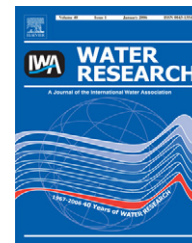


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# Partitioning of hydrophobic organic compounds within soil–water–surfactant systems

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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 ( $\sim 20$  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 behavior within soil–water–surfactant systems 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):

$$K_d^* = \frac{K_d + f_{\text{soc}}K_{\text{ss}}}{1 + K_{\text{mn}}X_{\text{mn}} + K_{\text{mc}}X_{\text{mc}}}, \quad (1)$$

where  $K_d^*$  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);  $f_{\text{soc}}$  is the surfactant-derived organic-carbon fraction in the solid;  $K_{\text{ss}}$  is the carbon-normalized HOC distribution coefficient with the sorbed surfactant-derived organic carbon (L/kg);  $X_{\text{mn}}$  and  $X_{\text{mc}}$  are the surfactant monomer and micellar concentrations in water, respectively (g/L); and  $K_{\text{mn}}$  and  $K_{\text{mc}}$  are the HOC partitioning coefficients with the surfactant monomer and micellar phases, respectively (L/g). Basically, the partitioning of HOC between soil and water ( $K_d^*$ ) is enhanced by the presence of sorbed surfactants ( $f_{\text{soc}}K_{\text{ss}}$ ) and decreased by the enhanced aqueous solubility of the HOC in the presence of surfactant monomers ( $K_{\text{mn}}X_{\text{mn}}$ ) and micelles ( $K_{\text{mc}}X_{\text{mc}}$ ).

The influence of the charge nature, the hydrophilic–hydrophobic balance and the effect of surfactant concentrations below or above the CMC on  $K_{\text{ss}}$  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 ( $X_{\text{mn}}+X_{\text{mc}}$ ) 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  $K_{\text{ss}}$  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  $K_{\text{ss}}$ ? Second, is  $K_{\text{ss}}$  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-dichlorophenyl)-1,1-dimethylurea) was purchased from ChemService Inc. (West Chestnut, PA) with a reported purity >99%. Triton-100 (t-octylphenoxypolyethoxyethanol (TX)), 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 0.01M CaCl<sub>2</sub> and 0.02% NaN<sub>3</sub>. The 0.01M CaCl<sub>2</sub> background electrolyte was used to minimize ionic strength change. The 0.02%

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