University of Alberta

Surfactant-assisted Remediation of Weathered Creosote Contaminated Soils

by

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ABSTRACT

Weathered creosote contaminated soils may pose serious environmental and health risks and are often difficult to remediate. Mass transfer limitations of hydrophobic contaminants found in creosote, including polycyclic aromatic hydrocarbons (PAHs), and dissolution of nonaqueous phase liquids (NAPLs) limit many remediation applications. Surfactant washing may provide a means to overcome the limitations associated with creosote mass transfer. Dowfax-8390, a dianionic surfactant, was employed in a sequential batch washing design. Total soil and solution PAHs and total extractable organics (TEO) were analyzed before and after treatment. Micellar solubilization significantly enhanced the solubility of hydrophobic PAHs. Emulsions were produced during Dowfax washing of more heavily contaminated soils. Emulsions only formed in the presence of lower Dowfax concentrations and elevated soil TEO. Emulsions significantly enhanced PAH solubility. Sequential washing significantly reduced PAH and TEO levels within selected soils. Dowfax-8390 demonstrated limited losses during soil washing.

For My Parents

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Chapter 1. Introduction

Accidental spills, uncontrolled disposal and inadequate containment of creosote have produced extensive soil contamination at many industrial sites throughout Canada creating serious environmental and health risks. Certain polycyclic aromatic hydrocarbons (PAHs) found within creosote mixtures may be carcinogenic requiring their removal from contaminated soils. While conventional pump-and-treat approaches can effectively manage the dilute portion of the contaminant plume, innovative technologies are required to facilitate source zone material decontamination of industrial site soils. Mass transfer limitations of hydrophobic contaminants from media surfaces and dissolution of trapped or pooled dense nonaqueous phase liquids (DNAPLs) limit conventional pump-and-treat techniques.

Surfactant-assisted remediation of contaminated soils has been evaluated as a potential means to overcome these mass transfer concerns. This potential has been elucidated within artificially contaminated or spiked soil samples where micellar solubilization of PAHs is often extensive. These results should be tempered by the fact that soil and contaminant conditions within weathered creosote contaminated soils are vastly different from those observed within spiked batch studies. The present research examined the interactions of surfactants within weathered creosote contaminated soils to address these concerns.

Micellar solubilization has received the majority of research attention and is relatively well understood. Mobilization and emulsification of discrete oil droplets that may result during surfactant washing of NAPL contaminated soils requires additional study. The present study was intended to quantitatively and qualitatively evaluate the role of these various surfactant mechanisms in facilitating PAH mass transfer from creosote contaminated soils.

The overall objective of this research was to examine the efficacy of surfactant washing for remediating weathered creosote contaminated soils. More specifically, the present research was designed to examine:

1) the extent to which target PAHs and total extractable organic material (TEO) can be removed from weathered contaminated soils through surfactant washing,
2) the extent of surfactant losses to the contaminated soil matrix during soil washing and
3) those surfactant mechanisms (solubilization, emulsification and mobilization) responsible for PAH and TEO mass transfer.

Chapter 2. Literature Review

2.1. Creosote Contaminated Soils

Wood-preservative manufacturing uses more pesticides worldwide than any other industry (Mueller et al., 1989). The major chemicals utilized for this purpose include: 1) creosote, 2) pentachlorophenol (PCP) and 3) copper, chromate and arsenate (CCA). The treatment mixture is a combination of an active agent and a carrier that is applied to wood. The carrier that allows for the appropriate dilution of preservative agent can be: 1) water, 2) diesel or 3) fuel oil. Further, these carrier agents facilitate wood cell penetration (Pollard et al., 1993). Within the United States between 415 and 550 creosoting operations consume approximately 4.5×10^7 kg of creosote annually (Mueller et al., 1989). Misuse, accidental spillage and improper disposal of creosote produce contaminated environments where potential ecological and human health risks may result.

Creosote is a complex mixture composed of chemicals possessing diverse chemical structures (Table 2.1). Coal tar creosote is composed of approximately 85% (w/w) polycyclic aromatic hydrocarbons (PAHs); 10% (w/w) phenolic compounds and 5% (w/w) N-, S- and O-heterocyclics (Mueller et al., 1989). Although there are hundreds of chemicals within creosote, relatively few are present in quantities greater than 1%. As such, relatively few compounds comprise 40-50% of a given creosote mixture (Mueller et al., 1989).

Across Canada, creosote contaminated sites pose environmental and health hazards as the contaminants commonly identified include: metals such as arsenic and hexavalent chromium; the polycyclic aromatic hydrocarbons (PAHs); benzene, toluene, ethyl benzene and xylene (BTEX); pentachlorophenol (PCP), lower chlorophenols and associated polychlorinated furans and dioxins (CCME 1991a, CCME 1991b). In Alberta, several abandoned wood-preserving facilities have been identified as potentially posing a risk to human health and the environment (Pollard et al., 1993).

The study of creosote mixture toxicity has not been thoroughly addressed, although limited evidence from prolonged occupational exposure suggests that creosote is likely to cause cancer in humans (ATSDR 1990a, Karlehagen et al., 1992). Further, creosote

Table 2.1 Components of Coal-Tar Creosote (Mueller et al., 1989)

Compound Class	Compound	Relative Weight Percentage within Class
Polycylic aromatic	Naphthalene	13
Hydrocarbons	2-Methylnaphthalene	13
	Phenanthrene	13
	Anthracene	13
	1-Methylnaphthalene	8
	Biphenyl	8
	Fluorene	8
	2,3-Dimethylnaphthalene	4
	2,6-Dimethylnaphthalene	4
	Acenapthene	4
	Fluoranthene	4
	Chrysene	2
	Pyrene	2
	Anthraquinone	1
	2-Methylanthracene	1
	2,3-Benzo(b)fluorene	1
	Benzo(a)pyrene	1
Phenolic compounds	Phenol	20
	o-Cresol	10
	m-Cresol	10
	p-Cresol	10
	Pentachlorophenol	10
	2,5-Xylenol	7.5
	3,5-Xylenol	7.5
	2,3-Xylenol	5
	2,4-Xylenol	5
	2,6-Xylenol	5
	3,4-Xylenol	5
	2,3,5-Trimethylphenol	5
Heterocyclic N-Heterocycles	Quinoline	10
Compounds and N-containing	Isoquinoline	10
aromatics	Carbazole	10
	2,4-Dimethylpyridine	10
	Acridine	5
	Aniline	5
	2-Methylquinoline	5
	4-Methylquinoline	5
	Pyrrole	5
	Pyrrolidine	5
S-Heterocycles	Benzo(b)thiophene	10
	Dibenzothiophine	10
O-Heterocycles	Dibenzofuran	10

exposure can produce a number of non-carcinogenic responses including embryo toxicity, feto toxicity and dermatitis (ATSDR 1990b).

2.2. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic pollutants in contaminated soils and groundwater at many industrial sites throughout North America. Certain high molecular weight homocyclic PAHs and heterocyclic compounds present in coal-tar creosote have the capacity to form carcinogenic and mutagenic diols and epoxides (Pollard et al., 1993). Benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, dibenz(a,h,)anthracene and indeno(1,2,3,cd-pyrene) are classified as probable human carcinogens by the U.S. Environmental Protection Agency (U.S. EPA 1984).

PAHs possessing three or more rings have very low water solubilities and high octanol-water partition coefficients (K_{OW}) (Grimberg et al., 1995). Thus, they can be expected to either sorb extensively to the soil matrix or to exist within a separate hydrocarbon phase, or nonaqueous phase liquid (NAPL), within the soil. A wide variety of bacteria, fungi and algae have the capacity to metabolize PAHs (Cerniglia, 1992). Lower molecular weight PAHs, including naphthalene and phenanthrene are degraded rapidly in sediments whereas higher molecular weight PAHs, including chrysene and benzo(a)pyrene, are resistant to microbial attack (Cerniglia, 1992). Generally, the higher molecular weight PAHs are more slowly desorbed and thus less bioavailable for microbial metabolism (Aronstein et al. 1991). Higher molecular PAHs, such as benzo(a)pyrene, are recalcitrant and persist indefinitely ($t_{1/2}$ = 200-300 weeks) in contaminated matrices (Cerniglia, 1992).

2.3. Mass Transfer of PAHs from Complex DNAPL Mixtures

PAHs are often present within soil as components of dense nonaqueous phase liquids (DNAPLs) such as coal tars and creosotes. These DNAPLs are often complex and incompletely characterized mixtures that possess constituents that may pose substantial health hazards due to their toxicity and/or carcinogenicity (Neff, 1979). PAH dissolution from DNAPLs into raw water sources often produces aqueous concentrations in excess of safe drinking water standards (Neff, 1979). Although many PAHs are sparingly soluble, large volumes of water can be contaminated by small DNAPL sources. DNAPLs have relatively low aqueous solubilities (hundreds to several thousands ppb) and exhibit significant sorption within soil and sedimentary systems (Fountain et al., 1995). Further, as they continuously dissolve, DNAPLs act as sources of long-term contamination requiring extensive remediation time frames unless contaminant sources are removed (Fountain et al., 1995, Mackay and Cherry, 1989). Removal of DNAPL sources are limited by difficulties associated with identifying their locations, resulting in the utilization of *in-situ* and *ex-situ* water-based remediation technologies (Mukherji et al., 1997). These remediation designs are usually rendered ineffective by the low aqueous phase concentrations produced by the slow mass transfer and low solubility of contaminants from DNAPL sources. Successful remediation of creosote-contaminated soils is contingent upon reducing the concentrations of higher molecular weight PAH compounds below regulatory limits. The limitations associated with cleaning up weathered creosote contaminated soils has led to the investigation of surfactant washing as an alternative remediation measure.

2.4. Surfactant Background

2.4.1. Surfactant Properties

Surfactants are a class of compounds that are surface active (Rosen, 1989; Shiau et al., 1995). Surfactants are amphiphilic molecules consisting of two distinct structural moieties: a hydrophilic head and a hydrophobic tail (Rosen, 1989). Surfactant molecules migrate to interfaces (air-water, oil-water and water-solid) where both structural components may reside in their preferred phases minimizing the free energy of the system; i.e. the hydrophilic head moiety resides in water and the hydrophobic tail moiety resides in oil (Shiau et al., 1994; Sabatini et al., 1995).

Synthetic surfactants are categorized according to the electrostatic charge of the hydrophilic portion of the molecule (West and Harwell, 1992). The head group may possess a: 1) positive charge (cationic), 2) a negative charge (anionic), 3) both cationic and anionic charges (amphoteric) or 4) zero charge (nonionic) (West and Harwell, 1992; Rosen, 1989). Cationic surfactant head groups are usually comprised of an amino or quaternary nitrogen group and do not perform well in soils possessing a negative surface charge due to strong adsorption of the surfactant to soil particles. The hydrophobic portion of a cationic surfactant is attached to a basic group (Rosen, 1989). Anionic surfactants are used in petroleum recovery due to their high aqueous solubility and repulsion from soils that possess a negative surface charge. Head groups of anionic surfactants include sulfonates, sulfates, and phosphates (Ouyang et al., 1995). Hydrophobic portions of anionic surfactants are attached to an acid group (Rosen, 1989). Both anionic and cationic surfactants are dissolved as ions and are influenced by solution pH. Nonionic surfactants are uncharged and soluble through hydrogen bonding at oxygen or hydroxyl groups (Ouyang et al., 1995). Nonionic surfactants contain a polyoxyethylene group as the soluble head group (Ouyang et al., 1995). The water solubility of nonionic surfactants is contingent upon the length of the ethoxylated chain; i.e. the longer it is, the greater its solubility (Rosen, 1989). Amphoteric surfactants combine both a basic and an acid group in the same molecule. They behave as anionic surfactants when the solution is acidic and as cationic surfactants when the solution is basic (Rosen, 1989).

The hydrophile/lipophile balance (HLB) value, which quantifies the relative dominance of the hydrophilic group over the lipophilic group of the surfactant molecule, is a useful parameter to characterize the emulsification behavior of surfactants (Rosen, 1989). The HLB number is calculated for nonionic surfactants as the weight percent of ethoxylate groups (EO= OCH_2CH_2) divided by 5 (Currie et al., 1992). Surfactants possessing a strong hydrophobic portion relative to the hydrophilic portion will have a low HLB value (Grimberg et al., 1995). Surfactants with HLB values of 8-18 are categorized as oil in water emulsifiers, and surfactants with lower HLB values are termed water in oil emulsifiers (Rosen, 1989). Attempts at soil remediation typically utilize oil in water emulsifiers.

2.4.2. Surfactant Mechanisms

2.4.2.1. Micellar Solubilization

Surfactant molecules have the capacity to self-assemble into dynamic aggregates termed micelles once a particular aqueous concentration of surfactant monomers has been reached (Sabatini et al., 1995). This concentration is referred to as the critical micelle concentration, or cmc. Critical micelle concentration values are a function of both system conditions (e.g. water hardness, temperature) and surfactant type. Nonionic surfactants generally have lower cmcs than anionic surfactants (Rosen, 1989). Typical cmc values range from 0.1 to 10 mM (West and Harwell, 1992). The number of surfactant molecules that form each micelle is referred to as the coordination number (Grimberg et al., 1995). Micelles have characteristic sizes within the low nanometer range (Attwood and Florence,1983).

Micelles contain the hydrophobic tail portions of surfactant molecules within their interior while the hydrophilic portions of the surfactant molecules comprise the micelle exterior (Sabatini et al., 1995). The polar exterior of the micelle imparts high aqueous solubility while the nonpolar interior functions as a pseudo-oil phase into which nonpolar organic compounds may partition (Shiau et al., 1994). The resulting enhanced aqueous solubility of organic compounds through partitioning into the hydrophobic core of the micelle at supra-cmc surfactant concentrations is termed solubilization (Sabatini et al., 1995). Hydrophobic compounds, including PAHs, partition into the hydrophobic core of micelles (Grimberg et al., 1995). When the hydrophobic solute is present in excess, the apparent solubility (total solute in the aqueous and micelle phases) increases linearly with an increase in surfactant concentration above the cmc. The slope of this increase is defined as the solubilization capacity (Grimberg et al., 1995).

Solubilization has been defined as the spontaneous dissolution of a substance (solid, liquid, or gas) by reversible interaction with surfactant micelles in a solvent to produce a thermodynamically stable isotropic solution (Rosen, 1989). Solubilization is believed to occur at a number of sites (Rosen, 1989): 1) at the micelle-solvent interface on the micelle surface; 2) between the hydrophilic head groups (in polyethylenated materials); 3) in the palisade layer of the micelle between the hydrophilic head group and the hydrophobic tail; and 4) in the micellar core. Thus polar molecules are solubilized in the outer regions of micellar structures whereas nonpolar solubilizates are contained within inner portions (Rosen, 1989).

2.4.2.2. Mobilization

In addition to solubilization, aqueous surfactant solutions also have the capacity to displace or mobilize residual NAPLs from porous media. DNAPL movement through the subsurface is governed by capillary forces (Hunt et al., 1989). In order to enter a water filled pore, the DNAPL must overcome a capillary displacement pressure (Fountain et al., 1995). Capillary pressure is generally greater in fine-grained material which function as barriers to vertical migration until sufficient DNAPL head pressure develops to overcome the displacement pressure. DNAPL will generally exist as residual saturation along its flow path and as pools upon relatively impermeable layers.

Surfactants reduce interfacial tensions between NAPLs and water. Depending on the surfactant employed, the reduction in interfacial tension may range up to four orders of magnitude (Fountain et al., 1995). Capillary pressures are known to decrease directly with reductions in interfacial tension. Mobilization occurs once viscous and/or gravitational forces acting on the NAPL exceed those capillary forces that are responsible for its immobilization. Once mobilization occurs, NAPL is removed from the soil/sediment as a discrete phase. Residual NAPL mobilization continues until a mechanical equilibrium governed by the Young-Laplace equation is reached. To produce substantial mobilization, interfacial tension must be reduced to near 10^{-3}mN m^{-1} (Fountain et al., 1995).

2.4.2.3. Emulsification

Water/NAPL/surfactant systems exhibit complex behavior and mechanisms of contaminant removal cannot be attributed solely to solubilization and/or mobilization. An additional mechanism for facilitating NAPL removal is through the process of emulsification. When two immiscible liquids of different densities such as oil and water are mechanically shaken together, two distinct layers commonly form. Surfactant may be added to lower the interfacial tension between the liquids. If the resulting mixture is shaken, the milling together of constituents forces one of the liquids to become dispersed in the other, forming an emulsion (Rosen, 1989). An emulsion is defined as a dispersion of droplets of one liquid into another with which it is completely immiscible (Ouyang et al., 1995).

At the cmc, solution interfacial tension is minimized and remains constant as surfactant concentration increases (Rosen, 1989). The retention of oil and other contaminants present as NAPL within a porous medium is a function of viscous, capillary and gravitational forces. The mobility of trapped oil increases at the cmc where the ability of viscous forces to overcome capillary forces is elevated due to the reduction in interfacial tension (Ang and Abdul, 1991). Once mobilized the contaminant can be suspended in the surfactant solution as an emulsion or be displaced and remain as a distinct NAPL. Two types of emulsions can be formed depending on system conditions: 1) macroemulsions with droplets having diameters greater than 1 *um* and 2) microemulsions with droplets of 0.01 - 0.1 *um*. Oil in water microemulsions are transparent, isotropic, clear, and thermodynamically stable (Shaw 1980). Conversely, macroemulsions are opaque and thermodynamically unstable, although they are classified as kinetically stable (Fortin et al., 1997). Surfactant solutions rarely reduce interfacial tensions below the 0.1 dyne cm^{-1} requirement to induce microemulsion formation.

Table 2.2. Operational Definitions and Characteristics of Various Components in Water-NAPL-Surfactant Systems[1]

Experimental Fraction	**Form**	**Dimension**	**Thermodynamic Stability**	**Description**
solubilized NAPL	dissolved	molecular	stable	dissolved
	micelle	< 1 *um*	stable	dissolved
emulsified NAPL	macroemulsion	> 1 *um*	not stable or metastable	polydispersed NAPL droplets dispersed in aqueous phase
mobilized NAPL	coalescable droplets			separate-phase NAPL released once capillary force acting on residual NAPL is overcome by viscous and gravitational forces

[1] Adapted from Okuda et al., 1996.

2.5. Surfactant-Assisted DNAPL Removal From Contaminated Soils

Surfactants can remove a portion of the DNAPL mass rapidly and cost effectively but the ultimate remediation level is based on site conditions (Fountain et al., 1995).

Surfactants increase the mobility of contaminants by combinations of the following three mechanisms (Fountain et al., 1995): 1) increasing contaminant solubilization, 2) reducing contaminant sorption and 3) lowering interfacial tension between water and DNAPLs. Surfactant enhanced remediation can be cost-effective for DNAPL sites as the DNAPL zones are usually restricted in size (Fountain et al., 1995).

Numerous studies have demonstrated the ability of surfactants in facilitating the solubilization of a variety of hydrophobic organic compounds from spiked soil samples (Deitsch and Smith, 1995; Di Cesare and Smith, 1994). Abdul et al. (1992) examined the efficiency of surfactants in removing automatic transmission fluid from batch samples of a sandy textured soil. Results demonstrated that surfactant removed between 56 and 84% of the contaminant whereas, washing with water alone removed only 23% of contamination. Peters et al. (1992) utilized synthetic surfactants solutions to leach undisturbed soil samples from a site contaminated with No.2 diesel fuel. Results demonstrated that water and surfactants removed generally less than 1% of No. 2 diesel fuel from soil. This discrepancy in NAPL removal efficiency between batch and column studies has been attributed to channeling of solution through large pores in columns. Column flooding involved nonequilibrium extractions, whereas batch screening extractions reached equilibrium (Ouyang et al., 1995).

Few studies have explored the use of surfactants within DNAPL contaminated soils, while fewer still have incorporated aged soil conditions (Pennell et al., 1994). Yeom et al. (1995) studied the micellar solubilization of PAHs in weathered coal tar-contaminated soils from manufactured gas plant sites using nonionic polyoxyethylene surfactants at supra-cmc dosages. It was reported that hydrophobic organic contaminant mobilization from artificially contaminated soils appeared to be unrealistically high compared to that determined in weathered, contaminated soils. Nash and Traver (1986) also reported that *in situ* soil washing of various hydrocarbons, including PCBs and benzo(a)pyrene, with aqueous surfactants was not effective. They concluded that this same ineffectiveness would occur at other chronic spill sites containing contaminants with high sorption values. These conditions certainly prevail at many DNAPL contaminated sites. Thus attempts at *in situ* surfactant-assisted soil washing appear to be ill advised.

Studies have demonstrated that a high sand and low silt plus fines content make *ex situ* soil washing with surfactants a promising remediation alternative (Tobia et al., 1994; Ganeshalingam et al., 1994). Deschenes et al. (1996) found that anionic SDS (Sodium Dodecyl Sulfate) enhanced the *ex situ* solubilization of sorbed PAHs from aged creosote-contaminated soils. The sandy loam soil contained 13% clay, 16% silt and 71% sand. At supra-cmc concentrations, increases in the solubilization of fluorene, phenanthrene, anthracene, fluoranthene and pyrene were witnessed. Pennell et al. (1993) studied the solubilization of dodecane by a nonionic surfactant (polyoxyethylene (20) sorbitan monooleate) as a means for recovering NAPLs from contaminated aquifers. In batch experiments, application of surfactant at supra-cmc doses resulted in the linear enhancement of the apparent solubility of dodecane.

The solubility enhancement provided by surfactants for a given contaminant is a function of the aqueous solubility of the compound; i.e. the greater the aqueous solubility or lower the K_{ow}, the lower the solubilization increase (Fountain et al., 1995). The presence of multi-component DNAPLs impose certain limitations on surfactant performance. DNAPLs are comprised of chemicals that possess different polarities, as assessed through their aqueous solubilities (Fountain et al., 1995). While data on the dissolution of PAHs from weathered DNAPL-contaminated soils is sparse, the remediation of these soils appears to be limited primarily by the slow rate of contaminant mass transfer to the aqueous phase (Yeom et al., 1996). Surfactant micelles greatly enhance the solubility of individual PAHs, however their utility in enhancing the rate of release of PAHs from DNAPL contaminated soils has yet to be thoroughly studied. Further, the study of emulsion formation with surfactant treatment of NAPL contaminated soils and the role this mechanism may play in remediation is relatively unknown.

Past research on surfactant flushing of contaminated soils for removing NAPLs has focused on two mechanisms: 1) mobilization of large NAPL volumes and 2) micellar solubilization of the organic phase. Recent studies have demonstrated that macroemulsion formation and transport can be an important mechanism in the remediation of soils containing NAPLs by surfactant flushing, accounting for up to 30% of its removal (Okuda et al., 1996). Okuda et al. (1996) further suggest that the formation and transport of macroemulsions are significant as: 1) surfactants that are effective solubilizers tend to form macroemulsions; 2) macroemulsions can modify the permeability within porous media; and 3) solubilization kinetics may be influenced by macroemulsification.

2.6. Potential Limitations of Surfactants within Contaminated Soils

2.6.1. Surfactant-Soil Interactions

Since surfactants are organic compounds, sorption onto soil may be significant (Liu et al., 1991; Rouse and Sabatini, 1993). Sorption reduces the efficiency of the surfactant system and increases costs. Surfactant sorption is a function of total organic carbon content, percentage of clays present in the soil, soil water chemistry and surfactant type (Liu et al., 1992; Rouse and Sabatini, 1993). Surfactant sorption typically increases with organic carbon or smectitic clay content (Fountain et al., 1995). Sorption of surfactant onto soil may result in much of the surfactant being unavailable for micellar solubilization (Edwards et al., 1992). Sorption of nonionic surfactant onto soils may elevate the fractional organic carbon of the soil, thus altering its sorptive characteristics (Liu et al., 1992). Thus, sorbed surfactant has the capacity to modify hydrocarbon sorption behavior, by functioning as an additional sorptive media to which the contaminant may adhere (Liu et al., 1991; Edwards et al., 1992).

The influence of water chemistry on the solubility of surfactants is well documented (Rouse and Sabatini,1993). While surfactants with hydrophile-lipophile balance (HLB) values greater than 12-13 will freely dissolve in distilled water, ionic strengths of as low as a few hundred mg L^{-1} may promote surfactant precipitation. Site specific water chemistry must then be used during testing to evaluate whether a given surfactant is effective under given conditions (Fountain et al., 1995). As surface area is a critical factor controlling surfactant sorption, any change in surface area may produce erroneous sorption estimates. Application of distilled water will mobilize clays present in a system producing different sorption characteristics emphasizing the need for using water chemistry similar to site conditions to avoid changing clay surface properties (Fountain et al.,1995).

Surfactant sorption is generally greater for nonionic than for anionic surfactants, but nonionics tend to have greater solubilization capacities (Rouse and Sabatini, 1993; Allred and Brown, 1994). Surfactant adsorption reduces the aqueous concentration of surfactant, thus increasing the concentration of surfactant that must be added in order to reach cmc. This new cmc that incorporates sorption to the soil matrix is termed the effective cmc (Liu et al., 1992). Surfactant sorption must be determined for individual soil systems due to its dependence on contaminated soil characteristics and surfactant type (Rouse and Sabatini, 1993).

Nonionic surfactants may partition into trapped residual phases if their solubilities in the NAPL are high; i.e. they possess lower HLBs (West and Harwell, 1992). Further, nonionic surfactants are subject to coacervation, the formation of a separate aqueous phase at a high critical temperature termed the cloud point (West and Harwell,1992). This point is noted by solution turbidity. Ionic surfactants are usually insoluble in NAPLs, however their divalent salts may have appreciable solubility in the nonaqueous phase (West and Harwell, 1992).

2.6.2. Contaminant-Soil Interactions

DNAPL interactions with soil systems are poorly understood. Methylene chloride used in soxhlet extraction has the capacity to extract 100% of PAHs in contaminated soils containing 6 benzene rings or less (Yeom et al., 1995). The remaining unextractable organic contaminant matrix is referred to as residual. Generally, this residual fraction consists of a collection of condensed aromatic nuclei that contain aliphatic and cycloaliphatic substituents, with heteroatoms such as oxygen, sulfur and nitrogen distributed throughout the structure (Speight,1991; Nelson et al., 1996). While this matrix itself is virtually insoluble in water, it may control the desorption of lower molecular weight compounds that are of regulatory importance by functioning as a highly effective partitioning media due to its hydrophobicity.

Brusseau (1991) has reported that equilibrium sorption constants determined in binary-solute systems were 1.5-3.0 times greater than those measured for single solute systems. The partitioning behavior of PAHs between soil surfaces and surfactant micelles is negatively affected in the presence of other hydrocarbons (Ganeshalingam, 1994). The sorption of PAHs on sand was enhanced by the presence of toluene, reducing removal rates of the PAHs by surfactant solutions (Ganeshalingam, 1994). Thus, substantially more surfactant treatment may be necessary for removing multicomponent DNAPLs than indicated by single contaminant solubility testing. Successful removal of PAHs may require that other less toxic hydrocarbons (oil and grease) are also adequately extracted from the soil, which is often overlooked from a regulatory point of view (Ganeshalingam, 1994). Finally, soil characteristics including: 1) organic matter quantity, 2) organic matter quality and 3) soil texture will also play a primary role in determining DNAPL desorption. With elevated soil organic matter content comes enhanced contaminant sorption as the organic matter fraction functions as a highly effective media that hydrophobic organic constituents may partition into or onto (Chiou, 1990). Further, the organic matter fraction becomes more nonpolar over time resulting in an enhanced capacity to sorb organic compounds (Chiou, 1990).

2.7. Perceived Research Needs

While surfactant-assisted remediation has recently received increased research attention, a number of fundamental and practical aspects of this technology must be investigated. The use of surfactant washing as a technologically viable means to remediate weathered contaminated soils is still questioned. The present study will attempt to provide insight into this potential through the examination of surfactant washing of various weathered creosote contaminated soils. The economic viability of surfactant washing as a remediation alternative also needs to be addressed. Economic viability is contingent upon the ability to recycle surfactant from spent soil washing solutions (Krebs-Yuill et al., 1995). In order to eventually develop recycling capabilities the surfactant should exhibit minimal losses to the soil matrix even in the presence of excessive contamination. The present study will evaluate surfactant losses to creosote contaminated soils during soil washing. Finally, the potential formation and persistence of emulsions during surfactant-assisted remediation has remained relatively unexamined. The present study will attempt to explore emulsification in an attempt to provide some fundamental knowledge on this mechanism.

Chapter 3. Materials and Methods

3.1. Soil Sampling

Three subsurface soil samples were collected in late 1994 from the former Saskatchewan Forest Products site located in Prince Albert, Saskatchewan. Soil samples were chosen to provide a range of contaminant conditions consisting of: 1) low (0.92%) 2) moderate (1.90%) and 3) high levels (8.20%) of total methylene chloride extractable organic material (TEO_{MC}). Samples were collected in 20-liter plastic buckets and stored within a temperature controlled cold room (4°C) until commencement of experimental work. In the summer of 1996, soils were allowed to air dry and were subsequently manually mixed. Soils were then separated using a 2 mm brass sieve and stored in 1-liter glass mason jars at 4°C. Only soil fractions less than 2mm were used in experimental studies.

3.2. Materials

3.2.1. Surfactant

A dianionic surfactant, Dowfax 8390, was selected for soil washing trials as it: 1) exhibits minimal losses to the soil matrix through precipitation and sorption reactions and 2) maintains a high micellar solubilization capacity (Rouse and Sabatini, 1993). Chemical characterisitcs of Dowfax 8390 are represented in Figure 3.1. Dowfax 8390 was supplied by Dow Chemical (Midland, MI). Dowfax 8390 was received in liquid form as an aqueous solution at a concentration of 1M. Dowfax 8390 was a high-purity product (contained low salts and no methylene chloride) and was used without further purification. Dowfax solutions of various concentrations were prepared with 10^{-4}M $HgCl_2$ (to inhibit microbial growth) and 10^{-2} M K_2SO_4 (background electrolyte) and stored in amber glass vials at 4° C when not in use.

Table 3.1. Physical-Chemical Properties of Dowfax-8390

Surfactant	Type	Chemical Formula	Mol.Weight (g mol^{-1})	cmc (mM)
Dowfax-8390	Anionic	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	642	3.00[1], 6.00[2]

[1] obtained from Dow Chemical, [2] Rouse and Sabatini (1993)

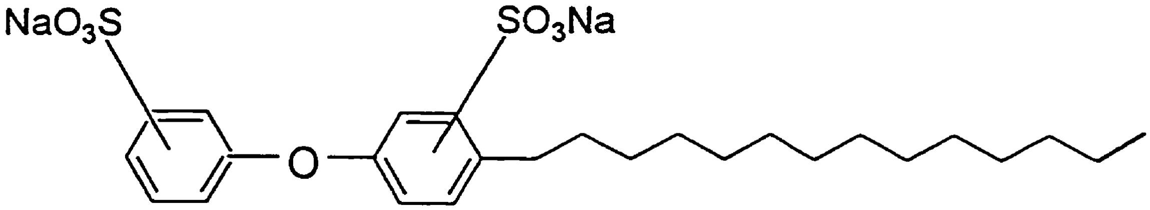


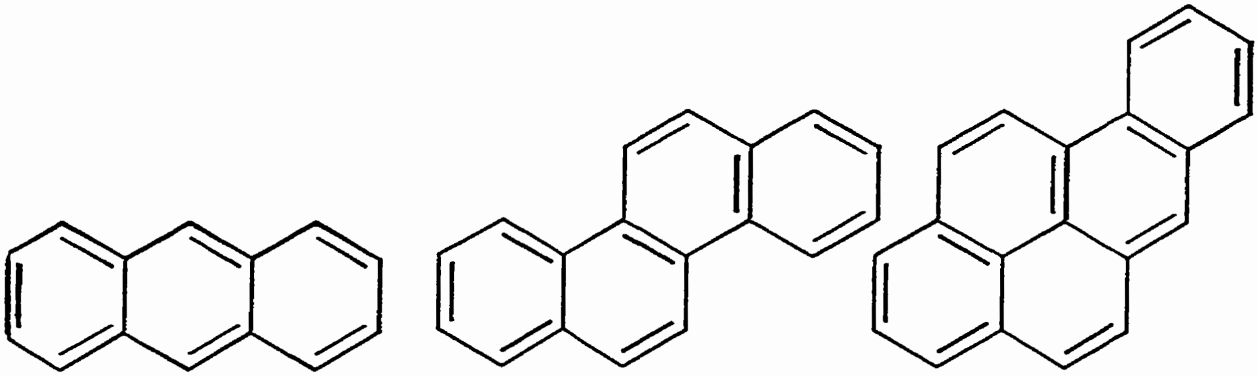
Figure 3.1. Chemical Structure of Dowfax-8390

3.2.2. Polycyclic Aromatic Hydrocarbons

Three PAHs were selected for examination within batch soil washing experiments. Anthracene, chrysene and benzo(a)pyrene were chosen as they: 1) possess variable chemical properties (water solubility, biodegradability, molecular size), 2) are all Environmental Protection Agency priority pollutants and 3) were present in the creosote contaminated soils. HPLC detection limits for anthracene = 1ug L^{-1}, chrysene = 3ug L^{-1} and benzo(a)pyrene = 7 ug L^{-1}. Chemical properties and structures of these 3 PAHs are given in Table 3.2 and Figure 3.2.

Table 3.2. Physical-Chemical Properties of Target PAHs (Mackay et al., 1992)

PAH	Molecular Formula	Molecular Weight (g mol^{-1})	Aqueous Solubility (mg L^{-1})	Log K_{ow}	Vapor Pressure at 25°C (Pa)
Anthracene	$C_{14}H_{10}$	178.2	0.045	4.54	0.001
Chrysene	$C_{18}H_{12}$	228.3	0.002	5.86	5.70×10^{-7}
Benzo(a)pyrene	$C_{20}H_{12}$	252.3	0.0038	6.04	7.40×10^{-7}



Anthracene Chrysene Benzo(a)pyrene

Figure 3.2. Chemical Structures of Target PAHs

Organic solvents (acetonitrile, methanol and methylene chloride) were of HPLC grade (Fisher Scientific, Fair Lawn, NJ). Deionized water was distilled through a MilliQ water purifier (ddH_2O). Anthracene, chrysene and benzo(a)pyrene were supplied by Supelco (Sigma-Aldrich, Canada). Anthracene was dissolved in methanol at 200 ug mL^{-1}, chrysene and benzo(a)pyrene were dissolved in dichloromethane at 200 ug mL^{-1}. Stock mixtures of PAH standards were made up from individual solutions in methanol. The solutions were stored in amber glass vials and stored at 4° C when not in use.

High performance liquid chromatography (HPLC) with an UV-Visible detector was selected for quantifying PAH and Dowfax 8390 concentrations. HPLC analysis was chosen to achieve high resolution, sensitivity and selectivity of PAHs (Dridi et al., 1998). Experimental trials revealed that simultaneous quantification of PAHs and Dowfax could be achieved by analyzing at 254nm.

3.3. Methods

3.3.1. Physical Analysis

Approximately 30 g of bulk soil samples were sieved to less than 2 mm (brass sieve) and were repeatedly washed with ddH_2O until dispersed. Ultrasonification was used as a dispersion technique. Clay separation was achieved through repeated dispersion and gravity sedimentation cycles according to Jackson (1979). Sand and silt fractions were separated through wet sieving, and oven dried at 105 °C for 24 hours. Sand and silt fractions were then weighed with clay calculated by difference.

