Partitioning of hydrophobic organic compounds within soil–water–surfactant systems

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ABSTRACT
Understanding the partitioning of hydrophobic organic compounds (HOCs) within soil–water–surfactant systems is key to improving the use of surfactants for remediation. The overall objective of this study was to investigate the soil properties that influence the effectiveness of surfactants used to remediate soil contaminated with hydrophobic pesticides, as an example of a more general application for removing strongly sorbing HOCs from contaminated soils via in-situ enhanced sorption, or ex-situ soil washing. In this study, the partitioning of two commonly used pesticides, atrazine and diuron, within soil–water–surfactant systems was investigated. Five natural soils, one nonionic surfactant (Triton-100 (TX)) and one cationic surfactant (benzalkonium chloride (BC)) were used. The results showed that the cation exchange capacity (CEC) is the soil property that controls surfactant sorption onto the soils. Diuron showed much higher solubility enhancement than atrazine with the micelles of either surfactant. Within an ex-situ soil washing system, TX is more effective for soils with lower CEC than those with higher CEC. Within an in-situ enhanced sorption zone, BC works significantly better with more hydrophobic HOCs. The HOC sorption capacity of the sorbed surfactant ($K_{ss}$) was a non-linear function of the amount of surfactant sorbed. For the cationic surfactant (BC), the maximal $K_{ss}$ occurred when around 40% of the total CEC sites in the various soils were occupied by sorbed surfactant. Below a sub-saturation sorption range ($<20$ g/kg), under the same amount of BC sorbed, a soil with lower CEC tends to have higher $K_{ss}$ than the one with higher CEC.

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1. Introduction

More than 2.3 billion kg of pesticides are used worldwide, with over 0.5 billion kg in the US alone (USEPA, 2004). Unfortunately, the manufacture, retailing, use and end-of-life activities are not perfectly controlled, resulting in spills, accidental and even intentional releases at various points. In particular, during the preparation of formulations for application there is a higher risk of release at relatively high concentrations, resulting in contaminated soils (Mata-Sandoval et al., 2002). There are many other situations where soils or sediments are contaminated with hydrophobic organic compounds (HOCs) that are strongly sorbed and not bioavailable for natural or enhanced biodegradation. Recently, the use of surfactants in ex-situ soil washing and in-situ enhanced sorption zones has been studied to some extent (Sun et al., 1995; Mata-Sandoval et al., 2002; Chu, 2003; Sanchez-Camazano et al., 2003; Rodriguez-Cruz et al., 2006; Gellner et al., 2006). However, there are a number of important issues that need to be better understood to improve the use of surfactants in these applications. This study focused on understanding how soil properties influence the effectiveness of surfactants used to remediate soil contaminated with hydrophobic pesticides, as an example of a more general

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application for removing strongly sorbing HOCs from contaminated soils, in situ or ex situ.

At low concentrations, surfactants are present as dispersed molecules (monomers); above a critical aqueous concentration, specific to each surfactant, the critical micelle concentration (CMC), surfactant monomers aggregate in solution to form micelles, which consist of a hydrophobic core and a hydrophilic shell (Rosen, 1989). The ability of the micelles of nonionic surfactants to enhance the water solubility of HOCs provides a potential means of enhancing soil-washing treatment efficiency for HOC-contaminated soils (Mata-Sandoval et al., 2002; Sanchez-Camazano et al., 2003; Rodriguez-Cruz et al., 2006).

Many surfactants (e.g., nonionic and cationic) may sorb efficiently onto soils. It is generally believed that surfactants can sorb onto solid surfaces only as monomers (Ko et al., 1998; Zhu et al., 2003). Sorption of surfactants onto soils results in surfactant loss and reduced performance for the solubilization of HOCs. More importantly, the sorbed surfactants can serve to increase the organic matter content of the soil particles, which serves as a new partitioning medium for HOCs (Sun et al., 1995; Ko et al., 1998; Zhu et al., 2003; Jones-Hughes and Turner, 2005). Due to their positive charge, the sorption of cationic surfactants onto soils or aquifer materials is so large that significant reduction in HOC mobility has been observed (Ko et al., 1998). Recent laboratory, field and numerical modeling studies have shown that under certain conditions, cationic surfactants can be used to form stable zones of enhanced sorption for HOCs, such as pesticides, migrating in groundwater (Gellner et al., 2006; Hayworth and Burris, 1997a, b). Thus, understanding of HOC partitioning within a soil–water–surfactant system is key to improving the application of surfactants for remediation.

