

THESIS

FATE AND TRANSPORT OF SURFACTANTS IN GRAYWATER WHEN APPLIED TO
SOIL

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ABSTRACT

FATE AND TRANSPORT OF SURFACTANTS IN GRAYWATER

WHEN APPLIED TO SOIL

Graywater reuse for irrigation has been considered an efficient way to reduce demand on water supply. Concerns, however exist regarding the potential impacts that graywater pose to soil quality. In particular, the fate of surfactants, the primary component in personal care and cleaning products, is not well understood. The objective for this study was to gain a better understanding of the adsorption behavior of surfactant onto soils, with particular attention on the effect of the organic matter and soil texture, then provide a suggestion about the kind of surfactants and soil be reused during graywater irrigation.

Surfactants linear alkylbenzene sulfonates (LAS) (anionic), alcohol ethoxysulfates (AES) (anionic) and alcohol ethoxylates (AE) (nonionic) were applied to three different soils with varying organic matter (OM) and clay fraction column studies. Adsorption results were obtained from leachate and soil samples. The fraction ranges of leached surfactants to sorbed of LAS, AES and AE were 0.10-0.42, 0.42-2.35, 0.06-0.77 respectively. The results indicated that AES had the most potential leaching capacity, which mean they could reach deeper soil layer even groundwater systems. On the other hand, from soil properties, OM played an important role in the adsorption of surfactants, both anionics and nonionics, whereas, the clay fraction content had a negative effect on anionic surfactants sorption ($p=0.006$, 0.002 for LAS and AES), possibly due to an increase in negative charge, repulsion forces as clay content increasing, but not significant on nonionic surfactants with clay content increased from 33% - 46% ($p=0.986$ for

AE). Meanwhile, AES homologues which contained different number of ethylene oxide (EO) groups were studied. Results indicated that adsorption increased as EO chain increased. Based on the results above, AE were recommended for graywater irrigation in terms of surfactants with relative high OM.

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1.0 Introduction

1.1 Research Motivation

Water availability has become a more and more urgent concern in recent years. U.S. Geological Survey shows United States residents consumed more than 148 trillion gallons of water for residential, commercial, agriculture, and manufacturing uses in the year of 2000. The combination of rising temperatures, drought, population growth, urban sprawl, waste and excess, has prompted implementation of many water reuse projects.

Graywater reuse has the potential to achieve substantial water savings in domestic residences when used for irrigation and toilet flushing. It was reported that we can reduce potable water use up to 50% if graywater is reused for irrigation especially in arid region (DHWA, 2002). Studies revealed that 7% of U.S households were reusing graywater (Group, 1999) and 13% of the household in Arizona used graywater for irrigation with the most utilized source being from clothes washers (Little, 1999).

However, there are substantial concerns about the safety of graywater reused for irrigation purpose. Surfactants, have been recognized as being the most abundant type of organic chemical in graywater (Eriksson et al., 2002). Research experiments showed that accumulation of surfactants in the soil from graywater might form water repellent soils that have a significant effect on agricultural productivity and environmental sustainability (Shafran et al., 2005). In addition, surfactants may affect the mobility and degradation of hydrophobic organic compounds in soil or sediment (Edwards et al., 1994). Also of concern is surfactants may reach deeper soil and be transported into groundwater. Studies on the fate and transport of surfactant after applied for graywater irrigation are still limited. In particular, little is known about how soil texture and organic content affect surfactants transport after application of graywater.

1.2 Hypotheses Evaluation

H-1 There is a correlation between sorption of surfactants and organic matter content of the soil.

Because surfactants are organic in nature and have a hydrophobic end, it is expected that organic matter content in soil will affect their transport.

H-2 There is a correlation between sorption of surfactant and clay content of the soil.

Because the hydrophilic groups of surfactants are generally charged and clay in soils is negatively charged, it is expected that clay content will affect their transport. For anionic surfactants, there may be a negative correlation between sorption and clay.

H-3 Ethylene oxide (EO) group have a positive effect on sorption of AES homologues.

Because ethoxylate surfactants may be adsorbed onto charged surface by hydrogen bonding between the EO groups and the surface, it is expected that EO group in AES homologues will affect their sorption. With the EO groups increased, the sorption behaviors may also be increased.

1.3 Research Objective

The objective of this project is to determine the fate and transport of surfactants, linear alkylbenzene sulfonates (LAS), alcohol ethoxysulfates (AES) and alcohol ethoxylates (AE) in varying soil types through a column study. Three types of soil including sandy loam, sandy loam with compost, and sandy loam with clay are studied. Surfactants measured in leachate and soil. The mobility and sorption behavior of three different types of surfactants with soils varying

organic matter and clay content were compared and evaluated. Also a homologue series with varying numbers of ethoxylate groups was evaluated.

1.4 Thesis overview

Chapter 2 provides background on surfactants used in this study and a literature review on the fate of surfactants particularly in relation to clay and organic matter content. Experiment setup, materials, and methods are given in Chapter 3. In Chapter 4, a detailed analysis on mobility of surfactant is presented. Conclusions and future works are discussed in Chapter 5.

2.0 Background and Literature Review

2.1 Surfactants

Surfactants, also named as “surface-active-agents”, are chemicals that stabilize mixtures of oil and water by reducing the surface tension at the interface between the oil and water molecules. It may act as a detergent, wetting agent, emulsifier, foaming agent and dispersant. Surfactants are a class of synthetic compounds commonly found in graywater as components of laundry detergent (Smulder, 2002) and other household cleaning and personal care products (Eriksson, 2003). They are organic molecules consisting of a hydrophilic head and a hydrophobic tail (Karsa and Porter, 1995). The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Based on nature of the hydrophilic group, surfactants are classified as anionic, cationic, nonionic or zwitterionic (Fig 2-1) (West and Harwell, 1992). The nonionic surfactants contain active molecules with no electrical charge, while ionic surfactants contain a head carrying a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If surfactant contains a head with two oppositely charged groups, it is termed zwitterionic. Unlike ionic surfactant, nonionic surfactants do not react with other ions. As a result, they do not form insoluble salts, they can be used in strong acidic solution and tend to have low toxicity profiles.

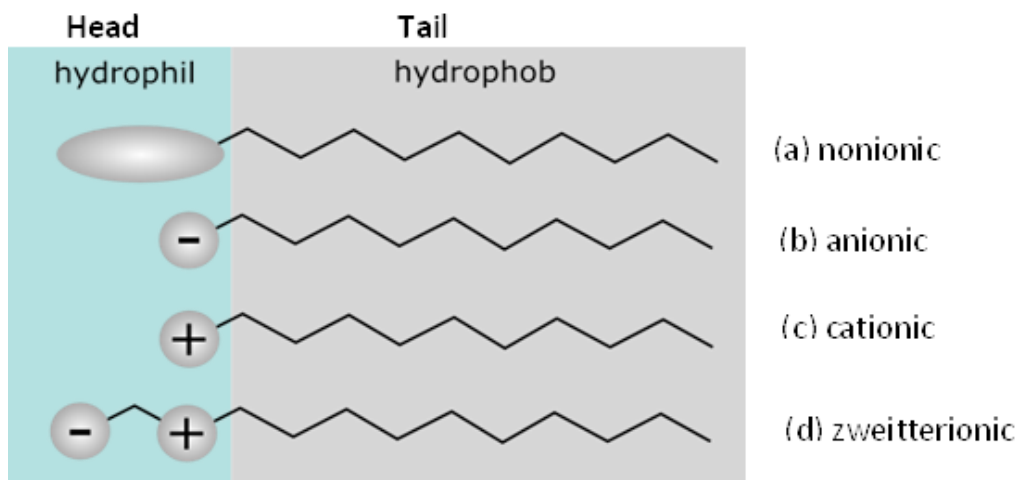


Figure 2-1 Surfactants Classification According to Composition of their head

The most commonly used surfactants are LAS, AES, AS, AE and APE (Aklylphenol ethoxylates), with LAS being the most popularly used anionic surfactant (Ying, 2006). Table 2-1 lists surfactant consumption in the United State and Canada for the 2000. Table 2-1A shows consumption of the various surfactant charge types by percentage. Table 2-1B, shows the consumption of the five major types of surfactant by tonnage.

Table 2-1 Surfactant Consumption in United States and Canada (excluding soap) in 2000

<i>A. Surfactant, by Charge Type</i>	
TYPE	%
Anionics	59
Cationics	10
Nonioncs	24
Zwitterionics and others	7
	100
<i>B. Major Surfactants, by Tonnage</i>	
SURFACTANT	THOUSAND METRIC TONS
Linear alkylbenzene sulfonates (LAS)	420
Alcohol ethoxysulfates (AES)	380
Alcohol sulfates (AS)	140
Alcohol ethoxylates (AE)	275
Alkylphenol ethoxylates (APE)	225
Other	1625
TOTAL	3065

Source: Colin A Houston and Associates, Inc.

LAS molecule contains an aromatic ring sulfonated at the para position and attached to linear alkyl chain at any position except the terminal carbons (Schonkaes, 1998, Cavalli and Valtorta, 1999, Valtorta et al., 2000). The alkyl carbon chain typically has 10 to 14 carbon atoms and the linearity of the alkyl chains ranges from 87% to 98% (Figure 2-2). LAS are the primary cleaning agent used in many laundry detergents and cleaners at concentration up to 25 percent in consumer products, and up to 30% in commercial products. LAS will be biodegraded rapidly in aerobic conditions (Janicke, W. et al., 1979). Anaerobic biodegradation is limited to particular conditions like deficiency in sulfur source (Denger and Cook, 1999, HERA, 2002) or when a small amount of oxygen is present to start the process.

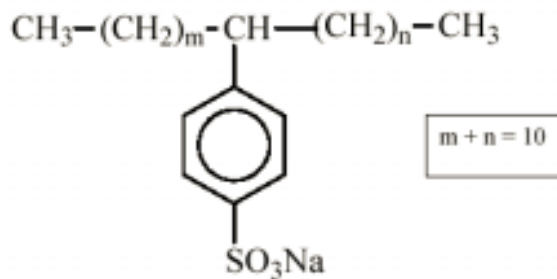


Figure 2-2 Linear Alkylbenzen Sulfonates (m+n=10) (HERA, 2002)

AE are a class of nonionic surfactants that are composed of a long-chain fatty alcohol with an ether linkage to a chain of ethylene oxide (EO) with 7 to 10 being the average number of EO units with a common ranges of 12 to 15 carbon units for the alkyl chain length for commercial grade materials (Figure 2-3) (McAvoy, et al., 1998). They are rapidly biodegraded, and have low to moderate foaming ability and tolerance to water hardness (HERA, 2009b).

AES are a widely used class of anionic surfactant. They are used in household cleaning products, personal care products, institutional cleaners and industrial cleaning processes, and as industrial process aids in emulsion polymerization and as additives during plastic and paint production (HERA, 2003). The alcohol ethoxysulfate family is defined as

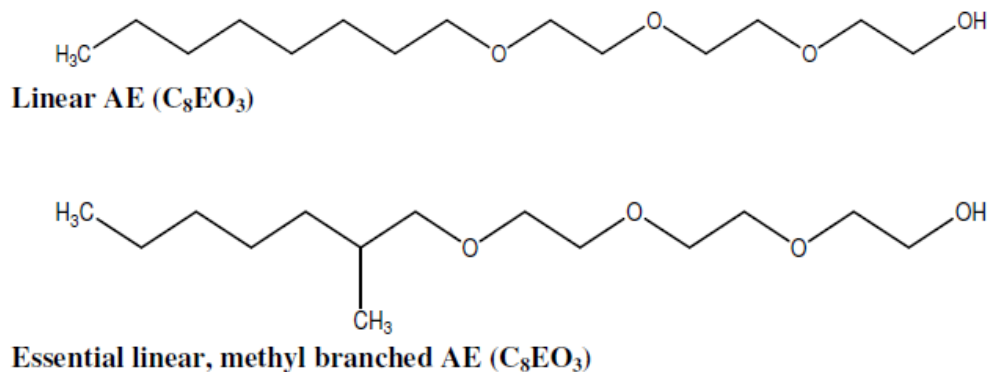


Figure 2-3 Two Principle Structures of AEs in Household Cleaning Products (HERA 2009b)

linear-type primary alcohol ethoxysulphates containing AES components of basic structure $C_n H_{2n} (C_2 H_4 O)_m SO_3 X$, where $n=12-18$ and $m=0-8$ and X =Sodium, ammonium or triethanolamine (TEA) (Figure 2-4). Sodium salts of AES are the most commonly used grades (HERA 2003). C12 through C15 grades were feedstocks for HERA AES. Ethoxylation of detergent alcohols typically is carried out by a base catalyzed reaction with ethylene oxide. The average value of n for the important sulphation grades is 1-3 moles EO per mole alcohol (HERA, 2003).