3.3.2. Chemical Analyses

Saturated paste extracts were collected from homogenized samples according to the method developed by Rhoades (1982). The pH of each soil was measured in distilled water. Electrical conductivity (EC) measurements of the extracts were performed with a conductivity bridge. Total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC) was determined for each soil sample. Total carbon (TC) analysis was performed using a LECO furnace. The carbonate fraction was determined through the titration method (Bundy and Bremner., 1972). Total organic carbon (TOC) was determined by subtracting carbonate C from Total C value. Subsamples for the determination of gravimetric moisture content were oven-dried at 105°C for 24 hours, placed in a dessicator to cool and re-weighed.

3.3.3. Total Extractable Organics Determination/Soxhlet Procedure for PAHs

Determination of total methylene chloride extractable organics (TEO_{MC}) was done on a gravimetric basis (ASTM, 1995; ESTAC 1995). TEO protocols included Soxhlet extracting 6 g of soil with 150 mL of methylene chloride for 16 hours. To facilitate drying, 1.0 g anhydrous sodium sulfate (Fisher Scientific) was mixed into samples prior to extraction. Refluxing cycles within the soxhlet apparatus ranged from 9-12 per hour for each heating pocket. Following extraction, extracts were reduced down to a known volume through rotary evaporation (Buchler Instruments, Fort Lee, NJ). Extracts were then brought up to volume in 50 mL glass volumetric flasks. 4 mL of extract was transferred via a glass volumetric pipette to 4 mL amber glass vials and stored at 4°C until needed for HPLC analysis. 40mL of extract was then transferred via 20 mL glass volumetric pipette to a preweighed aluminum dish and allowed to evaporate for 16 hours. The weight of the aluminum dish plus extract was then recorded and extract weight was determined by difference.

3.3.4. Critical Micelle Concentration Determination

Critical micelle concentrations (cmc) were estimated by surface tension measurements using the Fisher Tensiomat 2100 tensiometer (Fisher Scientific, Fair Lawn, NJ). For Dowfax 8390 a series of dilutions were placed in 30 mL glass beakers. Tensiometric measurements were then taken from lower to higher concentrations, measuring the force (dyne cm^{-1}) required to pull the tensiometer ring through the solution surface. Between each measurement the tensiometer ring was rinsed with ddH_2O. Between each triplicate measurement the ring was rinsed with acetone and passed through a flame to remove any residual Dowfax. The cmc was determined from the inflection point witnessed in surface tension reduction with increasing surfactant concentration.

3.3.5. Batch Equilibration/Kinetics

Batch equilibration washing was conducted to determine the appropriate mixing times for subsequent soil washing experiments. Batch equilibrations were conducted using 5:1, 10:1 and 20:1 surfactant solution : soil ratios. Three Dowfax concentrations were employed: 0.1mM , 1.0mM and 30mM. These concentrations were selected to obtain a range from sub- to supra-cmc Dowfax levels. Appropriate amounts of soil (6 g, 3 g and 1.5 g) were weighed out, corresponding to desired solution : soil ratio, in 40 mL clear glass vials. Thirty milliliters of Dowfax was applied to soil using a 10 mL glass pipette. Samples were then placed in 2 L plastic vessels, that were wrapped in aluminum foil to minimize photolysis, and placed on a flat bed shaker at 21°C in the dark. Sample triplicates were then removed from the shaker at 1, 3, 6, 12, 24 and 48 hours. Samples were then centrifuged at 1500g for 70 minutes using a Damon/IEC UV centrifuge. Supernatant was removed with a disposable glass pipette and stored in amber glass vials until needed. Supernatant was analyzed for both surfactant and PAHs with high performance liquid chromatography (HPLC).

The HPLC system was composed of two Waters (Milford, MA) Model 510 solvent delivery systems, a Waters Model 481 tunable UV absorbance detector, a Waters 712 sample injector, a Waters System Interface Module integrator, a Supelcosil LC-PAH column (Sigma-Aldrich, Canada), 15cm x 4.6 mm I.D., 5 μm particulate size, and a Supelguard LC-18 guard column (Sigma-Aldrich, Canada). The mobile phase (acetonitrile-water) gradient was: 50% acetonitrile + 50% water for 3 min, increasing linearly to 100% acetonitrile in 13 min, 100% acetonitrile was maintained between 13 and 23 min with linear return to 50% acetonitrile + 50% water at 26 min and maintained to 28 min. The flow rate was 1.8 mL min^{-1} and the temperature was 23° C. Prior to chromatography the mobile phase was degassed by vacuum filtration through a 0.5 *u*m Type FH filter (Millipore). All injections were via 150 *u*L syringes (Hamilton; Sigma-Aldrich, Canada). Dowfax and PAHs were analyzed at a wavelength of 254 nm using the UV absorbance detector. Sample concentrations were determined based on known Dowfax and PAH standards. Dowfax concentrations were calculated from total peak areas. PAH concentrations were calculated from peak heights.

3.3.6. Sequential Soil Washing

Sequential washing experiments were conducted using 6 g of soil and 30 mL of surfactant solution in 40 mL glass vials. Increasing molar concentrations of Dowfax-8390 (0.1, 0.5, 0.8, 1.0, 10, 30, and 100mM) plus a ddH_2O control were applied to each soil in triplicate. Soil and surfactant samples were mixed for 24 hrs on a flat bed shaker at 21° C. Following shaking all samples were centrifuged at 1500g for 70 minutes. Supernatant was removed with a disposable glass pipette and fresh Dowfax was added to the same soil pellet and again placed on shaker for 24 hrs. HPLC analysis was conducted on supernatants for both Dowfax and PAHs as described in Section 3.3.5. Sequential washing was conducted until PAHs of concern were no longer detected within wash solution. Soil was then washed with ddH_2O for 24 hrs to remove residual surfactant. The sample was then centrifuged for 70 min at 1500g. The water was then removed with disposable glass pipettes and supernatant was analyzed with HPLC. The soil pellet was then removed from the 40 mL vial with a metal spatula and quantitatively transferred with ddH_2O to an aluminum dish. The sample was then air dried in the fume hood. Following extraction, 1.0g of anhydrous sodium sulfate was added to the remaining soil pellet and placed in a single cellulose thimble and soxhlet extracted, Section 3.3.3, for 16 hours with methylene chloride. A 4 mL aliquot of the methylene chloride extract was used for HPLC analysis to determine soil PAH levels, while 40 mL of extract was used for gravimetric determination of TEO levels as described in Section 3.3.3.

Sequential washing was halted when PAH levels within the highest Dowfax treatment (100mM) were below HPLC detection limits. In order to compensate for the presence of residual Dowfax and contaminant solution within soil pores between successive treatments, the following correction factor (CF_{res}) was incorporated:

$$\text{Residual PAH [mg]} = \text{residual supernatant weight[kg]} \times \text{PAH concentration in supernatant [mg kg}^{-1}]$$

$$CF_{res}\ [\text{mg kg}^{-1}\ \text{dry soil}] = \frac{\text{Residual PAH [mg]}}{\text{Dowfax weight [kg]} + \text{Residual weight [kg]}}$$

Correction factors were determined in this manner for each PAH following each sequential wash and CF_{res} [mg kg^{-1}] was then subtracted from the treatment concentration.

The mass balance of target PAHs, on an oven dry soil basis, within the system was calculated at the completion of sequential washing experiments as the total concentration within the system:

$$C_{tot}\ [\text{mg kg}^{-1}] = C_{sol}\ [\text{mg kg}^{-1}] + C_{soil}\ [\text{mg kg}^{-1}]$$

where:

C_{tot} = total PAH concentration
C_{sol} = PAH concentration within solution
C_{soil} = PAH concentration within soil

3.3.7. Surfactant Adsorption Studies

Sorption studies were conducted using a 24-hour batch equilibration technique (Rouse and Sabatini, 1993). In surfactant adsorption studies, both initial and equilibrium concentrations of Dowfax-8390 within batch soil washing assays were determined and by mass balance the amount of surfactant adsorbed was calculated. Soil water blanks allowed correction for background interference. Dowfax sorption studies were done in conjunction with soil washing studies.

3.4. Statistical Analysis

Statistical analyses were conducted using SAS^{TM} version 6.11. ANOVA with accompanying Tukey tests ($P<0.05$) were utilized to examine if target PAH concentrations and TEO concentrations were significantly different amongst treatments.

Chapter 4. Results and Discussion

4.1. Soil Characterization

4.1.1. Soil Physical Properties

Creosote contaminated soils were abbreviated based on their levels of respective contamination into: 1) Low Prince Albert (LPA), 2) Moderate Prince Albert (MPA) and 3) High Prince Albert (HPA). Creosote contaminated soils used within experimental trials were all coarse textured and were classified according to the Canadian System of Soil Classification as indicated in Table 4.1.

Table 4.1. Particle Size Distribution of Creosote Contaminated Soils

Soil	% Sand	% Silt	% Clay	Texture
LPA	95.15 ± 1.55	2.95 ± 0.103	1.90 ± 1.45	Sand
MPA	95.31 ± 0.480	2.43 ± 0.224	2.26 ± 0.256	Sand
HPA	96.78 ± 0.653	1.01 ± 0.005	1.38 ± 0.523	Sand

4.1.2. Soil Chemical Properties

The concentrations of selected PAHs, total methylene chloride extractable organics (TEO_{MC}), total inorganic carbon (TIC), total organic carbon (TOC) and total carbon (TC) are presented in Table 4.2.

Table 4.2. PAHs and Carbon Constituents Within Creosote Contaminated Soils

Soil	Anthracene mg kg^{-1}	Chrysene mg kg^{-1}	Benzo(a)pyrene mg kg^{-1}	TIC %	TOC %	TC %	TEO_{MC} %
LPA	256	162	89	0.99	0.81	1.80	0.92
MPA	425	230	156	1.02	1.65	2.67	1.90
HPA	1705	905	620	1.12	7.44	8.56	8.20

Note: all PAH Concentrations expressed on dry weight basis

The pH and EC values obtained through saturated paste extract analysis are provided in Table 4.3.

Table 4.3. Soluble Components Within Saturated Paste Extracts

Soil	pH	EC dS m^{-1}
LPA	7.6	1.41
MPA	7.9	0.96
HPA	8.0	0.40

4.2. Critical Micelle Concentration Determination

Surface tension measurements were taken for various concentrations of Dowfax-8390 as outlined in Section 3.3.3,to determine the critical micelle concentration. The value for cmc_{tens} was determined by the inflection point in surface tension reduction relative to the log surfactant concentration (Figure 4.1). The observed cmc_{tens} value was approximately 0.5-0.8mM Dowfax.

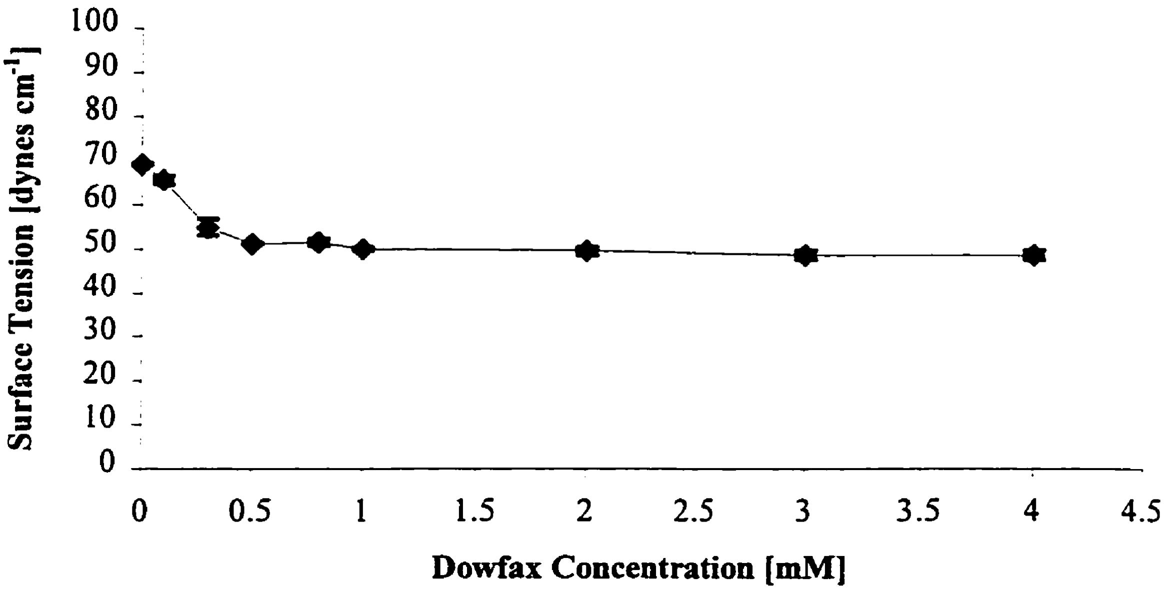


Figure 4.1 Critical Micelle Concentration Determination for Dowfax-8390

Effective cmc (cmc_E) determinations were attempted in the presence of contaminated soil extracts; however, the presence of a separate oil phase interfered with surface tension measurements. As a result, cmc_E values were not determined in this study. Dowfax-8390 has been utilized in many soil washing/flushing studies and has demonstrated minimal losses to soil through either sorption or precipitation mechanisms (Rouse and Sabatini, 1993). The lack of reaction between Dowfax and soil matrices led to the assumption that the cmc_E will not vary greatly from the cmc_{tens}. The observed depression in the cmc_{tens} value, relative to known literature values (Refer to Table 3.1) may have resulted through the addition of K_2SO_4 as a background electrolyte. K_2SO_4 was used as a background electrolyte within surfactant studies by members of the ESTAC research team to maintain consistency amongst studies. In aqueous solution the presence of electrolyte produces a decrease in the cmc of most surfactants with the greatest effect found in ionic surfactants (Myers, 1988). Observed cmc depression is primarily caused by a reduction in the electrostatic repulsion between surfactant head groups (Myers, 1988). The potential of a given electrolyte to alter the micellization process is related to the radius of hydration of the added ions, with the contribution of the anions and cations being approximately additive (Myers 1988). The order of effectiveness of cations in decreasing the cmc has been given by Ray and Nemethy (1971) as:

$$NH_4^+ > K^+ > Na^+ > Li^+ > \tfrac{1}{2}\, Ca^{2+}$$

For anions, the order is:

$$\tfrac{1}{2}\, SO_4^{2-} > F^- > BrO_3^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$$

Both K^+ and SO_4^{2-} electrolytes have the capacity to produce the observed cmc_{tens} depression relative to literature values. The reduction in cmc_{tens} does not mean it is a poor measurement, but rather cmc_{tens} values are system specific. Micellar surface tension values were similar to published values of 49.2 dynes cm^{-1} (Rouse and Sabatini, 1993). The cmc_{tens} used throughout research protocols was between 0.5 and 0.8mM Dowfax.

4.3. Reaction Kinetics and Surfactant Mechanism Determination

Batch equilibration experiments were conducted using two creosote contaminated soils (LPA and MPA) to determine: 1) the role of hydrocarbon and surfactant concentrations in controlling surfactant mechanism(s) and 2) appropriate mixing times to reach apparent equilibrium conditions for soil washing experiments. Apparent equilibrium was determined through the measurement of the aqueous concentrations of anthracene, chrysene and benzo(a)pyrene at 0, 1, 3, 6, 12, 24 and 48 hours. Three solution to soil ratios (5:1, 10:1 and 20:1) were evaluated as it was hypothesized that variable hydrocarbon concentrations may influence surfactant mechanism(s). Three Dowfax-8390 concentrations of 0.1, 1.0 and 30mM were used as they represent a range from sub- to supra-cmc$_{tens}$ levels.

4.3.1. Batch Equilibration Washing of Low Prince Albert Soil

4.3.1.1 Batch Equilibration Washing of LPA Soil using a 5:1 Dowfax Solution to Soil Ratio

Batch equilibration washing was conducted using a creosote contaminated soil with lower levels of hydrocarbon (LPA:TEO$_{MC}$=0.92%). LPA soil characteristics are provided in Tables 4.1 through 4.3. LPA soil washing with 0.1mM Dowfax did not facilitate HPLC detectable PAH transfer from soil to solution (Recall Section 3.2.2. for detection limits). LPA soil washing with 1.0mM Dowfax facilitated PAH transfer from the soil to solution as represented in Figure 4.2. PAH mass transfer may have resulted through either monomer or weak micellar solubilization as this concentration is in the vicinity of measured cmc$_{tens}$. Supernatants following washing appeared clear, with a light yellow color for both 0.1 and 1.0mM Dowfax treatments. Neither emulsification nor mobilization of creosote was witnessed for 0.1 and 1.0mM Dowfax washing.

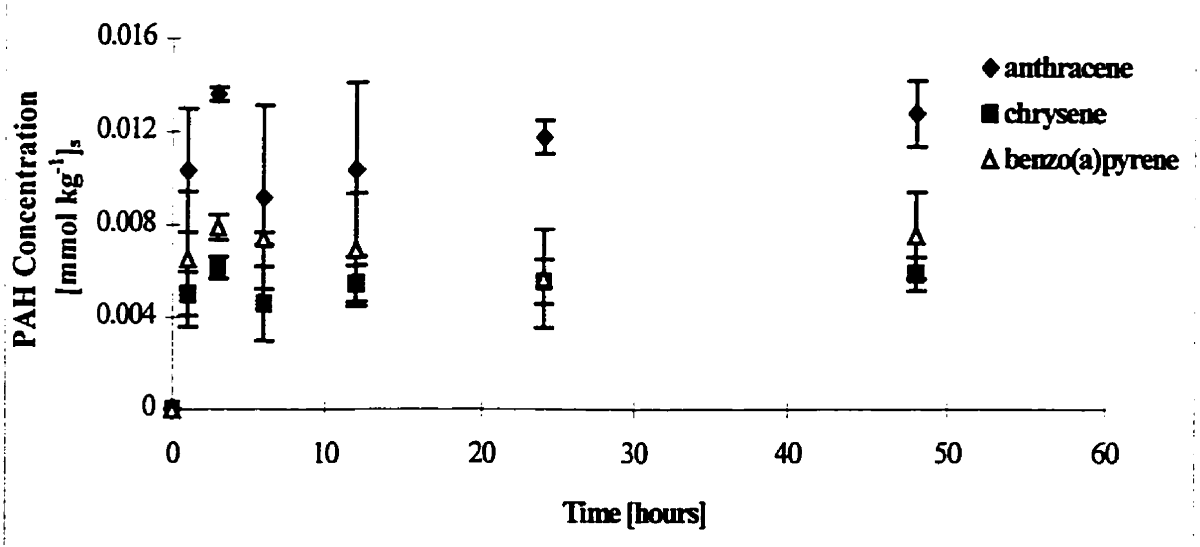


Figure 4.2. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] over time during 1.0mM Dowfax washing of LPA soil using a 5 : 1 solution to soil ratio

LPA washing with 30mM Dowfax also facilitated PAH mass transfer as represented in Figure 4.3. Aqueous PAH concentrations appeared to plateau between 12 to 24 hrs of mixing for 30 mM Dowfax treatment. Supernatant appeared clear with a light yellow color during 0.1 and 1.0mM Dowfax washings. A clear, dark brown colored solution was observed following 30mM Dowfax washing indicating micellar solubilization of organic compounds. Neither mobilization nor emulsification of NAPL was detected with 30mM Dowfax washing.

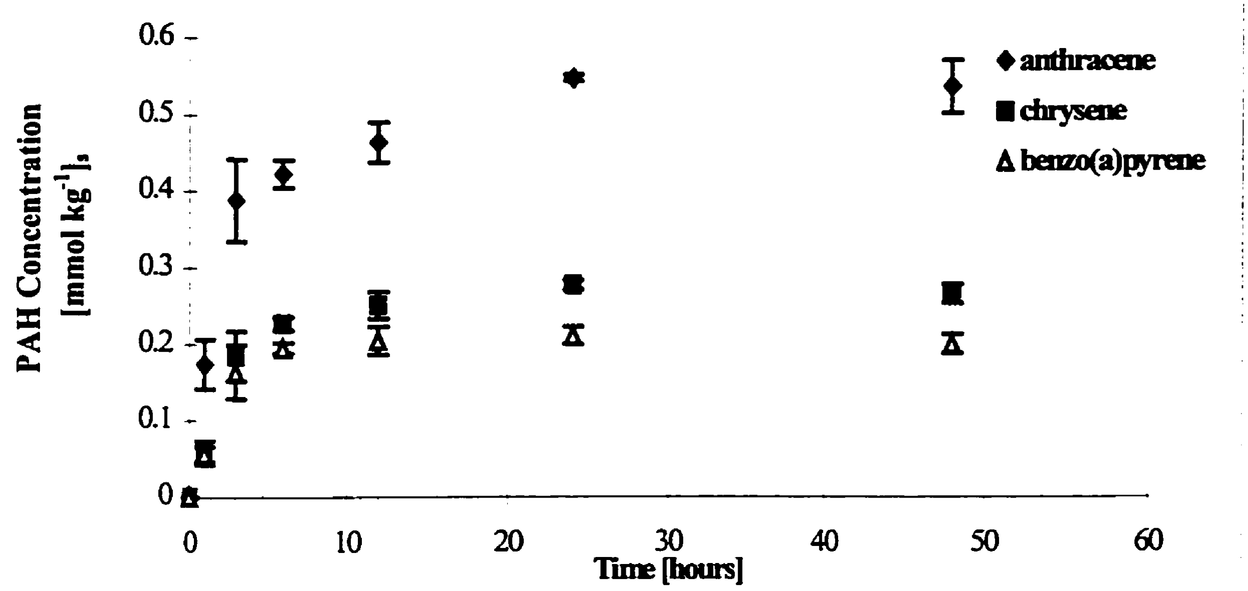


Figure 4.3. **Apparent PAH concentrations [mmol kg$^{-1}{}_{(s)}$ dry soil] over time during 30mM Dowfax washing of LPA soil using a 5 : 1 solution to soil ratio**

4.3.1.2. Batch Equilibration Washing of LPA Soil using a 10:1 Dowfax Solution to Soil Ratio

Batch equilibration experiments were then conducted utilizing a 10 : 1 Dowfax solution to soil ratio. LPA soil washing with 0.1mM Dowfax did not facilitate detectable PAH mass transfer from the soil to solution phase as determined by HPLC analysis. LPA soil washing with 1.0mM Dowfax facilitated PAH mass transfer from the soil to solution phase as represented in Figure 4.4. PAH mass transfer may have resulted through monomer and/or weak micellar solubilization. Qualitative assessments of samples indicated that 0.1 and 1.0mM Dowfax supernatants were clear and slightly yellow in color indicating that neither mobilization nor emulsification was witnessed with 0.1 and 1.0mM Dowfax treatments.

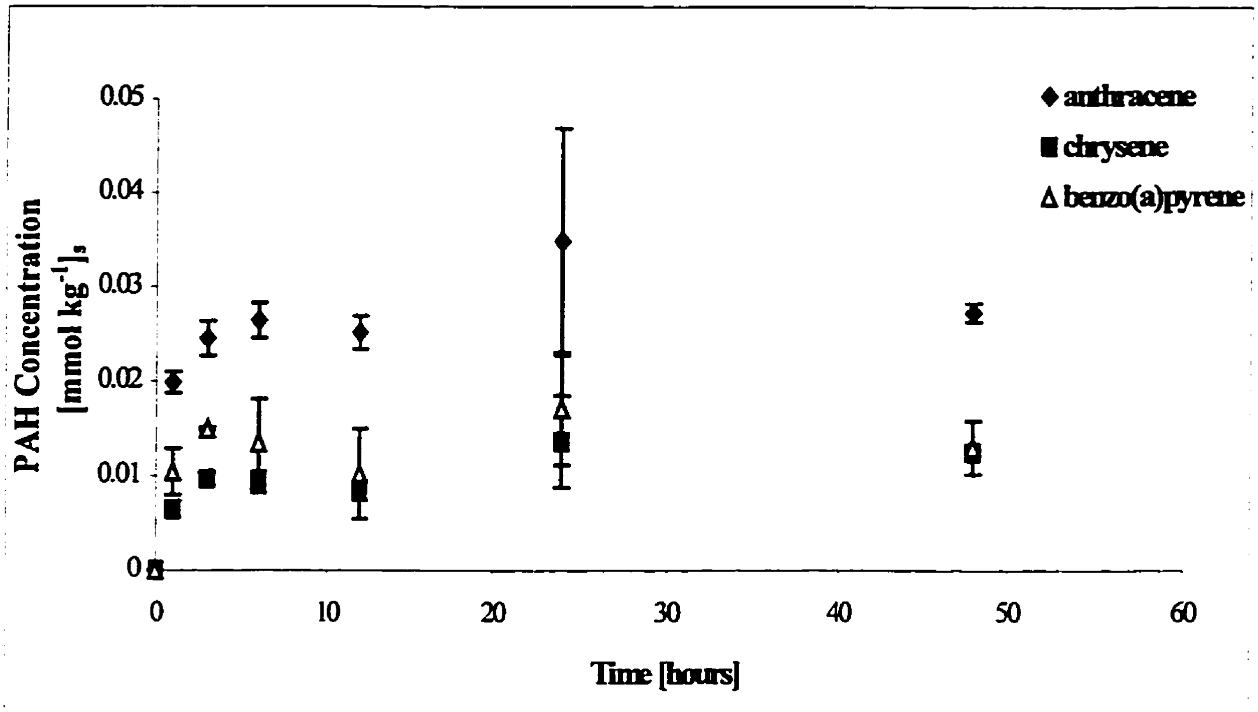


Figure 4.4. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] over time during 1.0mM Dowfax Washing of LPA Soil using a 10:1 solution to soil ratio

LPA washing with 30mM Dowfax also facilitated the transfer of PAHs to the solution phase (Figure 4.5). Clear, dark brown supernatants were noted following 30mM Dowfax washing again indicating creosote solubilization. While micellar solubilization was responsible for facilitated PAH mass transfer with 30mM Dowfax treatment, neither mobilization nor emulsification was observed. Maximum aqueous phase PAH concentrations were observed following 12 to 24 hours of mixing. Greater PAH mass transfer was observed following 30mM Dowfax washing using a 10 : 1 surfactant solution to soil ratio than with a 5 : 1 ratio, suggesting that micellar solutions using a 5:1 ratio became saturated (recall Figure 4.3).

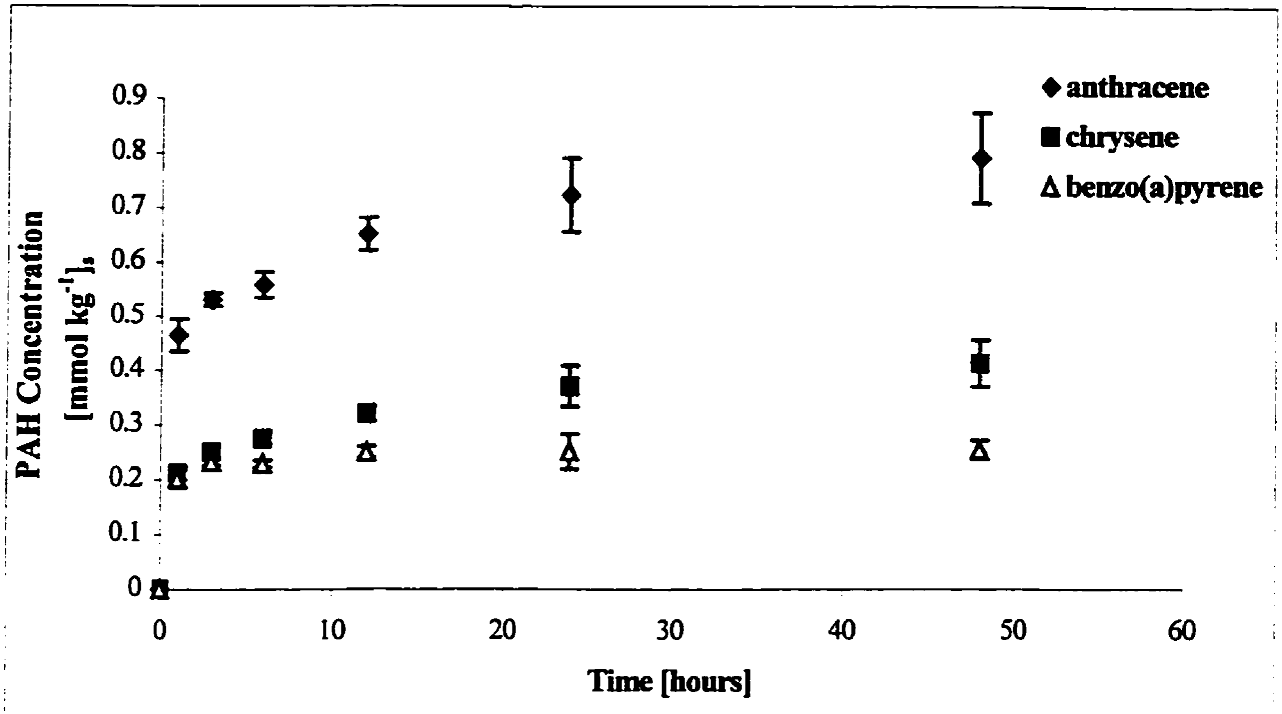


Figure 4.5. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry weight] over time during 30mM Dowfax washing of LPA soil using a 10 : 1 solution to soil ratio

4.3.1.2 Batch Equilibration Washing of LPA Soil using a 20 : 1 Dowfax Solution to Soil Ratio

Batch equilibration experiments were then conducted using a 20 : 1 Dowfax solution to soil ratio. LPA soil washing with 0.1mM Dowfax did not facilitate detectable PAH mass transfer from the soil to solution phase as determined by HPLC analysis. LPA soil washing with 1.0mM Dowfax facilitated transfer of PAHs from the soil to solution phase as represented in Figure 4.6. Enhanced PAH solubilities may have resulted from monomer and/or weak micellar solubilization. Qualitative assessments of samples indicated that 0.1 and 1.0mM supernatants were clear and slightly yellow in color indicating that neither mobilization nor emulsification occurred during 0.1 and 1.0mM Dowfax treatments.

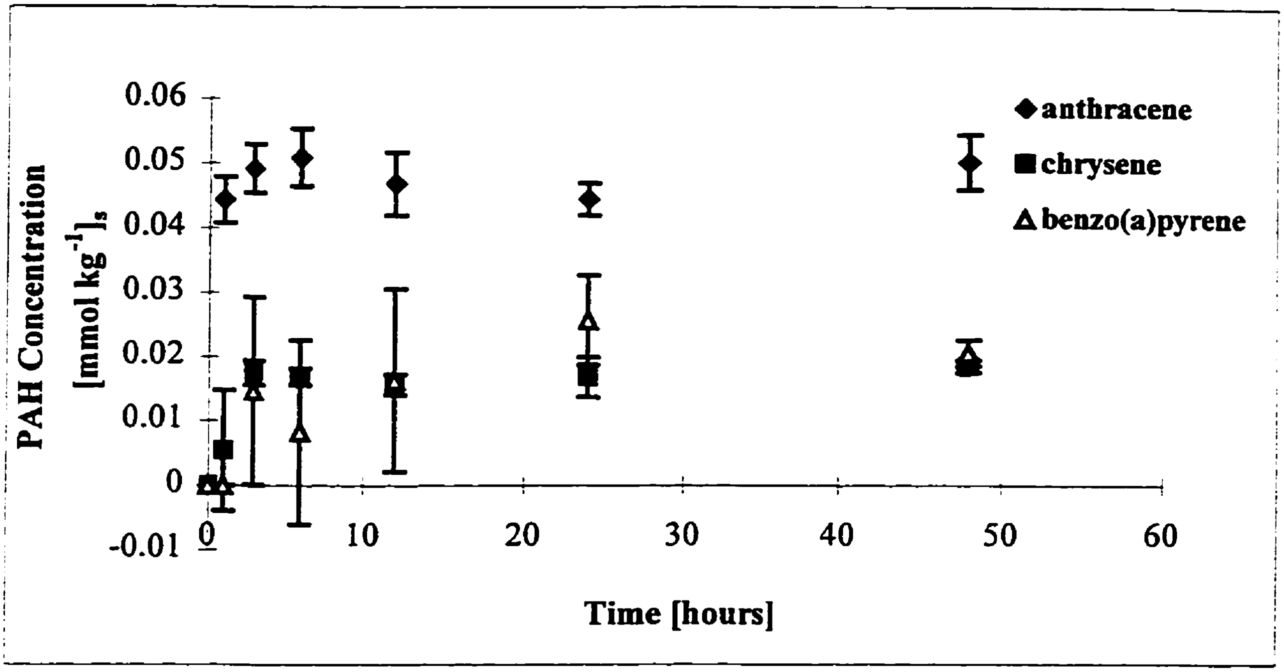


Figure 4.6. **Apparent PAH concentrations [mmol $kg^{-1}{}_{(s)}$ dry weight] over time during 1.0mM Dowfax washing of LPA soil using a 20 : 1 solution to soil ratio**

LPA washing with 30mM Dowfax facilitated PAH mass transfer to the solution phase through micellar solubilization (Figure 4.7). Clear, dark supernatants were observed following 30mM washing again indicating creosote solubilization. Maximum aqueous phase PAH concentrations were observed following 24 to 48 hours of mixing for 30mM treatments. Results suggest that increasing the solution to soil ratio during 30mM Dowfax washing of LPA soil facilitated increased PAH mass transfer. This result may suggest that micellar solutions become saturated during soil washing. The apparent trend of micellar saturation with anthracene is presented in Figure 4.8. Similar trends were observed for both chrysene and benzo(a)pyrene.

