to groundwater.

References

- [1] A.S. Abdul, T.L. Gibson, Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyl from sandy material, *Environ. Sci. Technol.* 25 (1991) 665–671.
- [2] K.H. Dma, N.C. Ann, M. Megehee, Soil clean-up by surfactant washing. III. Design and evaluation of the components of the pilot-scale surfactant recycle system, *Sep. Sci. Technol.* 28 (1993) 2319–2349.
- [3] R.A. Griffiths, Soil-washing technology and practice, *J. Hazard. Mater.* 40 (1995) 175–189.
- [4] E.P.S. Cheah, D.D. Reible, K.T. Valsaraj, W.D. Constant, B.W. Walsh, L.J. Thibodeaux, Simulation of soil washing with surfactants, *J. Hazard. Mater.* 59 (1998) 107–122.
- [5] S. Deshpande, B.J. Shiao, D. Wade, D.A. Sabatini, J.H. Harwell, Surfactant selection for enhancing ex situ soil washing, *Water Res.* 33 (1999) 351–360.
- [6] W. Chu, C.Y. Kwan, Remediation of contaminated soil by a solvent/surfactant system, *Chemosphere* 53 (2003) 9–15.
- [7] W. Chu, K.H. Chan, The mechanism of the surfactant-aided soil washing system for hydrophobic and partial hydrophobic organics, *Sci. Tot. Environ.* 307 (2003) 83–92.
- [8] J.F. Lee, P.M. Liao, C.C. Kuo, H.T. Yang, C.T. Chiou, Influence of a nonionic surfactant (TritonX-100) on contaminant distribution between water and several soil solids, *J. Colloid Interf. Sci.* 229 (2000) 445–452.
- [9] Y. You, H. Zhao, G.F. Vance, Surfactant-enhanced adsorption of organic compounds by layered double hydroxides, *Colloid Surf. A* 25 (2002) 161–172.
- [10] W. Zhou, L. Zhu, Distribution of polycyclic aromatic hydrocarbons in soil–water system containing a nonionic surfactant, *Chemosphere* 60 (2005) 1237–1245.
- [11] H. Rupprecht, T. Gu, Structure of adsorption layers of ionic surfactants at the solid–liquid interface, *Colloid Polym. Sci.* 269 (1991) 506–522.
- [12] S. Paria, K.C. Khilar, A review on experimental studies of surfactant adsorption at the hydrophilic solid, *Adv. Colloid Interf.* 110 (2004) 75–95.
- [13] P. Levitz, H.V. Damme, Fluorescence decay study of the adsorption of nonionic surfactants at solid–liquid interface. 2. Influence of polar chain length, *J. Phys. Chem.* 90 (1986) 1302–1310.
- [14] Y.-H. Shen, Sorption of nonionic surfactants to soil: the role of soil mineral composition, *Chemosphere* 41 (2000) 711–716.
- [15] P.E. Levitz, Adsorption of nonionic surfactants at the solid/water interface, *Colloid Surf. A* 205 (2002) 31–38.
- [16] J.-F. Lee, M.-H. Hsu, H.-P. Chao, H.-C. Huang, S.-P. Wang, The effect of surfactants on the distribution of organic compounds in the soil solid/water system, *J. Hazard. Mater.* 114 (2004) 123–130.
- [17] C.T. Chiou, J.P. Louis, H.F. Virgil, A physical concept of soil–water equilibria for nonionic organic compounds, *Science* 206 (1979) 831–832.
- [18] C.T. Chiou, P.E. Porter, D.W. Schmedding, Partition equilibria of nonionic organic compounds between soil organic matter and water, *Environ. Sci. Technol.* 17 (1983) 227–231.
- [19] S.E. McGroddy, J.W. Farrington, Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston harbor, *Environ. Sci. Technol.* 29 (1995) 1542–1550.
- [20] O. Gustafsson, F. Haghseria, C. Chan, J. MacFarlane, P.M. Gschwend, Quantification of dilute sedimentary soot phase: implication for PAH speciation and bioavailability, *Environ. Sci. Technol.* 31 (1997) 203–209.
- [21] S. Mitra, R.M. Dickhut, S.A. Kuehl, K.L. Kimani, Polycyclic aromatic hydrocarbon (PAH) sediment deposition patterns and particle geochemistry as factors influencing PAH distribution coefficients in sediments of the Elizabeth River, VA, USA, *Mar. Chem.* 66 (1999) 113–127.
- [22] H.-C. Huang, J.-F. Lee, H.-P. Chao, P.-W. Yeh, Y.-F. Yang, W.-L. Liao, Influence of solid-phase organic constituents on the partition of aliphatic and aromatic organic contaminants, *J. Colloid Interf. Sci.* 286 (2005) 127–133.
- [23] J.H. Harwell, D.A. Sabatini, R.C. Knox, Surfactants for ground water remediation, *Colloid Surf. A* 151 (1999) 255–268.
- [24] M.I. Kuhlman, T.I. Greenfield, Simplified soil washing processes for a variety of soils, *J. Hazard. Mater.* 66 (1999) 31–45.
- [25] D.-H. Lee, R.D. Cody, D.-J. Kim, S. Choi, Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil, *Environ. Int.* 27 (2002) 681–688.
- [26] W. Huang, P. Pang, Z. Yu, J. Fu, Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments, *Appl. Geochem.* 18 (2003) 955–972.
- [27] P. Conte, A. Agreto, R. Spaccini, A. Piccolo, Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils, *Environ. Pollut.* 135 (2005) 515–522.
- [28] K. Urano, M. Saito, C. Murata, Adsorption of surfactants on sediments, *Chemosphere* 13 (1984) 293–300.
- [29] T. Gu, B.Y. Zhu, H. Rupprecht, Surfactant adsorption and surface micellization, *Prog. Colloid Polym. Sci.* 88 (1992) 74–85.
- [30] J.-F. Lee, M.-H. Hsu, C.-K. Lee, H.-P. Chao, B.-H. Chen, Effects of soil properties on surfactant adsorption, *J. Chin. Inst. Eng.* 28 (2005) 375–379.
- [31] S. Sun, W.P. Inskeep, S.A. Boyd, Sorption of nonionic organic compounds in soil–water systems containing a micelle-forming surfactant, *Environ. Sci. Technol.* 29 (1995) 903–913.
- [32] S.M. Lambert, Functional relationship between sorption in soil and chemical structure, *J. Agric. Food Chem.* 15 (1989) 572–576.
- [33] T.D. Gauthier, W.R. Seitz, C.L. Grant, Effects of structural and compositional variations of dissolved humic materials on pyrene K_{oc} values, *Environ. Sci. Technol.* 21 (1987) 243–248.
- [34] D.E. Kile, C.T. Chiou, Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration, *Environ. Sci. Technol.* 23 (1989) 832–838.