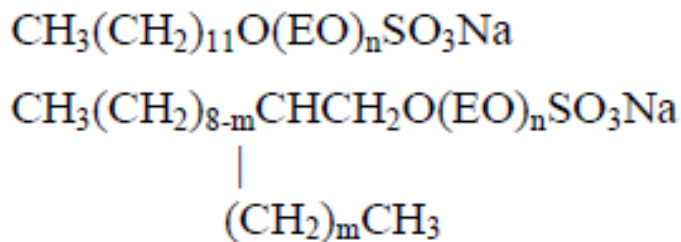


Figure 2-4 The Principle Structure in C_{12} AES (HERA 2003)

AS are a widely used class of anionic surfactants. They are used in household cleaning product include laundry detergents, hand dishwashing liquids, and various hard surfaces cleaner.

The AS family encompasses commercial grades of linear-type primary alkyl sulphates in the C₁₂ to C₁₈ range. They have a basic structure C_nH_{2n+1}SO₄ M, where n=12-18 and M =sodium, ammonium or triethanolamine (TEA) (Figure 2-5). Sodium neutralized AS are the predominant grades. Of the AS used in consumer cleaning applications, a preliminary estimate give 85% - 90% derived from even carbon number linear alcohols, with the remaining 10-1% derived from odd and even carbon number essentially linear-oxo alcohols (HERA, 2002).

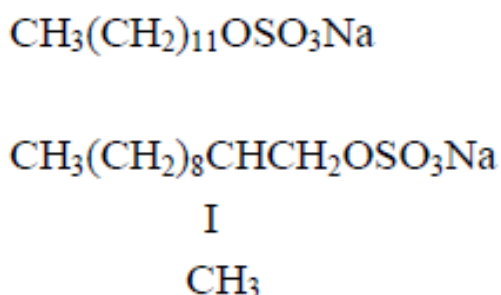


Figure 2-5 The Principle Structure in C₁₂AS

2.2 Surfactant Sorption to Soil

The literature review is divided into four sections. The first section describes mechanism of sorption on soil. The following two sections consist of brief discussions on the relationship between adsorption and clay fraction and organic matter content. Mobility studies on surfactants used in our project are described in the last section.

2.2.1 Mechanism of surfactant adsorption to soil

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors:

- (1) The nature of the structural groups on the solid surface-whether the surface contains highly charged sites or essentially nonpolar groupings and the nature of the atoms of which these sites or grouping are constituted.
- (2) The molecular structure of the surfactant being adsorbed (the adsorbate)- whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic, or aromatic.
- (3) The environment of the aqueous phase -its pH, electrolyte content, presence of any additives such as short-chain polar solutes (alcohol, urea, etc.) and its temperature (Milton, 2004).

Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

There are a number of mechanisms by which surface-active- molecules may adsorb onto solid substrates from an aqueous solution (Rosen, 2004). In general, most adsorption behavior tests are at concentration below the critical micelle concentration (CMC), because of higher micellar solubilization that occurs at higher CMC. The adsorption of surfactants involves single ions rather than micelles (Griffith and Alexander, 1967). The following mechanisms have been identified by Griffith & Alexander (1967) as important for surfactant adsorption:

- (1) Ion exchange (Fig 2-6): Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactants ions.
- (2) Ion pairing (Fig 2-7): Adsorption of surfactant ions from solution onto oppositely charge sites unoccupied by counter ions.

- (3) Hydrophobic bonding: Adsorption occurs by this mechanism when there is an attraction between a hydrophobic group of adsorbed molecule and molecule present in the solution.
- (4) Adsorption by polarization of π electrons: When the surfactants contain electron-rich aromatic nuclei and there are positive sites on the adsorbent adsorption may occur.
- (5) Adsorption by dispersion forces (Fig 2-9): Occurs via London-van der Waals dispersion force acting between adsorbent and adsorbate molecules. Adsorption by this mechanism generally increases with an increase in the molecular weight of the adsorbate and is important not only as an independent mechanism, but also a supplement mechanism in all other types.

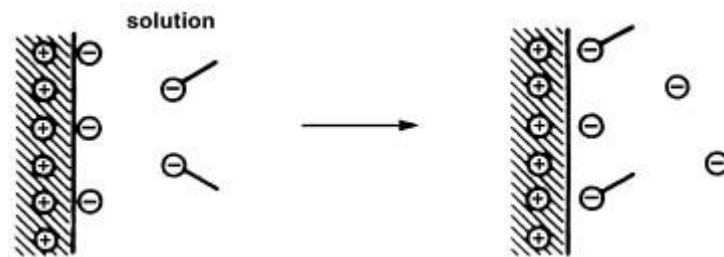


Figure 2-6 Ion Exchanges. M. J. Rosen, et al., 1975

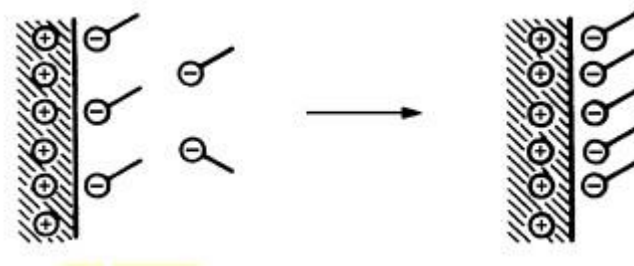


Figure 2-7 Ion Pairing. M. J. Rosen, et al., 1975

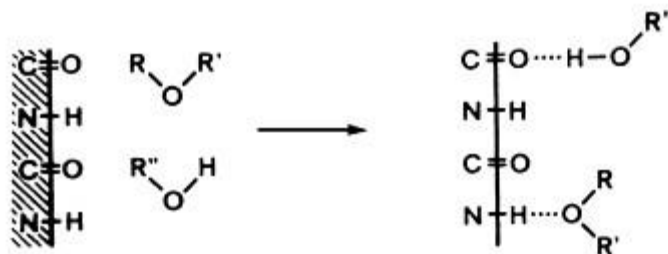


Figure 2-8 Hydrogen Bonding. M. J. Rosen, et al., 1975

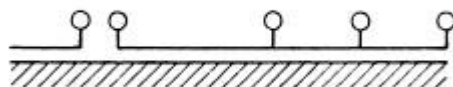


Figure 2-9 Adsorptions via Dispersion Forces on Nonpolar Surface. M. J. Rosen, et al., 1975

2.2.2 Relationship between surfactant sorption and clay content

There are two ways for nonionic surfactants to adsorb to clay. One is hydrogen bonding, the other is Van der Waals' attraction forces. Among the studies on sorption of nonionic surfactants to clay, Muherei and Junin (2009) found that the possible sorption mechanism for nonionic surfactants was adsorption by hydrogen bonding and sorption seemed to show correlation with clay minerals. The adsorption on soil was governed primary by the fraction of swelling clays and not by the organic carbon content of the soil (Brownwell et al., 1990). This finding was also supported by Abdul and Gibson. In their studies, they used 10 commercial surfactants for washing oil from sandy soil. They found adsorption of nonionic surfactants by sandy soil was low, and 1% aqueous solution of surfactants washed more than 80% oil from

sandy soil, the sorbed nonionic surfactants was easily washed out and biodegraded by native soil microbes (Rouse and Sabatini, 1993).

For anionic surfactants, due to negatively charged soil surface, adsorption onto soil is caused by ion exchange, rather than hydrophobic bonding or ion pairing or Van der Waals attraction forces. The correlation between surfactants and clay are not very clear yet. In 1966, Law and Kunze found no evidence of anionic surfactants adsorption based on adsorption studies and X-ray diffraction analysis. While in 2004, Rodriguez-Cruz claimed the total clay fraction content on the adsorption of anionic surfactant was negative, but there was a greater effect of the type of minerals (Ca^{2+} , Mg^{2+}) present than the total clay fraction content. In recent years, some research has addressed the relationship between adsorption and clay content. One study discussed the mechanism of adsorption of anionic surfactant on reservoir sand mixed with clay of Daqing (An oil productive city in China) oil field. The results showed that adsorption of surfactant increased with the increasing surfactant equilibrium concentration and clay content (Song et al., 2011). Anionic surfactants have very low sorption onto soil, but some research has indicated that the adsorption can be promoted if surfactants are mixed (anionic and nonionic together) (Fu E., 1987). In this case of anionic-nonionic surfactants mixture, they do not usually adsorb themselves but co-adsorb in the presence of another component. In this column study, there were three types of anionic surfactants, LAS, AS and AES. Their behavior with clay will be described in Chapter 4.

2.2.3 Correlation between surfactant sorption and organic matter (OM) content

There are three ways for nonionic surfactants to interact with soil organic matter (Baker, 1991):

- (1) Hydrophobic surface interaction between the hydrocarbon chain of the surfactant molecules and hydrophobic regions of the humic matter.
- (2) Hydrogen bonding between surfactant oxyethylene groups and polar groups of the humic matter, such as hydroxyl and phenolic groups.
- (3) Partitioning of the nonionic surfactant into the bulk organic matter in a manner analogous to solute partitioning into an organic liquid such as octanol.

Based on the adsorption isotherm analysis, Shirren I. Hamadamin (2009) investigated the effects of soil organic matter content, soil clay content and exchangeable cation content of natural soil on the adsorption capacity of Triton X-100 (nonionic surfactant) in water-soil systems. Results showed that adsorption increased with increasing soil OM content, but varied irregularly with clay content. This study also supports the research of Chen Wei-wei's group (2011), which claimed both soil organic matter and mineral played important roles in the adsorption of surfactants. Meanwhile, their experiments showed the adsorption of the nonionic surfactants TX-100 and Brij3 decreased with the increase of the number of ethylene oxide (EO) groups.

2.2.4 Behavior of surfactants in soil

The sorption of LAS on natural soil has two stages: linear and exponentially increasing isotherms (Ou, et al., 1996). At low LAS concentration ($< 90 \mu\text{g/mL}$), the sorption isotherms were linear and the adsorption coefficient (K_d) ranged from 1.2 to 2.0. At high concentrations ($> 90 \mu\text{g/mL}$), cooperative sorption was observed and the sorption amount of LAS increased exponentially with the increasing of LAS concentration in solution. This enhanced sorption of LAS on soils was also observed by (Fytianos et al., 1999). In an actual soil or aquatic

environment where LAS levels are rather low, the LAS sorption ability of a soil or sediment is very weak. The focus of this study is graywater, in which the concentration of LAS is low ($< 34 \text{ mg L}^{-1}$) (Leal et al., 2010), and therefore the adsorption of LAS on soil is expected to follow the linear stage as well.

AS adsorbs to the sediment via a hydrophobic interaction (Marchesi et al., 1991), however adsorption of AS on kaolinite was negligible compared with the adsorption of C_{10} - C_{13} homologues of LAS studied. The adsorption of AS increased as the increasing of carbon chain length (SIAM, 2007).

AE adsorption on soil and sediment depends on both properties of AE homologues and the soil characteristics, but it is higher than LAS and AES in general (Nakis and Ben-David, 1985; Yuan and Jafvert, 1997; HERA, 2002; HERA, 2003; HERA, 2009b).

For AES, the sorption of individual homologues within the mixture increased with the increasing EO chain length (Kiewiet et al., 1996). No correlation was found between the sorption capacities (and/or partition coefficient) and the organic content for the soil. However, soil with greater amount of mineral content had slightly higher sorption capacities.