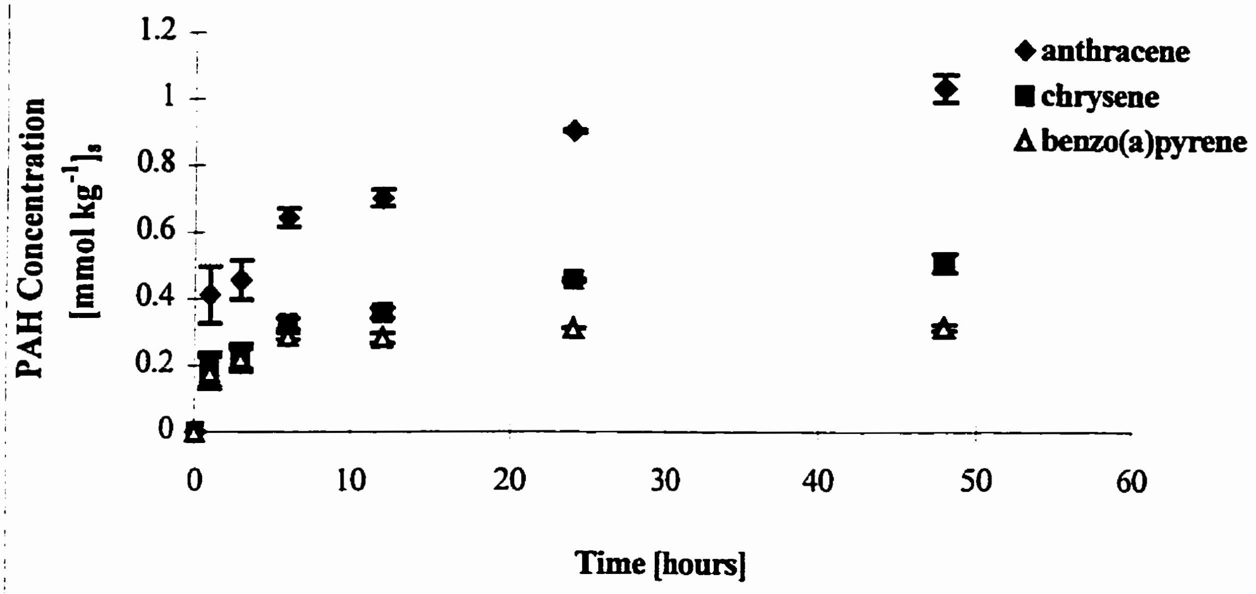


Figure 4.7. Apparent PAH concentrations [mmol kg$^{-1}_{(s)}$ dry weight] over time during 30mM Dowfax washing of LPA soil using a 20:1 solution to soil ratio

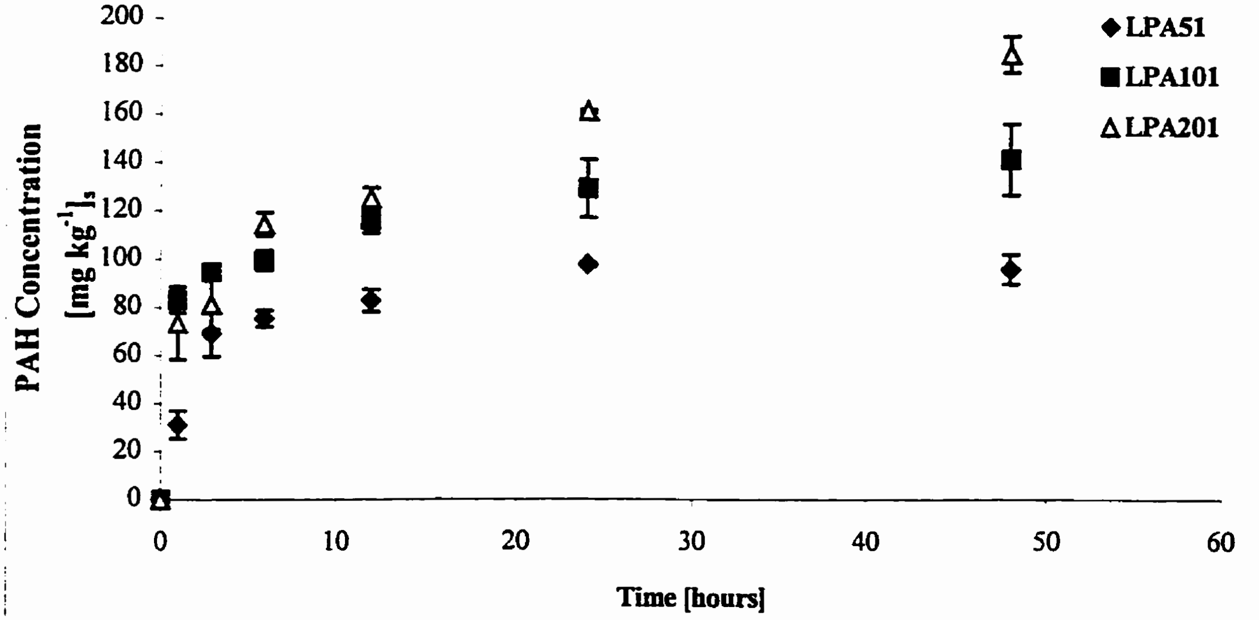


Figure 4.8. Apparent anthracene concentration [mg kg$^{-1}_{(s)}$ dry weight] over time during 30mM Dowfax washing of LPA soil using various solution to soil ratios

4.3.2. Batch Equilibration Washing of Moderately Contaminated Prince Albert Soil

4.3.2.1. Batch Equilibration Washing of MPA Soil using a 5:1 Dowfax Solution to Soil Ratio

Batch equilibration washing was then conducted using a moderately contaminated soil (MPA; TEO_{MC} = 1.9%). MPA soil characteristics are provided in Tables 4.1 through 4.3. Soil washing with 0.1mM Dowfax facilitated PAH transfer to the solution phase through macroemulsification. Recall that LPA soil washing with 0.1mM did not facilitate HPLC detectable PAH mass transfer. Qualitative observations indicated that a milky white, opaque solution was formed following mixing. Upon passing this solution through 0.2*u*m filter, as per HPLC protocols, a clear solution was noted that contained reduced Dowfax concentrations. The solution was then prepared without 0.2*u*m filtration and analyzed through HPLC. PAH mass transfer was observed through emulsification (Figure 4.9). The exclusion of the PAHs following separation indicated that the emulsion was greater than 0.2*u*m in size and was thus retained on the filter. Emulsions are polydispersed in size and generally have diameters exceeding 1.0 *u*M (recall Table 2.2). Maximum aqueous phase PAH levels were observed following 12 to 24 hours of mixing. After 48 hours of mixing, aqueous PAH levels declined as the emulsion appeared to be separating. Emulsions are not thermodynamically stable systems and will eventually separate back to their original components of oil and water. The observed breakdown of emulsion following 48 hrs of mixing demonstrates this instability. Emulsion separation was attempted, without success, through the addition of acetonitrile, methanol, methylene chloride and hexane. Freezing the emulsion followed by thawing broke the emulsion into oil and water components. Fine soil particles were observed within the frozen emulsion system and upon thawing settled out of solution. This observation may indicate a potential role of fine particulates in stabilizing emulsions. Further the exclusion of PAHs by the 0.2*u*m filter may have resulted from the retention of suspended silt and clay within the emulsion. Finally, this observation suggests that silt and clay remained in the supernatant following centrifugation.

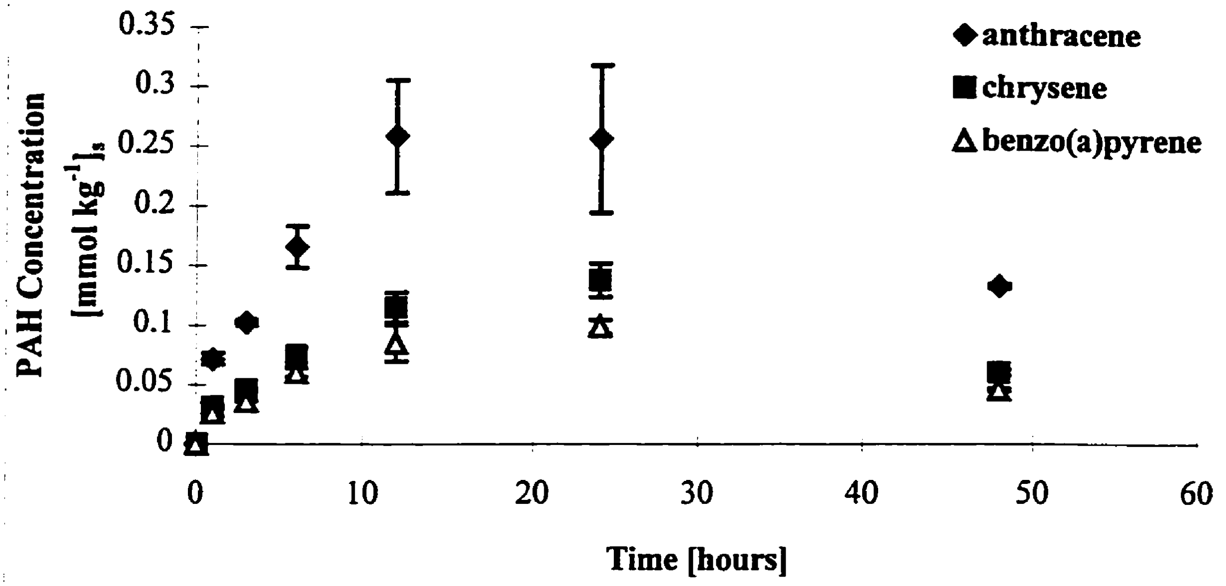


Figure 4.9. **Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry weight] over time during 0.1mM Dowfax washing of MPA soil using a 5:1 solution to soil ratio**

MPA soil washing with 1.0mM Dowfax facilitated the aqueous dissolution of PAHs from the soil (Fig 4.10). Emulsification was not noted at this concentration indicating the potential for emulsion formation to be dependent upon both surfactant and TEO concentration. Soluble PAH levels were similar to those observed following LPA soil washing with 1.0mM Dowfax (Figure 4.2). PAH mass transfer may have occurred through monomer and/or weak micellar solubilization as this Dowfax concentration is in the vicinity of cmc$_{tens}$. Qualitative observations indicated that the supernatant was clear with a light yellow discoloration.

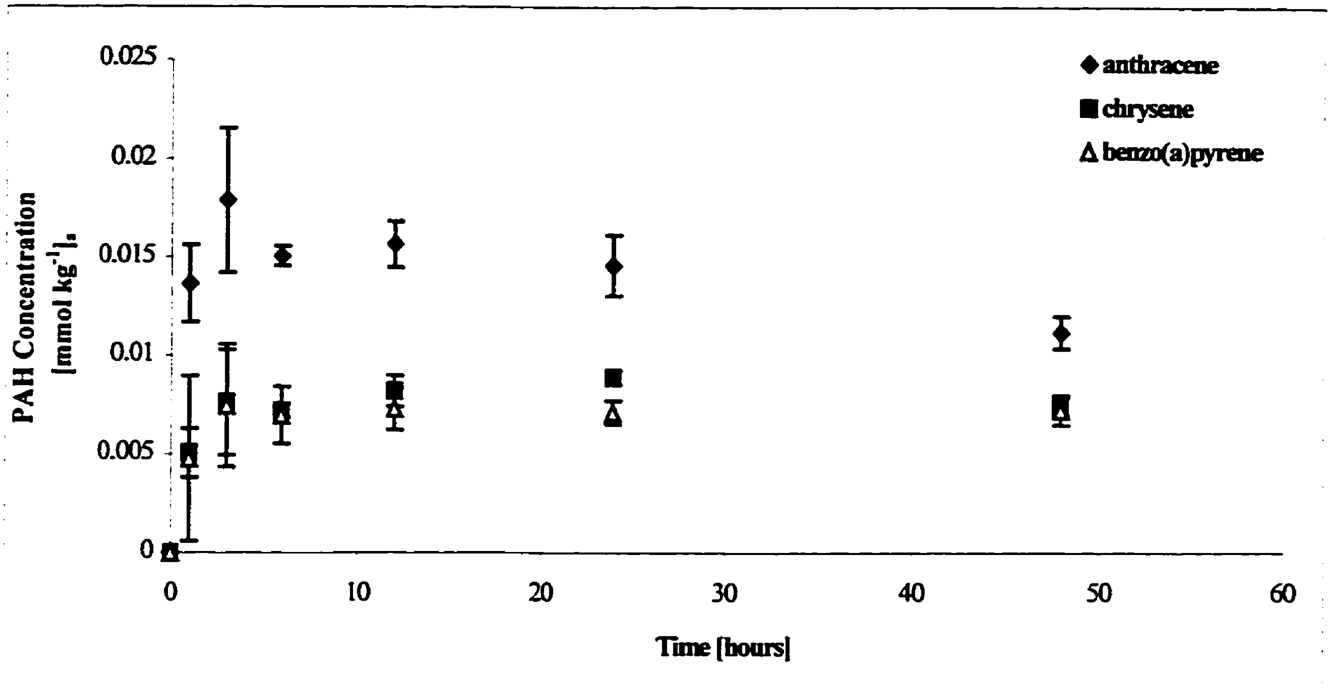


Figure 4.10. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry weight] over time during 1.0mM Dowfax washing of MPA soil using a 5:1 solution to soil ratio

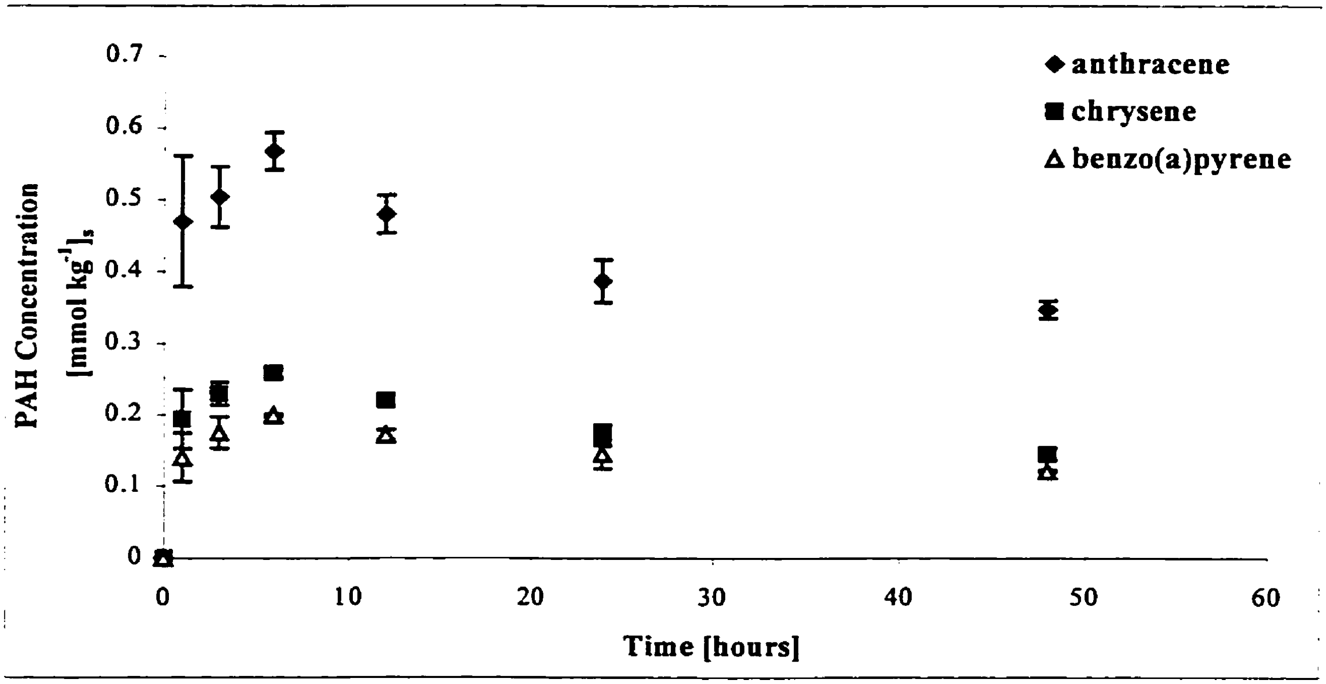


Figure 4.11. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry weight] over time during 30mM Dowfax washing of MPA soil using a 5:1 solution to soil ratio

MPA soil washing with 30mM Dowfax facilitated PAH mass transfer to the solution phase (Fig. 4.11). Aqueous PAH levels were similar to those observed following 30mM Dowfax washing of LPA soil using a 5:1 (v/w) ratio (Figure 4.3). This observation could indicate that the micellar solution had a finite capacity to solubilize organic contaminants, regardless of soil, and became saturated. Maximum aqueous PAH levels were reached within 3 hours of washing indicating that the micelles became saturated more rapidly in the presence of higher levels of organic contaminants. Recall that micellar solubilization with LPA soil washing required between 12-24 hours of mixing to achieve a plateau in aqueous PAH concentrations (Section 4.3.1.1.). Further, aqueous PAH concentrations were observed to decrease following 6 hours of treatment potentially due to the exclusion of swollen micelles by the 0.2uM filter used in HPLC preparation. Once micelles are saturated they tend to swell in size approaching the 0.2uM range (Myers, 1988). Qualtitative observations included a clear, dark brown colored supernatant, with neither emulsification nor mobilization detected during 30mM Dowfax treatment.

4.3.2.2. Batch Equilibration Washing of MPA Soil using a 10:1 Dowfax Solution to Soil Ratio

Batch equilibration washings were then conducted using a 10 : 1 Dowfax solution to MPA soil ratio. PAH mass transfer from the soil to solution was observed (Figure 4.12). In this instance, the supernatant was less opaque than those emulsions formed using 5:1 solution to soil ratios. Reduced mass transfer of PAHs to the solution phase through emulsification was observed using a 10:1 compared to a 5:1 solution to soil ratio. These results may indicate the potential dependency of emulsion formation on the level of hydrocarbon, or NAPL, present within the system.

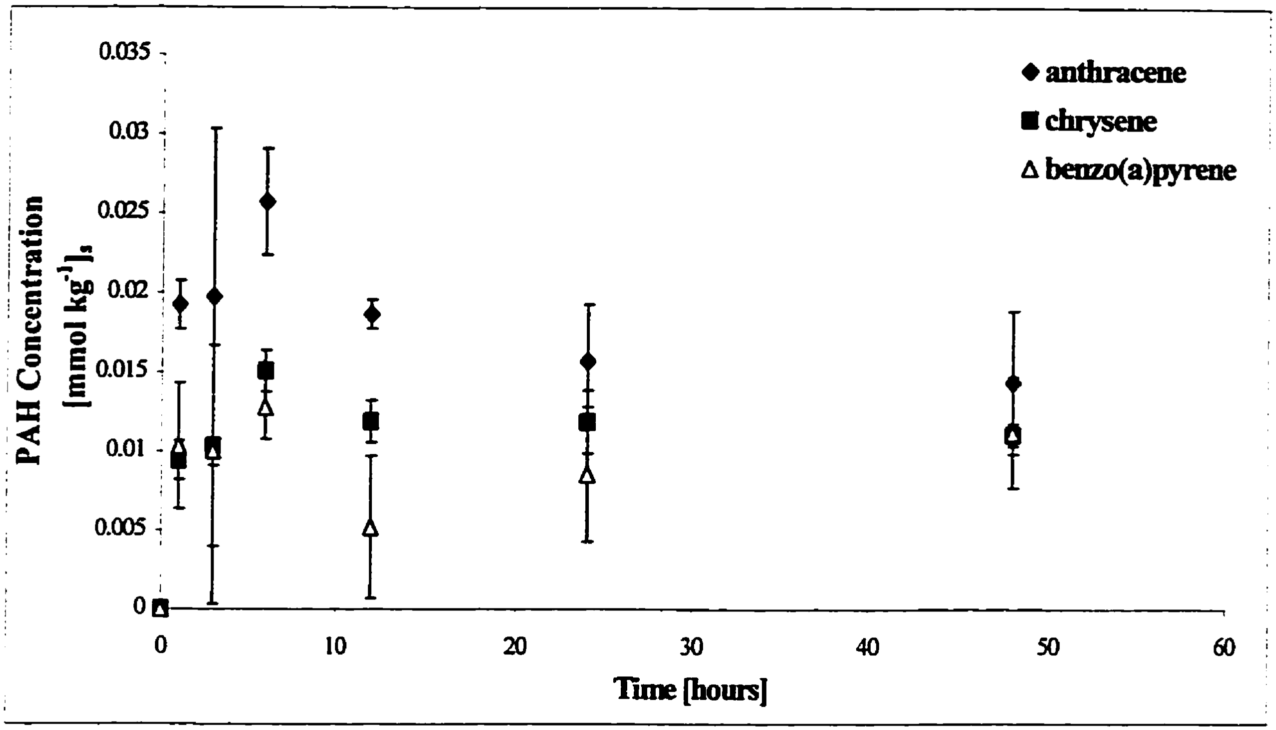


Figure 4.12. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] over time during 0.1mM Dowfax washing of MPA soil using a 10:1 solution to soil ratio

MPA soil washing with 1.0mM Dowfax facilitated the aqueous dissolution of low levels of PAHs (Fig. 4.13). Qualitative observations indicated a clear, yellow colored solution with no evidence of either emulsification or mobilization.

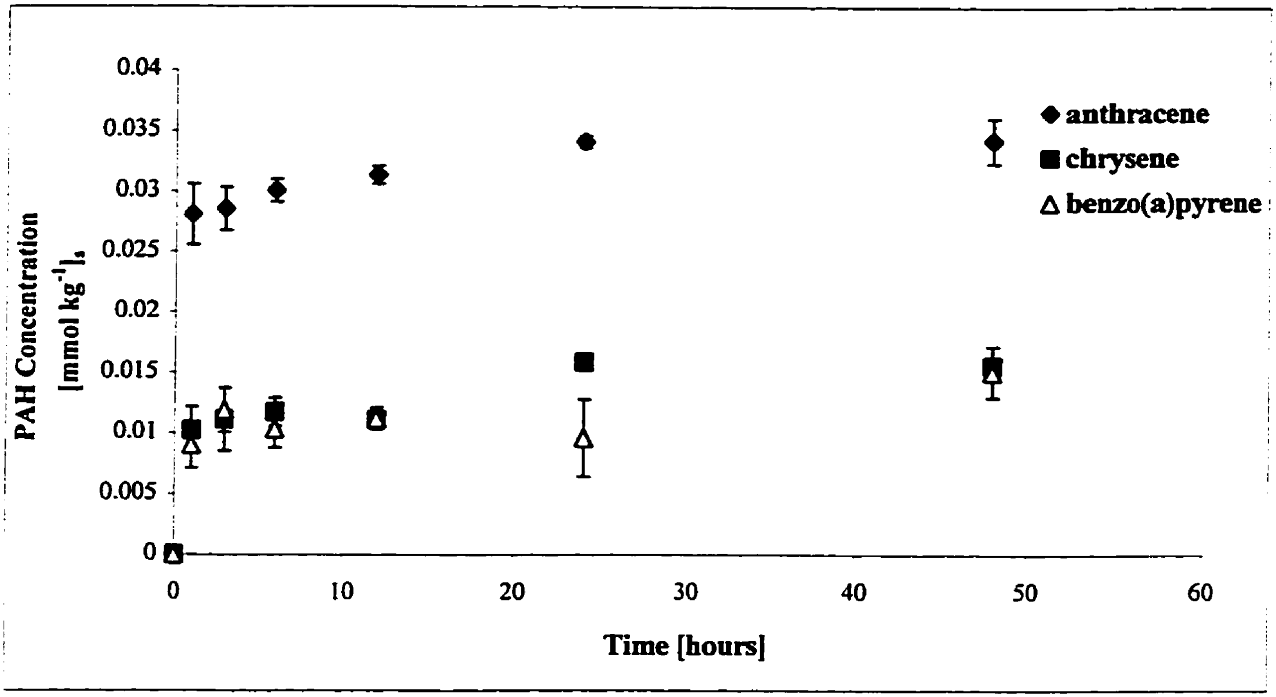


Figure 4.13. Apparent PAH concentrations [mmol $kg^{-1}_{(s)}$ dry soil] over time during 1.0mM Dowfax washing of MPA soil using a 10:1 solution to soil ratio

MPA soil washing with 30mM Dowfax facilitated PAH mass transfer through micellar solubilization (Fig. 4.14). Qualitative observations indicated a clear dark brown supernatant, indicative of solubilization, with neither emulsification nor mobilization detected. Aqueous PAH concentrations were observed to plateau between 6-12 hours. Soil washing using a 10 : 1 Dowfax to soil ratio provided for elevated PAH mass transfer compared to 5 : 1 (v/w) ratio, indicating the potential for micellar solutions to saturate.

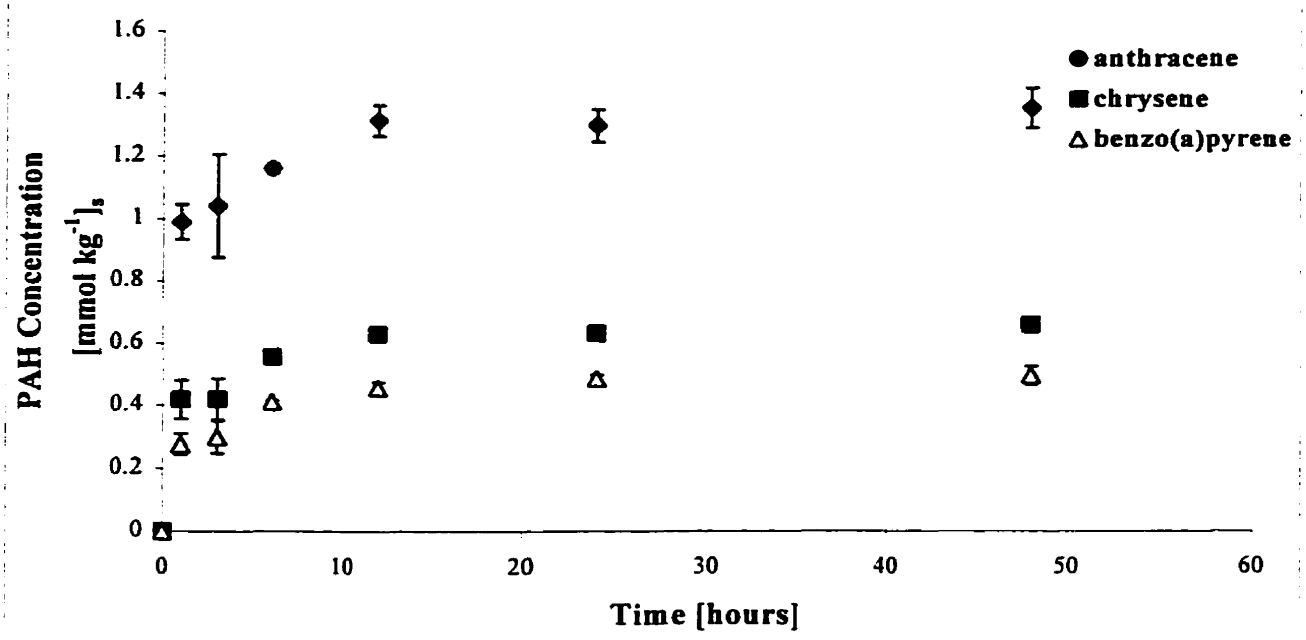


Figure 4.14. **Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] over time during 30mM Dowfax washing of MPA soil using a 10:1 solution to soil ratio**

4.3.2.3 Batch Equilibration of MPA Soil using a 20 : 1 Dowfax Solution to Soil Ratio

Batch equilibration experiments were conducted employing a 20 : 1 Dowfax solution to MPA soil ratio. MPA soil washing with 0.1mM Dowfax did not facilitate emulsion formation. PAH mass transfer to the solution phase was observed (Figure 4.15). Benzo(a)pyrene mass transfer was not detected during this treatment potentially due to its lower detection limit and/or lower concentration within the soil. No detectable anthracene and chrysene levels were observed at 48 hours (recall section 3.2.2.).

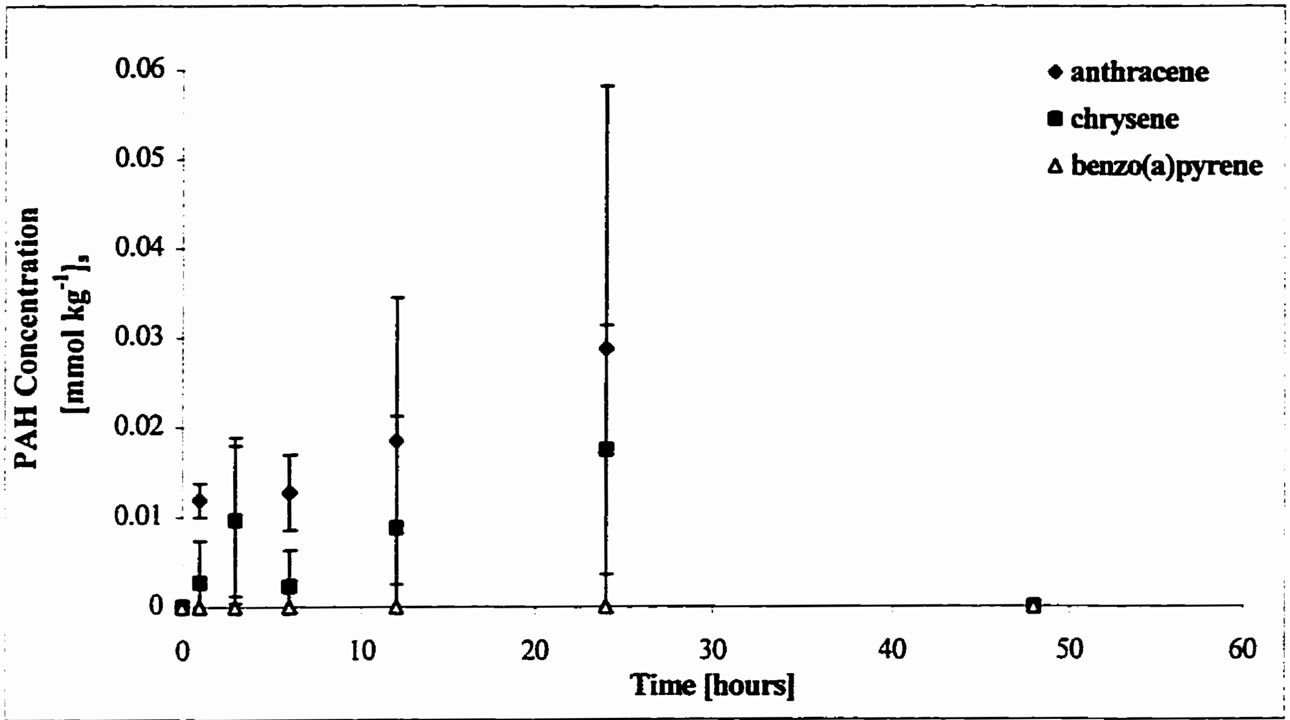


Figure 4.15. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] over time during 0.1mM Dowfax washing of MPA soil using a 20:1 solution to soil ratio

MPA soil washing with 1.0mM Dowfax facilitated the aqueous dissolution of low levels of PAHs (Figure 4.16). Qualitative observations indicated a clear, yellow colored solution with no evidence of either emulsification or mobilization.

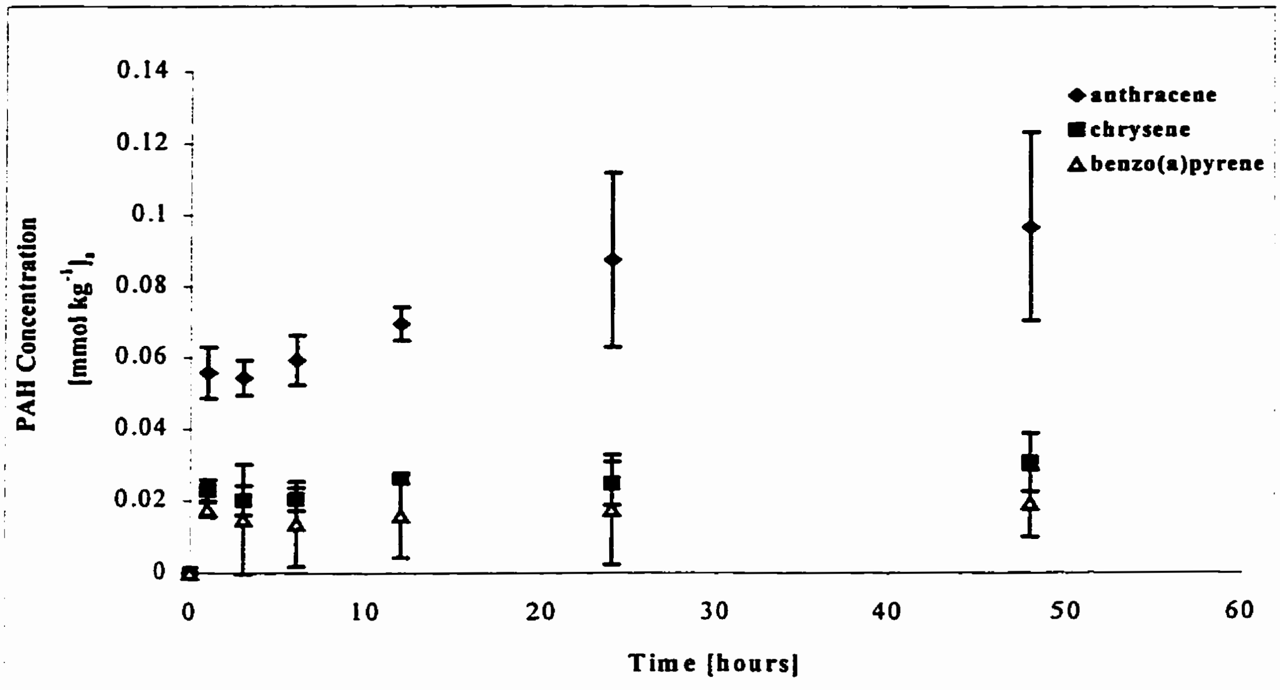


Figure 4.16. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] over time during 1.0mM Dowfax washing of MPA soil using a 20:1 solution to soil ratio

MPA soil washing with 30mM Dowfax facilitated PAH mass transfer through micellar solubilization (Figure 4.17). Qualitative observations indicated a clear dark brown supernatant indicative of creosote solubilization, with neither emulsification nor mobilization detected. Aqueous PAH concentrations were observed to plateau between 6 to 12 hours of mixing. Micellar solubilization using a 20:1 solution to soil ratio produced greater PAH mass transfer than witnessed with either 10:1 or 5:1 solution to soil ratios. The apparent trend of micellar saturation with anthracene is presented in Figure 4.18. Similar trends were observed for both chrysene and benzo(a)pyrene. Further, micellar solubilization using a 20 : 1 solution to soil ratio required a longer period for aqueous PAH levels to plateau.