The following governing equation has been used to describe HOC partitioning within a soil–water–surfactant system (Zhu et al., 2003; Lee et al., 2000; Sun et al., 1995):

$$K_d^s = \frac{K_d + f_{soc}K_{soc}}{1 + K_{mm}X_{mm} + K_{nc}X_{nc}},$$

(1)

where $K_d^s$ is the ratio of sorbed HOC to mobile HOC in aqueous solution (L/kg); $K_d$ is the HOC sorption coefficient with the soil in the absence of surfactant (L/kg); $f_{soc}$ is the surfactant-derived organic-carbon fraction in the solid; $K_{soc}$ is the carbon-normalized HOC distribution coefficient with the sorbed surfactant-derived organic carbon (L/kg); $X_{mm}$ and $X_{nc}$ are the surfactant monomer and micellar concentrations in water, respectively (g/L); and $K_{mm}$ and $K_{nc}$ are the HOC partitioning coefficients with the surfactant monomer and micellar phases, respectively (L/g). Basically, the partitioning of HOC between soil and water ($K_d^s$) is enhanced by the presence of sorbed surfactants ($f_{soc}K_{soc}$) and decreased by the enhanced aqueous solubility of the HOC in the presence of surfactant monomers ($K_{mm}X_{mm}$) and micelles ($K_{nc}X_{nc}$).

The influence of the charge nature, the hydrophilic–hydrophobic balance and the effect of surfactant concentrations below or above the CMC on $K_{soc}$ has been studied to some extent (Mata-Sandoval et al., 2002; Sanchez-Camazano et al., 2003; Rodriguez-Cruz et al., 2006; Deitsch and Smith, 1995; Doong et al., 1996; Sun et al., 1995). In a study of the sorption of HOCs within a soil–water–nonionic surfactant system, Sun et al. (1995) found that the $K_d$ of $p,p’$-DDT; 2,2’, 4,4’,5,5’-PCB and 1,2,4-TCB increased first with increasing aqueous surfactant concentrations ($X_{mm}+X_{nc}$) before the CMC of the surfactant was reached and decreased thereafter. On the sorbent side, the effect of soil organic matter (SOM) on the $K_d$ and $K_{soc}$ has also been reported by a number of authors (Zhu et al., 2003, 2004; Lee et al., 2000; Edward et al., 1994). These studies have improved the understanding of surfactants and HOC interactions. Despite this, there are still some important questions remaining. First, since soil cation exchange capacity (CEC) can have a significant impact on surfactant sorption, whether cationic, anionic or nonionic, what is the effect of soil CEC on HOC partitioning behavior within these systems and on $K_{soc}$? Second, is $K_{soc}$ a function of sorbed surfactant concentration?

In this study, five natural soils with similar soil organic carbon content but different CEC were selected. Sorption of two of the most commonly used pesticides was then carried out in the presence of a nonionic surfactant or a cationic surfactant as relevant to ex-situ soil washing and in-situ surfactant enhanced sorption zone. This research was designed to answer these questions.

2. Materials and methods

2.1. Chemicals

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was purchased from Supelco Inc. (Bellefonte, PA) with a reported purity >97%, and diuron (3-(3,4-dichlorofenyl)-1,1-dimethyleurea) was purchased from ChemService Inc. (West Chestnut, PA) with a reported purity >99%. Triton-100 (t-octylphenoxypolyethyoxethanol), a nonionic surfactant, and benzalkonium chloride (BC), a cationic surfactant, were purchased from Sigma-Aldrich. The chemicals were used as received. Selected physicochemical properties of these compounds can be found in the Supporting information. The selection of the surfactants was based on their cost and potential use in soil treatment systems.

2.2. Soils

Four soils and one sediment (denoted as Ag#1, Ag#2, Ag#3, Clayey and Sediment) were collected from Santa Barbara, CA. All samples were collected from the top 15 cm of the soil profile, air-dried and gently passed through a 2 mm sieve. The total organic carbon (TOC), CEC, BET surface area and pH were measured using the methods described by Carter (1993) (Table 1).