2.3 Toxicity of Surfactants

The harmful effects of surfactants on the environment have been well characterized on plants and soil organisms, and include remobilization of organic pollutants and inhibition of enzyme activity such as microbial dehydrogenase and algae nitrogenase (Margesin and Schinner, 1998). Several studies have been conducted on risk assessment of LAS, AES/AS and AE mainly in aquatic environment and river sediments (DK-EPA 2001). These studies showed that anionic surfactants are less toxic to bacteria than nonionic ones. Also the relationship between toxicity

and molecular weight of surfactants was found. The increase of toxicity along with the increase of molecular weight was observed (Ewa et al., 2004). Surfactants also have been shown to have toxic effects on stream microorganism with lowest no observed effect concentration (NOEC) was reported at concentrations between 0.22-0.29 mg L⁻¹ surfactant (Negahban-Azar M., 2012). The presences of surfactants in soils are of concern if they are toxic to some organisms. In addition, surfactants applied in graywater may be transport to groundwater.

2.4 Summary

Most studies address fate of surfactants in soil when they are applied at a concentration higher than observed in graywater and generally, solutions containing only one type of surfactants have been studied. The mobility and transport of surfactants in soil are different and complicated when we use surfactants contained in graywater for irrigation. On one hand, the adsorption behavior and mechanism may be derived from the complex composition in graywater. On the other hand, the formulation of commercial surfactant is generally a mixture of homologues, thus rending them more complex than individual surfactants alone. Soil organic matter and clay content are two major factors that affect adsorption behaviors of surfactant. Studies to date showed a positive relationship between adsorption of surfactants and organic matter content of soil, and behaviors of surfactants onto soil. However, research to date does not address the following issues:

- (1) There is little consensus on the mechanism of anionic surfactant adsorption onto clay.
- (2) Limited soil types and specific surfactants that are present in graywater;
- (3) Limited data on adsorption of surfactant mixtures to natural soil.

There is a need for detailed studies on transport of surfactants (LAS, AES and AE) in soil. In addition, the effects of organic matter and clay content related to surfactants adsorption are needed. Such studies will provide guidance on soil types that are appropriate for graywater reuse. For example, when leaching of surfactants to groundwater after graywater application is a concern, soils that adsorb surfactants are ideal. The lack of knowledge on surfactant interaction with soil limits our ability to predict and model what would happen under varying graywater irrigation scenarios (soil types and application rates).

3.0 Experiment Setup, Materials and Methods

Sorption and biodegradation are the most relevant processes acting simultaneously in soil (Boluda-Botella et al., 2010). For this study, columns were set up to study the transport of surfactants with a focus on physicochemical interactions with soil. To evaluate the fate and transport of surfactants in soil, environmental condition was attended to be abiotic to prevent biodegradation. To gain an understanding of how different soil types affect surfactant sorption, three kinds of soil were studied (sandy loam, sandy loam with added organic matter and sandy loam with added clay). For each soil type, there were four columns including three replicates and one control. The control column was irrigated with deionized (DI) water as feed water from the beginning to end, while other replicates were irrigated with a sequence of synthetic graywater and DI water. DI water was first used to irrigate soil columns until equilibrium was reached. In this state, inflow rate was nearly equal to outflow with no more than 5% variation observed over three data points, and electronic conductivity (EC) in leachate was constant with no more 5% variation over three sampling points. After that, synthetic graywater was applied to the columns for four hours after which DI water was again applied. Leachate was collected throughout the experiments for analysis of surfactants. Upon completion of the experiment (60-70 hrs), soil was removed from three locations in each column and analyzed for surfactant concentrations. A tracer test was conducted on soil columns twice, before initiation of the tests and at the end of each study.

3.1.1 Soil

Three soil types were used in column experiments; native sandy loam (supplied by Pioneer Sand Company, Fort Collins, CO), compost (supplied by Richlawn company) and clay soil (supplied by CSU ARDEC farm). Compost and clay soil were added to the native sandy

loam to change organic matter and clay content respectively. Before mixing together, all these soil materials were passed through a 10mm sieve. Native sandy loam (SL) was used in the first set of columns. The soil composition (Table 3-1) was 50% sand, 17% silt and 33% clay with organic matter (OM) content of 0.65%. Sandy loam combined with organic matter (SL+O) was made of native sandy loam with addition of 0.03:1(wt/wt) compost. Sandy loam added with clay (SL+C), was made from 3:7 (wt/wt) of clay soil and sandy loam. All soil characteristics are shown in Table 3-1. Note that methods for parameter analysis are included in section (3.3.3). Due to high OM% content of clay soil (2.1%), the SL+C also had higher OM% (1.1%) compare with SL. This might result a higher adsorption of SL+C as we addressed the effect of clay content between SL and SL+C. Results are interpreted considering the relatively high organic content of the SL+C soil.

Table 3-1 Soil Characteristics

Soil	Sand(%)	Silt(%)	Clay(%)	PH	EC($\mu\text{S cm}^{-1}$)	OM(%)	TN(%)	SAR
¹ SL	50	17	33	7.4	1150	0.65	0.09	3.3
Clay soil	31	18	51	7.5	1800	2.1	0.154	1.1
Compost	77	2	21	8	5100	41.7	1.53	3.3
² SL+O	46	16	38	7.4	1400	1.1	0.13	3.7
³ SL+C	42	12	46	7.1	1350	1.1	0.081	2

¹SL: native sandy loam

²SL+O: native sandy loam+ organic matter

³SL+C: native sandy loam+ clay

3.1.2 Surfactants

The source of LAS was Biosoft D-40 (38% LAS), which contains carbon chain lengths of 10 to 13, and was obtained from Proctor and Gamble (Cincinnati, OH, USA). AES was

purchased from Stepan Co (Northfield, IL, USA) in the form of STEOL CS 130, CS 270 and CS 330 respectively. STEOL CS 130, CS270 and CS330 contain sodium lauryl ether sulfate derived from fatty alcohols that are ethoxylated to an average of 1, 2 and 3 mols. Each of them has purity of 30%, 70% and 30% respectively. NEODOL 25-9[®], containing 98% of pure AE, was obtained from Shell Chemical Co (Houston, TX, USA). STEPANOL DCFAS-N, which is an alkyl sulfate (AS) with no ethoxylate group, was purchased from Stepan Co (Northfield, IL USA).

3.1.3 Water

Synthetic graywater (Table 3-3) and DI water were used in the experiments. DI water came from Atmosphere Simulation Lab. Synthetic graywater was prepared in the laboratory the same day which it was applied to columns for irrigation. The formula of synthetic graywater contains constituents typically found in actual graywater including nutrients (Finley, et al., 2009, Jefferson, et al., 2001, Ramon, et al., 2004, Gross, et al., 2005, Roesner, et al., 2006, Pidou, et al., 2008) Yeast extract was added in the synthetic graywater to simulate organics in graywater of which the source is not surfactants. The concentration of total surfactants is 35 mg L⁻¹ which is in a range from 0.7 to 70 mg L⁻¹ found by Alit Wiel et al. (2006) in graywater. LAS, AS/AES and AE have a concentration of 15, 16 and 4 mg L⁻¹ respectively.

Table 3-2 Synthetic Graywater Recipe

Reagent	Concentration(mg L ⁻¹)
Ammonium Chloride (NH ₄ Cl)	8.50
Sodium Nitrate(NaNO ₃)	15.8
Sodium Borate(Na ₂ B ₄ O ₇ ·10H ₂ O)	4.40
Potassium Phosphate monobasic(KH ₂ PO ₄)	3.50
Magnesium Sulfate Anhydrous power(MgSO ₄)	57.5
Potassium Chloride crystalline(KCl)	11.4
Calcium Chloride (CaCl ₂ ·2H ₂ O)	47.1
Sodium Chloride(NaCl)	25.6
Calcium Sulfate (CaSO ₄)	144
Sodium Sulfate(Na ₂ SO ₄)	40.5
Biosoft D-40 (LAS)	15.0
Neodol 25-9 (AE)	4.00
Steol CS-130 (AES)	4.00
Steol CS-270 (AES)	4.00
Steol CS-330 (AES)	4.00
Stepanol DCFAS-N (AS)	4.00
Yeast Extract	248

3.2 Column Setup

PVC columns of 45 cm in length and 12 cm internal diameter were used for the experiments (Figure 3-1). They were (1) cleaned and washed with nonionic surfactant soap and water, (2) rinsed with tap water and followed with DI water, (3) then rinsed with methanol followed by a rinse with methylene chloride. After that they were air dried one week before using. Three different holes with 1cm internal diameter on the side of column, which were located at 15cm, 30cm and 40cm from the bottom, were created for soil sampling. Feed water was pumped upward from the bottom of column and exited from the top to create completely saturated conditions. Three replicate columns were prepared for each soil type. Also one controlled was set up by using DI water as feed water thoroughly. This control column was used

for making a comparison with other three replicates. As there was no surfactant feeding into the control column, irrigation process would not change soil physicochemical characteristics. Soil particle density (Table 3-3) was measured prior to packing. When filling columns, particle density was adjusted by vibration or compaction to the value measured before. We removed the top surface of each layer before adding the next increment. Then we packed the soil into the column so that uniform density was achieved. This could be checked by visual observation of the soil in the transparent column. Soil was added to the column to the desired final height 41.0cm, ensuring each replicate had approximate same height. After filling the column, soil weight (Table 3-3) was determined. All of the soils were air dried and autoclaved at 215°C for 45 minutes three times prior to insertion in columns. In addition during the experiments, 5% (wt/wt) formaldehyde was added to synthetic graywater to prevent microbial growth in columns. The soil packing process followed ASTM standard D4874-95.

Table 3-3 Soil Parameters

Soil Type	Weight(g)	¹D_b(g cm⁻³)	²D_p(g cm⁻³)	³P_s
SL	5057	1.55	2.65	42.5%
SL+O	5057	1.36	2.04	33.0%
SL+C	4500	1.25	2.39	47.7%

¹D_b: Bulk density

²D_p: Particle density

³P_s: Pore space



Figure 3-1 Column Set up

3.2.1 Experiment Conditions

All experiments were conducted at room temperature (20-25°C) and attended to be abiotic saturated conditions. To achieve these conditions, soil was autoclaved at 215°C for 45 minutes three times before mixing homogenously. In addition, 0.5% (m/m) formaldehyde was added to synthetic graywater to prevent growth. This method was used by others who studied surfactant sorption to soil (Boluda-Botella et al., 2010).

3.2.2 Experiment Procedure

Each column was irrigated with DI water using a Masterflex[®] L/S[®] pump (Vernon Hill, IL 60061) (Fig 3-2) until they reached equilibrium (approximately 50 hours). Polyethylene

tubing (0.25 in diameter, Spindale, NC 28160) was used to connect the pump and the bottom of column. Electronic conductivity (EC) and flow rate were used as indicators for equilibrium. After 48 hours, EC, inflow rate, and outflow rate were measured once per hour. The EC in the leachate was constant and inflow was nearly equal to outflow with no more than 5% variation observed over three data points. Synthetic graywater was prepared the same experiment day to prevent changes in composition. After reaching equilibrium, synthetic graywater was applied to the columns at a constant flow rate for 4 hours 5.0 mL min^{-1} . This irrigation hours and flow rate were applied to mimic the flow rate studied by Boluda-Botella et al. (2010). Homogeneity of surfactants solution was maintained with adequate stirring during the experiment. After 4 hours of irrigation with graywater, a continuous input of DI water was maintained.