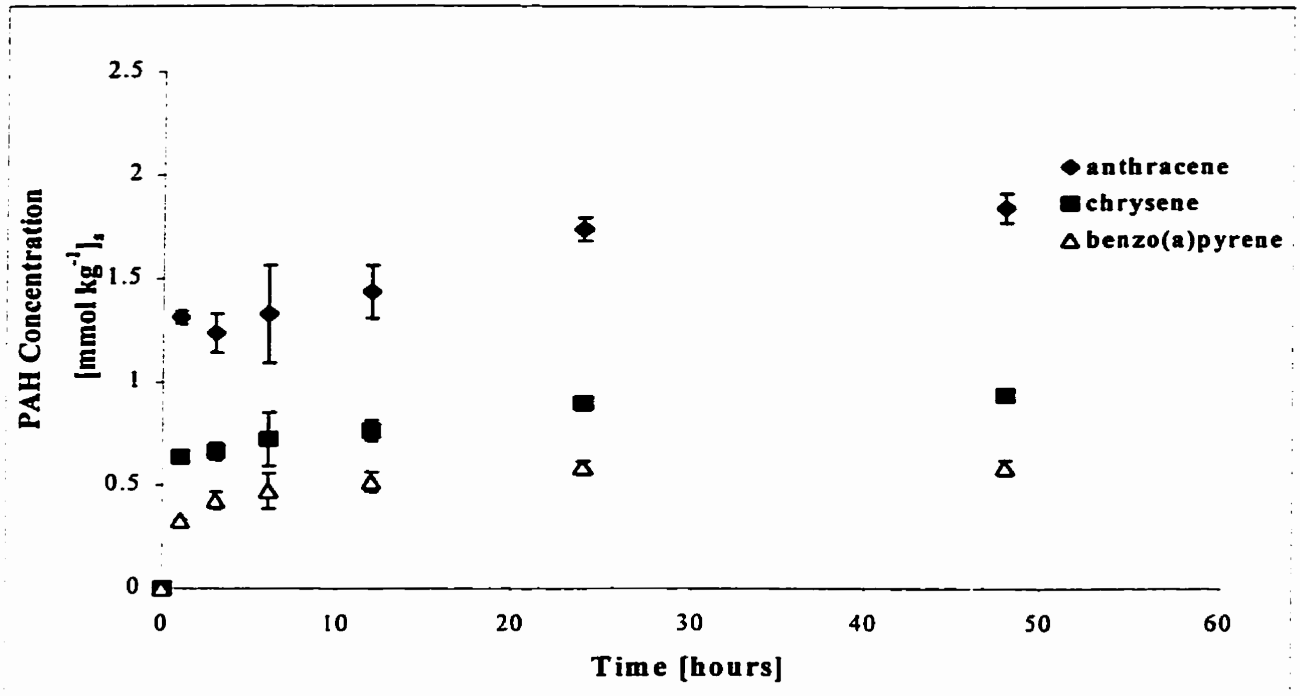


Figure 4.17. Apparent PAH concentrations [mmol kg$^{-1}_{(s)}$ dry soil] over time during 30mM Dowfax washing of MPA soil using a 20:1 solution to soil ratio

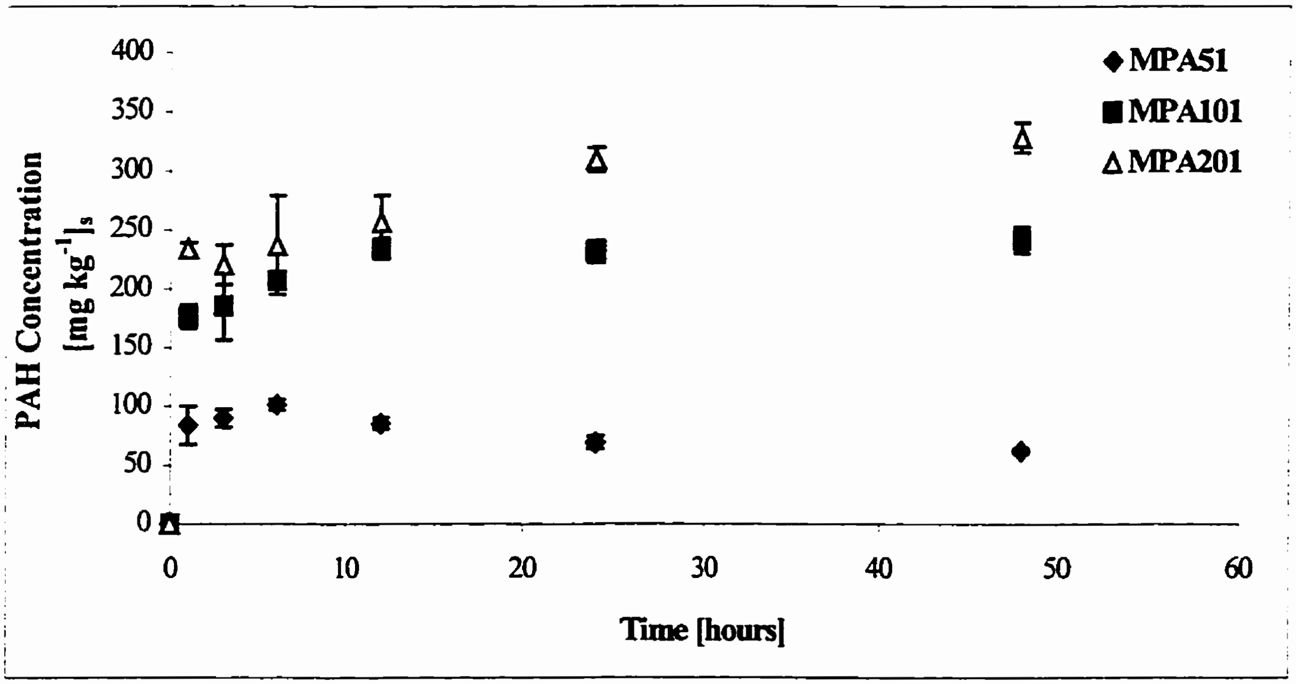


Figure 4.18. Apparent anthracene concentration [mg kg$^{-1}_{(s)}$ dry soil] over time during 30mM Dowfax washing of MPA soil using various solution to soil ratios

4.4. Implications of Batch Equilibration Washings

Based on the batch equilibration results, a number of insights were gained with respect to both fundamental surfactant mechanisms and the design of subsequent experimental protocols. Emulsion formation occurred only: 1) at sub-cmc_{tens} surfactant levels, 2) in the presence of elevated hydrocarbon levels (MPA 5 : 1, MPA 10 : 1) and 3) following certain mixing times (1, 3, 6, 12 and 24 hrs). Subsequent experiments were designed to evaluate the potential of emulsification in facilitating PAH removal from weathered creosote contaminated soils. In doing so, the boundaries of the emulsification domain were sought. These results may further indicate the potential dependency of emulsion formation on the level of hydrocarbon, or NAPL, present within the system. Emulsification was seen to operate within more heavily contaminated systems (MPA 5 : 1), did not operate as effectively with decreasing levels of oil (MPA 10:1) and finally did not form (MPA 20:1).

Soil washing with 1.0mM Dowfax facilitated limited PAH mass transfer in either LPA or MPA soils, compared to 0.1 (MPA) and 30mM Dowfax treatments (LPA and MPA). Monomer and/or weak micellar solubilization may have accounted for the observed PAH mass transfer during1.0mM Dowfax washing.

Soil washing with 30mM Dowfax led to the conclusion that the micellar solutions were becoming saturated with organic contaminants. Aqueous PAH levels following 30mM Dowfax soil washing of the two creosote-contaminated soils were not significantly different (recall Figures 4.3 and 4.11). However, the rate to reach saturation was accelerated within the more heavily contaminated MPA soil system. Observations suggest that increasing Dowfax solution : soil ratios facilitated greater PAH mass transfer. Elevated PAH mass transfer, with a 20:1 Dowfax solution to soil ratio, required longer equilibration periods (24-48 hrs) compared to both 5:1 and 10:1 ratios. Dowfax washing of soil systems with decreasing levels of hydrocarbon (MPA 10:1, MPA 20:1) demonstrated that micellar solubilization was effective at facilitating PAH mass transfer. Alternatively, Dowfax washing of soil systems with elevated levels of hydrocarbon (MPA 5:1) produced extensive PAH mass transfer through both emulsification and micellar solubilization.

Increasing the solution to soil ratio provided for enhanced PAH mass transfer during micellar solubilization, suggesting the finite capacity that micelles have for organic constituents (recall Figs 4.8 and 4.18). The observed solubilization enhancement, with increasing solution to soil ratios in both LPA and MPA soils, may have resulted from a greater micelle to contaminant ratio. Dowfax washing resulted in higher aqueous anthracene concentrations followed by chrysene and then benzo(a)pyrene. This observation may have resulted from the amount of each PAH within the system (recall Table 4.2) and not preferential solubilization of one PAH with respect to another. The solubilization of PAHs relative to one another will be discussed in Section 4.6.1.

To account for micellar saturation, and the accompanying cessation of PAH mass transfer, a sequential washing design was incorporated. The sequential Dowfax design was incorporated to address the extent to which the addition of fresh surfactant solution can facilitate PAH mass transfer from weathered soil matrices. Further, a broad range of Dowfax concentrations will be incorporated to encompass sub- to supra-cmc_{tens} surfactant levels. Based on equilibration experiments the following protocols were selected for subsequent experiments: 1) a 24 hr mixing time, 2) a 5 : 1 Dowfax solution to soil ratio, and 3) no filtration of surfactant supernatant prior to HPLC analysis due to the exclusion of emulsion.

4.5. Influence of Extraction Frequency and Surfactant Concentration on PAH Mass Transfer From Weathered Creosote-Contaminated Soils

Sequential washing experiments were conducted to examine the efficacy of surfactant washing as a remediation option for weathered creosote-contaminated soils. PAHs are typically the sentinel compounds employed to evaluate the risk associated with creosote-contaminated sites and their concentrations within soils dictate remediation goals. Both PAH concentrations within the surfactant solution during sequential washing and within the soil following sequential washing were evaluated. Several Dowfax-8390 concentrations: 0.0, 0.1, 0.5, 0.8, 1.0, 10, 30 and 100mM were incorporated to evaluate the role of surfactant concentrations on creosote extraction. Reduction in TEO_{MC}, also known as total oil and grease, was also evaluated following treatment. Alberta Tier I

Standards in addition to CCME guidelines for both PAHs and TEO are represented in Table 4.4.

Table 4.4. Regulatory Limits Associated with Creosote Contaminated Soils

		CCME Guidelines[2]		
Constituent	Alberta Tier I[1]	Agriculture	Residential/ Parkland	Commerical/ Industrial
Individual PAHs Nonchlorinated (mg kg^{-1})	0.1	0.1	1	10
Total Extractable Organics (mg kg^{-1})	1000	1000	1000	1000

[1]Alberta Tier I Criteria 1994; [2] CCME Guidelines 1991b.

4.5.1. Sequential Washing of LPA Soil

Sequential washing, as outlined in Section 3.3.5, was conducted with LPA soil. In order to evaluate the influence of Dowfax treatments on contaminant mass transfer, PAH solution concentrations following successive 24 hr soil washings in conjunction with PAH reductions within the soil at the completion to sequential washing period were determined. Apparent PAH concentrations following initial soil washing treatments (24 hr) are provided in Table 4.5. Apparent PAH concentrations throughout the entire sequential washing period, for each treatment, are provided in Appendix A.

Table 4.5. Enhanced PAH mass transfer [mg kg^{-1} dry soil] following 24 hour Dowfax washing of LPA Soil

	Dowfax Concentration [mmol L^{-1}]							
PAH	0	0.1	0.5	0.8	1.0	10	30	100
Anthracene	1.84	4.29	11.03	8.36	9.91	32.04	89.01	157.11
Chrysene	1.16	2.33	6.61	4.46	5.54	14.40	40.522	95.07
Benzo(a)pyrene	nd[1]	2.41	5.65	5.49	5.28	11.70	34.10	61.02

1) indicates non detectable: benzo(a)pyrene detection limit = 7 ug kg^{-1}.

Anthracene and chrysene concentrations following the first ddH_2O washing are approximately 41 and 580 times higher, respectively, than literature values of PAH solubility in water (Refer to Table 3.2). Benzo(a)pyrene was not detected within the aqueous phase potentially due to less being present in the system and its lower detection limit (7 ug kg^{-1}). Elevated anthracene and chrysene levels tended to persist over the entire sequential washing period (Appendix A). Elevated aqueous PAH levels, following ddH_2O washing, may have resulted through partitioning into the diesel carrier used in creosote application. Diesel or a gasoline compound was observed, as a LNAPL sheen, on the surface of ddH_2O following the first extraction period. PAHs have much higher solubilities within these more nonpolar carriers, than they have in water (Chen and Delfino, 1996). Further, polar partially miscible organic solvents within the creosote mixture, including soluble phenolic and heterocyclic compounds, may have acted as cosolvents for PAHs (Pinal et al. 1990). Alternatively, dissolved humic substances have also demonstrated the capacity to enhance the apparent solubility of hydrophobic compounds like PAHs. Recall that all soils used within experimental protocols were subsurface in origin and would contain reduced levels of native organic matter. The role of humic acids was then thought to be negligible. Finally, biosurfactants may also facilitate the mass transfer of PAHs from soil to the aqueous phase. The incorporation of $HgCl_2$ was thought to inhibit microbial growth rendering this process void. Partitioning of PAHs into diesel appears to be the predominant mechanism involved in facilitating PAH mass transfer during ddH_2O washing. Enhanced PAH mass transfer relative to literature solubility values (Figure 3.2) was evident throughout sequential washing (Fig 1. Appendix A). The observed increase in PAH concentration after the sixth extraction resulted as the experiment was halted for 24 hrs, with supernatant not decanted, due to HPLC malfunction.

Apparent mass transfer of PAHs following the first soil washing period was observed with surfactant addition (Table 4.5). Statistical evaluation of apparent PAH mass transfer is provided in Section 4.5.1.2. Supernatants following 0.1, 0.5, 0.8 and 1.0mM treatments were clear and light yellow in color. Although numerous researchers have reported PAH mass transfer from contaminated soil during sub-cmc surfactant washing (Kile and Chiou 1989;Yeom et al. 1995) few have provided experimental evidence on the exact mechanism(s) involved. Enhanced PAH concentrations following 0.1, 0.5, 0.8 and 1.0mM Dowfax treatments may potentially be explained through a number of mechanisms. Immature micellar forms with small aggregation numbers (dimer, trimer etc.) may exist below the cmc that may account for the observed enhanced solubility, particularly for the more hydrophobic PAHs (Yeom et al. 1995). As surfactants are amphipathic molecules, they are capable of interacting with PAHs while maintaining fairly high aqueous solubility. Depending on the hydrophobicity, as determined by the octanol-water partition coeffecient K_{ow}, a PAH can exhibit a solubility enhancement in the presence of surfactant monomers (Yeom et al. 1995). Kile and Chiou (1989) attributed solubility enhancement in this instance to a partition-like interaction of the nonpolar portion of dilute surfactant solutions with highly hydrophobic molecules. Anthracene, chrysene and benzo(a)pyrene have high K_{ow} values (4.54, 5.86 and 6.04 respectively) and would be expected to exhibit solubility enhancement in the presence of surfactant monomers.

Alternatively, the dispersion of fine soil particles during sequential washing may have produced errors in the dissolved PAH concentrations. Mackay and Powers (1987) describe the phenomenon whereby part of the chemical allegedly in solution is actually sorbed to suspended colloidal matter. Recall that fine soil particles were observed in destabilized emulsions (Section 4.3.2.1) indicating that dispersed or suspended soil fines did not sediment out of the supernatant with centrifugation. Also recall that the HPLC filtering procedure was abandoned due to exclusion of emulsion (Section 4.3.2.1). Thus suspended clays with associated PAH, could produce the observed dissolved PAH concentrations. The notion of suspended silt and clay particles in facilitating apparent contaminant mass transfer will be discussed in Section 4.5.1.4. PAH solubility enhancement with 0.1, 0.5, 0.8 and 1.0mM treatments continued for the duration of the sequential washing period as represented in Figures 2 through 5 (Appendix A).

Results indicate that micellar solubilization began between 0.6 and 1mM, as noted by the inflection point in the apparent PAH solubility curve provided in Figure 4.19. The observed cmc value obtained from solubility enhancement data (cmc_{sol}), determined from the inflection point of apparent solubility curve (Figure 4.19) does not differ significantly from the cmc_{tens} (Figure 4.1).

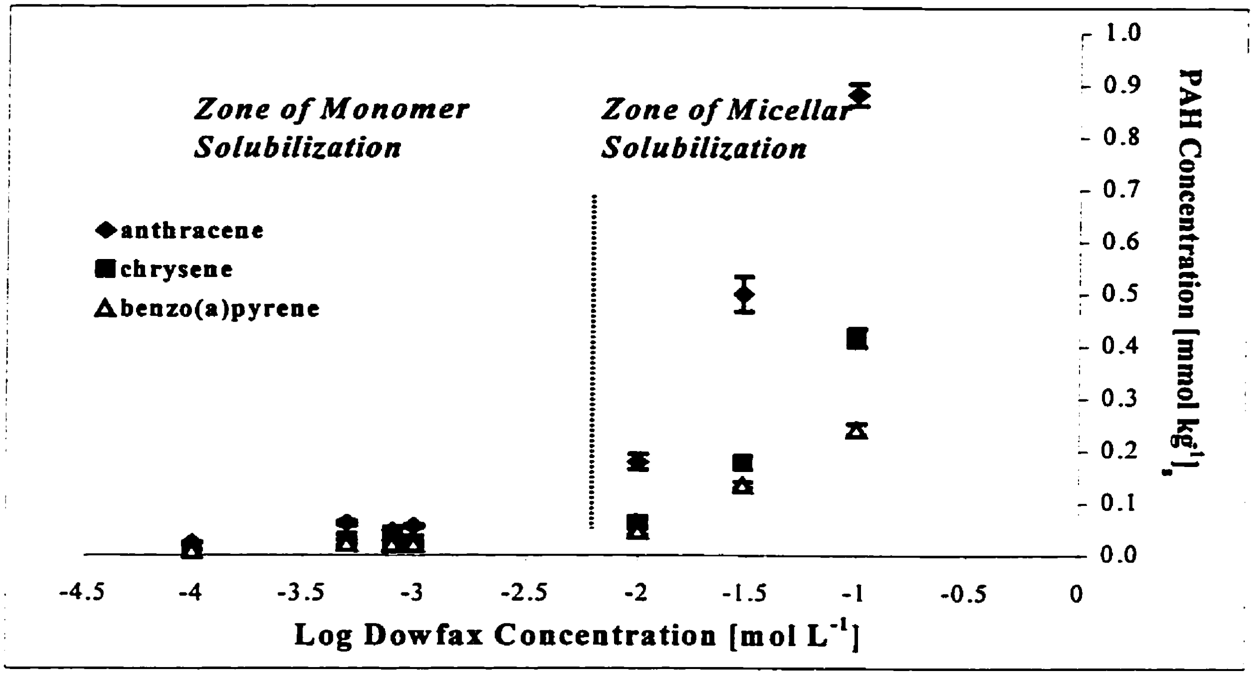


Figure 4.19. Apparent PAH concentrations [mmol $kg^{-1}{}_{(s)}$ dry soil] following 24 hour Dowfax washing of LPA soil

Sequential washing with 10mM Dowfax facilitated PAH mass transfer throughout the sequential washing period, without reducing supernatant PAH concentrations below HPLC detection limits (Figure 6, Appendix A). Sequential washing with 30mM Dowfax facilitated the bulk of PAH mass transfer within 2-3 extractions (Figure 7, Appendix A). Although the majority of PAH mass transfer occurred after the first 2-3 successive treatments, an additional 5 washings (4 Dowfax + 1 ddH_2O) did not reduce aqueous PAH concentrations below HPLC detection limits. Sequential washing with 100mM Dowfax facilitated the bulk of PAH mass transfer within two sequential extractions (Figure 8, Appendix A). Soil washing for an additional 6 extraction periods (5 Dowfax + 1 ddH_2O) was required to reduce aqueous PAH concentrations below HPLC detection limits. Results suggest that there is a more readily extractable PAH pool that is removed rapidly (within 2-3 successive washings), while a more refractory/nonlabile PAH pool requires extensive washing periods to remove from soil. The mass balance of target PAHs, as outlined in Section 3.3.5, during sequential washing are presented in Figures 4.20 through 4.22. Mass balance figures also serve to represent the relative reductions in soil PAH concentrations relative to pretreatment values.

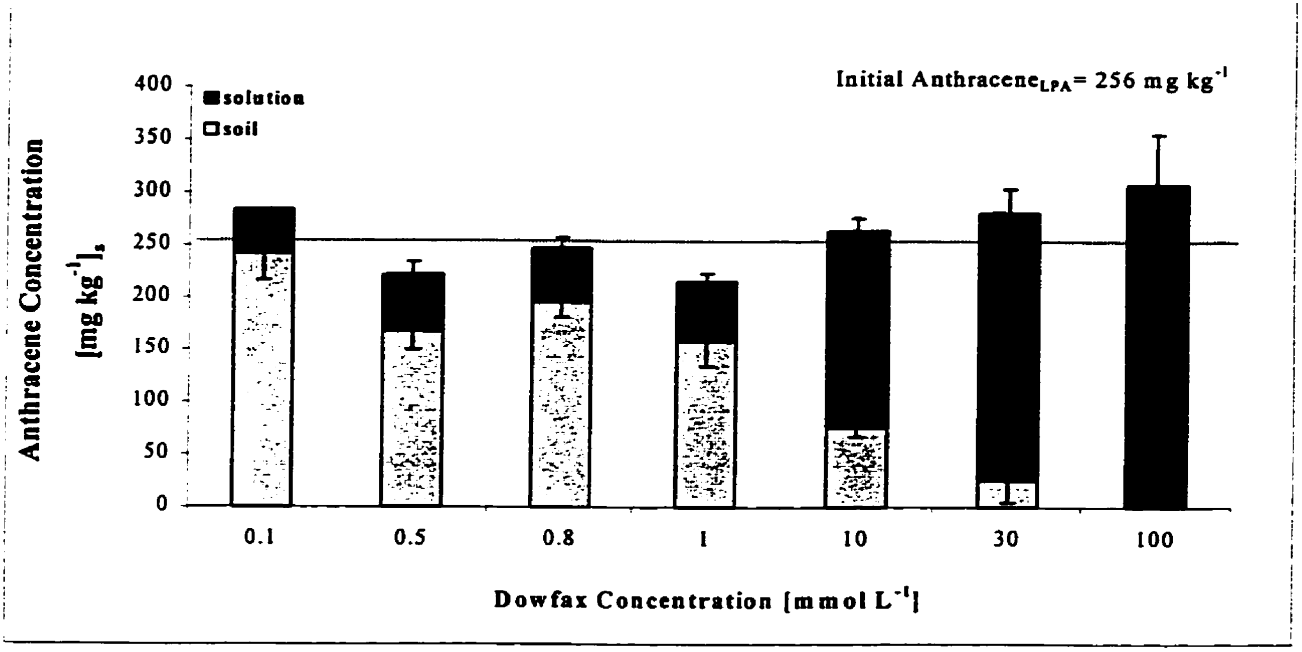


Figure 4.20. Anthracene mass balance [mg kg^{-1}$_{(s)}$ dry soil] following completion of sequential Dowfax washing of LPA soil

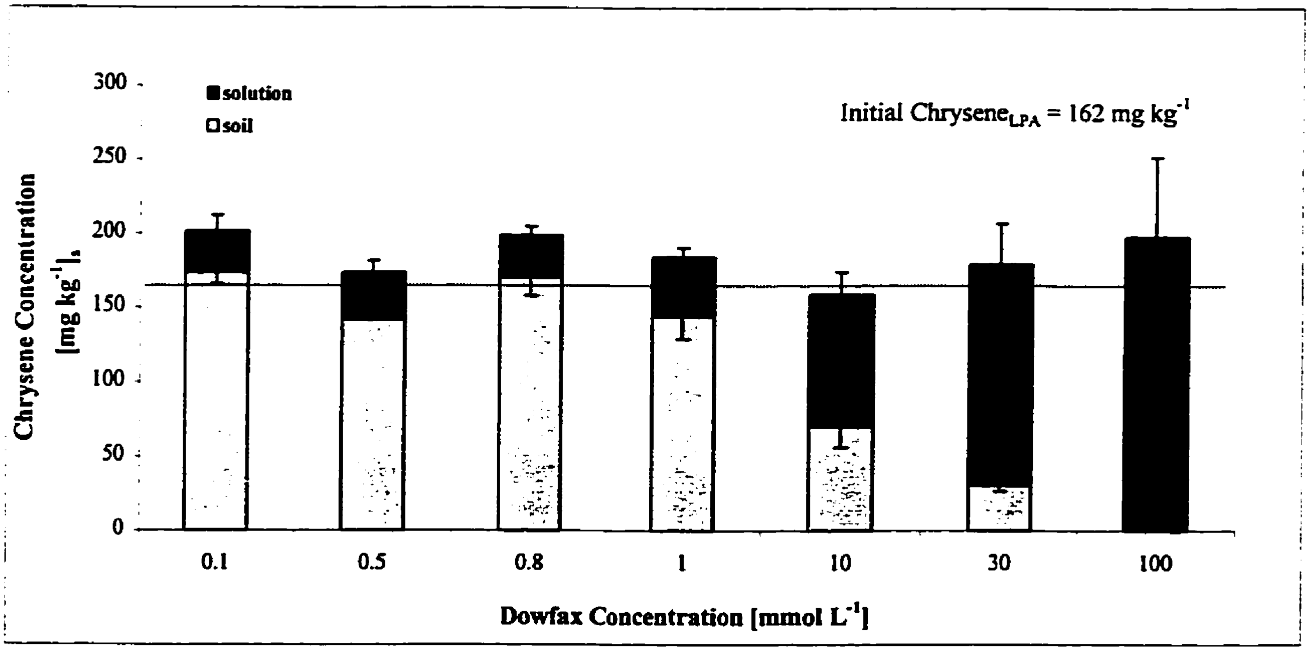


Figure 4.21. Chrysene mass balance [mg kg^{-1}$_{(s)}$ dry soil] following completion of sequential Dowfax washing of LPA soil

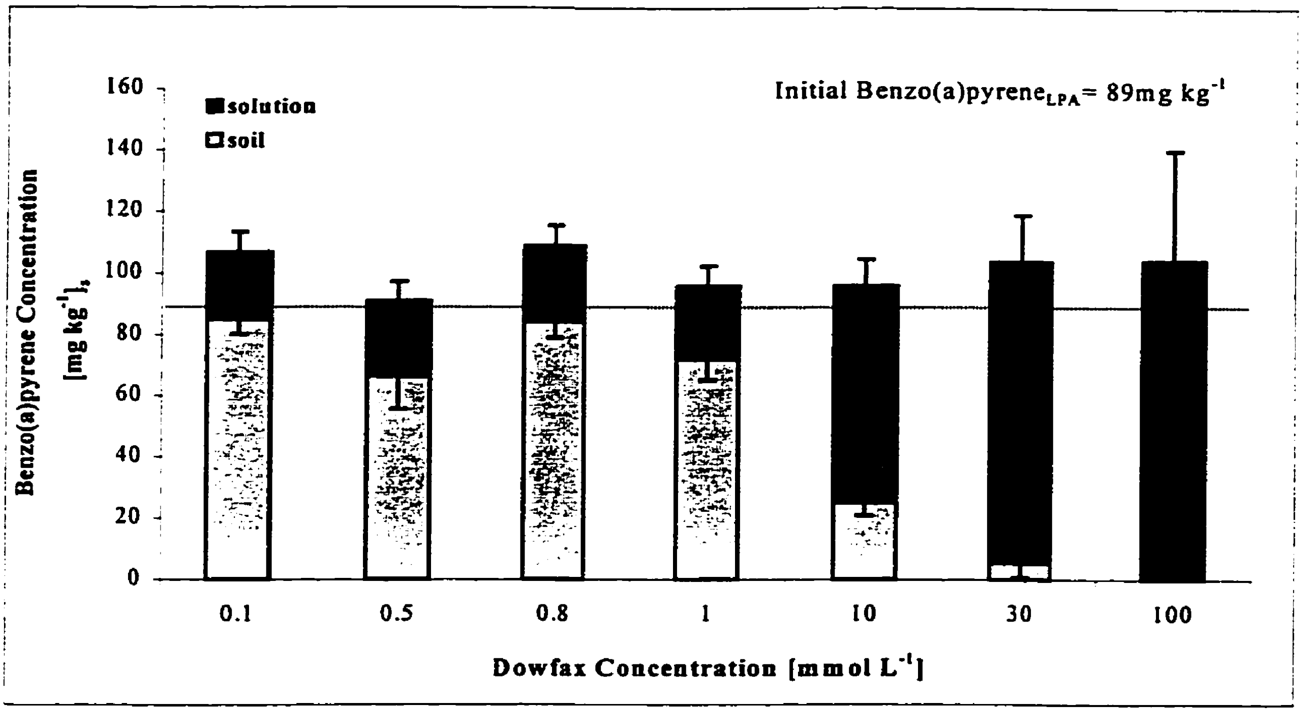


Figure 4.22. Benzo(a)pyrene mass balance [mg kg^{-1}$_{(s)}$ dry soil] following completion of sequential Dowfax washing of LPA soil

Mass balances for all PAHs were acceptable over the course of an eight day sequential washing period. Anthracene recovery ranged from 87 to 120 %. Chrysene recovery ranged from 99 to 123 %. Benzo(a)pyrene recovery ranged from 102 to 122%. Sequential washing with 10, 30 and 100mM Dowfax produced substantial apparent reductions in target PAH concentrations within soil. Sequential washing with 0.1, 0.5, 0.8 and 1.0mM Dowfax produced apparent reductions in soil anthracene and benzo(a)pyrene levels. Apparent soil PAH reductions were statistically analyzed in Section 4.5.1.3.

4.5.1.2. Statistical Evaluation of PAH Mass Transfer Following Dowfax Washing of LPA Soil

Changes in solution PAH concentrations following the initial Dowfax washing period (24 hrs) of the LPA soil sequential washing experiment were examined through ANOVA (SAS) using a Tukey test ($P<0.05$). Statistical analyses are summarized in Table 4.6.

Table 4.6. PAH Mass Transfer Following Dowfax Washing of LPA Soil

	Anthracene		Chrysene		Benzo(a)pyrene	
Dowfax [mM]	Dowfax vs ddH_2O	Amongst Treatments	Dowfax vs ddH_2O	Amongst Treatments	Dowfax vs ddH_2O	Amongst Treatments
0.1	nsd[1]	*	nsd	*	nsd	*
0.5	nsd	*	nsd	*	nsd	*
0.8	nsd	*	nsd	*	nsd	*
1.0	nsd	*	nsd	*	nsd	*
10	nsd	*	nsd	*	nsd	*
30	sd[2]	**	sd	**	sd	**
100	sd	***	sd	***	sd	***

Note: 1) nsd indicates not significantly different from ddH_2O control ($P < 0.05$)
2) sd indicates significantly different from ddH_2O control ($P < 0.05$)
3) Treatments with same number of * are not significantly different ($P<0.05$)
4) Treatments with different number of * are significantly different ($P<0.05$)

Statistical evidence suggests that only 30 and 100mM Dowfax treatments produced significant ($P<0.05$) PAH mass transfer following the first extraction period. Monomer (0.1 and 0.5mM) and dilute micellar (0.8 and 1.0mM) solutions were not effective treatments for enhancing PAH mass transfer. Although 10mM Dowfax produced an apparent increase in PAH solubility, the increase was not statistically significant ($P<0.05$).

4.5.1.3. Statistical Evaluation of LPA Soil PAH Reductions Following Sequential Washing

Changes in soil PAH concentrations following sequential washing were evaluated through ANOVA (SAS) with a Tukey test ($P < 0.05$). Sequential Dowfax-8390 washing produced variable reductions in PAHs within the LPA soil. Statistical analyses are summarized in Table 4.7.

Table 4.7. Soil PAH Reductions Following Sequential Washing of LPA Soil

	Anthracene		Chrysene		Benzo(a)pyrene	
Dowfax [mM]	Treatment	Amongst Treatments	Treatment	Amongst Treatments	Treatment	Amongst Treatments
0.1	nsd[1]	*	nsd	*	nsd	*
0.5	sd[2]	**	nsd	*	sd	**
0.8	sd	*,**	nsd	*	nsd	*
1.0	sd	**	nsd	*	nsd	*,**
10	sd	***	sd	**	sd	***
30	sd	***,****	sd	***	sd	****
100	sd	****	sd	***	sd	****

Note: 1) nsd indicates not significantly different from pretreatment concentrations ($P < 0.05$)
2) sd indicates significantly different from pretreatment concentrations ($P < 0.05$)
3) Treatments with same number of * are not significantly different ($P < 0.05$)
4) Treatment with different number of * are significantly different ($P < 0.05$)

Soil anthracene concentrations were significantly reduced ($P < 0.05$) with every treatment except 0.1mM Dowfax. Anthracene reductions with 0.5, 0.8 and 1.0mM Dowfax treatments may in part be due to its higher aqueous solubility (0.045 mg L^{-1}) compared to chrysene and benzo(a)pyrene (0.002 and 0.004 mg L^{-1} respectively). Soil chrysene and benzo(a)pyrene concentrations were significantly reduced through micellar solubilization. Note that 10mM Dowfax treatment produced significant reductions over the course of sequential washing experiment in contrast to results of 24 hr washing (Table 4.6). The significant reduction in soil benzo(a)pyrene concentrations following 0.5mM Dowfax sequential washing may have resulted from soil variability. Note that the significant reduction in soil benzo(a)pyrene levels produced with 0.5mM Dowfax was not statistically different than the soil benzo(a)pyrene reduction produced with 1.0mM Dowfax.

4.5.1.4. Total Extractable Organic Reductions in LPA Soil after Sequential Washing

Following the conclusion of sequential washing experiments, total methylene chloride extractable organic (TEO_{MC}) determination was conducted on the remaining soil pellet as outlined in Section 3.3.5. Changes in TEO_{MC} content with treatment are represented in Figure 4.23. The overall trend indicates that increasing Dowfax-8390 concentrations facilitated elevated TEO_{MC} reductions following LPA soil washing.

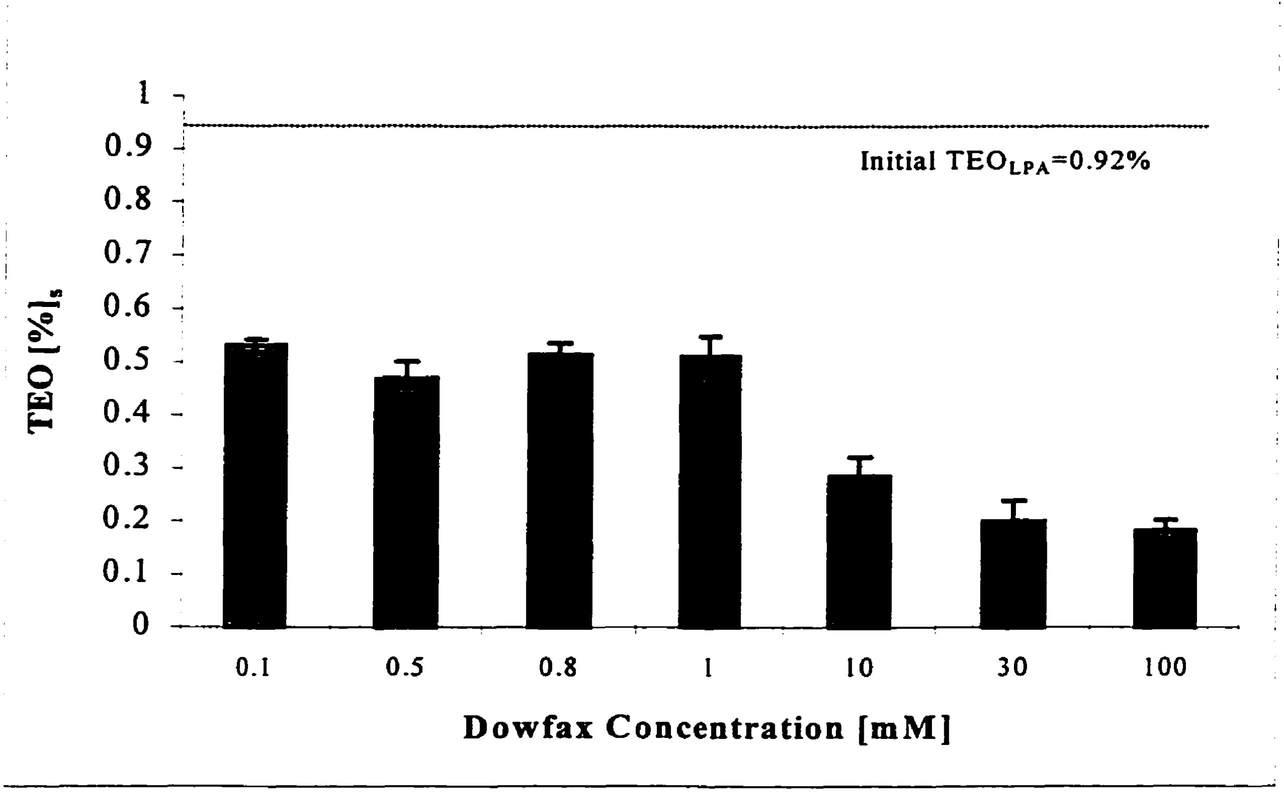


Figure 4.23. **TEO_{MC} [% $_{(s)}$ dry soil] reductions following sequential Dowfax washing of LPA soil**

Surfactant washing of LPA soil produced significant reductions in TEO_{MC} content as determined through ANOVA (SAS) using a Tukey test ($P < 0.05$) for each Dowfax-8390 concentration compared to pretreatment TEO_{MC} values (Table 4.8). Low concentrations of Dowfax (0.1, 0.5 and 0.8mM) were able to dissolve or disperse almost 50% of the TEO in the LPA soil. The addition of Dowfax may have served to disperse or suspend silt and clay particles within the supernatant. The centrifuge treatment of 2500 g for 70 minutes was likely inadequate to produce sedimentation of highly dispersed silt and clay particles. Recall that suspended silt and clays were observed within emulsions following centrifugation (Section 4.3.2.1). The suspended silt and clay fractions were then lost from the system through the decanting of surfactant supernatant between successive washings. A total soil mass balance was conducted following sequential washing experiments and the average % loss of soil, for each Dowfax treatment, is provided in Appendix B. The observed soil losses of 3-5% may correspond to the total silt + clay fractions present in the LPA soil (4.85 %; Table 4.1). Suspended fine particulates have been identified as a reservoir for hydrophobic chemicals in aqueous solutions (Mackay and Powers, 1987). Contaminant losses through association with suspended silt and clay particles may account for the large TEO reductions observed while washing with low concentrations of Dowfax and may also contribute to TEO reductions with higher Dowfax concentrations (10, 30 and 100mM).