2.3. Sorption

The sorption of the surfactants and pesticides was determined in duplicate by the batch equilibration technique. The initial surfactant concentration spanned over a large range below and above the surfactant CMCs. The surfactant and pesticide solutions were prepared in water containing 0.01 M CaCl$_2$ and 0.02% Na$_2$S. The 0.01 M CaCl$_2$ background electrolyte was used to minimize ionic strength change. The 0.02%
\[ S^*_w = 1 + X_{mc}K_{mn} + X_{mc}K_{mc}, \]

where \( S^*_w \) is the apparent HOC solubility at a total stoichiometric surfactant concentration of \( X = X_{mc} + X_{mc} \) (g/L). \( S^*_w \) is the intrinsic HOC solubility in water in the absence of the surfactant (mg/L). \( S^*_w \) and \( S_w \) were measured directly on the HPLC. The results of the HOC solubility enhancement experiments are presented in Fig. 1.

The results showed that at concentrations below the CMC of either surfactant there was no interaction between the surfactant monomers and the HOC, and thus no solubility enhancement was observed, while, once the surfactant concentrations exceeded the respective CMC, a solubility enhancement was observed for either HOC but to a different extent (Fig. 1). The lack of interaction between the surfactant monomers and either HOC was expected. According to the literature, only extremely hydrophobic organic compounds such as DDT (octanol–water distribution coefficient \( K_{ow} = 10^{6.36} \)) are known to be associated to a significant degree with surfactant monomer in the aqueous phase (Kile and Chiou, 1989; Park and Jaffe, 1993; Chiou et al., 1982). In a study conducted by Park and Jaffe (1993), the interaction between phenanthrene (\( K_{ow} = 10^{4.46} \)) and the monomers of anionic surfactants was also determined to be insignificant. In this study, since both HOCs were moderately polar (\( K_{ow} < 10^{2.3} \)), they exhibited negligible interaction with the surfactant monomers and thus \( K_{mn} = 0 \). As a result, before the CMC was reached, \( S^*_w / S_w = 1 \), while, after CMC had been reached, \( S^*_w / S_w \) was greater than unity and increased monotonically with increasing surfactant concentration.

Linear regression was conducted with the solubility enhancement data for \( S^*_w / S_w > 1 \), using the average of duplicate measurements. The results of the regression and the calculated CMC and \( K_{mc} \) are presented in Table 2. The CMC

### Table 1 – Measured soil properties and fitted Langmuir parameters of the TX and BC sorption

<table>
<thead>
<tr>
<th>Soil</th>
<th>TOC (%)</th>
<th>CEC (cmol/kg)</th>
<th>pH</th>
<th>BET surface area (m²/g)</th>
<th>TX</th>
<th>BC</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag#1 (sandy loam)</td>
<td>1.51</td>
<td>6.2</td>
<td>7.3</td>
<td>3.5</td>
<td>4390</td>
<td>7.0</td>
<td>0.89</td>
</tr>
<tr>
<td>Ag#2 (loam)</td>
<td>1.50</td>
<td>15.4</td>
<td>7.4</td>
<td>9.4</td>
<td>27,189</td>
<td>9.4</td>
<td>0.92</td>
</tr>
<tr>
<td>Ag#3 (loam)</td>
<td>1.52</td>
<td>15.2</td>
<td>7.6</td>
<td>14.1</td>
<td>28,662</td>
<td>6.5</td>
<td>0.90</td>
</tr>
<tr>
<td>Clayey (sandy clay loam)</td>
<td>1.37</td>
<td>15.7</td>
<td>7.1</td>
<td>13.1</td>
<td>33,910</td>
<td>8.3</td>
<td>0.89</td>
</tr>
<tr>
<td>Sediment (loamy sand)</td>
<td>1.12</td>
<td>5.4</td>
<td>8.1</td>
<td>2.0</td>
<td>4090</td>
<td>7.1</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*\( K_l \) is the Langmuir constant (L/g).
was calculated as the intersection between the regression line and $S_w^*/S_w = 1.0$ line (Fig. 1). The calculation of $K_{mc}$ can be seen in the Supporting information.