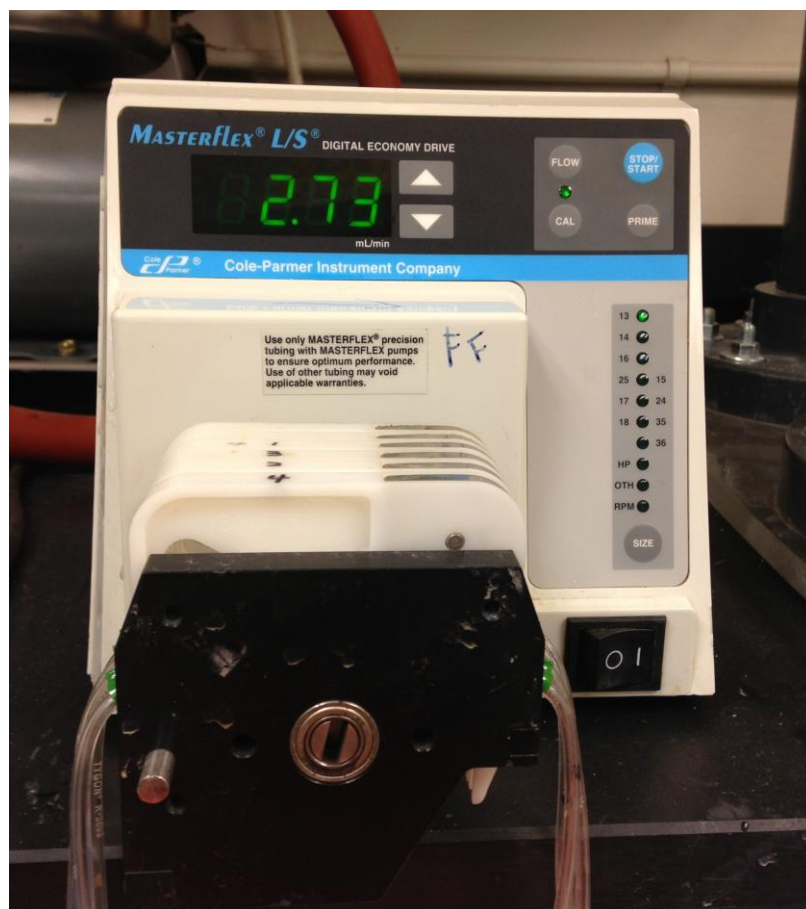


Figure 3-2 Masterflex® L/S® Irrigation Pump

(Cole-Parmer Instrument Company, IL 60010 USA)

3.2.3 Leachate Sample Collection

Based on the experiment with different soil types, leachate sampling schedules and DI water irrigation duration (Table 3-4) were different. The first leachate sample from SL and SL+O was collected at 0.5 hour after starting irrigation with graywater. For SL+C, as clay soil was added into native sandy loam, soil porosity was increased which caused an increased residence time. So the first sampling time was changed to 3 hours after initiation of graywater irrigation. Leachate flowed through a tube which connected to the outlet of column (Figure 3-3). Samples were stored in a refrigerator (4°C) during the experiment. They were extracted (section 3.3.1.1)

and analyzed for surfactants (section 3.3.1.3) within 1 to 2 days. It should be noted that for the surfactants, though the sample extraction was performed within the specified period, measurement of the surfactant concentration did not occur immediately. The extracted samples were stored in a freezer (-6 °C).

To enable the mass balance determinations for surfactants in the columns, soil samples were collected from three different depths, 15, 30 and 40 cm from the bottom of column respectively. At least 20g of soil was collected at each sampling point in 50 ml centrifuge tubes. Soil samples were weighed and extracted (section 3.3.1.2) within 1 to 2 days after sample

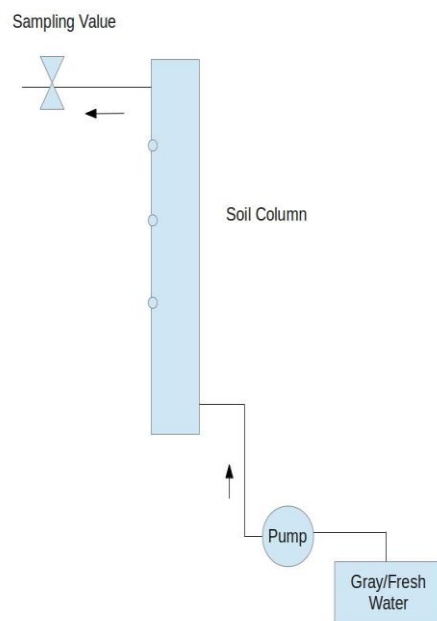


Figure 3-3 Schematic of Column Setup

collection. Soil samples were kept in a freezer at -6 °C to inhibit microbial activity until they were tested.

Table 3-4 Leachate Sampling Intervals

Sample No.	¹SL Sampling Time (h)	²SL+O Sampling Time (h)	³SL+C Sampling Time (h)
1	0.5	0.5	3
2	3.5	3.5	7
3	7	7	11
4	10.5	10.5	15
5	20.5	20.5	30
6	30.5	30.5	48
7	40.5	40.5	69
8	50.5	50.5	
9	60.5	60.5	
10	70.5	70.5	

¹SL: Native sandy loam

²SL+O: Native sandy loam added with compost

³SL+C: Native sandy loam added with clayed soil

3.2.4 Tracer Test

At the beginning and the end of experiments, tracer tests were conducted to characterize the hydrodynamic parameters of soil columns. According to Sardin et al. (1998) CaCl₂ is considered a good tracer in experiments with sand columns and clay for this study. Tracer solution with concentration of 0.98g L⁻¹ CaCl₂ was prepared with DI water with electrical conductivity (EC) of 2000 µS cm⁻¹. Before the tracer tests, soil columns were irrigated with DI water to reach equilibrium. Then tracer solution was added through a tube which connected to the bottom of columns at a rate of 5 mL min⁻¹ then flowed out from the top of column. EC was continuously measured with a GRANT field probe (Smithfield, RI 02917) in the effluent every

30 minutes. The tracer test was terminated when EC in effluent reached a constant value with no more 5% vibration over three observations for three consecutive measurements. The breakthrough curves were utilized to calculate transport parameters with ACUAINTRUSION TRANSPORT as Boluda-Botella et al. (2010) did for each column setup. This graphical user interface calculates the best fit of experimental data, e.g., Cl^- concentration (mmol L^{-1}) or conductivity versus experimental time (h). The analytical solution of the convection-dispersion equation (Japidus & Amundson, 1952) is:

(Equation 3-1)

$$C(L, t) = C_i + \frac{(C_0 - C_i)}{2} \left[\text{erfc}\left(\frac{L - vt}{\sqrt{4D_L t}}\right) + \exp\left(\frac{vL}{D_L}\right) \text{erfc}\left(\frac{L + vt}{\sqrt{4D_L t}}\right) \right]$$

Where (for example, for the EC experimental data): $C(L, t)$, is the Cl^- EC at the output stream of the column; C_i , the initial Cl^- EC in the water; C_0 , the EC of chloride at the inlet; L , column length; t , time; v , interstitial water velocity in the direction of propagation (equal to Darcy velocity u divided by porosity); and D_L , the longitudinal dispersion coefficient.

The program then provided the following calculated transport parameters: mean residence time t_m (L/v), Darcy velocity u , (u =flow rate divided by column crossing area) Péclet number, ($Pe = vL/D_L$), effective porosity ε , interstitial velocity v (u/ε), D_L , and dispersivity α (L/Pe).

3.3 Testing Methods

3.3.1 Surfactant analysis

3.3.1.1 Liquid Extraction

Surfactants were extracted from leachate samples, using solid phase extraction (SPE) by methods developed by Negahban-Azar, M. et al. (2013). The process includes the use of Waters® OASIS extraction cartridges (Waters, Milford, MA, USA) and an SPE vacuum (Fig 3-3). The extraction cartridges contain a unique hydrophilic-Lipophilic Balance (HLB) sorbent, which is a universal polymeric reversed-phase sorbent that was developed for the extraction of a wide range of acidic, basic, and neutral compounds from various matrices using a simple, generic protocol. To start leachate extraction, the Oasis HLB extraction cartridges were placed on the vacuum manifold and the pressure of vacuum (Barnant CO, IL, USA) was kept at or below 5 in. Hg. A continuous vacuum was maintained on all cartridges throughout the process. The cartridges were first conditioned by adding 2mL of methanol. To equilibrate the system, 2mL of DI water was added and drawn through the tubes. Then a sample volume of 2 mL was passed the cartridges. To wash out the cartridges, 2 mL of 5% methanol in water (v/v) was added and drawn through the cartridges. The vacuum was released, the manifold cover was removed and the waste fluids were discarded. The rack containing the collection vessels was inserted into the vacuum manifold. The cover was replaced and the vacuum was turned on. To elute, 2 mL of methanol was added to the tubes. The eluates were kept in 2 mL amber vials for LC-MS analysis (section 3.3.1.3). Recovery percentage for the SPE was ranged from 92-100%.

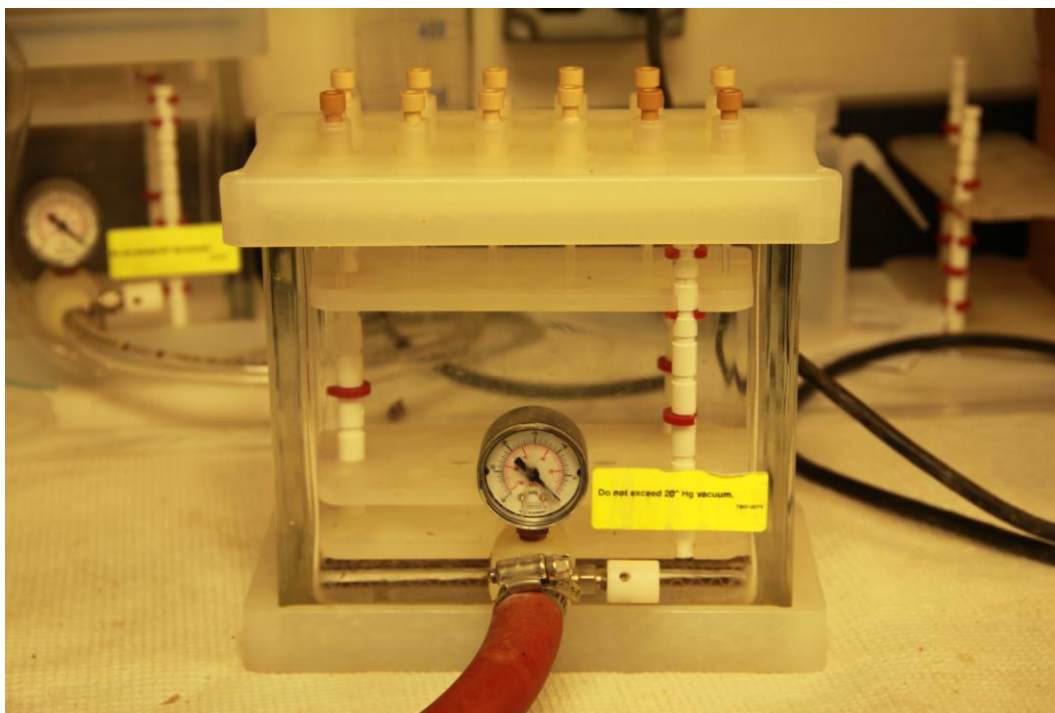


Figure 3-4 SPE Vacuum

3.3.1.2 Soil Extraction

Soil samples were collected in a 50mL centrifuge tube immediately after experiment. To extract the surfactants from soil, a volume of 20 mL methanol was then added to the soil contained in the centrifuge tubes using a pipette, close the caps and make sure they were tightly closed. Automated shaking was carried out for 20 minutes at 350 rpm followed by placement of the centrifuge tubes in a sonicator for 5 minutes. The samples were then centrifuged for 10 minutes at 2500 rpm. After centrifugation, the clear solvent was decanted to a separate centrifuge tube, and the tube was capped. This was repeated adding another 20 mL methanol, extracted from soil again. At the end of the process, approximately 40 mL of liquid was obtained in the centrifuge tube. The tube was then placed under nitrogen in order to evaporate the methanol extract. Following drying, 2 mL of methanol was added to the tube. This addition was followed by centrifugation for 5 minutes. After centrifugation, the samples were filtered using 0.45 μ m

sterile cellulose acetate membrane centrifuge filters. The filtered liquid was transferred to 2 mL autosampler vials for LC-MS analysis. These vials were stored in the freezer (-6°C) prior to surfactant measurement using the LC-MS machine. After extraction, soil samples were air dried for about one week before weighed. The concentration of surfactants in soil is reported on a dry mass of soil basis. Average rates of recovery were 85 ± 14 , 86 ± 15 , and 91 ± 11 for LAS, AES, and AE respectively for the various soil types.