Significant TEO_{MC} reductions witnessed with sub-cmc_{tens} Dowfax washings could also indicate that a large component of the organic contaminant matrix was somewhat water-soluble. Treatment with 0.1mM Dowfax produced significant reductions in TEO_{MC} although it did not significantly reduce PAHs within the soil. The diesel carrier used in creosote application, in conjunction with some of the more soluble PAHs, phenolic and heterocyclic compounds may constitute a portion of this sub-cmc extractable material. A combination of the aforementioned physical and chemical processes may account for the observed results.

Table 4.8. TEO_{MC} Reductions Following Sequential Washing of LPA Soil

Dowfax [mM]	Statistical Significance (P<0.05)	Statistical Significance Amongst Treatments (P<0.05)
0.1	sd	*
0.5	sd	*
0.8	sd	*
1.0	sd	*
10	sd	**
30	sd	**
100	sd	**

Note: 1) sd indicates that treatment produced a significant reduction in TEO_{MC} relative to pretreatment TEO values ($P<0.05$)
2) treatments with same number of * are not significantly different ($P<0.05$)

Significant reductions in TEO_{MC} with 10, 30 and 100mM Dowfax resulted from contaminant mass transfer through micellar solubilization. Additionally, the aforementioned dispersion of fine silt and clay with surfactant washing may also have contributed to TEO_{MC} losses (refer to Appendix B). Examination of TEO_{MC} reductions through micellar solubilization (10, 30 and 100mM Dowfax) suggests that although hydrophobic PAHs have been significantly reduced within the contaminated soil, a pool of relatively refractory organic material exist. As PAHs are only a portion of the entire creosote matrix, other organic constituents that are not extracted through surfactant washing may be left behind accounting for the remaining TEO_{MC}. Further, residual Dowfax within the soil matrix, not removed with ddH_2O washing, may also have contributed to the remaining TEO_{MC} fraction. TEO_{MC} levels following sequential washing exceed both Alberta Tier I Criteria and CCME Guidelines (Table 4.4).

4.5.1.4. Implications of Sequential LPA Soil Washing

A number of insights were gained from LPA soil washing. Sequential washing proved to be effective in reducing all target PAH concentrations within LPA soil through micellar solubilization with 10, 30 and 100mM. Additional mechanisms, including potential monomer and/or weak micellar solubilization produced statistically significant reductions in soil anthracene concentrations with 0.5, 0.8 and 1.0mM sequential treatments, however substantial anthracence levels remained within the soil. The more hydrophobic and less abundant PAHs, chrysene and benzo(a)pyrene, did not demonstrate significant reductions with 0.5, 0.8 and 1.0mM treatments. Results from 30 and 100mM sequential washings suggest the presence of two contaminant fractions within LPA soil: 1) a relatively accessible contaminant pool that can be removed relatively rapidly through micellar solubilization within 2-3 sequential extractions and 2) a more refractory contaminant matrix that requires an extensive extraction period for removal from soil. As PAH removal increases, micelles must solubilize contaminants from deeper areas within the contaminated soil matrix, and nonequilibrium effects resulting from mass transfer limitations become significant. Other studies have reported that nonequilibrium conditions exist in the solubilization of PAHs at such high surfactant dosages (Yeom et al., 1995).

4.5.2. Sequential Washing of Moderately Contaminated Prince Albert Soil

Sequential washing of MPA soil (TEO$_{MC}$ = 1.90%) was conducted following the procedure outlined in Section 3.3.5. Aqueous PAH concentrations following the first extraction period (24 hrs) treatment are provided in Table 4.9. PAH mass transfer during sequential washing are presented in Appendix C.

Table 4.9. Enhanced PAH mass transfer [mg kg^{-1}dry soil] following 24 hour Dowfax washing of MPA soil

	Dowfax Concentration [mmol L^{-1}]							
PAH	0	0.1	0.5	0.8	1.0	10	30	100
Anthracene	1.60	42.55	66.77	10.20	9.67	26.84	72.68	265.0
Chrysene	0.73	29.86	44.16	6.20	5.67	12.16	35.28	139.8
Benzo(a)pyrene	nd[1]	16.64	26.56	3.96	3.91	8.02	22.51	86.43

[1] indicates non-detectable:benzo(a)pyrene detection limit = 7ug kg^{-1}

Partitioning of PAHs into the diesel carrier and/or association of PAHs with suspended fine particulates, as discussed in Section 4.3.1, appears to be the predominant mechanism involved in facilitating apparent PAH mass transfer during ddH$_2$O washing. Elevated PAH concentrations persisted throughout ddH$_2$O sequential washing (Figure 1, Appendix C).

The addition of Dowfax produced enhanced apparent PAH solubility relative to treatment with ddH$_2$O. Statistical evaluation of apparent PAH solubility enhancements are provided in Section 4.5.2.1. Emulsion formation was observed following the first extraction period with 0.1 and 0.5mM Dowfax. Emulsification was responsible for elevated PAH mass transfer compared to 0, 0.8 and 1.0mM Dowfax treatments (Table 4.9). The range or domain of emulsification, within the context of the experimental parameters utilized, stretches from 0.1mM to 0.5mM Dowfax. Dowfax concentrations less than 0.1mM were employed in subsequent experiments to ascertain the lower boundary of emulsification within this system (Section 4.5.2.1). Emulsification continued to operate within the MPA-Dowfax system until a critical level of oil was removed, after which point emulsion formation ceased. This critical oil level was removed after 3 sequential extractions with 0.1mM Dowfax and after the first extraction with 0.5mM Dowfax (Figures 2 and 3 Appendix C). Evidence suggests that after this critical amount of oil was removed alternative mechanisms were responsible for enhanced PAH solubility observed for the duration of the experiment; including potential monomer solubilization similar to that witnessed during LPA soil washing with 0.1 and 0.5mM Dowfax (Figures 2 and 3, Appendix A). PAH mass transfer continued with 0.1 and 0.5mM washing for the remainder of the sequential washing experiment.

Emulsion separation had occurred by 0.8mM and continued at 1.0mM Dowfax. The cessation of emulsification reduced PAH mass transfer following these treatments (Table 4.9). Coalesced oil droplets were noticed on the soil surface following the initial soil extraction using 0.8 and 1.0mM Dowfax treatments. Emulsion stability is dependent upon the resistance of the dispersed oil within the system to coalescence (Myers, 1988). Results suggest that coalescence of oil droplets may have terminated the emulsification process. Fine silt and clay particles were also observed to settle out of solution with 0.8 and 1.0mM treatment. Emulsions may be stabilized by the presence of fine suspended particles, such as silt and clay, at the interface between the dispersed and continuous phases (Myers, 1988; Rosen, 1989). Dowfax is an anionic surfactant and increasing its concentration would elevate the amount of charge, and ionic strength, within the system. The elevated ionic strength may have destabilized the finely divided solids from the emulsion interface, facilitating oil droplet coalescence and terminating the emulsification process. However, this assertion is based on qualitative observation and requires quantitative verification. Soil washing with 0.8 and 1.0mM Dowfax facilitated limited PAH solubility enhancement (Figures 4 and 5, Appendix C). The observed PAH solubility enhancement may have resulted from a number of mechanisms including: partitioning of PAHs into the diesel carrier, adsorption to fine suspended particulates, monomer and/or weak micellar solubilization as discussed in Section 4.5.1. Washing of MPA soil with ddH$_2$O for the final extraction period, to remove residual surfactant, stimulated emulsion formation within 0.8 and 1.0mM Dowfax systems that facilitated PAH mass transfer (Figures 4 and 5, Appendix B). Evidence suggests that ddH$_2$O washing diluted the residual Dowfax within the soil pores to a concentration amenable to emulsion formation. This observation lends credence to the hypothesized role of reduced surfactant concentrations in emulsion formation. Figure 4.24. provides the relative zones of emulsification and solubilization following first 24 hr MPA soil washing period.

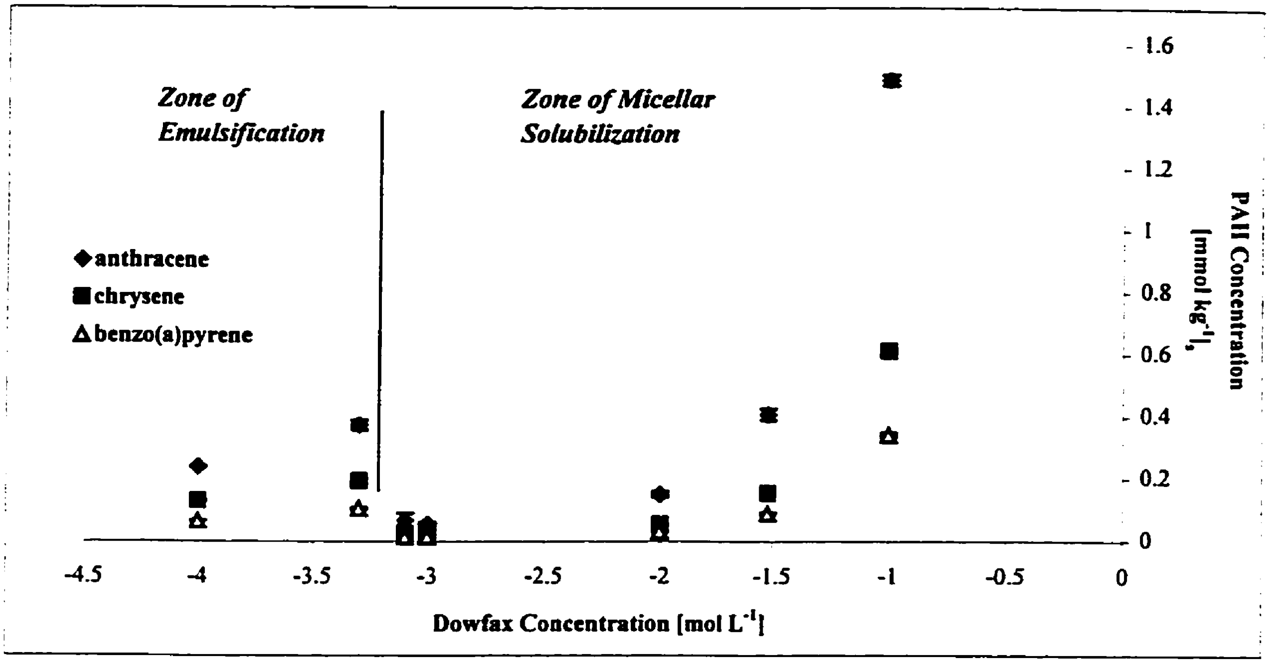


Figure 4.24. Apparent PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] following 24 hr Dowfax washing of MPA soil

Micellar solubilization was observed within 10, 30 and 100mM Dowfax treatments. Facilitated PAH mass transfer from soil to solution phase was witnessed throughout the sequential washing period with 10mM Dowfax treatment (Figure 6, Appendix C). The absence of a reduction in soluble PAH levels, over the course of sequential washing, indicated that 10mM Dowfax washing was unable to completely remove the accessible target PAH fraction of the contaminant pool. Micellar solubilization with 30mM Dowfax removed the majority of target PAHs within 4-5 successive washings (Figure 7, Appendix C). The remaining 5 extractions were unable to reduce aqueous PAH levels within the surfactant wash solution below HPLC detection limits (provided in Section 3.2.2). Micellar solubilization with 100mM Dowfax washing facilitated the majority of PAH mass transfer within 2-3 sequential extractions (Figure 8, Appendix C). While the majority of PAH mass transfer occurs within the first 2-3 successive surfactant washings, extensive washing periods were required to reduce soluble PAH concentrations below HPLC detection limits. Following 100mM Dowfax sequential washing, the concentration of selected PAHs within the soil phase (anthracene = 2 mg kg^{-1}, chrysene = 5 mg kg^{-1} ; benzo(a)pyrene = 5 mg kg^{-1}) exceeded certain regulatory limits (Table 4.4).

The mass balance of target PAHs, as outlined in Section 3.3.5, during sequential washing of MPA soil are provided in Figures 4.25 to 4.27. The mass balance figures also represent the relative reductions in soil PAH concentrations and the corresponding increase in PAH solubility with sequential Dowfax treatment. All target PAH concentrations demonstrated apparent reductions following sequential Dowfax treatment. These apparent soil PAH reductions were statistically analyzed in Section 4.5.2.3. Mass balances for all PAHs were within an acceptable range following 10 successive washings. Anthracene mass balance ranged from 81-124%, chrysene ranged from 95-127% and benzo(a)pyrene ranged from 91-112%.

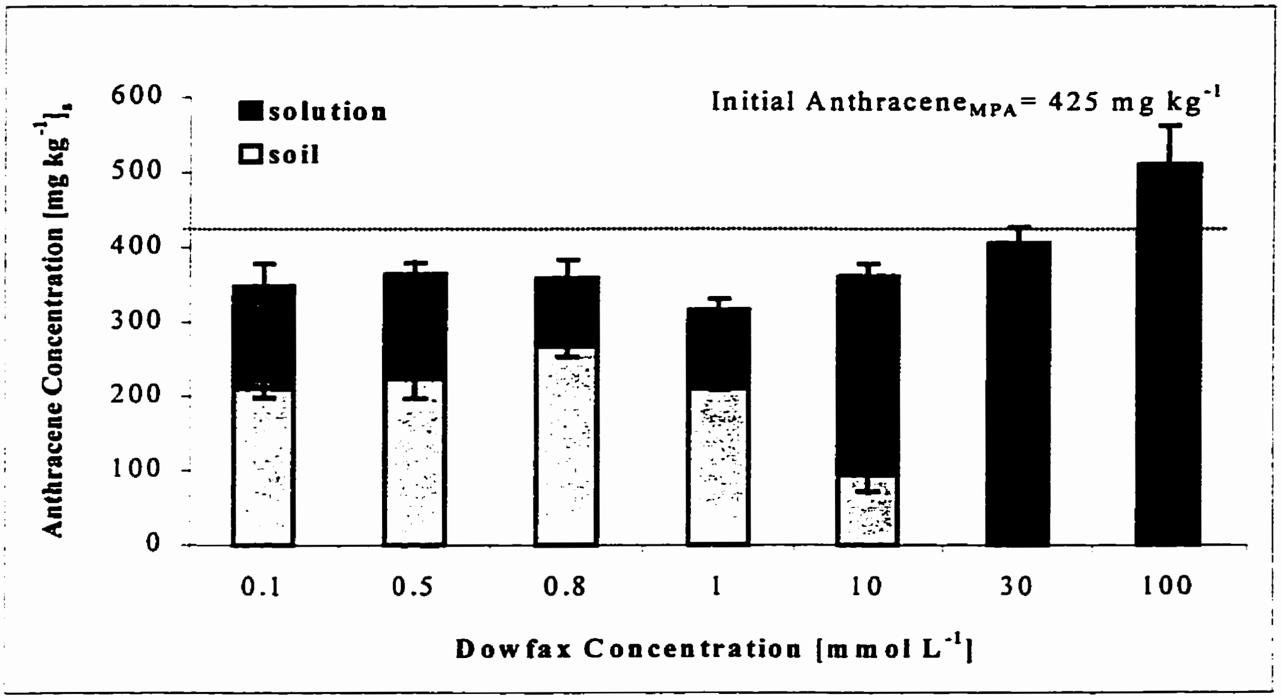


Figure 4.25. Anthracene mass balance [mg kg^{-1}$_{(s)}$ dry soil] following completion of sequential Dowfax washing of MPA soil

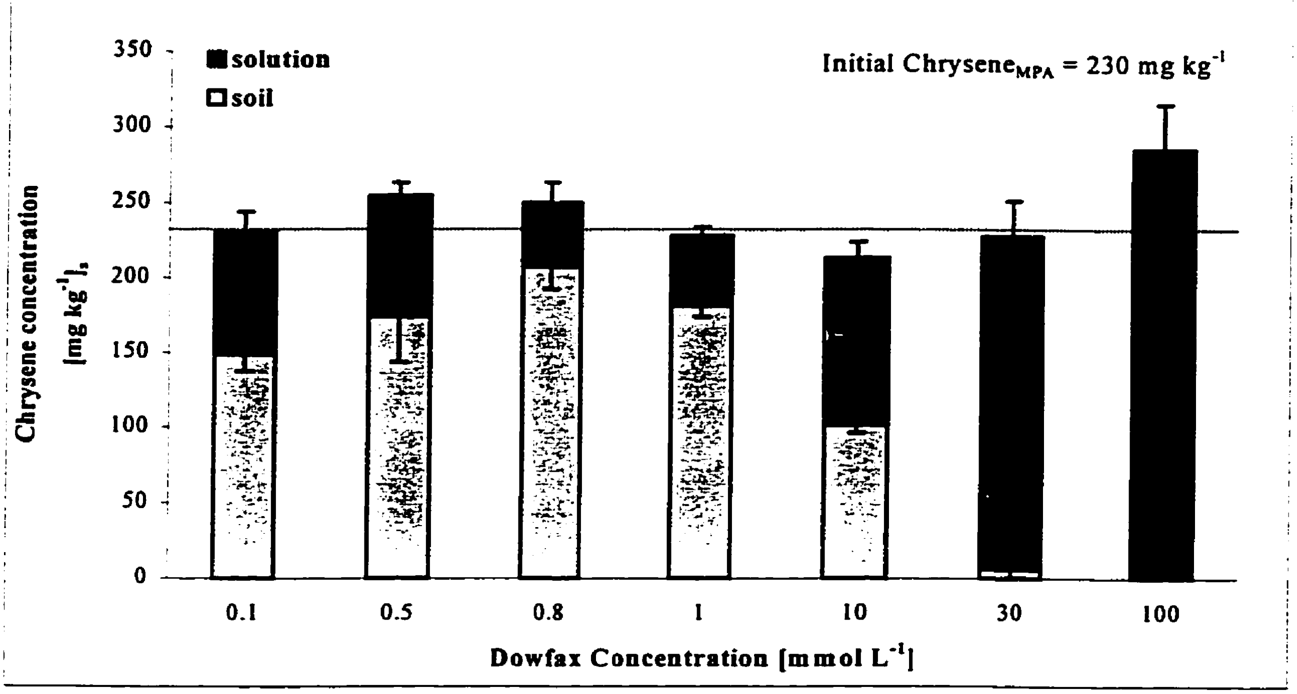


Figure 4.26. Chrysene mass balance [mg kg^{-1}$_{(s)}$ dry soil] following completion of sequential Dowfax washing of MPA soil

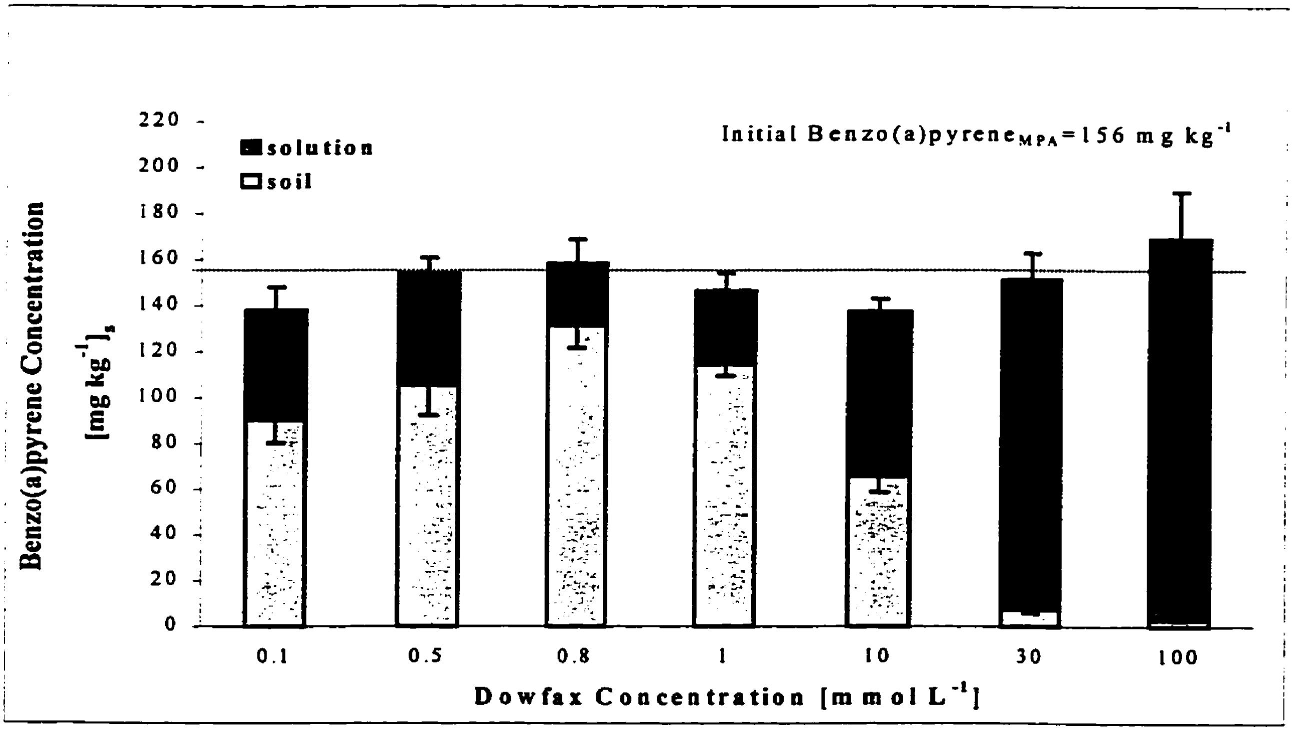


Figure 4.27. Benzo(a)pyrene mass balance [mg kg^{-1}$_{(s)}$ dry soil] following completion of sequential Dowfax washing of MPA soil

4.5.2.1. Discerning the lower bounds of emulsification within MPA Soil System

In order to discern the lower bounds of the zone of emulsification witnessed with surfactant washing of the MPA soil, 3 additional Dowfax concentrations (0.01, 0.05 and 0.08mM) were utilized in a single (24 hour) soil washing design. Note that the procedure is identical to that outlined in Section 3.3.5 but only a single Dowfax extraction was employed. Emulsion formation was not witnessed with 0.01mM Dowfax treatment but was noted at 0.05 and 0.08mM treatments. As a result, the lower bound of emulsification within the MPA soil system is between 0.01 and 0.05mM Dowfax. No emulsification was noted following LPA soil washing with 0.01, 0.05 and 0.08mM Dowfax. LPA soil washing with 0.01, 0.05 and 0.08mM Dowfax did not produce a significant increase in soluble PAH concentrations ($P<0.05$).

4.5.2.2. Statistical Evaluation of PAH Mass Transfer Following Dowfax Washing of MPA Soil

Changes in solution PAH concentrations following the initial Dowfax extraction of MPA soil were examined with an ANOVA (SAS) employing a Tukey test ($P<0.05$). Results of statistical analyses are provided in Table 4.10. Note that 0.01, 0.05 and 0.08mM Dowfax treatments were only included in statistical analysis for the initial MPA soil washing to encompass the zone of emulsification.

Table 4.10. PAH Mass Transfer Following Dowfax Washing of MPA Soil

	Anthracene		Chrysene		Benzo(a)pyrene	
Dowfax [mM]	Dowfax vs ddH$_2$O	Amongst Treatments	Dowfax vs ddH$_2$O	Amongst Treatments	Dowfax vs ddH$_2$O	Amongst Treatments
0.01	nsd	*	nsd	*	nsd	*
0.05	sd	*,**	sd	**	sd	**
0.08	sd	**	sd	**,***	sd	**,***
0.1	sd	**	sd	***,****	sd	**,***
0.5	sd	***	sd	******	sd	***
0.8	nsd	*,**	nsd	*,*****	nsd	*,**
1.0	nsd	*,**	nsd	*,*****	nsd	*,**
10	sd	**	sd	**,*****	sd	*,**
30	sd	***	sd	****	sd	***
100	sd	****	sd	*******	sd	****

Note: 1) nsd indicates not significantly different from ddH$_2$O control ($P<0.05$)
2) sd indicates significantly different from ddH$_2$O control ($P<0.05$)
3) Treatments with same number of * are not significantly different ($P<0.05$)

Emulsification that occurred with 0.05, 0.08 0.1 and 0.5mM Dowfax treatments facilitated significant target PAH solubility enhancement relative to ddH$_2$O ($P < 0.05$). Micellar solubilization with 10, 30 and 100mM Dowfax treatments produced significant PAH solubility enhancement relative to ddH$_2$O treatment ($P < 0.05$).

4.5.2.3. Statistical Evaluation of MPA Soil PAH Reductions Following Sequential Washing

Changes in soil PAH concentrations following sequential washing of MPA soil were examined through ANOVA (SAS) using a Tukey test ($P < 0.05$). Results of statistical analyses are provided in Table 4.11. Note that sequential washing was not conducted with 0.01,0.05 and 0.08mM Dowfax-8390. Dowfax-8390 washing of MPA soil produced variable results with respect to PAH reduction within the soil.

Table 4.11. Soil PAH Reductions Following Sequential Washing of MPA Soil

	Anthracene		Chrysene		Benzo(a)pyrene	
Dowfax [mM]	Treatment	Amongst Treatments	Treatment	Amongst Treatments	Treatment	Amongst Treatments
0.1	sd	*	sd	*	sd	*
0.5	sd	*	nsd	*,**	sd	*
0.8	sd	*	nsd	**	sd	**
1.0	sd	*	nsd	*,**	sd	*
10	sd	**	sd	*,**	sd	*
30	sd	***	sd	***	sd	***
100	sd	***	sd	***	sd	***

Note: 1) nsd indicates not significantly different from pretreatment PAH concentrations ($P < 0.05$)
2) sd indicates significantly different from pretreatment PAH concentrations ($P < 0.05$)
3) Treatments with same number of * are not significantly different ($P < 0.05$)

Soil washing with all Dowfax concentrations produced statistically significant reductions in both anthracene and benzo(a)pyrene soil levels. Soil washing with 0.5, 0.8 and 1.0mM Dowfax produced apparent reductions in soil chrysene levels (Fig. 4.26) but the reductions were not statistically significant ($P < 0.05$). Chrysene has very low water solubility (0.002 mg L^{-1}) that may account for its lower reduction following sequential washing. However, benzo(a)pyrene has a similar solubility (0.004 mg L^{-1}) and yet washing. However, benzo(a)pyrene has a similar solubility (0.004 mg L^{-1}) and yet demonstrated significant reductions within the soil following all treatments. Chrysene variability within the soil may account for the observed results.

4.5.2.4. Total Extractable Organic Removal From MPA Soil Following Sequential Dowfax Washing

Following the conclusion of sequential washing experiments, total methylene chloride extractable organics (TEO_{MC}) determination was conducted on the remaining soil pellet. Changes in TEO_{MC} content with treatment are represented in Figure 4.28.

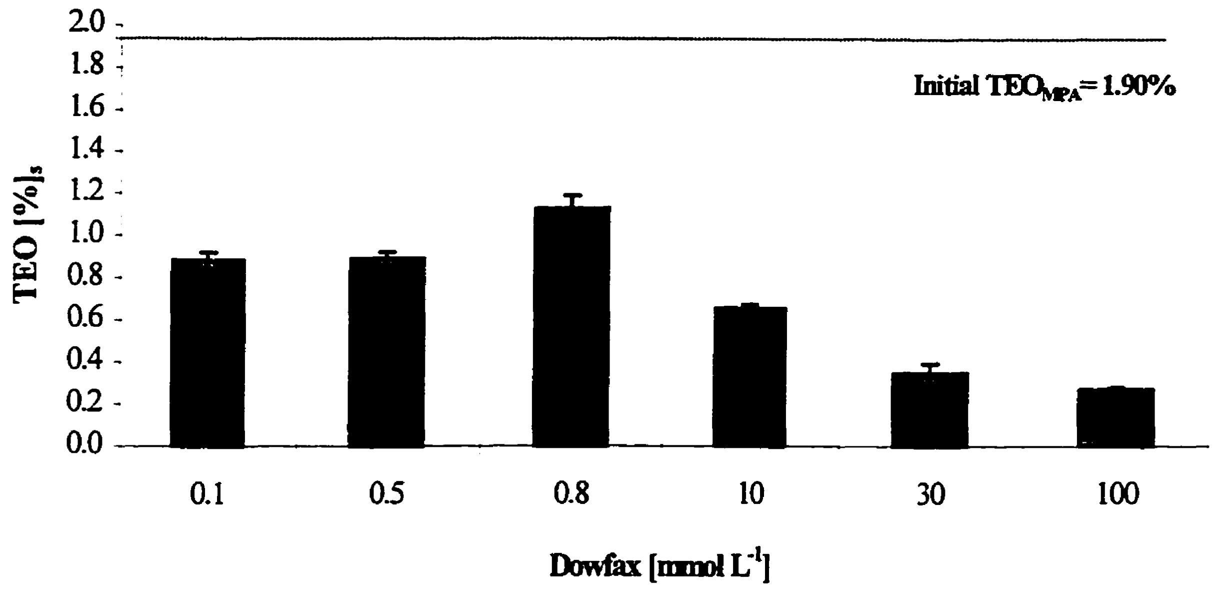


Figure 4.28. **TEO_{MC} [% $_{(s)}$ dry soil] reductions following sequential Dowfax washing of MPA soil**

The apparent trend indicates that Dowfax concentrations that facilitated micellar solubilization (10, 30 and 100mM) elevated TEO_{MC} reductions compared to the remaining treatments. Further, those Dowfax concentrations that facilitated emulsification (0.1 and 0.5mM) enhanced TEO_{MC} reductions compared to 0.8mM. Low concentrations of Dowfax (0.1, 0.5 and 0.8mM) were able to dissolve or disperse almost 50% of the TEO in the MPA soil. The loss of suspended fine particulates during sequential washing, and its associated contaminant fraction, has been described previously in Section 4.5.1.4. The results from the MPA soil mass balance indicate that approximately 5% of the soil mass was lost during sequential washing (Appendix B). The total fines fraction (silt + clay) accounts for approximately 5% of MPA soil mass (Table 4.1). Losses of this soil fraction could account for the substantial TEO reductions observed with low concentrations of Dowfax. Note that 1.0mM Dowfax samples were lost through experimental error and are therefore not included in Figure 4.26.

Sequential Dowfax washing of MPA soil produced significant reductions in TEO_{MC} content at each surfactant concentration compared to pretreatment TEO_{MC} values, as determined through ANOVA (SAS) with a Tukey test ($P < 0.05$).. Statistical analyses of TEO_{MC} reductions following sequential washing are summarized in Table 4.12.

Table 4.12. TEO_{MC} Reductions Following Sequential Washing of MPA Soil

Dowfax [mM]	Statistical Significance (P<0.05)	Statistical Significance Amongst Treatments
0.1	sd	*
0.5	sd	*
0.8	sd	**
10	sd	***
30	sd	****
100	sd	****

Note: 1) sd indicates TEO_{MC} values have demonstrated significant reductions ($P<0.05$) following sequential treatment relative to pretreatment values
2) Treatments with same number of * are not significantly different ($P<0.05$)
3) 1.0mM treatments broke in centrifuge

Examination of TEO_{MC} reductions suggests that although PAHs may have been removed from the contaminant matrix, a pool of relatively nonlabile organic material remains (Refer to Section 4.5.1.4.). TEO levels within MPA samples following sequential washing exceed both Alberta Tier I Criteria and CCME Guidelines (Table 4.4) for all treatments employed.

4.5.2.5. Implications of MPA Sequential Washing

A number of insights were gained from sequential washing experiments. First, sequential Dowfax washing of the more heavily contaminated MPA soil facilitated significant mass transfer of PAHs from the soil to surfactant solution phase. Micellar solubilization again proved to be effective in reducing all target PAH concentrations within the soil. Second, there exists a readily accessible contaminant pool that can be removed relatively rapidly through micellar solubilization (30 and 100mM) with 2-3 successive extractions (Section 4.5.1.5). In contrast, a more nonlabile contaminant fraction exists that requires extensive sequential washing for removal from the soil matrix. These results are consistent with the notions of contaminant aging and nonequilibrium desorption (Alexander, 1995). Third, emulsion formation appears contingent upon levels of both hydrocarbon and surfactant within the system. Emulsion formation occurred with 0.1 and 0.5mM Dowfax treatments and continued until a critical amount of hydrocarbon was removed through sequential washing. Emulsion formation ceased after one and three extraction periods, respectively, for 0.5mM and 0.1mM Dowfax treatments. Coalescence of oil droplets on the soil surface was observed following 0.8 and 1.0mM treatments that terminated the emulsification process. The reasons for observed oil droplet coalescence are unclear. Dilution of 0.8 and 1.0mM concentrations of Dowfax, while attempting to remove residual surfactant solution, also facilitated emulsion formation indicating the role of reduced surfactant concentrations in emulsification.

4.6. The Role of Hydrocarbon and Surfactant Concentrations in Defining the Zone of Emulsification

To examine the roles of hydrocarbon and surfactant concentrations on emulsion formation a more heavily contaminated soil (HPA; $TEO_{MC} = 8.20\%$), taken from the same creosote-contaminated site, was employed in a single, 24 hour, soil washing design as outlined in Section 3.3.5. Soil characteristics of HPA are provided in Tables 4.1

through 4.3. The ten Dowfax concentrations incorporated within previous soil washing experiments were utilized. Results from soil washing trials are presented in Table 4.13.