Clearly, the $K_{mc}$ of diuron was much greater than that of atrazine for either surfactant and $K_{mc}$ of either HOC was greater with BC than with TX. Interestingly, the ratio of the $K_{mc}$ of diuron to that of atrazine was much greater for BC (12.4) than for TX (4.7). The observed differences might be a combined effect of hydrophobicity and polarity. First, diuron is more hydrophobic than atrazine, as indicated by its higher $K_{ow}$, and thus can partition more into the hydrophobic micellar cores. Second, the polar heads of the HOCs can attach to the micellar shells, but the higher polarity of diuron, as indicated by its higher dipole moment, explains the greater solubility enhancement of diuron in the presence of these surfactants. Sanchez-Camazano et al. (2003) and Rosen (1989) had previously suggested that moderately polar pesticides could be additionally solubilized on the shell of the micelles. Since the attraction between two polar groups is much less significant than that between an ionic and a polar group, the attraction of these pesticides onto the micellar shells of TX is weaker than onto the micellar shells of BC due to the charge nature of BC. This explains the higher solubility enhancement of these pesticides with BC than with TX.

![Fig. 1](image1)  
**Fig. 1** – Pesticide solubility enhancement as a function of surfactant concentration. The equation refers only to the fit of data above the CMC: (a) TX; (b) BC.

![Fig. 2](image2)  
**Fig. 2** – Surfactant sorption isotherms: (a) TX; (b) BC.

<table>
<thead>
<tr>
<th>Table 2 – Pesticide solubility enhancement data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relationship</td>
</tr>
<tr>
<td>TX Atrazine</td>
</tr>
<tr>
<td>Diuron</td>
</tr>
<tr>
<td>BC Atrazine</td>
</tr>
<tr>
<td>Diuron</td>
</tr>
</tbody>
</table>

*Note: $Y = S_w^*/S_w; X =$ total aqueous concentration of surfactant.*
3.2 Surfactants sorption isotherms

Fig. 2 presents the sorption data (average value of duplicate measurements) for TX and BC, and Table 1 presents the saturation sorption capacity ($C_{\text{max}}$), along with the measured soil properties. Clearly, the behavior is non-linear, and cannot be fitted adequately with the Freundlich sorption model (Schwarzenbach et al., 1993). The data were fitted with a one-site Langmuir sorption model (Schwarzenbach et al., 1993), which adequately fits the high surfactant concentration range (>10 mg/L) but deviates for lower concentrations. The corresponding Langmuir coefficients are presented in Table 1. Error bars representing one standard deviation are presented for soil Ag#1 in Fig. 2. In all cases, the standard deviations were within 15% of the mean values. The error bars for the other soils are not presented for clarity.

Based on $C_{\text{max}}$, the surfactant sorption behavior can be separated into two soil groups: Ag#1 and sediment, denoted as Group 1 with lower CEC, and Ag #2, Ag #3 and clayey soil, denoted as Group 2 with higher CEC. The soils within Group 2 have consistently higher surfactant sorption than those within Group 1.

The results indicate that soil CEC controls surfactant sorption onto the soils for BC or TX, with the correlation coefficients between the $C_{\text{max}}$ of BC and TX and soil CEC being 0.99 and 0.96, respectively. The results did not show significant correlation between the surfactant sorption capacities and soil TOC, with the correlation coefficient being only 0.40. Thus, surfactant partitioning into SOM is not as significant for TX and BC, which is consistent with previous studies (Mata-Sandoval et al., 2002; Cano and Dorn, 1996).

Unlike cationic surfactant sorption, which takes place via the cation exchange reaction (Li and Bowman, 1998a, b; Xu and Boyd, 1995; Sheng et al., 1996), the sorption of nonionic surfactant is less clear. Edward et al. (1994) proposed a three-stage sorption model for TX sorption onto the sediment, which states that at high bulk solution surfactant concentrations, a patchy bilayer of the sorbed TX is formed, with the base layer consisting of the ‘head-on’ sorbed TX held on the hydrophilic (i.e., charged) patches of the sediment surface. The high correlation between TX sorption capacities and CEC in this study seems to support this hypothesis.