3.3.1.3 Surfactants Measurement

Surfactants (LAS and AES/AS) were quantified by mass spectrometer with an Agilent 1200 high-throughput HPLC system coupled with an Agilent 6220 Accurate Mass Time of Flight (Agilent Technologies, Santa Clara CA, USA; Negahban-Azar et al., 2012).

Chromatographic separation was carried out with Xterra® MS C18 column (2.5µm, 50mm 2.1mm) (Waters, Millford, MA, USA) from Waters. A gradient method with a mixture of water and 10 mM ammonium acetate and acetonitrile with 10 mM ammonium acetate was used. The flow rate was 0.32 mL min^{-1} was used for measurement. To determine LAS and AES/AS, electrospray ionization (negative ion mode) mass spectrometer was used. The negative ion molecular weight of LAS, AES(EO1), AES (EO2), AES (EO3) and AS are 325m/z, 309m/z, 353m/z, 397m/z and 265m/z respectively. For AE, chromatographic separation was carried out with an Allure C18 (150mm×2.1mm) and a 5µm Restek column (Bellefonte, PA 16823). A gradient method with a mixture of methanol with 5 mM ammonium acetate and water with 5 mM ammonium acetate were used. A flow rate of 0.32 mL min^{-1} and injection volume of 20µL were set. Detection of AE was carried out using an Agilent 6220 Accurate Mass Time of Flight mass spectrometer with positive ionization mode APCI source. The positive molecular weights of AE are 570m/z, 614m/z and 659 m/z respectively. Six surfactants standard concentrations (0.2,

0.02, 0.002, 0.0002, 0.00002 and 0.000002) were run firstly to get calibration curves. Mass Hunter Workstation software was utilized to process concentrations based on calibration curves. Detection limits for LAS, AS/AES and AE were $5\mu\text{g L}^{-1}$, $5\mu\text{g L}^{-1}$ and $3\mu\text{g L}^{-1}$ respectively.

3.3.2 Water quality analysis

Leachate samples were analyzed for total organic carbon (TOC) with the high temperature combustion method (referenced in part from Standard Method, 2005 (5310B)). The TOC was measured using TOC-VCSH Shimadzu organic carbon analyzer (Shimadzu, Columbia, MD). A volume of 50 mL of leachate samples were collected in amber glass bottles to ensure enough liquid for TOC and surfactant analysis. Due to the large organic content of formaldehyde added into feed water, TOC tests results were meaningless.

3.3.3 Soil quality analysis

3.3.3.1 Bulk density D_b , particle density D_p and pore space P_s

The bulk, particle density were determined by coated-clod method (GR Blake, 1965). A mass of soil was removed from the soil profile without changing its nature structure. The clod plus the paper clip and hair net was weighed, coated twice with a saran sealer and then given with hair net and paper clip for weighing and for determination of the weight of the 2 saran coats. The clod was then suspended in water and weighted. Archimedes Principle was used to determine the volume of the clod. Once the original moisture content of the clod was detained the bulk density of the clod can be determined. Since the displaced liquid equaled the volume of the object and water has a density of 1gram per cubic centimeter, the decrease in weight when the clod was suspended in water was equal to the clod's volume. The D_p was then determined by the equation 3-2, P_s was determined by the equation 3-3.

(Equation 3-2)

D_p = oven-dry wt./ volume of the soil solids

(Equation 3-3)

P_s = volume of the pores/ total volume of the sample, pore volume+ solid volume

3.3.3.2 Soil texture

Soil texture was determined for each sample using the hydrometer method (G.W et al., 1986). The hydrometer method is based on the change of density of a soil and water suspension upon the settling of the soil particles.

3.3.3.3 pH value

Soil pH was determined by the saturated paste method (USDA, 1954). A saturation paste was first prepared then standardized the pH meter. (1) Rinsed electrode with deionized water and placed in pH 7.00 primary standard buffer and adjusted as necessary; (2) rinsed electrode and place in pH 4.00 primary standard buffer; (3) adjusted the slope until response is ± 0.05 units to expected response; and (4) checked pH 7.00 primary standard buffer and adjust as necessary. For high pH soil (>7.00) use pH buffers 7.00 and 10.00. Followed that, inserted electrode into soil paste and gently rotated the container to remove entrapped air. When the meter had stabilized, soil pH was recorded as pH_{sp} to the nearest 0.001 pH unit. Finally, electrodes was removed, rinsed with deionized water and blot excess water with filter paper.

3.3.3.4 Organic matter

Soil organic matter was determined by Walkley-Black method (D.W Nelson & L.E Sommers, 1996). The Walkley Black method used for determining soil organic matter utilizes a specified volume of acidic dichromate solution reacting with a determined titration of the excess dichromate solution with ferrous sulfate with gives a volume of ferrous sulfate in mL. The organic matter was calculated using the difference between the total volume of dichromate added and the volume titrated after reaction.

3.3.3.5 Total inorganic nitrogen

Soil total inorganic nitrogen (TIN) was summed of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$. $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were measured using in-line UV/persulfate digestion and oxidation with flow injection analysis and ammonia-selective electrode method respectively (APHA & AWWA, 2005).

3.3.3.6 SAR

Soil SAR was calculated as $[\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+}) / 2^{0.5}]$ using sodium, calcium and magnesium concentration values normalized based on the molecular weight and valence charge of the ion. The ion concentration were measured using an inductively couple plasma atomic emission (ICP) spectrophotometer (Thermo Jarrel Ash Corp., Franklin, MA).

3.3.4 Statistical analysis

Statistical packages SPSS 20.0 for WINDOWS (SPSS Inc., Chicago, IL) and Microsoft Office Excel 2010 (Microsoft Corporation, Redmond, WA) were used for statistical analysis. The significance of the ratio of mass of leached to mass of retained effects on soil OM, clay and irrigation time (Time) was determined at the 95% confidence interval using regression analysis.

OM, clay and time were set as independent variables, and the fraction of mass of leached surfactants to mass of retained was as dependent variable. A multiple linear regression equation was developed between independent variables and measured parameter. The *p* values for equations were reported.

3.4 Microbial Activity Test

Due to our results from SL and SL+O columns, we found there may be microorganisms in experimental soils even though soils were autoclaved and 5% (m/m) of formaldehyde was added in feed water. Enumeration of the microbial population by the spread plate method is a simple and rapid method to count viable microbial cells in soil (Carter & Gregorich, 2009). Soil samples from SL+C were collected from three different columns with three depths and then kept into freezer (-6°C) until tests were conducted. Reasoner's 2A agar (R2A) was used as a growth medium for this test. Before doing the test, all the materials including R2A agar, pipettes, glass spreader, dilution bottle, D.I water were sterilized by autoclaving at 215°C for about one hour. A mass of 2g of soil sample was inserted into dilution bottle which contained 19 mL of DI water. Glass beads (6mm diameter) from Fisher Scientific® (Pittsburgh, PA 15275) were added to this dilution blank to facilitate mixing. Bottles were placed on a mechanical shaker for 10 minutes. After removing the bottle from the shaker, samples were vigorously shaken before removing aliquots. We transferred a 10 mL sample to a 90 mL dilution blank and shook the dilution bottle to make a 1:10 dilution soil sample. This sequence was continued until a dilution of 10^{-7} was reached. Subsequent spread plating of 0.1 mL aliquot of this dilution allowed enumeration of up to 1×10^7 colony-forming units (cfu) per g soil. The plates were incubated at 30°C for 72 hours (Fig 3-5).

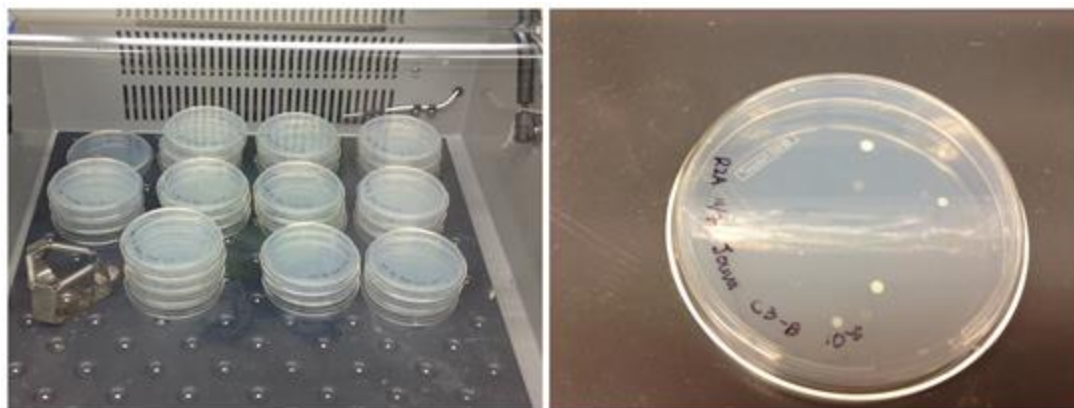


Figure 3-5 R2A Plates in Incubator

4.0 Results and Discussion

4.1 Tracer Tests

Hydrodynamic and physical characteristics of three different soil columns were determined at the beginning and the end of each experiment. A continuous inflow of CaCl_2 tracer permitted the production of breakthrough curves, which contained all the information with respect to the hydrodynamic and physical characteristics of the column. The determination of transport parameters was relevant to adequately explain surfactants behavior along the soil column. The different characteristics of transport parameters, for instance dispersivity $\alpha(cm)$, could modify the shape of fronts in the surfactants pulse and therefore affected the chemical composition of the groundwater across the flow path in field studies (Boluda-Botella et al., 2010). In particular, when the t_m is high in a column, we expect to see surfactants in the leachate at a later duration than when t_m is low.

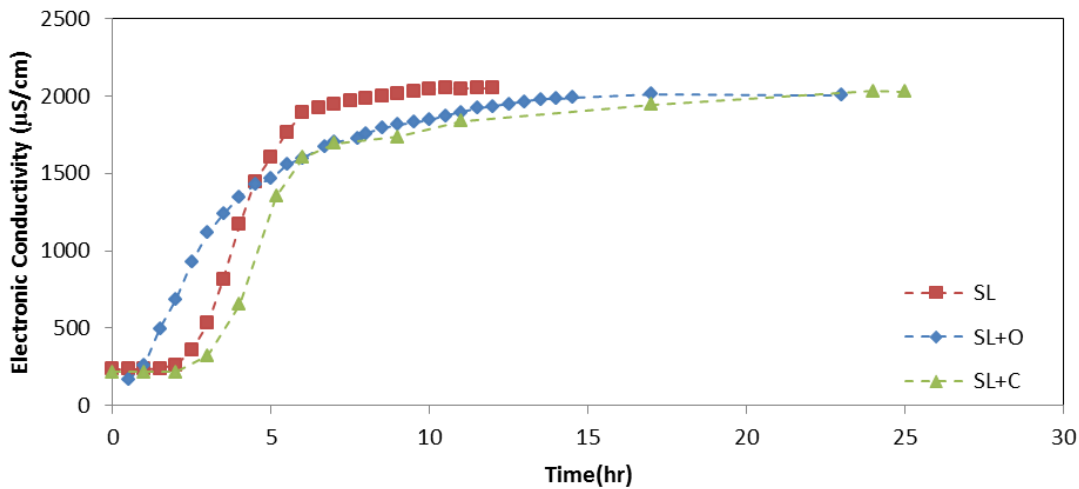


Figure 4-1 Tracer Tests Results. (SL: Native Sandy Loam, SL+O: Native Sandy Loam added with 5% Organic Matter, SL+C: Native Sandy Loam added with Clay Content)

Mean residence time was 4.20 ± 0.13 hr, 3.75 ± 0.34 hr and 5.30 ± 0.45 hr in SL, SL+O and SL+C respectively. With a difference of 27 min between SL and SL+O, adding compost had slightly decreased effective porosity of soil column, which from 0.38 ± 0.01 in SL to 0.35 ± 0.02 in SL+O. Lower effective porosity caused shorter residence time due to a lower volume of pore space for water to flow through, thus increasing the velocity of liquid. On the other hand, compared with SL to SL+C, 70 min lower residence time in SL than SL+C, with their effective porosity of 0.38 ± 0.01 in SL increased to 0.51 ± 0.03 in SL+C. The increased proportion of soil increased the effective porosity as a consequence of the higher clay content. A lower median grain size increased the water-storage capacity. It was also indicated that adding clay content has more effects on soil ε , which increased more t_m .