Table 4.13. Enhanced PAH Mass Transfer [mg kg^{-1}dry soil] Following 24 hour Dowfax Washing of HPA Soil

	Dowfax Concentration [mmol L^{-1}]									
PAH	0.01	0.05	0.08	0.10	0.50	0.80	1.0	10	30	100
Anthracene	1.18	8.29	9.98	19.47	55.39	144.56	207.59	37.50	75.97	237.07
Chrysene	nd[1]	4.45	5.41	14.17	44.09	115.93	153.93	20.21	36.38	122.63
BaP	nd[2]	3.37	4.12	9.52	31.53	77.52	106.74	13.51	23.79	81.89

[1] indicates chrysene not detectable (detection limit = 3 ug kg^{-1})

[2] indicated benzo(a)pyrene not detectable (detection = 7 ug kg^{-1})

The addition of Dowfax produced apparent increases in PAH mass transfer to the solution phase relative to ddH$_2$O. Statistical evaluation of apparent PAH solubility enhancement is provided in Section 4.6.1. Emulsification was evident within 0.1, 0.5, 0.8 and 1.0mM Dowfax samples. Emulsification occurred over a different range of Dowfax concentrations, than witnessed with MPA soil washing, and was effective at facilitating PAH mass transfer. Emulsification at 1.0mM facilitated greater chrysene and benzo(a)pyrene mass transfer than did micellar solubilization at 100mM Dowfax. Micellar solubilization was observed following 10, 30 and 100mM Dowfax treatments. PAH solubility enhancement through suspected monomer and/or weak micellar solubilization was observed following 0.01, 0.05 and 0.08 Dowfax treatments. The zones of emulsification and solubilization are presented in Figure 4.29.

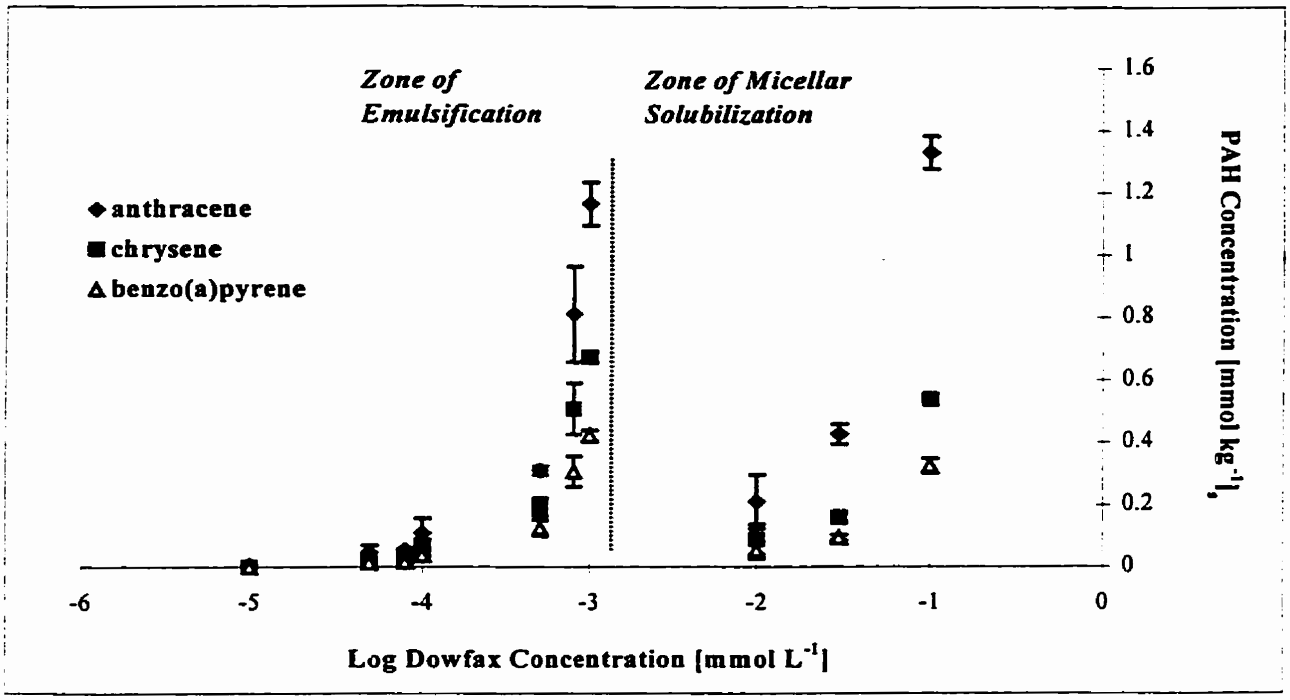


Figure 4.29. **Aqueous PAH concentrations [mmol kg$^{-1}{}_{(S)}$ dry soil] following 24 hour Dowfax washing of HPA soil**

4.6.1. Statistical Evaluation of PAH Mass Transfer Following Dowfax Washing of HPA Soil

Changes in solution PAH concentrations following 24 hour Dowfax-8390 washing of HPA soil were examined with ANOVA (SAS) and a corresponding Tukey test ($P < 0.05$). A summary of statistical analyses is presented in Table 4.14.

Table 4.14. PAH Mass Transfer Following Dowfax Washing of HPA Soil

	Anthracene		Chrysene		Benzo(a)pyrene	
Dowfax [mM]	Dowfax vs ddH$_2$O	Amongst Treatments	Dowfax vs ddH$_2$O	Amongst Treatments	Dowfax vs ddH$_2$O	Amongst Treatments
0.01	nsd	*	nsd	*	nsd	*
0.05	nsd	*	nsd	*,**	nsd	*
0.08	nsd	*,**	nsd	*,**	nsd	*
0.1	nsd	*,**	nsd	*,**	nsd	*
0.5	sd	**,***	sd	***	sd	**
0.8	sd	****	sd	*****	sd	****
1.0	sd	*****	sd	******	sd	*****
10	sd	**	sd	**,****	nsd	*,***
30	sd	***	sd	***,****	sd	**,***
100	sd	*****	sd	*****	sd	****

Note: 1) nsd indicates not significantly different from ddH$_2$O control ($P < 0.05$)
2) sd indicates significantly different from ddH$_2$O control ($P < 0.05$)
3) Treatments with same complement of * are not significantly different ($P<0.05$)

Significant increases in PAH solubility were observed through emulsification with 0.5, 0.8 and 1.0mM Dowfax treatments ($P<0.05$). HPA soil washing with 10mM Dowfax produced apparent PAH solubility enhancement (Table 4.14), however the enhancement was found to be non-significant ($P<0.05$).

4.6.2. Implications of HPA soil washing

The range of emulsification stretched from 0.1 to 1.0mM Dowfax suggesting that emulsion formation may be system dependent. Recall that emulsion formation within the MPA soil ranged from 0.05 to 0.5mM Dowfax. Emulsification was effective at facilitating PAH mass transfer following 24 hr washing of HPA soil. Chrysene and benzo(a)pyrene solubility enhancements following emulsification with 1.0mM Dowfax were greater than their observed concentrations following 100mM solubilization (Figure 4.29).

Coalesced oil droplets were noticed on the soil surface following 10mM Dowfax washing for 24 hours. Emulsion stability is dependent upon the resistance of the dispersed oil within the system to coalescence (Myers, 1988). Results suggest that coalescence of oil droplets may have terminated the emulsification process as described in Section 4.5.2. Fine silt and clay particles were also observed to settle out of solution with 10mM Dowfax treatment. Recall that silt and clay were observed to settle out of the emulsion following freezing and thawing experiments (Section 4.3.2.1). Emulsions may be stabilized by the presence of finely divided solids, such as silt and clay, at the interface between the dispersed (oil) and continuous (water) phases (Myers, 1988). As Dowfax is anionic, the addition of increasing concentration would elevate the amount of charge in the system. The elevated charge may have destabilized the finely divided solids from the emulsion interface, facilitated oil droplet coalescence and terminated emulsification (Myers, 1988). The influence of increasing Dowfax concentration on fine particulates may account for the observed cessation of emulsification prior to micellar solubilization at 10mM Dowfax (Figure 4.29). Note that this assertion is based on qualitative interpretation and requires experimental validation.

Within the HPA system, emulsification may persist longer under a sequential washing scheme than did the emulsions within the MPA system. The presence of a larger NAPL reserve may allow for the persistence of emulsion over several sequential washing treatments. As there is an elevated oil pool present, emulsion formation may continue for an extended period until the critical oil level is removed. Within the MPA system, (TEO_{MC}= 1.9%) this critical oil load removed with 2-3 successive extractions.

Utilizing emulsification may be desirable in remediating more heavily contaminated soils as lower surfactant concentrations can be employed until the critical NAPL load is removed from the system. Once cessation of emulsification occurs, micellar solubilization may be employed to facilitate the remainder of contaminant mass transfer. Emulsification may also enhance solubilization due to the increased contaminant surface area within an emulsion system. For instance, if 10mL of oil is emulsified in water to produce a droplet diameter of 0.2mm, the resulting oil-water interfacial area increases by a factor of 10^6 (Myers, 1988). Experimental results indicate that emulsification can facilitate PAH mass transfer, however, the factors controlling emulsion formation (surfactant concentration and oil content) are system specific.

Micellar solubilization with 10, 30 and 100mM Dowfax produced significant increases in all target PAH concentrations. Recall that similar results were observed during LPA and MPA soil washing trials.

4.7. The Role of Surfactant Mechanisms in PAH Mass Transfer From Weathered Creosote Contaminated Soils

The addition of surfactants to contaminated soils can enhance the apparent solubility of hydrophobic organic constituents through various mechanisms. Experimental results, provided in Sections 4.4, 4.5 and 4.6, suggest that emulsification and micellar solubilization can facilitate extensive PAH mass transfer. PAH mass transfer may vary amongst surfactant mechanisms and this section was designed to delineate how individual PAH mass transfer occurs during both micellar solubilization and macroemulsification relative to the other PAHs within the system.

4.7.1. PAH Mass Transfer Through Micellar Solubilization

While most studies of micellar solubilization of PAH have concentrated on individual compounds, PAHs exist within complex mixtures of multiple constituents at contaminated sites. Partitioning into the micelle has been found to be independent of the source of contamination (sorbed, residual saturation) and dependent only on the concentration of the contaminant outside the micelle (Rouse et al., 1993). Micellar solubilization was analyzed following the initial extraction of LPA, MPA and HPA soils with 10, 30 and 100mM Dowfax. The zones of micellar solubilization for LPA, MPA and HPA soils are provided in Figure 4.30 through 4.32. Note that Dowfax concentration is now expressed in these graphs in mol L^{-1}. The inflection point in the apparent PAH solubility curve indicates that the cmc_{tens} value (0.5-1.0mM) is close to the observed cmc_{sol} (0.8-1.0mM).

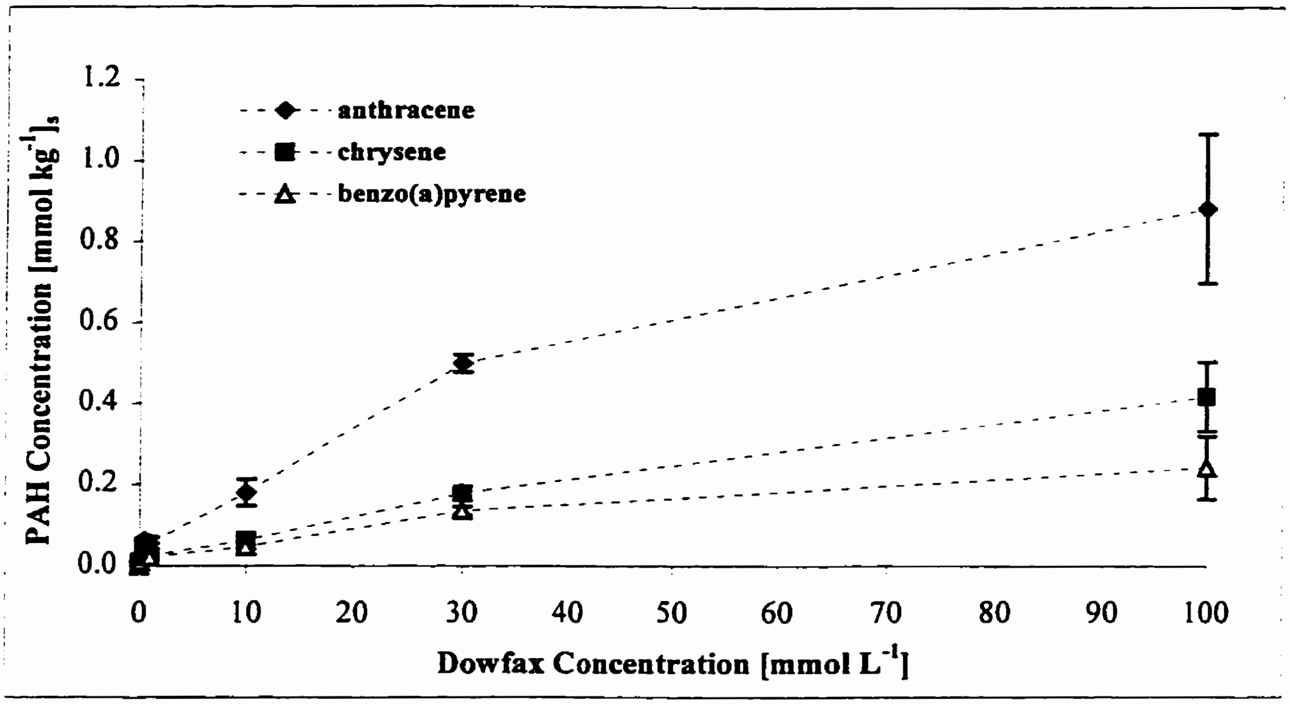


Figure 4.30. Micellar solubilization of target PAHs [mmol kg^{-1}$_{(s)}$ dry soil] following 24 hour washing of LPA soil

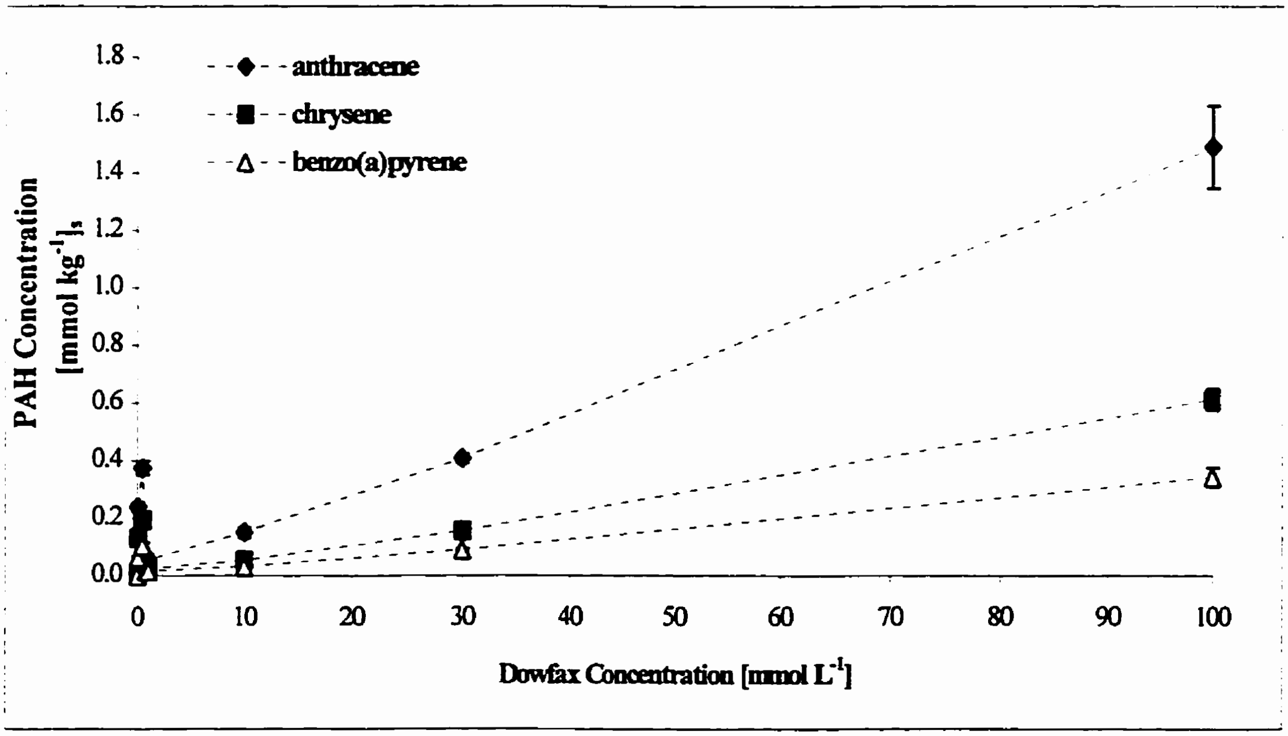


Figure 4.31. Micellar solubilization of target PAHs [mmol kg^{-1}$_{(s)}$ dry soil] following 24 hour Dowfax washing of MPA soil

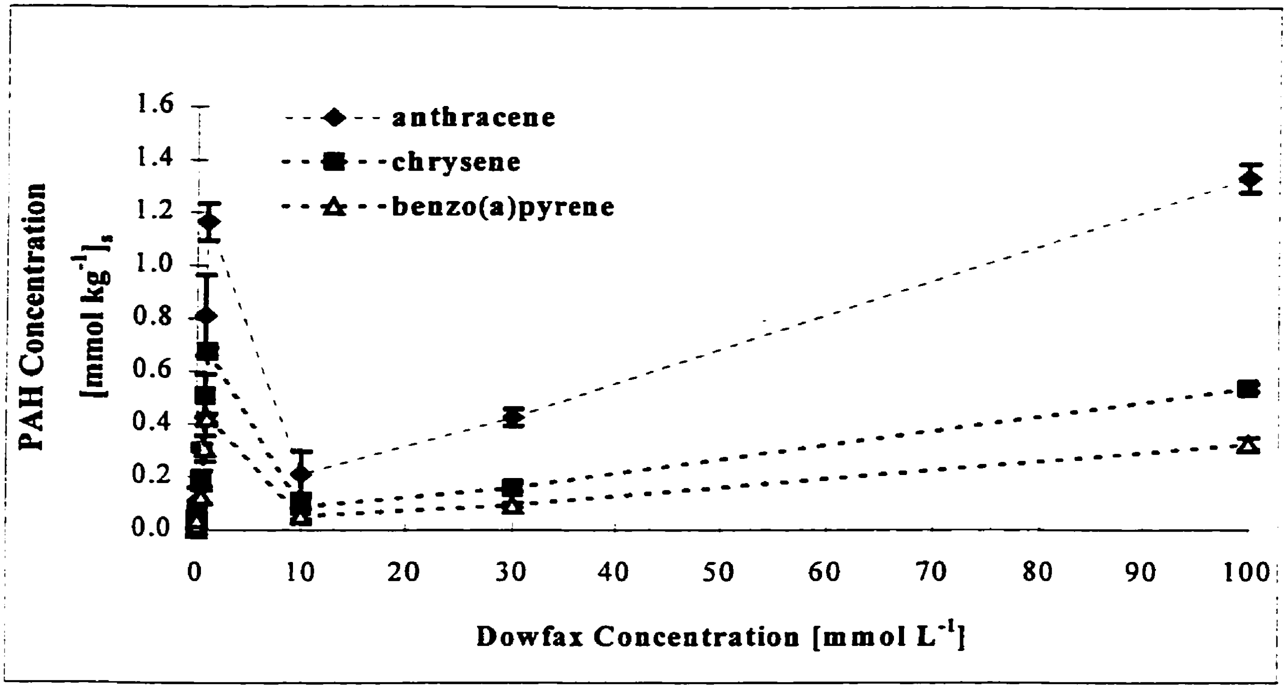


Figure 4.32. Micellar solubilization of target PAHs [mmol kg^{-1}$_{(s)}$ dry soil] following 24 hr Dowfax washing of HPA soil

The molar solubilization ratio (MSR) is the ratio of the moles of organic contaminant solubilized to the moles of surfactant in micellar form. The MSR can be obtained from the slope of the solubility curve above the cmc (Pennell et al., 1997). In this case the MSR was determined from the slope of solubilization curve above the cmc$_{sol}$ for each soil. Molar solubilization ratio calculations for target PAHs within each soil are provided in Appendix D. The MSR for anthracene, chrysene and benzo(a)pyrene are summarized in Table 4.15 for each soil.

Table 4.15. Molar Solubilization Ratios for Selected PAHs

	Molar Solubilization Ratios		
PAH	LPA Soil	MPA Soil	HPA Soil
Anthracene	0.007798	0.01485	0.01244
Chrysene	0.003932	0.006215	0.004985
Benzo(a)pyrene	0.002172	0.003453	0.003012

The observed reduction in MSR values for all target PAHs within the LPA soil, compared to MPA and HPA values, was unexpected. A possible explanation for this observation is that the concentration of contaminant outside the micelle, within the LPA system, is not sufficient to completely saturate the 100mM Dowfax solution. Recall that PAH solubility enhancement increases linearly with increasing surfactant concentration only in the presence of excess hydrophobic solute. The 100mM Dowfax solution may not be filled to capacity during LPA washing due to the lack of excess PAH. Conversely the 100mM solutions following MPA and HPA washing are saturated. The MSR values for the LPA soil without the inclusion of the 100mM data are: 0.015986, 0.005743 and 0.004438 for anthracene, chrysene and benzo(a)pyrene respectively. These adjusted MSR values are similar to those observed during MPA and HPA soil washing (Table 4.15). MSR results suggest that micellar solubilization operates similarly for individual PAHs regardless of the three soils analyzed.

Apparent PAH concentrations indicate that solubilization occurred in the following order within all examined soils: anthracene > chrysene > benzo(a)pyrene. Studies have suggested that hydrophobic PAHs will not compete for the limited residence volume within the micellar core (Yeom et al., 1995). Consequently, PAH concentrations were normalized for their respective concentrations within contaminated soils according to:

$$\mathrm{PAH}_{NORM} = \frac{\mathrm{PAH}_{SOL}\ [\mathrm{mmol\ kg^{-1}}]}{\mathrm{PAH}_{SOIL}\ [\mathrm{mmol\ kg^{-1}}]}$$

Where: PAH_{NORM} = normalized PAH concentration
PAH_{SOL} = PAH concentration within surfactant solution [mmol kg^{-1}]
PAH_{SOIL} = PAH concentration within soil [mmol kg^{-1}]

Normalized PAH solubility curves are supplied in Appendix E. The PAH_{NORM} values were then compared amongst PAHs for 10, 30 and 100mM Dowfax treatments. Results suggest that once the solubilization data is normalized for the amount of PAH within the soil, no significant difference amongst PAHs exists (SAS; ANOVA; $P<0.05$). Statistical examination amongst target PAHs with each Dowfax concentration was conducted with an ANOVA (SAS) using a Tukey test ($P<0.05$) and is reported in Appendix E (Tables 1-

3). The general outcome of this analysis supports the notion that hydrophobic PAHs will not compete for micelle volume.

4.7.2. PAH Mass Transfer Through Macroemulsification

The process of emulsification has received limited research attention within environmental applications. Results from this study suggest that both surfactant and hydrocarbon concentrations influence emulsion formation/deformation. While partitioning into the micelle is independent of whether contamination exists sorbed, or within residual or pooled NAPL; emulsification should be dependent on the contaminant source. Emulsification would not be able to access those contaminants that are sorbed to the contaminant matrix and could only mobilize, through interfacial tension reductions, those contaminants within residual or pooled NAPL of specific dimensions. Emulsions were composed, in this instance, of oil dispersed within water. Emulsified PAH levels were normalized for their concentration within the contaminated soil system (as described in 4.7.1) and were compared amongst PAHs for each treatment (Appendix E). The ratios of PAHs within the emulsion were expected to coincide with the relative PAH ratios within the contaminated soil matrix and once normalized should be close to one. Recall that emulsification operated within MPA and HPA soils and not in the LPA soil. Apparent increases in chrysene and benzo(a)pyrene relative to anthracene were observed during emulsification in MPA and HPA soil washing treatments. Statistical examination amongst target PAHs with each Dowfax concentration was conducted with ANOVA (SAS) using a Tukey test ($P<0.05$) and is reported in Appendix E.

Findings suggest that chrysene and benzo(a)pyrene may be removed preferentially through emulsification relative to anthracene. Emulsification produced significantly ($P<0.05$) greater mass transfer of chrysene compared to anthracene with 0.1 and 0.5mM treatments during MPA soil washing (Table 2, Appendix E). Emulsification during 1.0mM Dowfax treatment of HPA soil produced significantly ($P<0.05$) greater mass transfer of chrysene and benzo(a)pyrene relative to anthracene (Table 3, Appendix E). Emulsification during 0.8mM Dowfax treatment of HPA soil produced an apparent increase in chrysene and benzo(a)pyrene relative to anthracene, however the increase was not significant ($P<0.05$).

The unexpected discrepancy amongst PAH concentrations within the emulsion may result from: 1) the PAH ratios within those oil droplets that form emulsions not corresponding to the PAH ratios provided by total contaminated soil extracts, 2) different chemical properties of individual PAHs and 3) experimental error and sample variability. Emulsions form with smaller oil droplets of specific dimensions, those droplets that are too large may not engage in this process. The smaller droplets that can become emulsified have large surface area to volume ratios. Thus, the PAH concentrations within the smaller oil droplets may contain reduced levels of anthracene as it possesses both higher water solubility and vapor pressure (Table 2.1).

4.8. Surfactant Sorption During Washing of Creosote Contaminated Soils

One of the primary factors controlling the efficacy of surfactant washing is the monetary cost associated with surfactant losses to the soil matrix (Krebs-Yuill et al., 1995). Dowfax-8390 is a dianionic surfactant that has demonstrated limited losses to various soils through either sorption or precipitation mechanisms. Anionic surfactants are resistant to sorption within soils with alkaline pH values, due to charge repulsion from negatively charged surface sites. Twin head group anionic surfactants demonstrate a reduced tendency to precipitate in solution compared to single head group anionic surfactants due to increased solubility (Rouse et al., 1993). To evaluate surfactant losses to contaminated soil matrices, batch sorption assays were conducted for LPA, MPA and HPA soils (as described in Section 3.3.6).

Dowfax losses during LPA soil washing were not observed. The creosote-contaminated soils utilized within soil washing experiments were all slightly alkaline in nature (pH values ranged from 7.6 to 8.0) and would possess a negative surface charge. Further, these soils are subsurface in nature and partitioning into natural organic matter would be negligible. Results from additional Dowfax sorption assays within various non-contaminated soils, of various textures and levels of native organic matter, produced similar findings (Salloum et al., 1998). Increased charge and steric hindrance to sorption are provided by the presence of the dual ionic groups in the Dowfax structure, potentially accounting for these results (Rouse and Sabatini, 1993).

Low levels of Dowfax were observed to partition/sorb during MPA soil washing. The sorption isotherm is represented in Figure 4.33. Dowfax sorption follows a Langmuir isotherm with a plateau reached above the cmc value. Similar trends have been documented in numerous studies for other surfactants (Liu et al., 1992; Pennell et al., 1993). Surfactant may be expected to partition into soils possessing higher levels of organic contamination, or NAPLs, such as that found within the MPA soil (TEO_{MC} = 1.9%). While Dowfax partitioning may have been evident, the losses to the soil matrix appear inconsequential. Q_{MAX} is used to characterize the maximum surfactant load onto the soil in a micellar solution. A Q_{MAX} value of 26.3 ug kg^{-1} was observed during MPA washing at 100mM Dowfax.

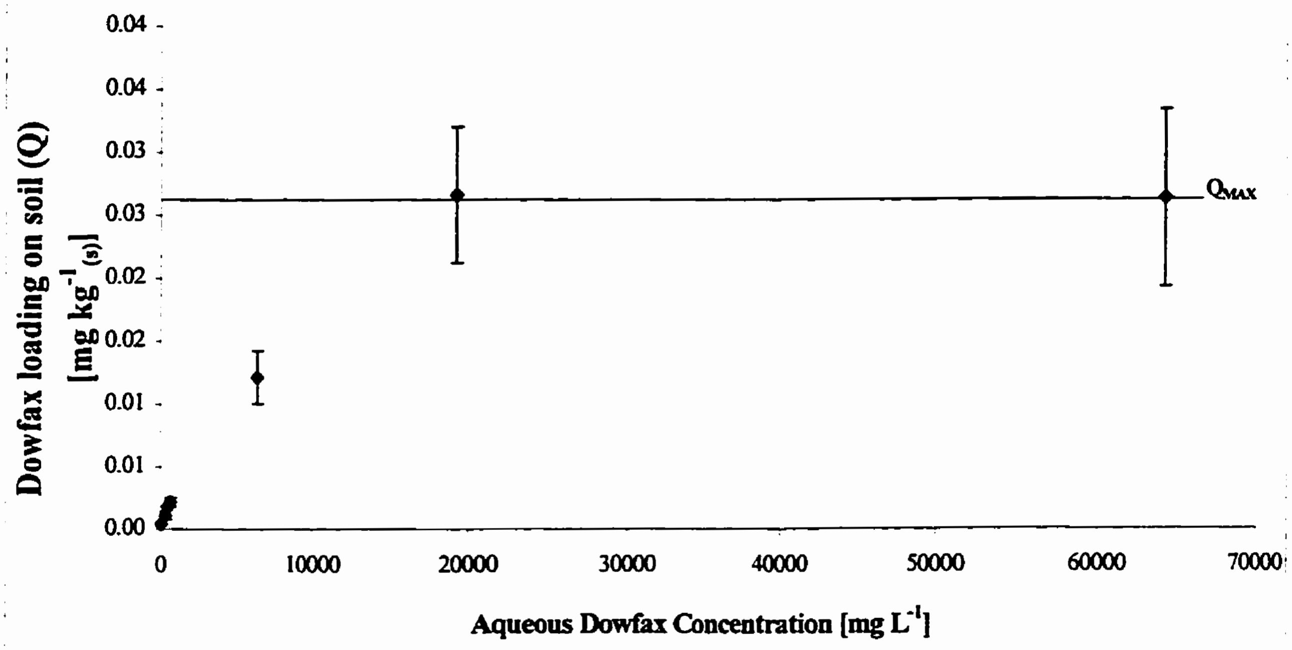


Figure 4.33. Sorption of Dowfax [mg $kg^{-1}_{(s)}$ dry soil] on MPA soil

Low levels of Dowfax-8390 were found to sorb/partition during HPA washing. The sorption isotherm is represented in Figure 4.34. A linear regression was plotted with an R^2 value 0.97 obtained for the isotherm. Dowfax losses may again be explained through partitioning into the NAPL phase. The oil content within the HPA system (TEO_{MC} = 8.2 %) is larger than that witnessed within the MPA system (TEO_{MC} = 1.9%) and as such

Dowfax losses through partitioning into the NAPL would be expected to be greater. A Q_{MAX} value of 100 ug kg^{-1} was observed following 100mM Dowfax washing.

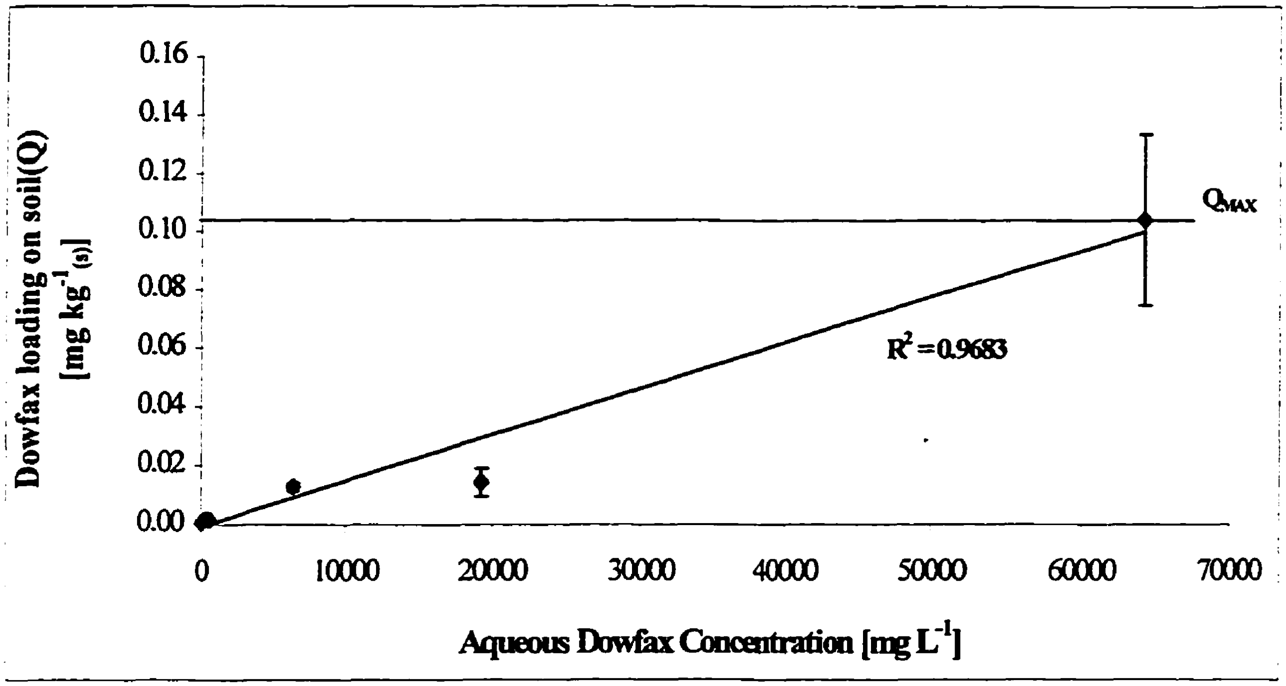


Figure 4.34. Sorption of Dowfax [mg $kg^{-1}{}_{(s)}$ dry soil] on HPA Soil

4.8.1. Implications of Sorption Assays

Losses of Dowfax to MPA and HPA soils were observed following 24 hr surfactant washing. Partitioning into the residual pooled NAPL has been identified as the potential mechanism of Dowfax loss within these soils. While some sorption losses were observed, the values were thought to be minimal in MPA and HPA soils as expressed by the Q_{MAX} values. Dowfax-8390 appears to be an ideal surfactant to utilize within soil remediation applications given its resistance to sorption losses even in the presence of gross levels of creosote contamination.

Chapter 5. Conclusions

The present study was undertaken to examine: 1) the efficacy of surfactant washing for facilitating the remediation of weathered creosote contaminated soils and 2) those surfactant mechanisms responsible for contaminant removal. The efficacy of surfactant washing was evaluated in terms of: 1) facilitating PAH and total extractable organic (TEO) removal from weathered contaminated soils and 2) surfactant losses to the contaminated soil matrix. Creosote contaminated soils were washed with various concentrations of surfactant. Soil and solution analyses, during and after soil washing, provided insights into both contaminant mass transfer and those mechanisms responsible for mass transfer.

5.1. PAH Removal

Dowfax washing of weathered creosote contaminated soils produced significant PAH mass transfer to the solution phase. Substantial reductions in soil PAH concentrations were observed upon completion of sequential washing experiments. Micellar solubilization was very efficient in facilitating the majority of PAH mass transfer from soil within 2-3 sequential extractions. Mass transfer limitations may be a factor involved in the slow removal efficiceny observed after most of the PAH mass was removed. Micellar solubilization operated within all soils studied, irrespective of the level of soil contamination (TEO_{MC}). Results suggest that micellar solubilization could be used to significantly reduce initial contaminant mass within weathered creosote contaminated soils.