3.3 Mobility of HOCs in the water–soil–surfactant system

Dependence of the aqueous HOC concentrations on the total concentration of the surfactants ($X = X_{\text{mm}}+X_{\text{mc}}$) in the mobile phase, e.g., aqueous phase, is presented in Fig. 3, describing the mobility of the HOC within the water–soil–surfactant systems.

In all cases, the aqueous HOC concentrations decreased first with increasing aqueous surfactant concentrations before the CMCs of the surfactants were reached. Within this surfactant concentration range, the surfactants were present as monomers, so the increase in surfactant concentration led to higher sorbed surfactant concentration, which consequently resulted in more HOC sorbed onto soil particles. After the CMC was exceeded, surfactant sorption became negligible and micelles started forming in the aqueous solution. The micelles then competed with the sorbed surfactants for the HOCs. With increasing micelle concentration, more HOC molecules partitioned into the micelles within the aqueous phase. This result is consistent with previous research (Sun et al., 1995).

Another general trend was that, in the presence of TX, the mobility of either HOC differed noticeably between the two soils groups. Due to the higher surfactant sorption, the soils within Group 2 had higher concentrations of HOC sorbed on
the solid phase than Group 1 soils, leading to lower aqueous HOC concentration and thus requiring more surfactant to transfer the sorbed HOC molecules into the aqueous phase. Besides, the HOC mobility in the presence of TX was much higher than in the presence of BC. The very high sorption of BC onto all soils blurred the difference between the soil groups, although at higher BC concentrations the differential behavior of the two soil groups can be seen (Figs. 3c and d). It is worth mentioning that at a particular BC loading onto the soils, the aqueous diuron concentrations were reduced as low as 0.1 mg/L (Fig. 3d). Thus, TX would be a better surfactant for in-situ mobilization for enhanced degradation or for ex-situ soil washing. For either of these remediation approaches, HOC mobility after CMC has been exceeded in the aqueous phase is very important. It is clear from these results that in the presence of TX the HOC mobility in Group 1 soils is higher than in Group 2 soils and thus TX is more effective for soils with lower CEC (Group 1) than those with higher CEC (Group 2) (Fig. 3a and b). As discussed earlier, diuron has much higher affinity to the surfactant micelles than atrazine, which explains the sharper increase in its aqueous concentrations in the presence of the surfactant micelles, i.e., after the CMC is reached.

3.4. HOC sorption and $K_{ss}$ as a function of the amount of surfactant sorbed

Fig. 4 presents the dependence of the amount of HOC sorbed on the amount of surfactant sorbed, describing the immobilization of the HOC within the water–soil–surfactant systems. Generally speaking, the sorbed HOC concentrations increased with increasing sorbed surfactant concentrations before the surfactant sorption saturation was reached. The plateau in sorbed diuron concentration in the case of BC (Fig. 4d) was the result of nearly complete sorption of diuron onto the soils in the presence of the sorbed BC. As can be seen from Fig. 4, the highest sorbed HOC concentration in the soils in the presence of BC was much higher than in the presence of TX. For an in-situ enhanced sorption zone, one would be interested in HOC immobilization in the presence of the surfactant before reaching the surfactant sorption capacities. HOC sorption in the presence of TX did not show significant difference across the soils due to TX’s lower sorption and presumably lower affinity for either HOC to the sorbed TX (Fig. 4a and b), while, interestingly, within a low BC sorption range (<20 g/kg for atrazine and <10 g/kg for diuron), the sorption of either HOC clearly was different for the two soils groups (Fig. 4c and d). Within these lower BC sorption ranges, the soils with lower CEC (Group 1) showed higher HOC sorption capacity than the soils with higher CEC (Group 2) in the presence of this surfactant.

In order to compare HOC sorption onto the sorbed surfactant, $K_{ss}$ needs to be calculated. Eq. (1) can be rearranged to obtain an expression for $K_{ss}$. The $f_{soc}$ was calculated using the following formula:

$$f_{soc} = \frac{Q_{ss} \times \%C}{10^6},$$

where $Q_{ss}$ is the amount of surfactant sorbed (mg/kg), %C is the percentage carbon within each surfactant molecule and $10^6$ is a conversion factor.