Table 4-1 Transport Parameters of Different Columns Experiments by Applying ACUAINTRUSION Model Conductivity.

Test	Flow (mL min ⁻¹)	Length (cm)	u(cm h ⁻¹)	t _m (h)	Pe(vL D ⁻¹)	Effective ε	α (cm)
SL	4.98 (± 0.23)	41.5 (± 0.08)	3.75 (± 0.17)	4.2 (± 0.13)	21.33 (± 8.05)	0.38 (± 0.01)	2.19 (± 1.00)
SL+O	4.96 (± 0.15)	40.5 (± 0.01)	3.73 (± 0.11)	3.75 (± 0.34)	1.82 (± 0.47)	0.35 (± 0.02)	24.33 (± 6.73)
SL+C	5.13 (± 0.12)	41 (± 0.03)	3.92 (± 0.09)	5.3 (± 0.45)	24.31 (± 22.78)	0.51 (± 0.03)	3.53 (± 3.47)

Pe relevant in the study of transport phenomena in fluid flows. It was defined by the fraction of the rate of advection and the rate of diffusion. The higher the Pe , the more important is advection. If $Pe \gg 1$, large thermal gradients can exist. If $Pe \ll 1$, diffusion dominates transport. In the three soil types studied, Pe were all larger than 1. This means the performance of chemicals transport in these three columns was all likely by advection. Also from dispersivities (α), which were calculated as L/Pe . The small dispersivities indicated that the column hydrodynamic characteristics were similar to plug flow. Therefore, we could consider all these three columns could be characterized by similar hydrodynamics. However, the Pe for the SL+O column was only slightly larger than 1, and much lower than other columns. It indicates higher diffusion in this column compared to others.

4.2 Surfactants Behaviors in Soil Columns

4.2.1 Leaching of Surfactants through Soil Columns

Due to their physical and chemical features, surfactants may sorb onto solid surfaces or may interact with sorbed surfactant or leached out with injection water or may be biodegraded by soil microbial. Three types of surfactants LAS, AES and AE were conducted in SL, SL+O and SL+C respectively. All of them were under abiotic conditions. From Fig 4-2, we used proportion of leached surfactants and proportion of surfactants retained in soils to gain a mass balance. In ideal conditions, these two values added up were equal to 100. The lost portion of surfactants might be due to the following reasons.

- (1) Surfactants might be biodegraded by soil microorganism during experiments.
- (2) Residual surfactants on PVC columns.

(3) The extraction efficiency of surfactants in liquid and soil are in a range of 85%-100%.

Surfactants might be lost during extraction process.

Biodegradation was the most important reason of lost, this was indicated that some surfactants were biodegraded and the soil columns still containing microorganisms.

The reason for microorganism living in soil columns might be due to the following reasons.

(1) Soil samples were not sufficiently autoclaved, might need more times.

(2) Amount of formaldehyde added into feed water was not enough.

(3) Residual microorganism on PVC columns or in feed water.

As a result of observations from the SL and SL+O experiments, microbial activity tests were conducted for SL+C column study, and the feed water was changed from fresh tap water to D.I water to overcome presence of microorganisms.

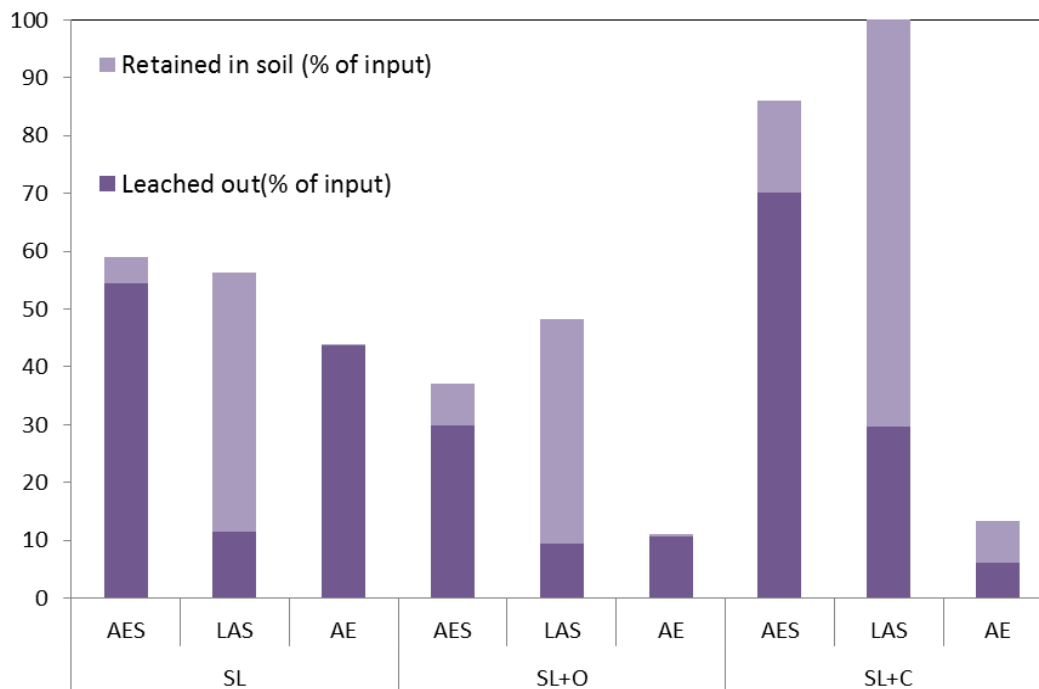


Figure 4-2 Mass Balance for Surfactants onto Soils

Of note that the typical value of microbes in soil is from 10^8 - 10^9 /g soil (Sylvia, et al., 1998). Results (Table 4-2) indicate that soils contained microorganism even after having been autoclaved for three times at five-hour duration. The microorganism appeared in all three locations (A, B and C) from soil column. After experiment, even though formaldehyde could inhibit organism rapid growth, the experiment conditions were still biotic, as indicated by the presence of microorganisms in several samples. It was determined that results from the mass balance were reasonable, and that surfactant adsorbed onto soil and was biodegraded by microorganism simultaneously.

Table 4-2 Results for Microorganism Tests

	Microbial Counts ($\times 10^5/\text{gsoil}$)				
	C1-B	C2-A	C2-B	C2-C	C3-B
Before GW	4	5	0	1.5	3
After GW	0.5	0	0	2	2

The biodegradivity in this study could be concluded as $\text{SL}+\text{O} > \text{SL} > \text{SL}+\text{C}$. Of note is that more measures were taken to prevent microorganism presence and/or growth in the $\text{SL}+\text{C}$ experiment (see above). Due to rapid biodegradation (HERA, 2009b), recovery rate of AE in this study ranged from 10%-40% indicating a large portion of AE was biodegraded. Because biodegradation of surfactants was not mitigated in all experiment, results are reported in terms of the ratio of mass leached to mass retained. Analysis of the data by this approach enables comparison of leaching potential despite some observed biodegradation.

Three different situations were evaluated for each type of surfactant (LAS, AES and AE) used in this study: SL , $\text{SL}+\text{O}$ and $\text{SL}+\text{C}$.

For anionic surfactants (LAS and AES), Fig 4-3 and Fig 4-4 show the adsorption isotherms in the three studied soils. Compared with SL , both surfactants in $\text{SL}+\text{O}$ showed that a lower ratio of mass leached to mass of retained. This indicates that higher soil organic matter enhanced the adsorption capacity of LAS and AES. This result was also consistent with other researchers about surfactant adsorption (Urano et al., 2009, Chen et al., 2011). An increase in clay resulted in more leaching of surfactants out of the columns, which indicated that adding clay content had a negative effect on anionic surfactant adsorption and increasing leaching of the surfactant. This was unexpected since soil organic matter tends to increase with clay content. This increase depends on two mechanisms. First, bonds between the surface of clay particles.

This can neutralize the mineral surface by acting like a bridge and adjusting the charge of the negatively charged mineral surface. In neutral and alkaline soil mostly Ca^{2+} and Mg^{2+} are present, whereas in acid soil additional Fe^{3+} and Al^{3+} form cation bridge resulting in sorption of organic matter (Lutzow, et al., 2006). Second, soil with higher clay content increase the potential for aggregate formation, macroaggregates physically protect organic matter molecules from further mineralization caused by microbial attack (Rice, 2002). One possible explanation for the relatively high leaching potential of anionic surfactant in clay is repulsion with negatively charged clay. SL+C were tested for cation exchange capacity of 13.10 meq/100 soil and SL had a CEC of 12.17meq/100g soil. Compared to these two with the normal range in soil groups (Table 4-3), CEC is in the low in both soils range of soils. CEC is indicative of the ability of particle to adsorb and store cations. The higher the CEC, the higher the negative charged and the more cations that can be held. SL+C which had higher CEC increased repulsion forces between soils and anionic surfactants, thus the hydrophobic bonding could have been diminished.

Table 4-3 Normal Range of CEC Values for Common Color/Texture Soil Groups

Soil groups	Examples	CEC in meg/100
Light colored sands	Plainfield	3-5
	Bloomfield	
Dark colored sands	Maumee	10-20
	Gilford	
Light colored loams and silt loams	Clermont-Miami	15-25
	Miami	
Dark colored loams and silt loams	Sidell	30-40
	Gennesee	
Organic soils	Carlisle musk	50-100

For nonionic surfactant AE (Fig 4-5), adsorption isotherms of surfactants onto the SL+O is similar to LAS and AES onto SL+O, where more surfactant adsorption occurred onto SL+O than SL. Moreover, comparing LAS and AES sorption onto SL+O, AE had lower ratio of leached to retained mass of columns. This showed that the adsorption of nonionic surfactants was more than of anionic LAS/AES on soil containing organic matter, indicating that there were stronger electrostatic repulsion between organic soil and anionic surfactants than that between soil and nonionic surfactants. Nonionic surfactants sorbed more to organic soils than anionic surfactant. This was also reported by several other researchers (Yuan, et al.,2007; Muherei & Junin, 2009). On the contrary, the adsorption of AE onto SL+C was less than SL (Fig 4-5). Most clay is negatively charged and SL+C had higher CEC than SL, which indicates a negative charge of the added clay material. Of note is that SL+C has the same OM as SL+O (1.1%), which is higher than SL. As previously discussed, higher OM matter will increase sorption capacity. Therefore, in SL+C, combining with the interaction of organic matter and clay content themselves, the adsorption of AE may dominated by OM instead of clay, and it may decrease

with clay content increase. This might be attributed to stronger electrostatic repulsion. The higher clay composition, the more negatively net charged the soil is thus resulting in less AE sorption.