Emulsions were observed to form during Dowfax washing of the more heavily contaminated MPA and HPA soils. Emulsions only formed in the presence of lower Dowfax concentrations and at specific mixing time frames. Emulsification substantially enhanced target PAH mass transfer particularly within the most contaminated soil (HPA). The cessation of emulsification may have resulted from the reduction of oil within the system, during sequential soil washing, to a level not amenable to emulsion formation. The observed influence of surfactant concentrations on emulsion formation and stabilization is not clear. Examination of emulsion formation demonstrates that this process is system specific.

5.2. Total Creosote Removal

Dowfax washing of weathered creosote contaminated soils produced significant TEO_{MC} reductions irrespective of surfactant concentration. The loss of suspended silt and clay, and their associated contaminant fraction, during soil washing may account for this result. Observed TEO_{MC} reductions in the absence of significant hydrophobic PAH reductions suggests that a large portion of the TEO_{MC} may consist of more soluble organic constituents including diesel, phenolic compounds, heterocyclic compounds and soluble PAHs (naphthalene, acenapthene etc.). Sequential washing treatments that reduced target PAHs below regulatory were unable to achieve acceptable TEO_{MC} levels. A fraction of the TEO_{MC} may be either unavailable and/or unextractable by sequential Dowfax washing.

5.3. Surfactant Losses to Soil Matrix

Limited Dowfax losses were observed within the more heavily contaminated MPA and HPA soils. Sorption isotherms suggest partitioning into the NAPL phase as the likely cause of Dowfax losses. The lack of significant losses within highly contaminated soils, coupled with its capacity to enhance contaminant mass transfer, should make Dowfax-8390 attractive for remediation applications.

5.4. Future Research Initiatives

The present study has provided some fundamental knowledge on the efficacy of surfactant washing as a remediation technology for weathered creosote contaminated soils. Due to the observed mass transfer limitations observed during sequential washing, micellar solubilization could be used with subsequent biotreatment once nonequilibrium conditions are reached. A more practical approach may then involve employing surfactant washing to significantly reduce the initial NAPL contamination trapped within weathered soils, followed by biotreatment to achieve remediation goals. Further research should also identify processes by which surfactant recycling from spent wash solutions can take place and then subsequently reused.

The potential role of emulsification within surfactant remediation applications needs to be addressed particularly within heavily contaminated soils. Emulsions are formed in the presence of low surfactant concentrations and may be more cost-effective than micellar solubilization within initial *ex-situ* soil remediation applications. Results suggest that surfactant and hydrocarbon concentration influence emulsion formation and stabilization. However, the role of fine particulates in stabilizing emulsions should be experimentally evaluated. Further research into emulsion formation and stability within surfactant remediation applications is necessary. While surfactant washing appears promising for facilitating the remediation of weathered creosote contaminated soils, further study is required to determine both field scale and economic viability.

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Appendix A

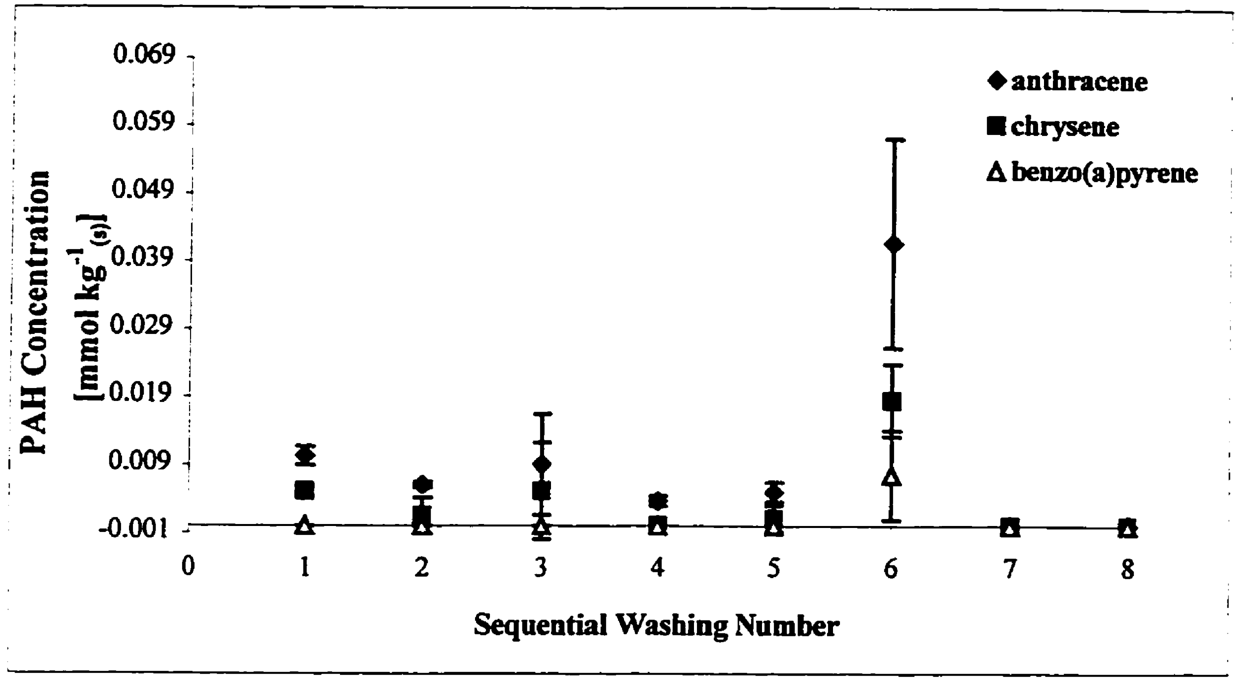


Figure 1. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential ddH$_2$O washing of LPA soil

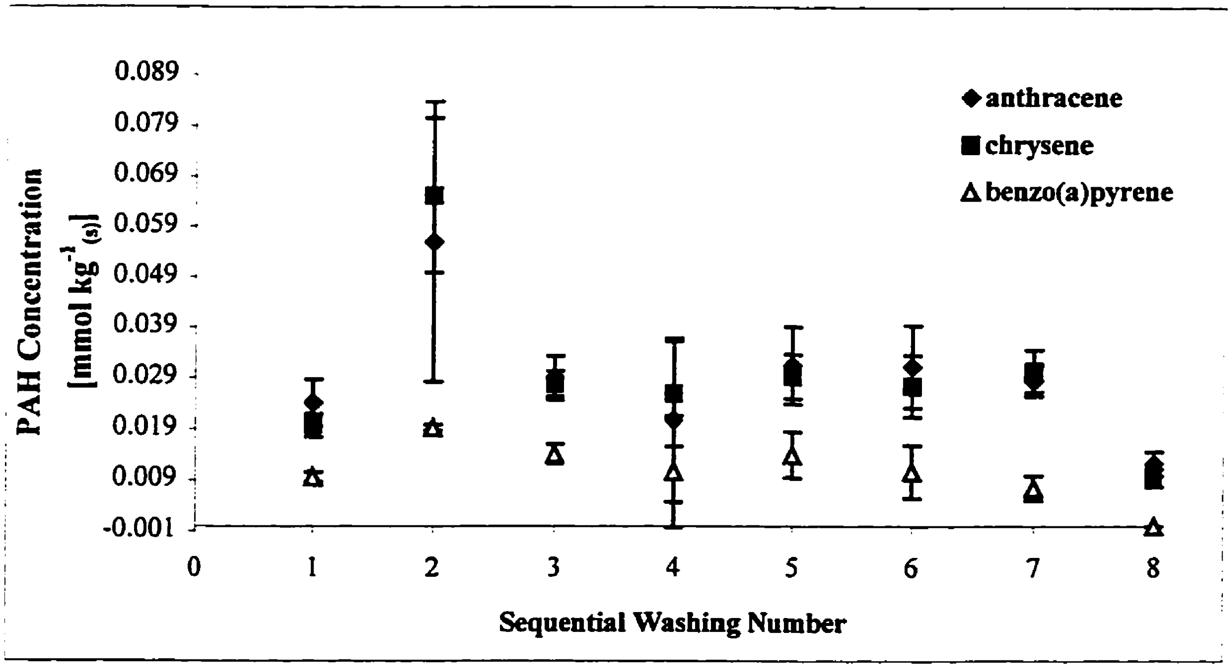


Figure 2. PAH Concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 0.1mM Dowfax washing of LPA soil

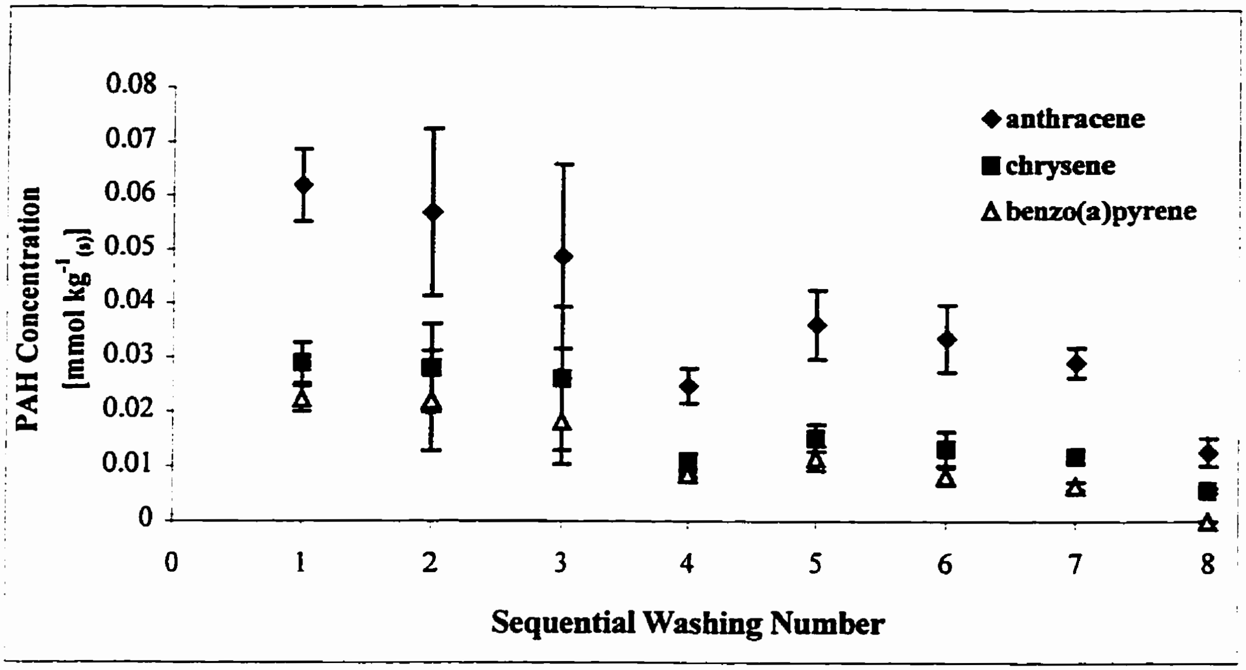


Figure 3. PAH concentrations [mmol kg$^{-1}_{(s)}$ dry soil] during sequential 0.5mM Dowfax washing of LPA soil

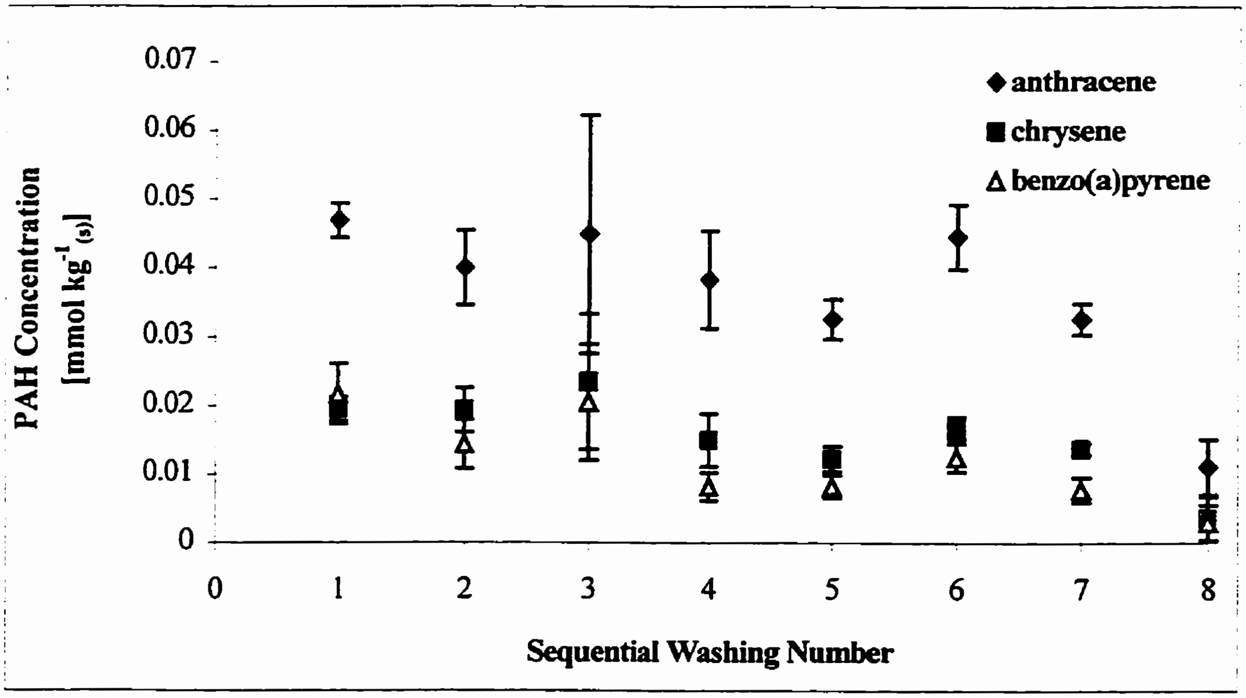


Figure 4. PAH concentrations [mmol kg$^{-1}_{(s)}$ dry soil] during sequential 0.8mM Dowfax washing of LPA soil

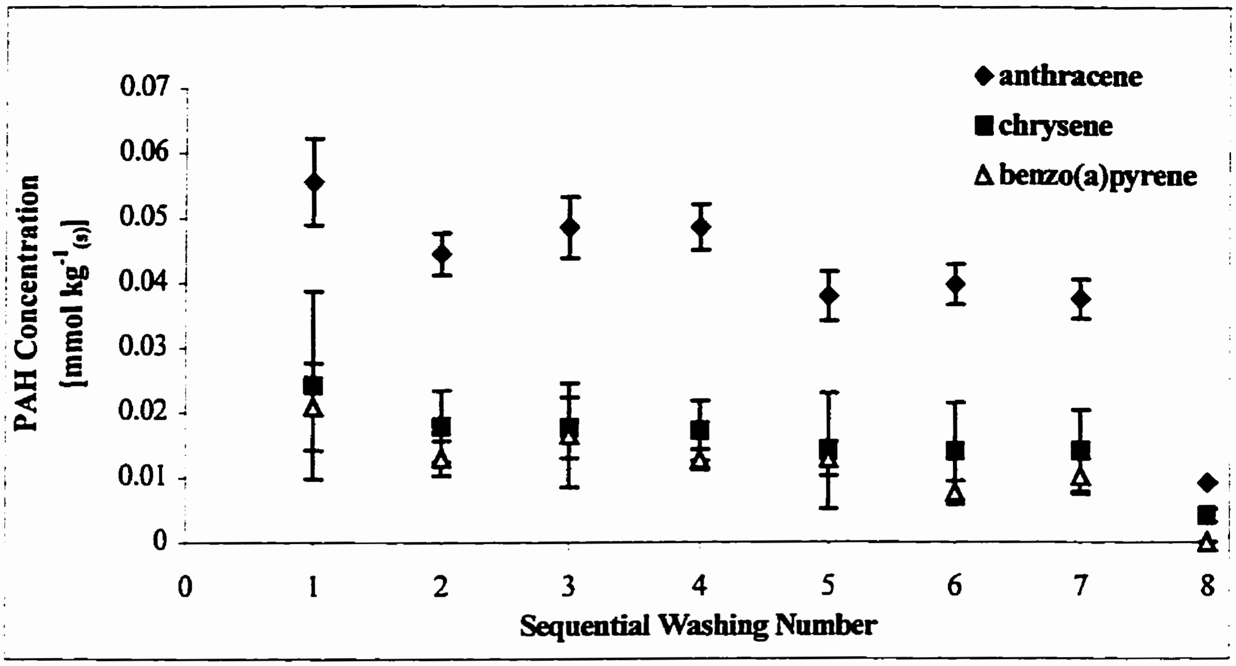


Figure 5. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 1.0mM Dowfax washing of LPA soil

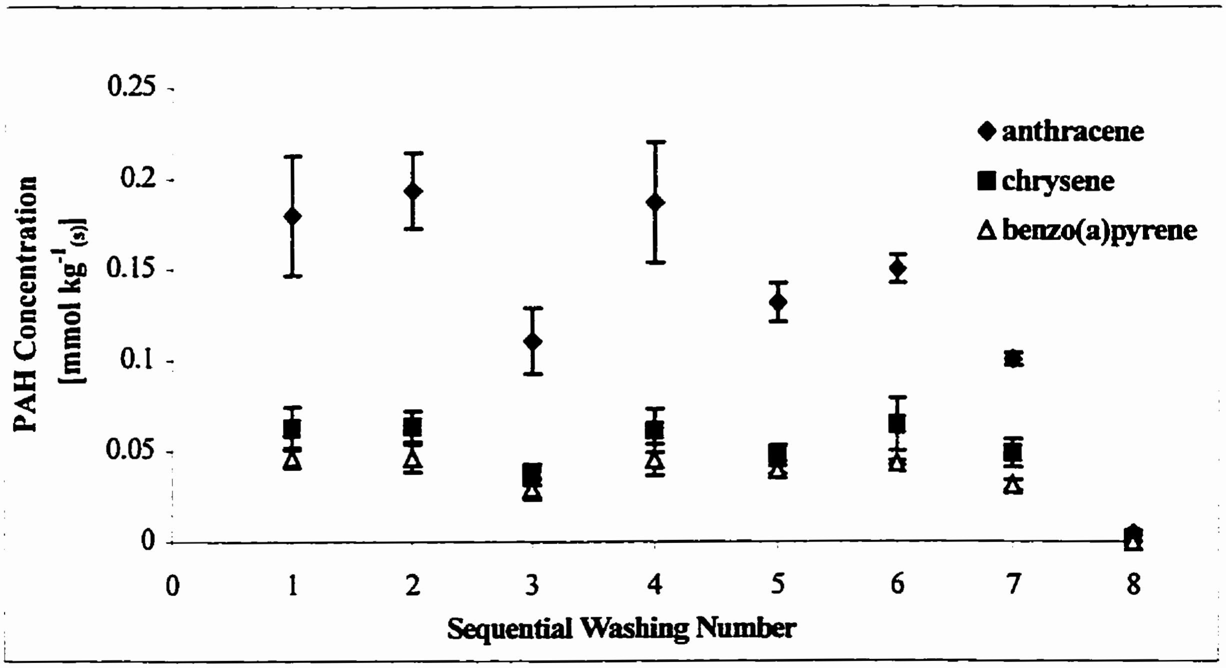


Figure 6. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 10mM Dowfax washing of LPA soil

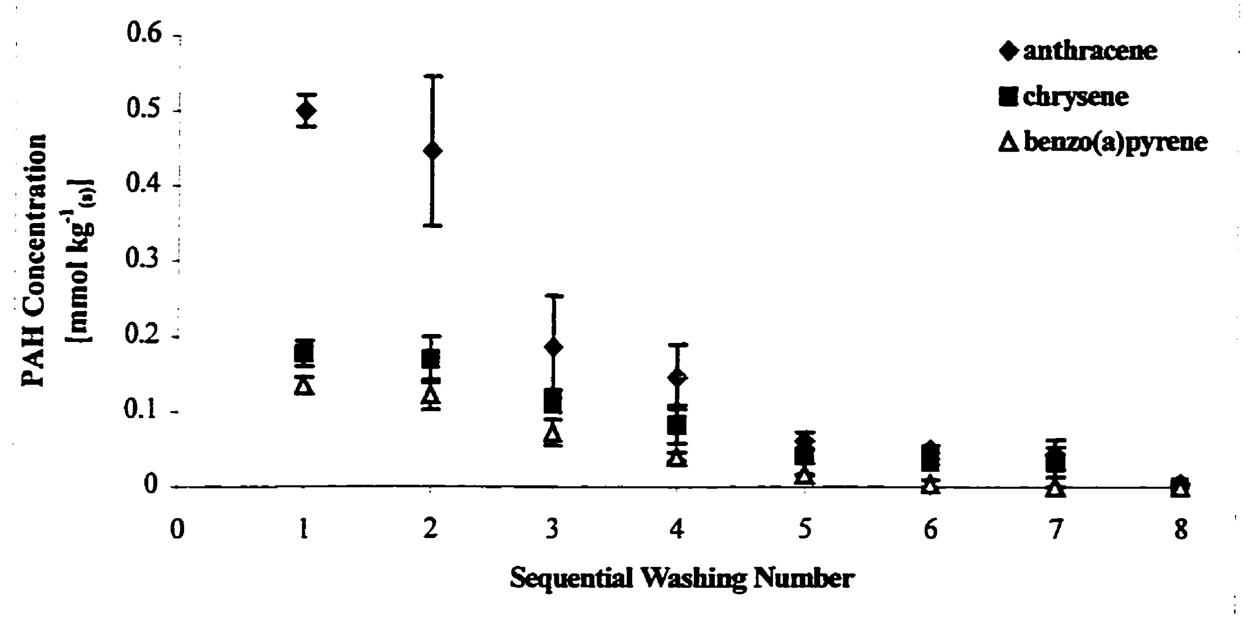


Figure 7. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 30mM Dowfax washing of LPA soil

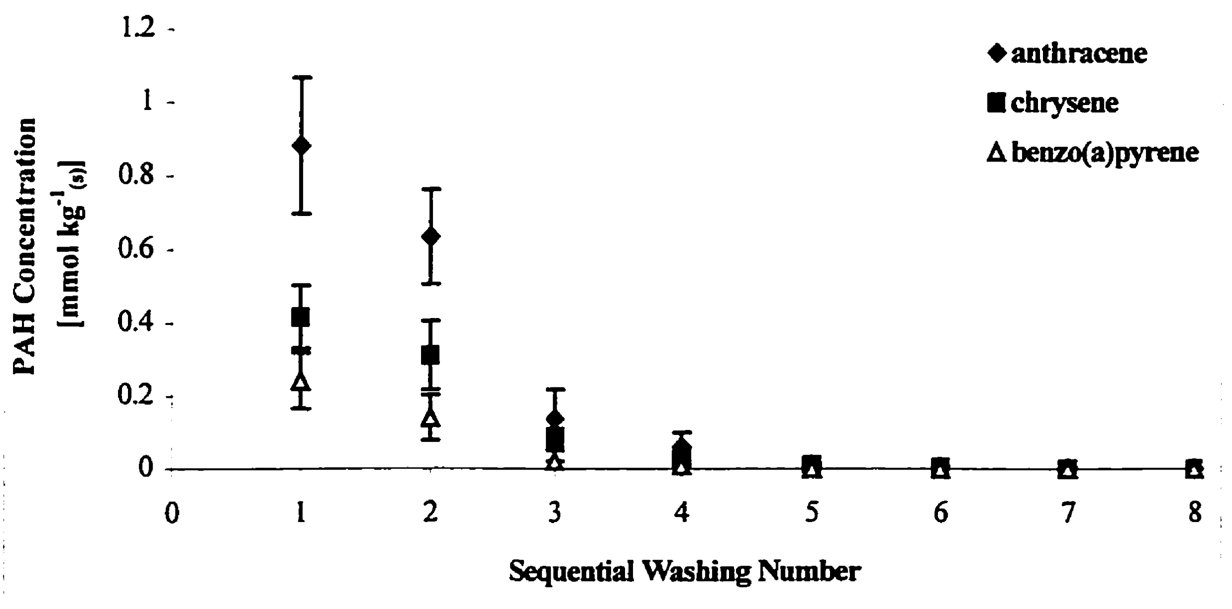


Figure 8. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 100mM Dowfax washing of LPA soil

Appendix B

Table 1. Soil losses [% dry weight] following sequential Dowfax washing of LPA and MPA soils

Dowfax Treatment	Mean % loss of LPA soil following sequential washing experiment	Mean % loss of MPA soil following sequential washing experiment
0	Undetermined*	4.61 ± 0.326
0.1mM	3.48 ± 0.077	4.37 ± 0.074
0.5mM	3.24 ± 0.088	4.51 ± 0.226
0.8mM	3.41 ± 0.134	4.61 ± 0.250
1.0mM	3.30 ± 0.280	4.33 ± 0.003
10mM	4.56 ± 0.420	5.46 ± 0.048
30mM	5.14 ± 0.001	6.28 ± 0.151
100mM	4.34 ± 0.043	6.02 ± 0.160

* denotes samples were lost due to experimental error

Appendix C

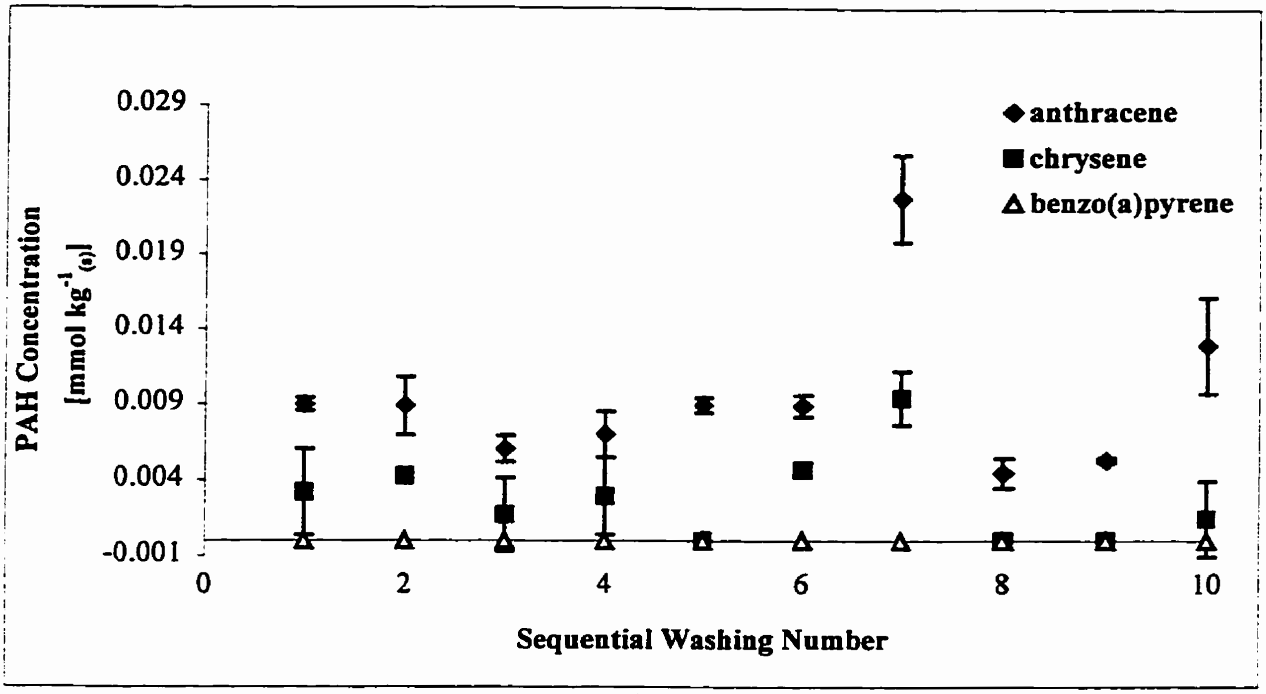


Figure 1. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil]during sequential ddH$_2$O washing of MPA soil

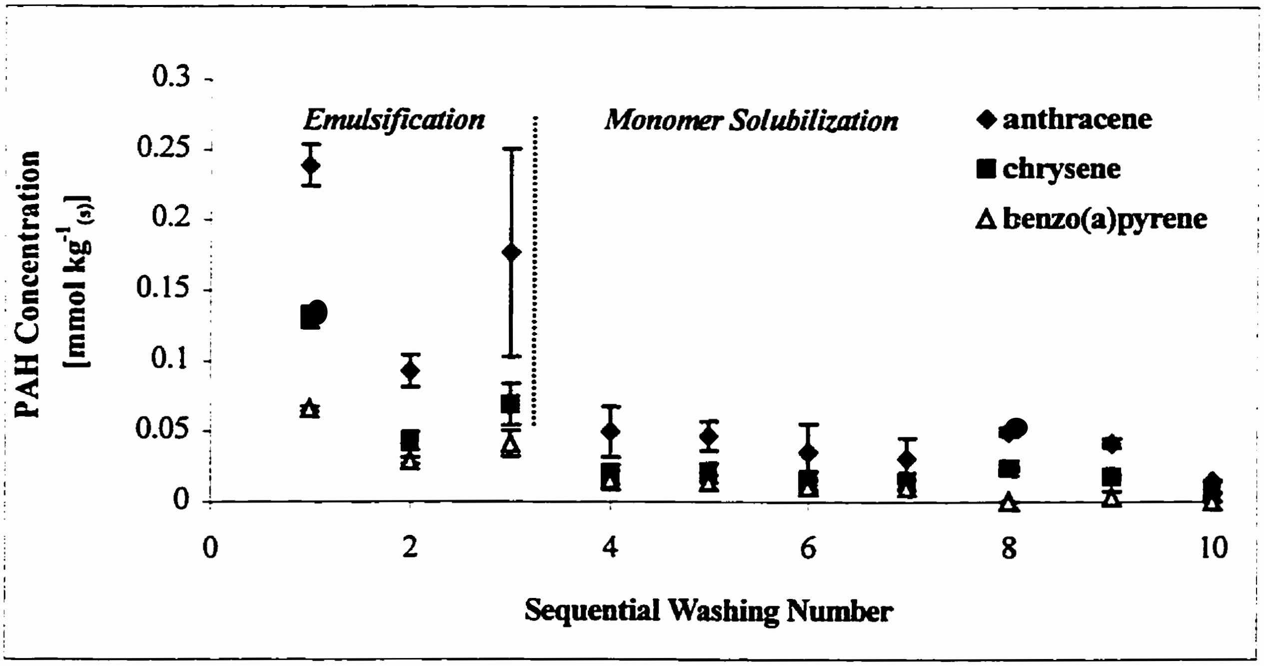


Figure 2. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 0.1mM Dowfax washing of MPA soil

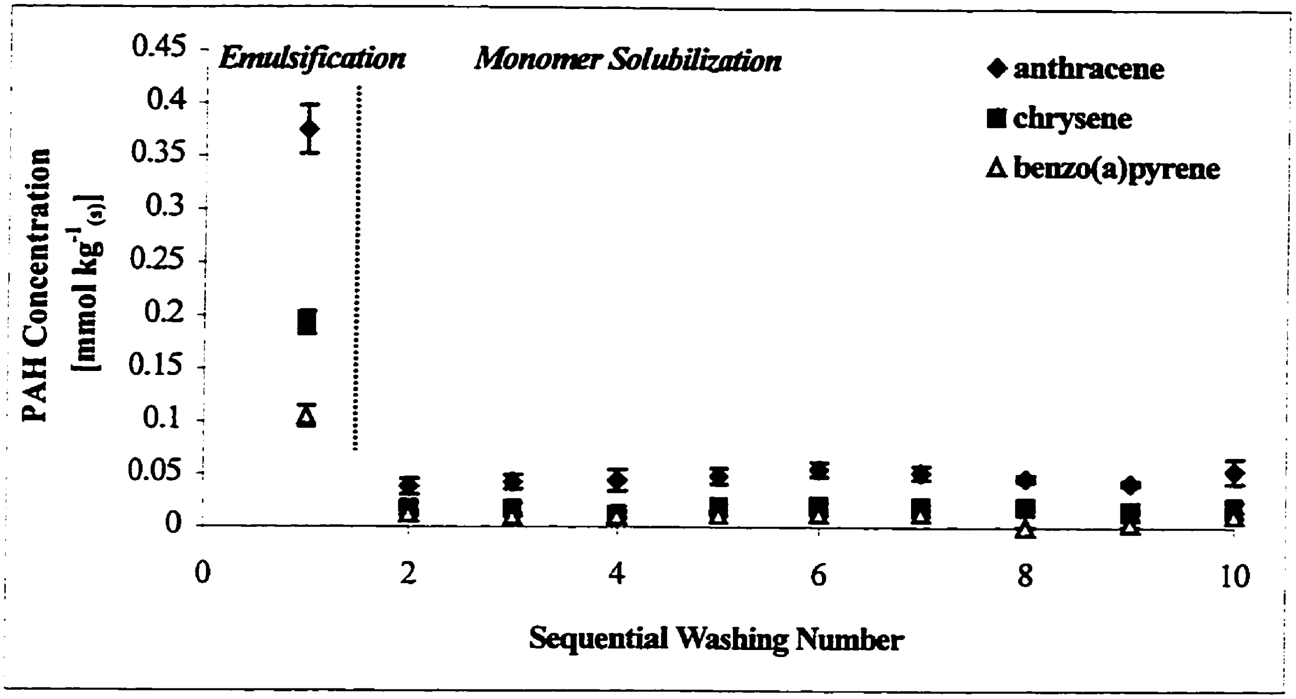


Figure 3. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 0.5mM Dowfax washing of MPA soil

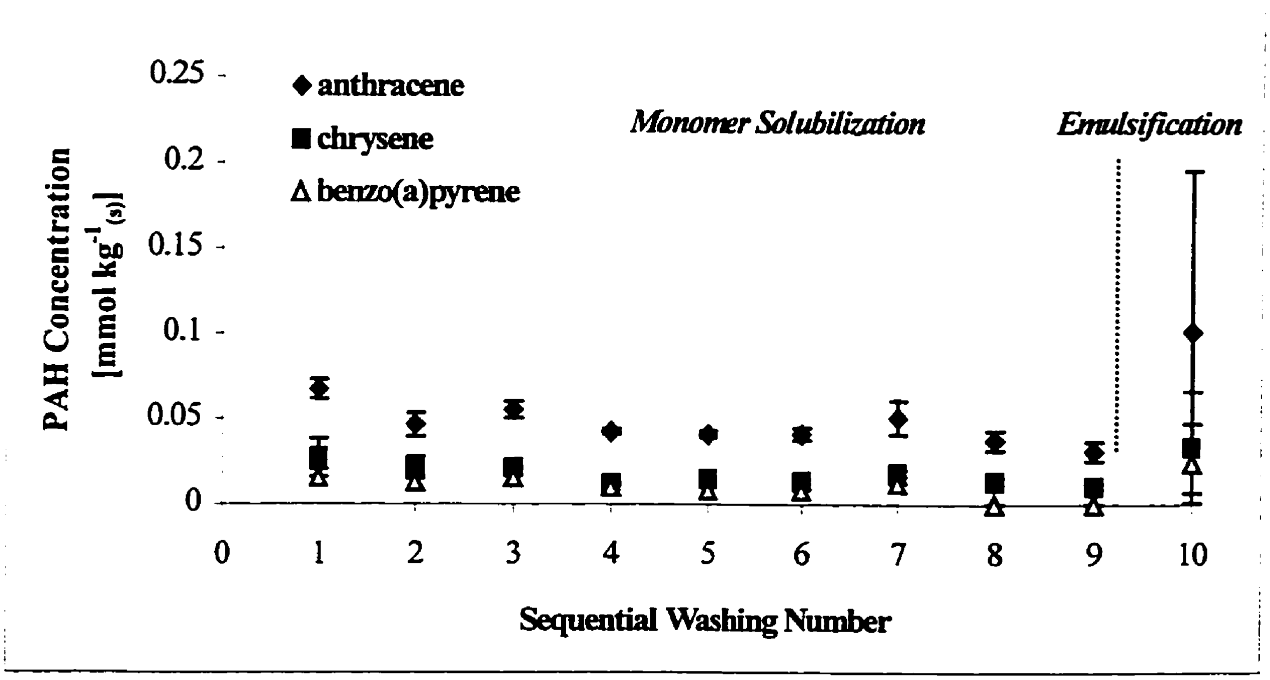


Figure 4. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 0.8mM Dowfax washing of MPA soil