The calculated $K_{ss}$ of the sorbed surfactant for each pesticide in relation to the amount of surfactant sorbed is presented in Fig. 5. Clearly, for either surfactant, $K_{ss}$ was a non-linear function of the amount of surfactant sorbed, with $K_{ss}$ increasing initially as the amount of sorbed surfactant

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Fig. 4 – Dependence of the sorbed pesticide concentrations on the concentrations of the sorbed surfactant (a) atrazine with TX; (b) diuron with TX; (c) atrazine with BC; and (d) diuron with BC.

increased, reaching a maximum $K_{ss}$ at a certain amount of sorbed surfactant before decreasing monotonically as more surfactant was sorbed onto the soil before the surfactant saturation sorption was reached.

Investigating Fig. 5 immediately reveals two distinct features, which are more clearly shown for BC (Fig. 5c and d) than for TX. First, when the amount of sorbed surfactant was below a certain level ($^{1/2}C_24^20$ g/kg for BC), the $K_{ss}$ of Group 1 soils was much higher than for Group 2 soils, given the same amount of BC sorbed (Fig. 5c and d), implying that the difference across soil groups in Fig. 4c and d was due to sorbed BC. Second, the $K_{ss}$ of the sorbed BC for either HOC peaked long before the saturation BC sorption was reached (Fig. 5c and d).

The observation that, with BC, the soils could be clearly classified into two groups with regard to both CEC and their $K_{ss}$ led us to consider a relationship between these two properties. It is believed that the sorption of cationic surfactants onto soils takes place initially via cation exchange (Li and Bowman, 1998a, b; Xu and Boyd, 1995; Sheng et al., 1996). Further analysis showed that the maximal $K_{ss}$ of the sorbed BC occurred uniformly when around 40% of the total CEC sites were occupied by BC (Table 3). The amount of sorbed BC at 40% occupancy of the total CEC sites of the soils, $Q_{BC}$ (mg/kg), was calculated using the following formula:

$$Q_{BC} = \frac{CEC \times (MW_{BC} - 35.5) \times 1000}{100} \times 40\% = 1216CEC,$$

where $MW_{BC}$ is the molecular weight of BC (339.5 g/mol). The molecular weight of chlorine is subtracted since BC is dissociated under these conditions.

To explain these findings, the surfactant sorption phases have to be taken into consideration. A double-layer model has been proposed and used for cationic surfactant sorption by some researchers (Zhu et al., 2003; Li and Bowman, 1998a, b), which states that the sorption of cationic surfactant consists

![Fig. 5 - Dependence of $K_{ss}$ on sorbed surfactant for (a) TX with atrazine; (b) TX with diuron; (c) BC with atrazine; and (d) BC with diuron.](image)

### Table 3 - Maximal $K_{ss}$ with the corresponding amount of BC sorbed, calculated amount of BC sorbed at 40% CEC occupancy and calculated double-layer sorption capacities

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>Diuron</th>
<th>Calculated 40% CEC occupancy (mg/kg)</th>
<th>BC sorbed at which max. $K_{ss}$ occurred (mg/kg)</th>
<th>Double-layer sorption capacities (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag#1</td>
<td>1067</td>
<td>54,000</td>
<td>7539</td>
<td>9300</td>
<td>15,078</td>
</tr>
<tr>
<td>Ag#2</td>
<td>1010</td>
<td>45,078</td>
<td>18,726</td>
<td>21,200</td>
<td>37,452</td>
</tr>
<tr>
<td>Ag#3</td>
<td>960</td>
<td>43,952</td>
<td>18,483</td>
<td>21,200</td>
<td>36,966</td>
</tr>
<tr>
<td>Clayey</td>
<td>803</td>
<td>47,863</td>
<td>19,091</td>
<td>21,200</td>
<td>38,182</td>
</tr>
<tr>
<td>Sediment</td>
<td>1225</td>
<td>54,408</td>
<td>6566</td>
<td>7200</td>
<td>13,132</td>
</tr>
</tbody>
</table>

of two phases: namely, monolayer formation and double-layer formation. Within the monolayer formation phase, the cationic surfactant molecules, taking a ‘head-on’ configuration, gradually occupy available CEC sites via cation exchange. Within the double-layer formation phase, the cationic surfactant molecules sorb onto the presorbed mono-layered surfactant molecules, taking an ‘end-on’ configuration.