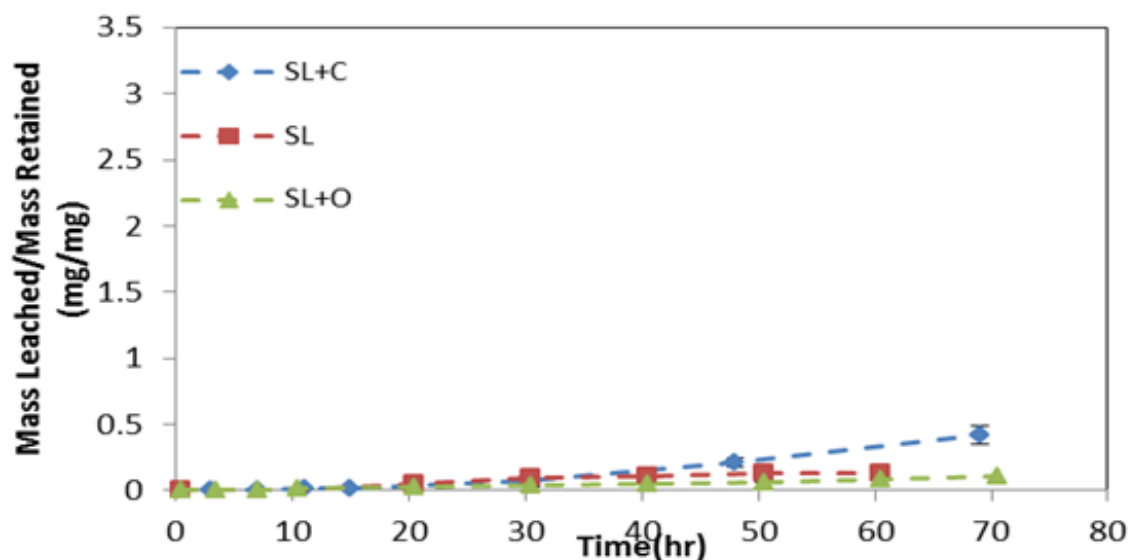


Figure 4-3 LAS Transport in Different Soil Types

Lipophilicity (or hydrophobicity) is measured as the octanol to water partition coefficient (K_{ow}). Lipophilicity was known as a good indicator of evaluating hydrophobicity of organic matter compounds (Table 4-4). The relative $\text{Log}K_{ow}$ of surfactants can be summarized as $\text{AE} > \text{LAS} > \text{AES}$ (HERA, 2002; HERA, 2003; HERA, 2009b). The lower the K_{ow} value the more hydrophilic the surfactant. Results from these experiments were consistent with the reported K_{ow} values in that AES had the highest leaching potential compare to LAS and AE (Fig 4-3 – 4-5). This result was also consistent with what we observed from initiation time of LAS leaching compare to AES and AE (Fig 4-3 – 4-5). The values for the time that leaching started for LAS, AES and AE were 18 ± 0.50 , 10 ± 0.96 and 20 ± 0.45 hours in SL respectively. It can be concluded

that AES leached out first and had higher potential to reach deeper soils, and thus also potentially groundwater.

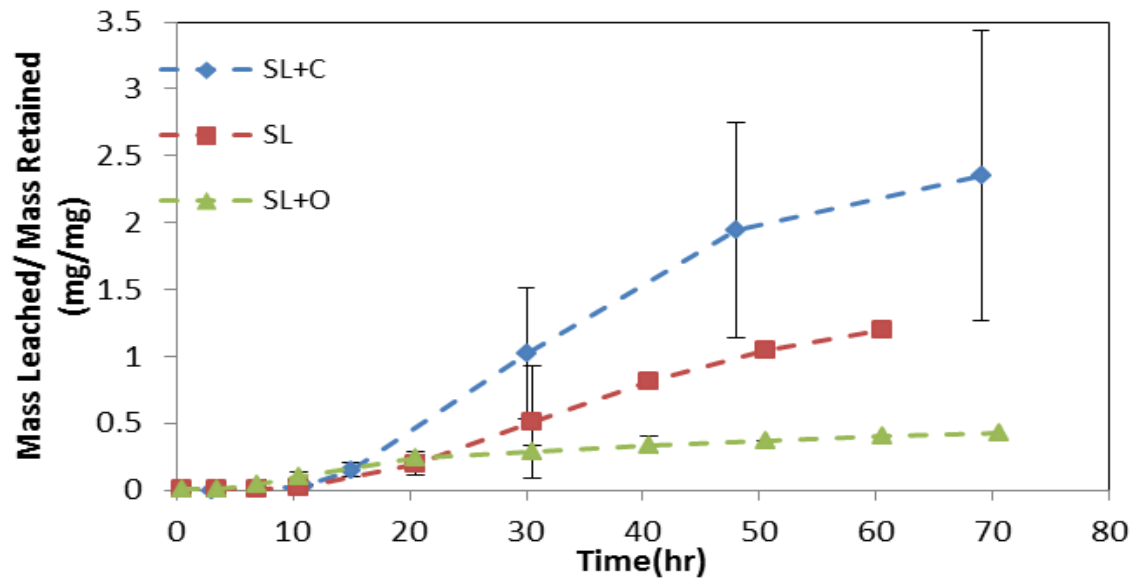


Figure 4-4 AES Transport in Different Soil Types

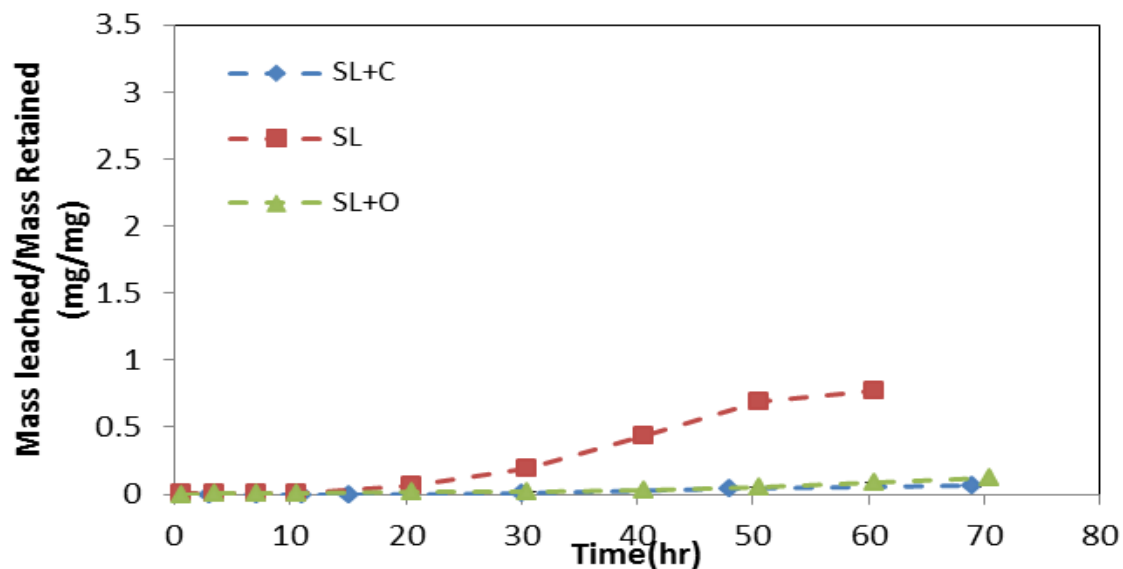


Figure 4-5 AE Transport in Different Soil Types

Table 4-4 Sorption Characteristics

(HERA 2002, 2003, 2009a.b and references there in)

Surfactants	K_d	Log K_{ow}
LAS	2-300	3.32
AES	-	0.1
AE	580-5900	5.36

In this study, for two anionic surfactants LAS and AES, the results from their adsorption behavior were a little different (Fig 4-3 and Fig 4-4). The mobility of AES was higher than LAS in all soils tested. This result was consistent with Allred (2001). He noted that the presence of an oxyethylene group significantly increases the transport of AES over LAS.

4.2.2 AES Homologues in Soil Columns

For experiments with different soils (SL, SL+O and SL+C) the variation of AES homologues eluted from soil column were observed (Fig 4-6 – Fig 4-8). Note that these experiments should have been conducted over a longer time period due to the observation of a continuing upward trend at 60 hr. AES homologues that leached first, and in great extent to the deeper soil layer were those with shorter EO chains (AS). However, the mass of AES (EO2) and AES (EO3) in the effluent were low, due to their higher sorption capacity on soil (Brownwell et al., 1990). Due to its stronger interaction with soil, AES (EO2 and EO3) needed more time to start leach out from SL column (Fig 4-6), and a lower fraction washed out than was leached with water over a long period compared to AS and AES(EO1).

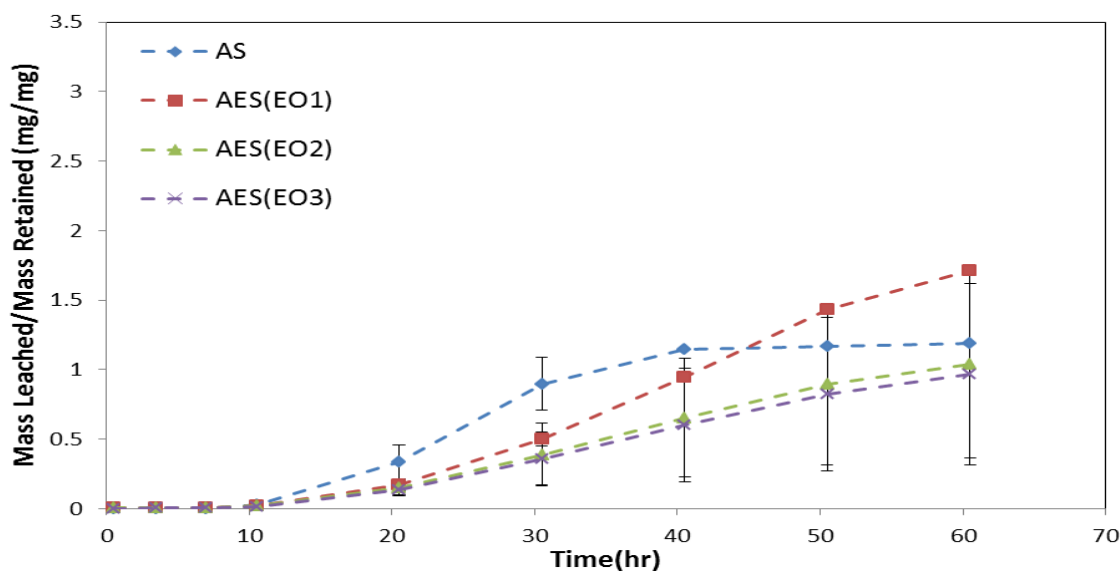


Figure 4-6 AES Homologues in Sandy Loam (SL)

Experiment results obtained with soils with added organic matter (SL+O), showed that the AES fraction of mass leached to mass retained was less than half that in SL or SL+C. This was likely a result of increased number of active surface sites for AES. It was also observed that

adding organic matter decreased the time (from 60 hrs to 20 hrs) to reach maximum values of mass leached to mass retained. This result is difficult to interpret since the retention time was also lower in SL+O (Table 4-1). Similar results were found when adding clay into sandy loam (Fig 4-8). For SL and SL+C, with their t_m value were 4.2 (± 0.13) hours and 5.3 (± 0.45) hours respectively, there was a delay of the maximum mass leached out at 48 hours in SL+C compare to 40 hours in SL (AES EO3).

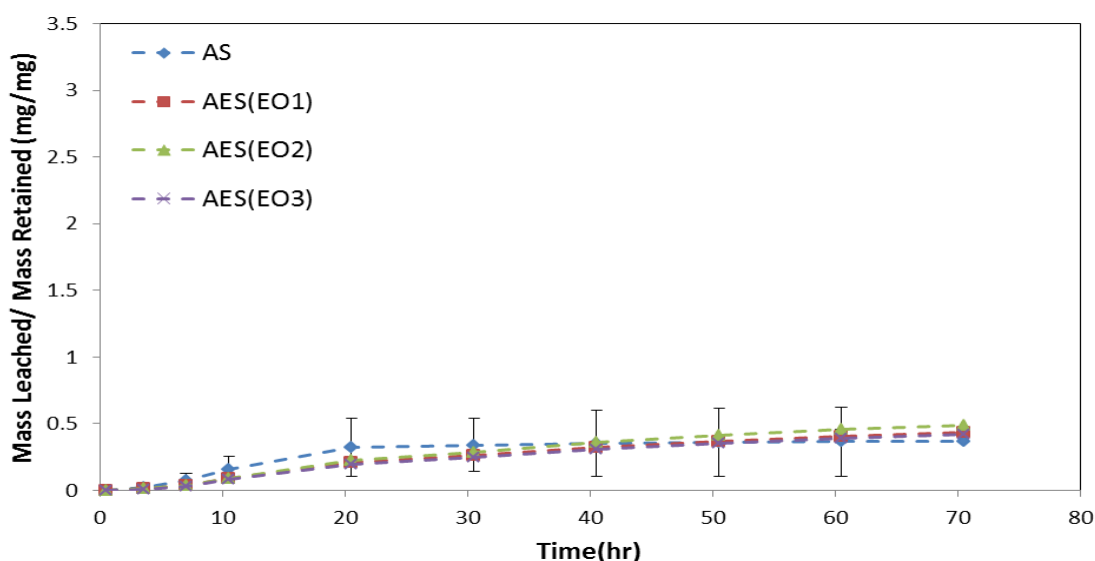


Figure 4-7 AES Homologues in Sandy Loam Added Organic Matter (SL+O)

The soil column acted as a reverse chromatographic column, with a higher separation capacity when the clay content was increased, which increased the mobility of surfactants. From soil analysis (Fig 4-9), AES homologues which had higher EO groups number adsorbed more to the soil. This was consistent with what we found in leachate samples. If the mass of AES eluted in the soil column and the column layer length (45cm) was considered, it was possible to estimate the potential distance that AES could be transported under experimental conditions. It is

possible that shorter EO groups could reach deeper soil at higher clay content. But this transport might be limited in the environment, because biodegradation occurs simultaneously.