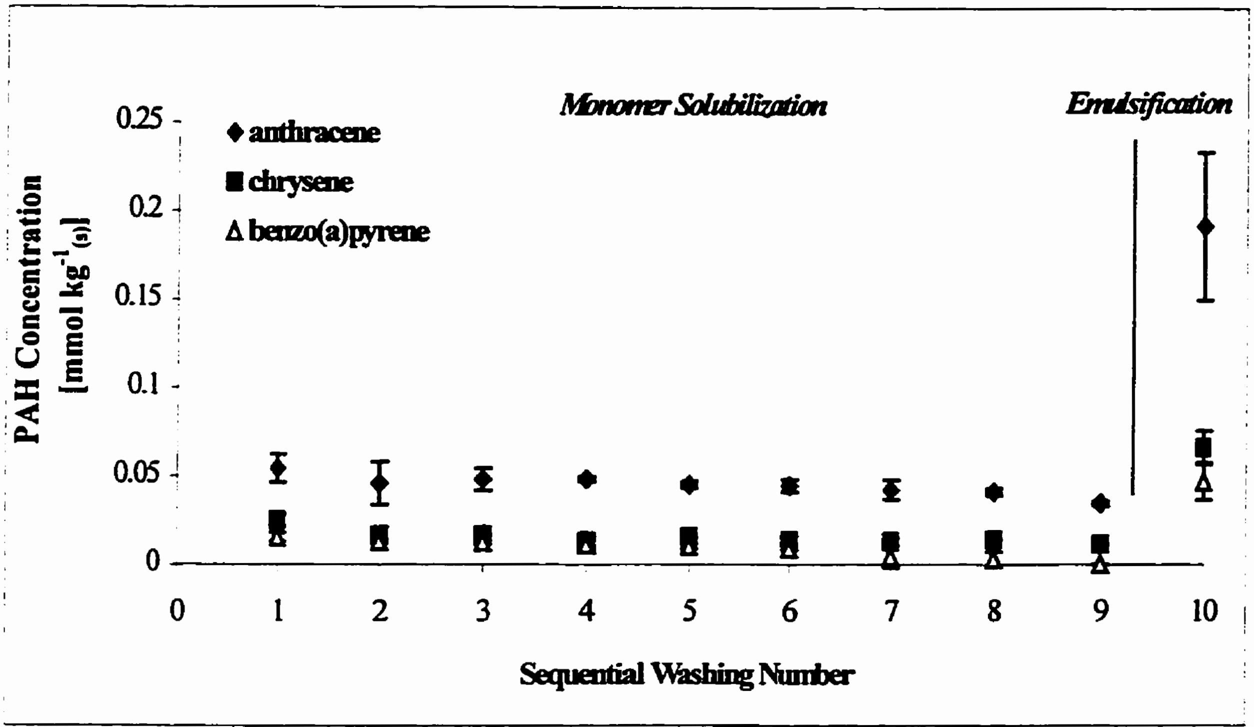


Figure 5. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 1.0mM Dowfax washing of MPA soil

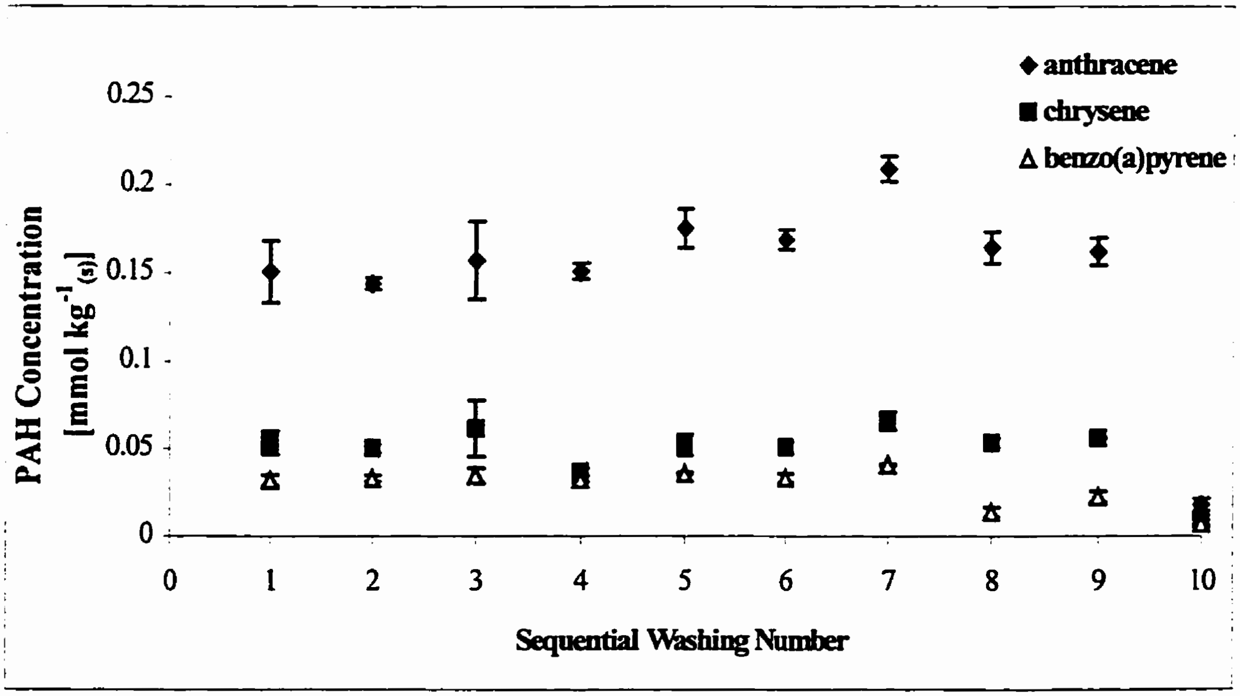


Figure 6. PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 10mM Dowfax washing of MPA soil

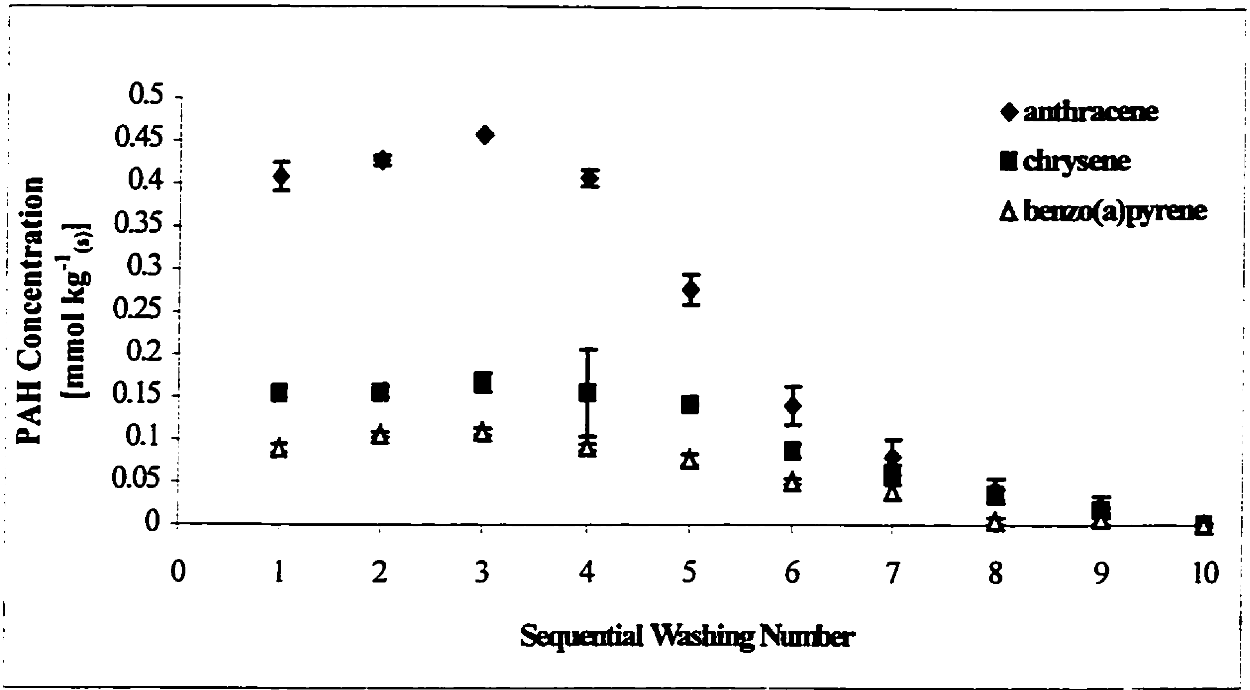


Figure 7. **PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 30mM Dowfax washing of MPA soil**

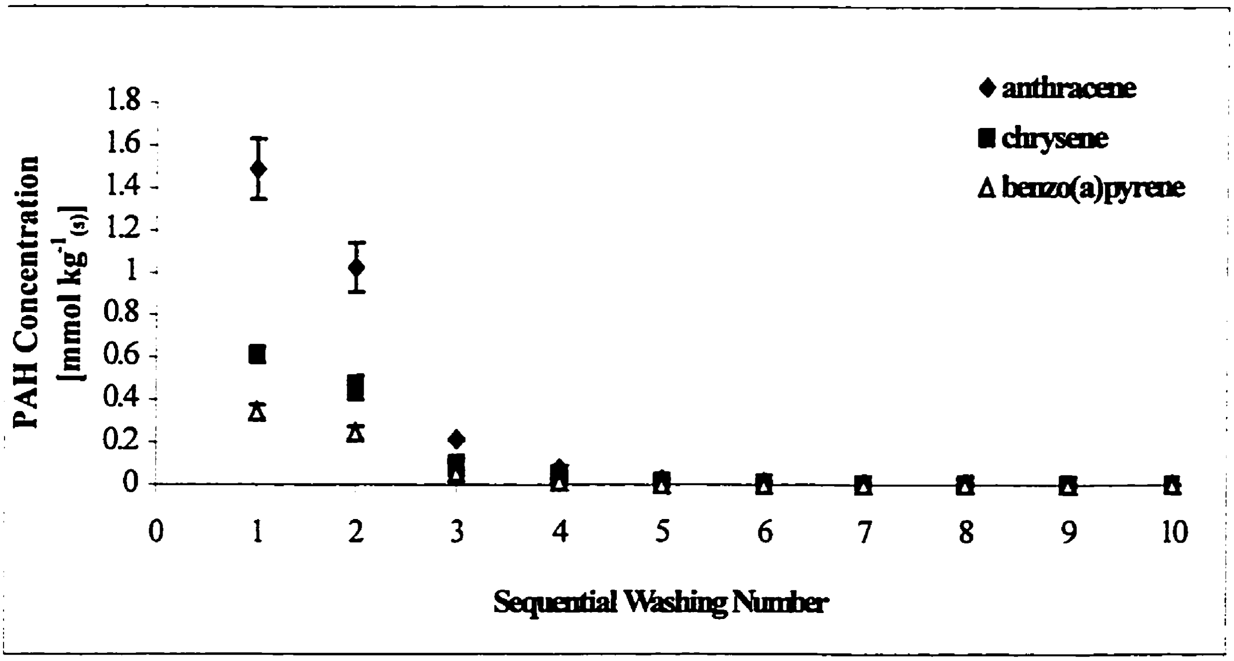


Figure 8. **PAH concentrations [mmol kg^{-1}$_{(s)}$ dry soil] during sequential 100mM Dowfax washing of MPA soil.**

Appendix D

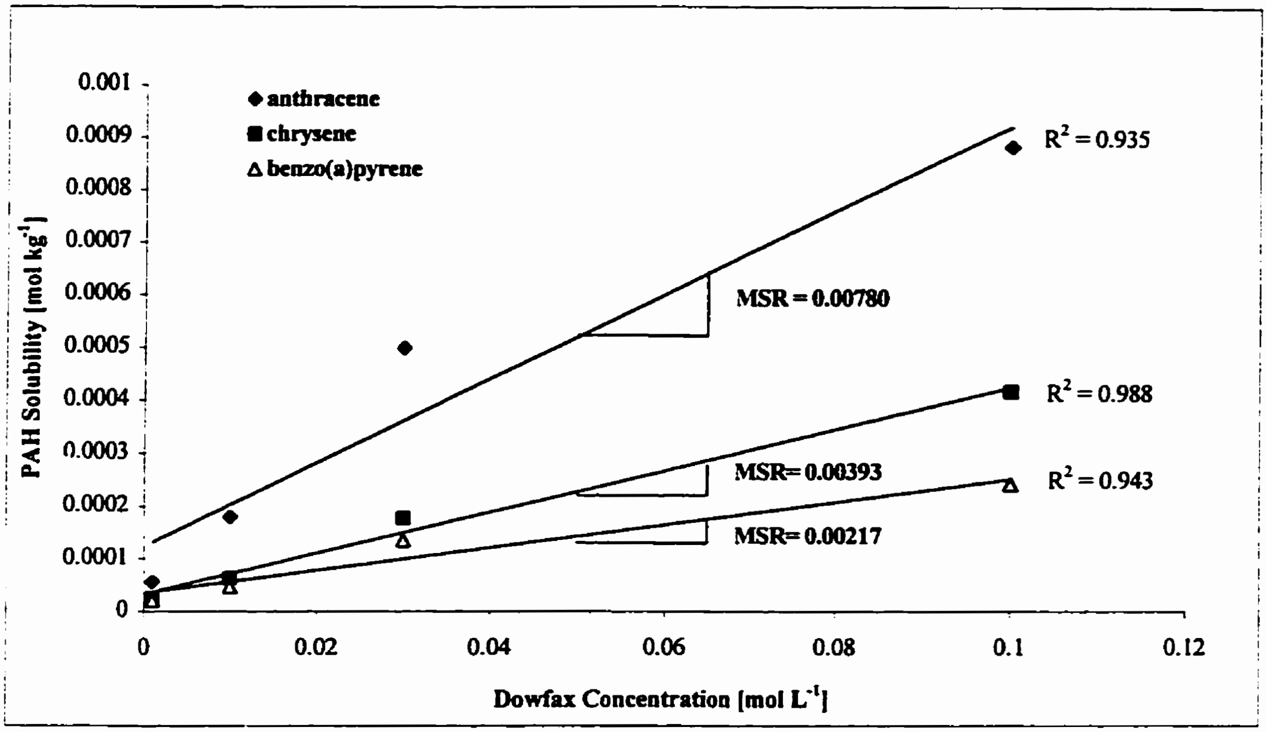


Figure 1. Molar solubilization ratios for target PAHs following 24 hr Dowfax washing of LPA soil

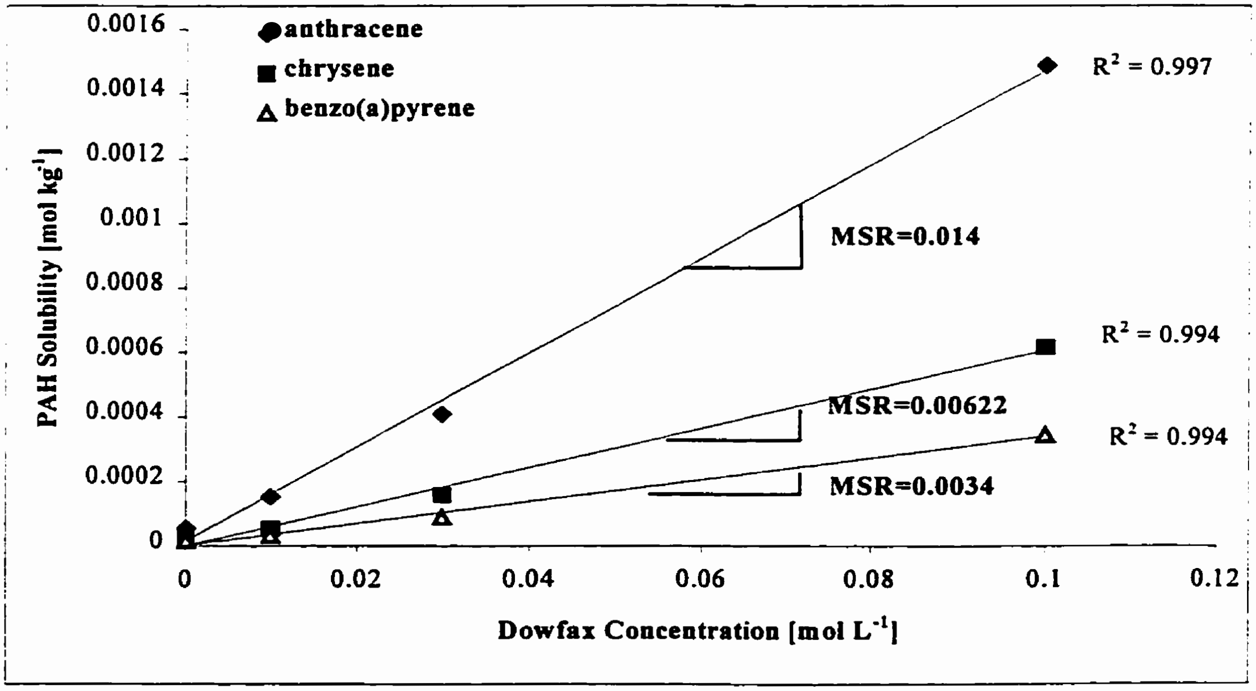


Figure 2. Molar solubilization ratios of target PAHs following 24 hr Dowfax washing of MPA soil

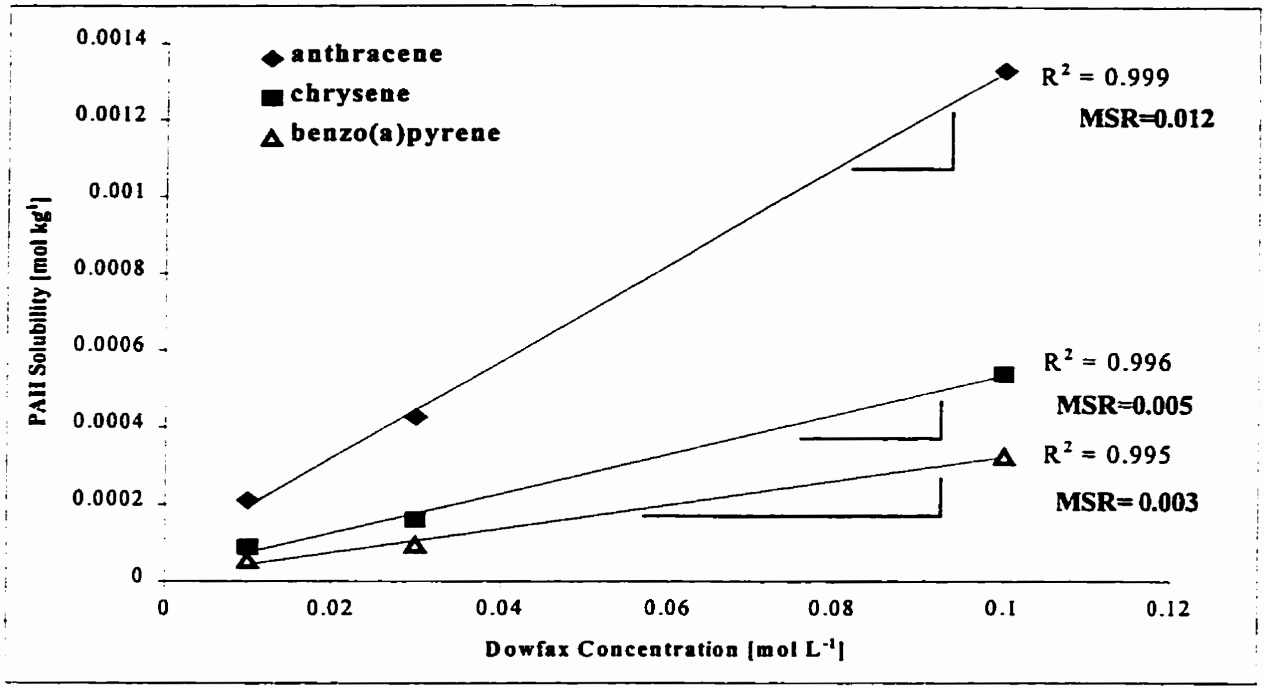


Figure 3. Molar solubilization for target PAHs following 24 hr Dowfax washing of HPA soil

Appendix E

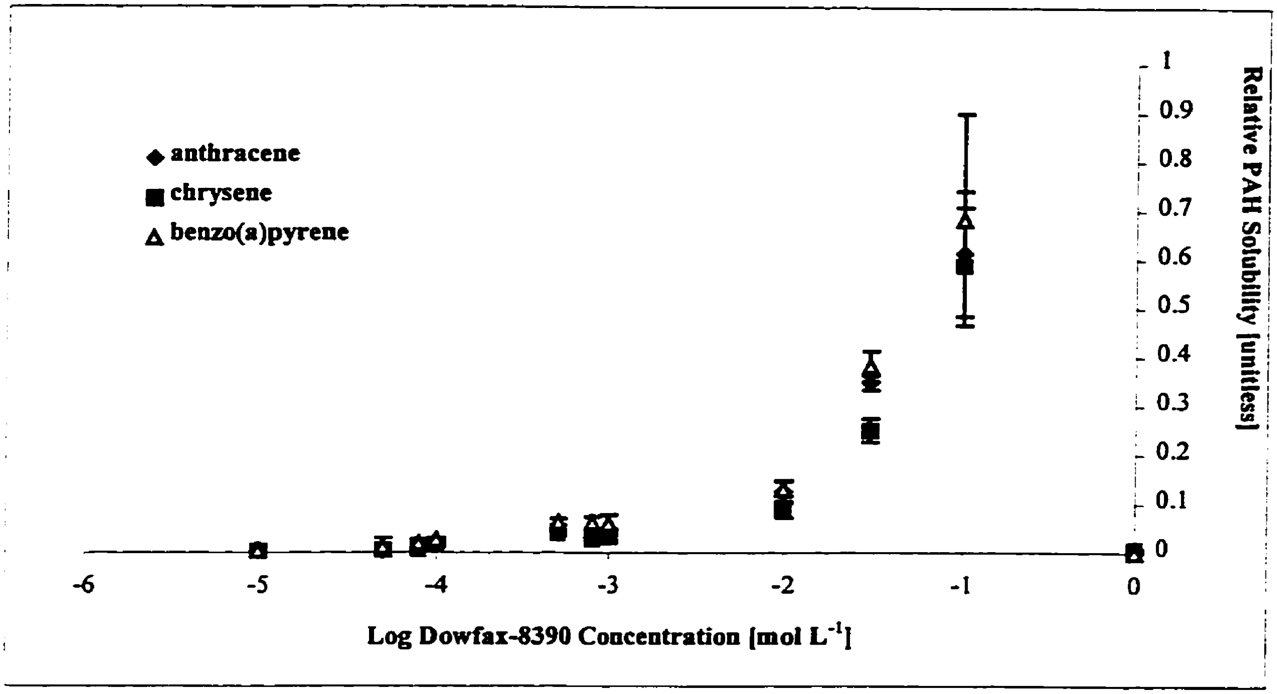


Figure 1. Normalized PAH solubility enhancement following 24 hr Dowfax washing of LPA soil

Table 1. Statistical summary of normalized PAH solubility enhancement following 24 hr LPA soil washing

	Dowfax Treatment [mM]									
PAH	0.01	0.05	0.08	0.1	0.5	0.8	1.0	10	30	100
Anth	*	*	*	*	*	*	*	*	*	*
Chry	*	*	*	*	*	*	*	*	**	*
BaP	*	*	**	**	**	**	*	*	*	*

Note: 1) same number of * indicates no significance difference amongst PAHs ($P<0.05$)
2) different number of * indicates significant difference amongst PAHs ($P<0.05$)

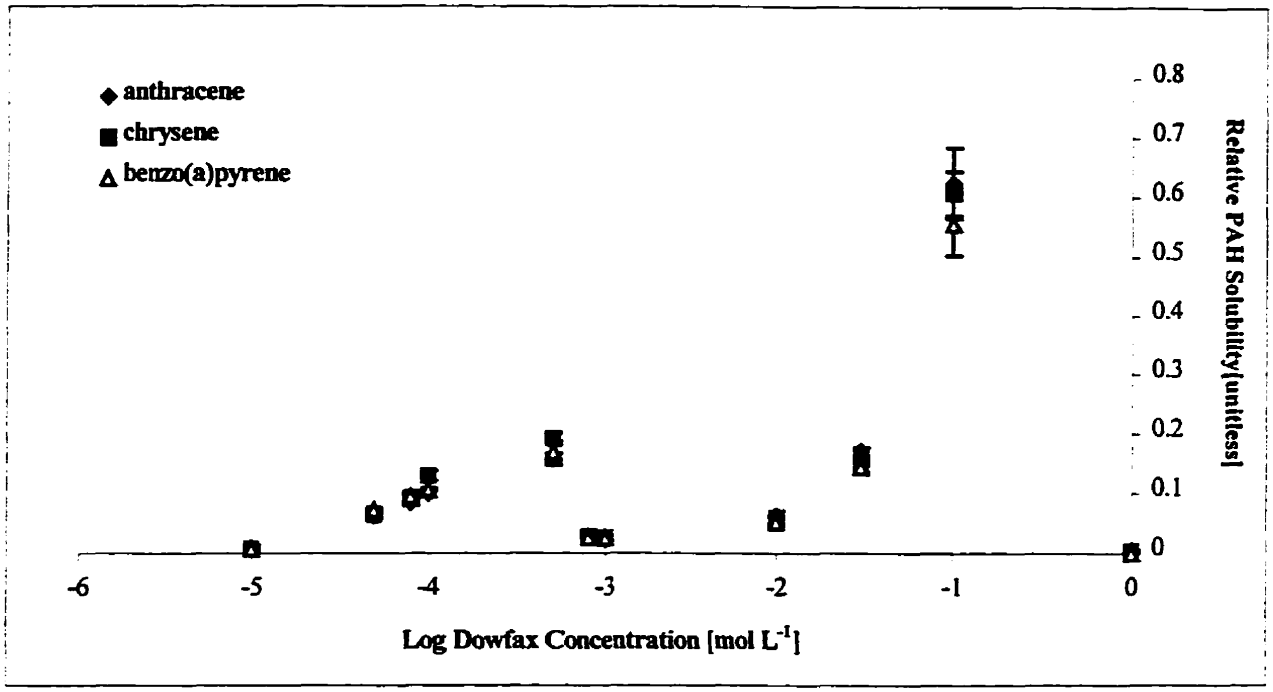


Figure 2. Normalized PAH solubility enhancement following 24 hr Dowfax washing of MPA soil

Table 2. Statistical Summary of normalized PAH solubility enhancement following 24 hr Dowfax washing of MPA soil

	Dowfax Treatment [mM]									
PAH	0.01	0.05	0.08	0.1	0.5	0.8	1.0	10	30	100
Anth	*	*	*	*	*	*	*	*	*	*
Chry	*	*	*,**	**	**	**	*	*	**	*
BaP	*	*	**	*	*,**	**	*	*	**	*

Note: 1) same number of * indicates no significance difference amongst PAHs ($P<0.05$)
2) different number of * indicates significant difference amongst PAHs ($P<0.05$)

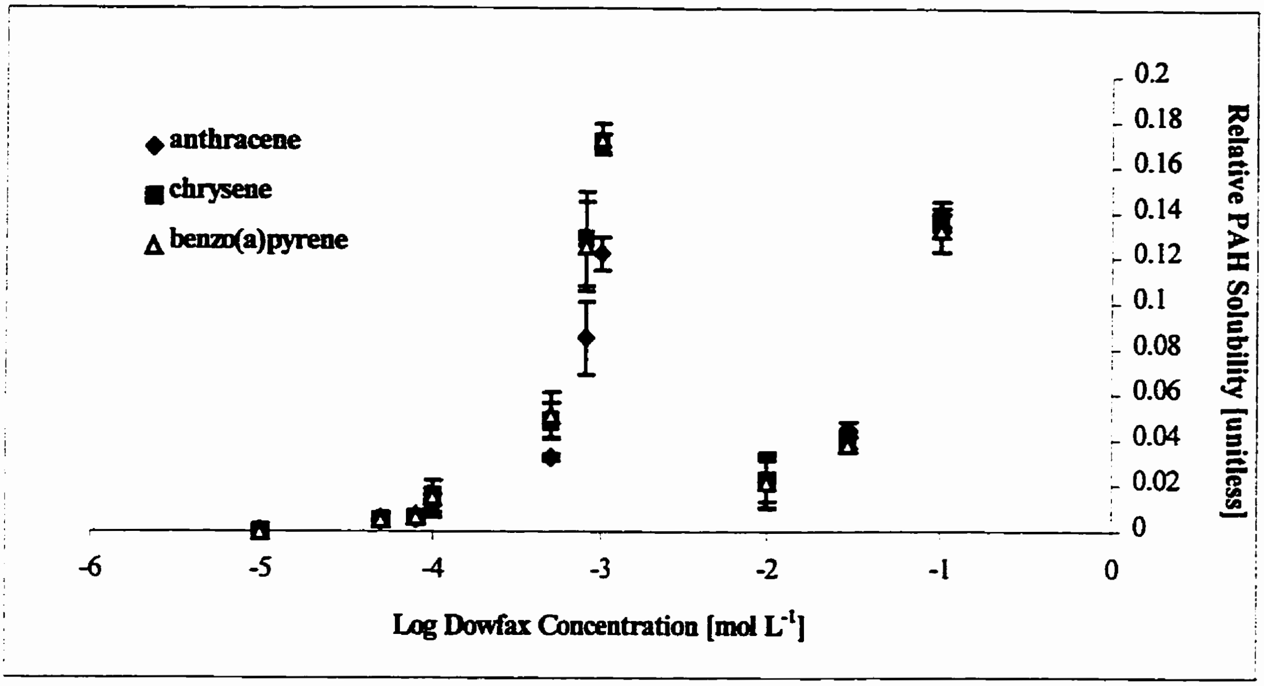


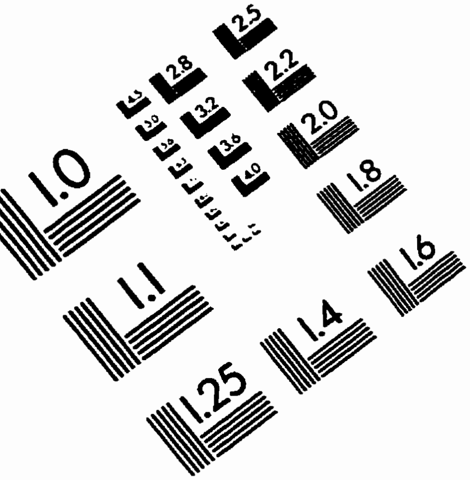
Figure 3. **Normalized PAH solubility enhancement following 24 hr Dowfax washing of HPA soil**

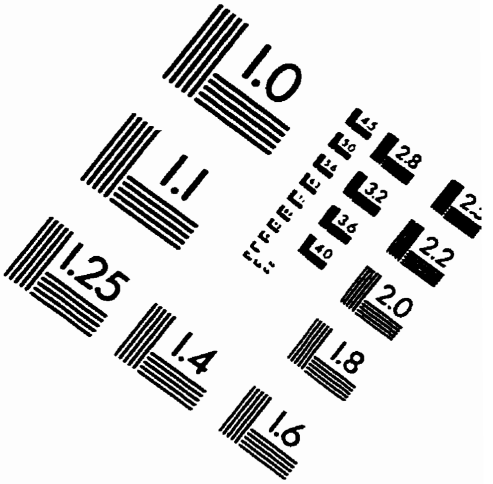
Table 3. **Statistical summary of normalized PAH solubility enhancement following 24 hr Dowfax washing of HPA soil**

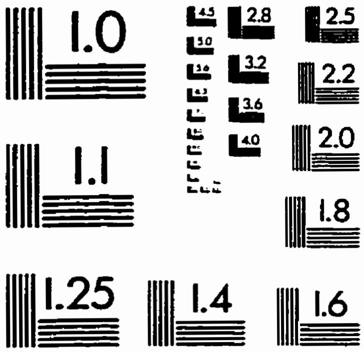
	Dowfax Treatment [mM]									
PAH	0.01	0.05	0.08	0.1	0.5	0.8	1.0	10	30	100
Anth	*	*	*	*	*	*	*	*	*	*
Chry	**	*	*	*	*	*	**	*	*	*
BaP	**	*	*	*	*	*	**	*	*	*

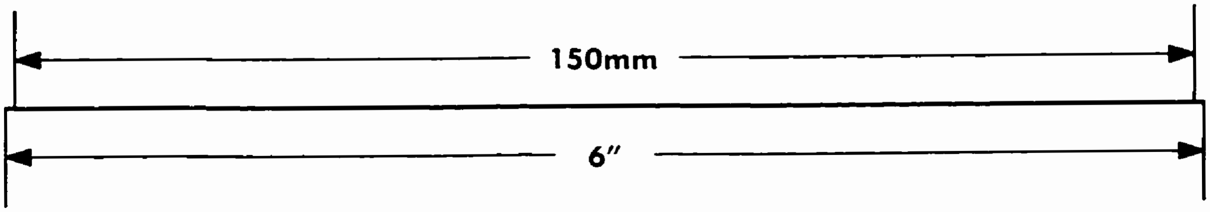
Note: 1) same number of * indicates no significance difference amongst PAHs ($P<0.05$)
2) different number of * indicates significant difference amongst PAHs ($P<0.05$)

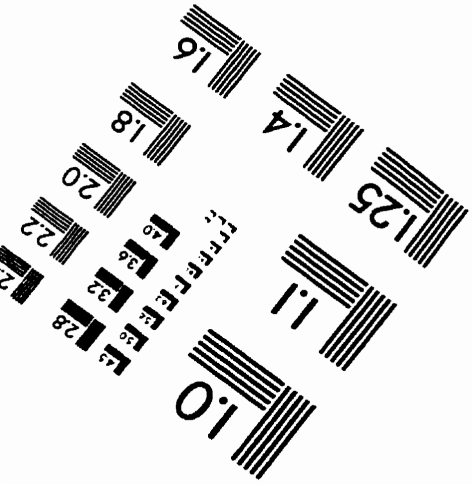
IMAGE EVALUATION TEST TARGET (QA-3)











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