Although 100% occupancy of CEC sites has been used by some authors in comparing the measured and calculated cationic surfactant sorption capacities onto natural sorbents (Zhu et al., 2003), it is very unlikely that all of the CEC sites would be physically available for surfactant sorption. CEC is measured at very high electrolyte concentrations (1.0 M), which are unlikely in natural conditions. In the current experimental conditions, the significantly lower ionic strength of the solution (<0.1 M) reduced the likelihood of replacing all exchangeable cations with cationic surfactant. Li and Bowman (1998b) investigated the sorption of a cationic surfactant (HDTMA) onto a pure zeolite mineral and found that only external CEC sites (80%) of the total CEC sites could be occupied at the saturation surfactant sorption. Thus, only a fraction of CEC is generally available for cationic surfactant sorption. In the soil–surfactant systems studied here only 40% of the CEC sites were available for BC sorption via cation exchange during monolayer formation. Within this phase, as the amount of the sorbed surfactant increased, an increasingly hydrophobic surface was formed, leading to an increasing Kss (Fig. 5, region before maximal Kss). The maximal Kss occurred at the end of the monolayer formation when a complete hydrophobic surface was formed. The maximal Kss was reached with a smaller amount of cationic surfactant sorbed for soils with lower CEC than soils with higher CEC and therefore these lower CEC soils tend to have a higher Kss than the soils with higher CEC because the former tends to have a more hydrophobic surface under the same amount of the surfactant sorbed than the latter. This is supported by the results shown in Figs. 4 and 5, where it can be seen that the greatest distinction in pesticide sorption behavior and Kss between the two soil groups occurred mainly within this monolayer sorption stage. Once the monolayer was completed and the double-layer started forming, an increasing amount of sorbed surfactant resulted in a decreasing Kss, since more polar surfaces formed (Fig. 5, region beyond maximal Kss and before sorption saturation).

Although the double-layer model can explain cationic surfactant sorption to some extent, the current experiments resulted in much higher sorption capacities for BC than would be predicted (Table 3) by the double-layer model. Thus, we believe that, in addition to a double-layered structure, admicelles, structurally similar to micelles in aqueous solution, were formed on the soil surfaces. Additional observational evidence is needed to determine whether these structures form, but the sorption data indicate that this is likely to occur.

Although a double-layered sorption model has been proposed for TX sorption (Edward et al., 1994), a clear correlation between CEC and Kss was not observed for TX in this study, presumably because being a nonionic molecule, TX sorption does not participate in cation-exchange interactions, and also due to TX’s much lower sorption and less affinity of either pesticide onto the sorbed TX relative to BC.

4. Conclusions

Understanding the behavior of HOCs within soil–water–surfactant systems is key to improving the use of this technology, in situ or ex situ. In addition to the choice of surfactant and the physicochemical properties of the HOC, it is important to consider soil properties such as CEC. Some surfactants, such as BC, are best used for in situ immobilization, while others such as TX can serve to mobilize and render the HOC more available for biotic or abiotic transformation, in situ or ex situ. The presence of surfactant can enhance the solubilization of HOCs, but only after the CMC has been reached, since surfactant monomers do not provide sufficient co-solvency. For nonionic and cationic surfactant, soils with higher CEC are better surfactant sorbents than soils with lower CEC.

The magnitude of Kss is neither constant nor a linear function of fsoec, but is rather a complex function of soil CEC and the amount of surfactant sorbed. Also, the maximal Kss occurs before the saturation surfactant sorption is reached. For even more hydrophobic compounds than atrazine or diuron, Kss is expected to be an even stronger function of sorbed surfactant as the compound would be attracted more to the sorbed surfactant in the monolayer stage and then repelled more in the stages thereafter. One of our major findings is that, at a low cationic surfactant sorption range, under the same amount of surfactant sorbed, a soil with lower CEC tends to have higher Kss than one with higher CEC.

Although other researchers have also found that the maximal Kss occurred before the surfactant sorption capacity was reached on certain pure minerals (Zhu et al., 2003; Li and Bowman, 1998a, b; Behrends and Herrmann, 1998), to our knowledge, this is the first study to find a relationship between Kss and real soil CEC and to offer an explanation for the variation of Kss with the amount of surfactant sorbed, based on the fraction of CEC that is available for surfactant sorption.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2007.11.015

References