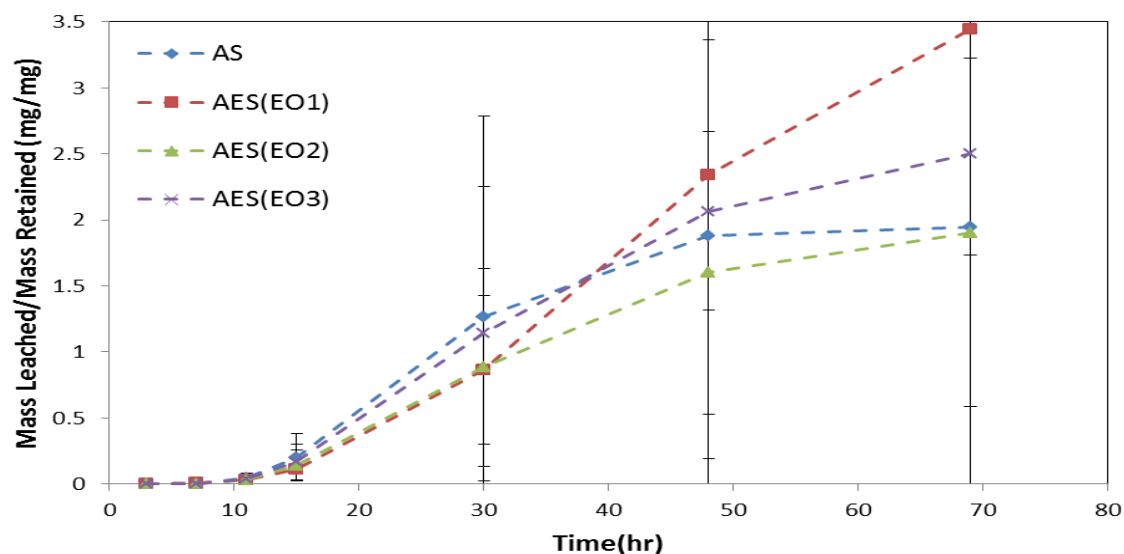


Figure 4-8 AES Homologues in Sandy Loam Added Clay Content (SL+C)

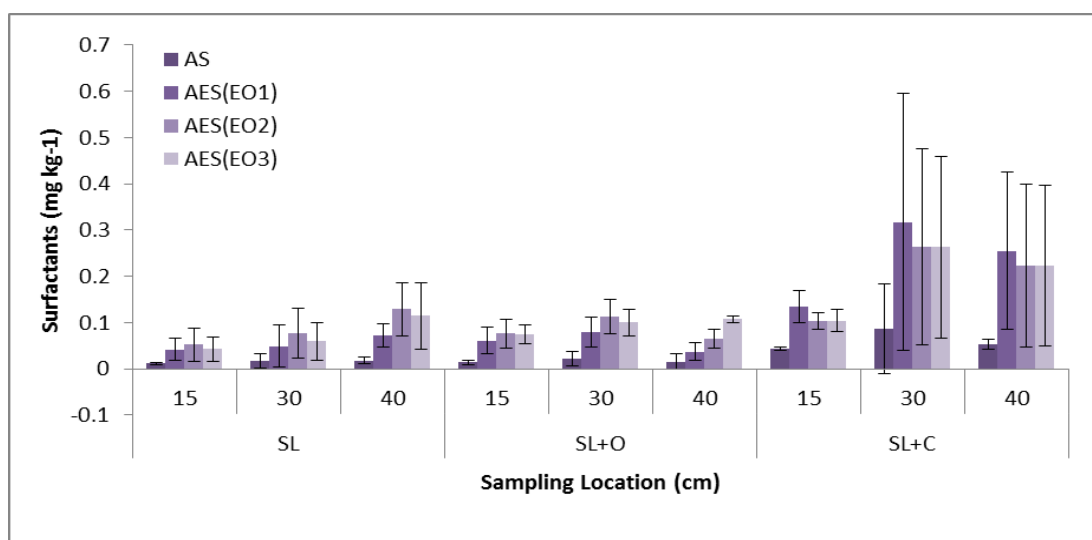


Figure 4-9 AES Homologues Concentration in Different Soil Depth

4.3 Multiple Linear Correlation Analysis

Some researchers have reported the existence of a positive relationship between adsorption and the organic matter content of soils (Urano et al., 1984;Litz et al., 1987;Fytianos et al., 1999;Paterson et al., 1999). Others have found a positive relationship between adsorption of nonionic surfactants and the clay content (Cano and Dorn, 1996;Ou et al., 1996;Brownawell et al., 1997;Shen, 2000). This indicates that the behavior of surfactants in the soil was not well known.

To gain a better understanding of the adsorption behavior of surfactant by soil, the influence of soil properties on the adsorption of surfactant was investigated by calculating multiple correlation coefficients.

The results obtained (Table4-5 and Table 4-6) shows a very significant negative correlation between OM and the value of mass leached verses mass retained of soils by LAS, AES and AE ($p<0.05$). As OM increased, less surfactant leached out. This indicates a positive correlation between surfactant adsorption and OM. Meanwhile, a significant positive correlation was found between clay fraction and mass leached to mass retained of anionic surfactant (LAS and AES), and no correlation between nonionic surfactant (AE) and clay content. The regression equations that describe the relationship between these variables are:

$$\text{LAS} = -0.23 - 1.86[\text{OM}] + 0.10[\text{Clay}]$$

$$\text{AES} = -1.70 - 1.53[\text{OM}] + 0.08[\text{Clay}] + 0.02[\text{Time}]$$

$$\text{AE} = 0.45 - 5.09[\text{OM}] + 0.01[\text{Time}]$$

The results of surfactants and clay correlation come to similar conclusion of field experiments in Nagahban-Azar M.'s thesis (2012). His work addressed the fate and occurrence of graywater chemical constituents and their potential impacts on soil quality, groundwater and plant health. The research using multivariate regression analysis showed that clay content was negatively correlated to soil surfactant concentration. Of note that the relative ratios of LAS: AES: AE are 15:16:4.

Table 4-5 Regression Analysis of Surfactants on Leachate Samples

	LAS ^a			AES ^b			AE ^c		
	R ²	t	Sig.	R ²	t	Sig.	R ²	t	Sig.
Constant		-2.712	0.013		-2.997	0.007		3.447	0.002
OM	0.706	-2.391	0.026	0.705	-2.918	0.008	0.514	-3.857	0.001
Clay		3.051	0.006		3.588	0.002		-	-
Time		6.637	0.000		6.486	0.000		3.938	0.001

^{a,b,c} Significant at level 0.001<p<0.05

Table 4-6 Multiple Correlation Coefficients between Experiment Results of Surfactants and the Properties of Soils

	LAS	AES	AE
Constant	-0.23	-1.70	0.45
OM	-1.86	-1.53	-5.09
Clay	0.10	0.08	-
Time	0.00	0.02	0.01

5.0 Conclusions and Future Work

Graywater has been widely reused in the United States in the recent years. Surfactants as one of the most abundant type of organic chemistry in graywater have rising concerns on several aspects: higher leaching potential surfactants may reach deeper soil layer even groundwater; the accumulation of surfactants may be toxic to soil microbes; surfactants may also affect the mobility and degradation of organic matter in soil. Previous researches (Ou, et al., 1996, Marchesi et al., 1991, Kiewiet et al., 1996) have not addressed these problems, because surfactants they applied are at a concentration higher than observed in graywater, on the other hand the type of surfactants they used are not generally used domestically. This study is more practical by using LAS, AES and AE at 15, 16 and 4 mg L⁻¹. Based on this research, recommendations can be provided for suitability of graywater irrigation in terms of type of surfactants and soils.

The adsorption capacity of the surfactant in this study is separated to anionics and nonionic. In general the nonionic surfactant AE, has higher sorption capacity than the anionic surfactants LAS and AES. Our statistical analysis of the results showed that the soil parameters with a significant effect on the adsorption of LAS and AES were OM and clay content. A positive correlation is observed for OM and negative correlation for clay content. However, the adsorption of AE mainly depends on OM. A statistically significant relationship was not found with clay content. Depending on the influence of these parameters, the mechanisms involved in surfactant adsorption are different. The surfactant must be adsorbed to the soil OM through a hydrophobic mechanism. As soil with a 70% OM increase, less surfactant leached from columns. This interaction had been also observed by other researchers (Urano et al., 1984; Litz et al., 1987; Fytianos et al., 1999). Anionic surfactants leached out of soil more easily as clay content

increased from 33% - 46% increase. As clay content increased, CEC increased in soil columns. The relationship between clay content and CEC indicates more negative charge existed and repulsion forces between anionic surfactants and soils likely increased.

For AES homologues, a positive correlation was observed between the EO group number and the adsorption. AES (EO2) and AES (EO3) adsorb more onto soil and require higher volumes of eluted water to be transported through the soil column. On the other hand, AS and AES (EO1), leached out from columns first and could access deeper soil layers more quickly. AES sorption is reversible in SL+C and especially in sand fractions, but could delay the transport of more hydrophobic homologues to deeper soil layers; these homologues especially AS and AES (EO1) could access deeper with sufficient irrigation water application.

Greenhouse study included the same surfactants studied here. Our study evaluated transport of surfactants under limited biological activity to observe behavior of surfactants in terms of physicochemical interactions. For the surfactants used in this study, AES had highest mobility than LAS and AE, particularly AS and AES (EO1) these two homologues. Concerns may be raised to contamination of groundwater when sufficient water applied. However, of note is that in a greenhouse study (Negahban-Azar M. et al., 2013), where leaching of graywater constituents were observed, it was observed that 92%-96% of added surfactants were biodegraded. Therefore, the concern for leaching is much lower in a natural system where biological reactions are present. In contrast, nonionic surfactants (AE) had highest sorption capacity than anionics. When transport of surfactants in graywater applied for irrigation is a concern, products containing AE are recommended over AES and LAS. In addition, leaching of surfactants will be a lower concern if soil has relatively high OM content ($> 0.5\%$).

Although this column study provided transport and mobility of surfactants in graywater used on soils, there are some improvements that can still be made in our future work.

- (1) For nonionic surfactants: even though no correlation was found between adsorption and clay content, it is not indicated that clay will not affect surfactants sorption. More soil physicochemical and mineralogical properties can be addressed, such as percentage of montmorillonite, illite and kaolinite in soil.
- (2) Based on statistical study by using SPSS, multiple correlation coefficients were obtained between adsorption and soil characteristics. Inclusion of more soil types and more extension data set would result in more meaningful results.
- (3) Surfactant-enhanced washing by using anionic-nonionic mixture is being considered to achieve contaminant removal. Mixed surfactant could be employed over a wide range of temperature, salinity and hardness conditions than the individual surfactants (Gu & Galera-Gomez, 1995, Al-Ghamdi & Nasr-El-Din, 1997, Goell, 1999). Therefore, surfactant mixtures with superior properties are always required in a wide variety of practical applications. Our study addressed an anionic-nonionic mixture of surfactants (7.75:1). Further studies could evaluate different mass ratios of anionic : nonionic surfactants (1:1, 1:2 or 1:3) to extend the knowledge of behavior of mixtures of surfactants.
- (4) The mobility and transport behavior of surfactants have been analyzed in this study. Our future research is to build models for graywater to evaluate the fate and transport of chemicals in soil. By models, we expect to see the safe level of surfactants used in our daily life to our plants, soil organisms and groundwater.

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