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TITOLO DELLA TESI

EFFICACIA DEL “SOIL WASHING” NELLA DECONTAMINAZIONE DA IDROCARBURI: IL RUOLO DI TEMPERATURA, CONCENTRAZIONE DEL TENSIOATTIVO E MINERALOGIA DEL SUOLO.

TITOLO IN INGLESE - EFFICIENCY OF SOIL WASHING IN HYDROCARBON REMOVAL: THE ROLE OF TEMPERATURE, SURFACTANT CONCENTRATION AND SOIL MINERALOGY

Settore Scientifico Disciplinare: GEO/09

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Abstract

The object of the current PhD research is to evaluate the effect of variations in the type and concentrations of surfactants, washing temperature and most importantly, mineral composition of the soil on washing efficiencies. In order for surfactant-enhanced soil washing to be a viable and efficient remediation strategy a series of requirements must be met. First, the soils being treated cannot have clay contents higher than 30% and organic materials exceeding 2 wt%, as it would result in excessive loss of surfactant to adsorption and subsequent difficulty in the removal of the washing solution. In addition, the soils should also have relatively low cation exchange capacity (CEC).

The study was articulated into three distinct phases. In the first phase fourteen samples representative of the various soils present in the Marche Region were collected and their grain size distributions, organic contents, cation exchange capacity, mineral composition and Atterberg limits were determined. Based on their grain size distributions, the soils are characterized by sand fractions between 7% and 49%, silt fractions between 2% and 49% and clay fractions between 2% and 52%. They have organic contents of 0.21 to 6.37 wt%, CEC's of 7.2 to 35 cmol+/kg and plasticity indexes that range from non-determinable (for non-plastic soils) to 25. The studied soils are rich in calcite, quartz and mica, and have minor amounts of clay minerals, feldspars and plagioclases. It was concluded that, in the event of contamination, most of the sampled soils would be unsuitable for surfactant-enhanced soil washing due to their high clay and organic contents. Of the remaining soils, two were chosen, MF-05 and MF-10, for the experimental phase of the project, based on their different mineralogy and locations in close proximity to population centers. Sample MF-05 has equal proportions of quartz, calcite and mica family minerals, while MF-10 has no calcite and lower CEC, organic contents and plasticity index.

The second phase of the project was focused on the development and fine-tuning of the laboratory washing procedure using the procedure described in Urum et al. (2014) as a setting off point. The procedure had to be modified to take into consideration a different contaminant and analytical method. Each step of the washing and extraction of residual hydrocarbon procedure was assessed. The final procedure involved the artificial contamination of the soil samples with 15 wt% diesel followed by washing in a temperature-controlled water bath for 30 minutes with surfactant-based washing solutions in a ratio of 4 to 1. The samples were then rinsed with deionized water, dried in an oven set to 60°C. The diesel remaining in the sample was then extracted using n-Hexane and analyzed using GC-MS (Gas Chromatography – Mass Spectrometry). Two surfactants were used in the experiments: SDS (anionic) and TWEEN80 (non-ionic).

The experiments were carried out at two washing temperatures (30°C and 40°C) and three surfactant concentrations. One below the critical micelle concentration (CMC) and two above. Experiments using deionized water as the washing liquid were used as a baseline of comparison. It was found that for sample MF-05, washing with SDS-based washing solutions had little effect at concentrations below the CMC, improving drastically once the CMC was exceeded; in sample MF-10, on the other hand, a drastic improvement in washing efficiency was already evident at concentrations below the CMC and continued to increase, at a lower rate, with increasing SDS concentrations. The initial delay in washing efficiency improvement in sample MF-05 is likely due to the adsorption of the negatively charged surfactant molecules to the positively charged calcite surfaces, absent in sample MF-10. For both samples, washing with TWEEN80-based solutions resulted in a significant improvement in efficiency at concentrations below the CMC, followed by less significant improvement at intermediate concentrations and a decrease in efficiency at the highest concentrations of TWEEN80. The similar performance of the TWEEN80 washing solutions in samples MF-05 and MF-10 is consistent with its neutral charge. Temperature did not produce significant differences in surfactant performance. When compared to each other, as expected, SDS slightly outperformed TWEEN80 and both are more effective at extracting n-Alkanes from sample MF-10 than MF-05. The decrease in TWEEN80 efficiency at higher concentrations may be due to a change in shape or loss of stability of micelles.

Abstract

(Italian)

L’oggetto del presente studio di dottorato è quello di valutare l´effetto delle variazioni del tipo e delle concentrazioni dei tensioattivi, delle temperature di lavaggio e, soprattutto, della composizione mineralogica sull´efficienza del “soil washing”. Affinché il lavaggio del suolo con l’aggiunta di tensioattivi possa risultare una strategia di risanamento praticabile ed efficiente, è in ogni caso necessario soddisfare una serie di requisiti. In primo luogo, sarebbe opportuno che i terreni da trattare non abbiano frazioni granulometriche di argilla superiori al 30% e materiali organici maggiori al 2% in peso, in quanto comporterebbero un'eccessiva perdita di tensioattivo per adsorbimento e conseguente difficoltà nella rimozione della soluzione di lavaggio. Inoltre, i suoli dovrebbero avere una capacità di scambio cationico (CEC) relativamente bassa.

Lo studio è stato articolato in tre fasi distinte. Nella prima fase sono stati raccolti quattordici campioni rappresentativi dei vari suoli presenti nella Regione Marche, sui quali è stata svolta una caratterizzazione riguardante la granulometria, il contenuto organico, la capacità di scambio cationico, la composizione mineralogica e i limiti di Atterberg. In termini di granulometria, i terreni sono caratterizzati da sabbia tra 7 e 49%, limo tra 2 e 49% e una frazione argillosa tra 2 e 52%. Il contenuto organico varia da 0.21 a 6.37%, CEC da 7.2 a 35 cmoli+/kg ed indici di plasticità da non-determinabili (per terreni non plastici) fino a 25. I suoli investigati sono ricchi in calcite, quarzo e mica e presentano quantità minori di minerali argillosi, feldspati e plagioclasio. La maggior parte dei suoli campionati non sarebbero pertanto idonei al lavaggio con tensioattivi in caso di inquinamento, a causa del loro alto contenuto di frazione argillosa e di composti organici. I due suoli con i migliori requisiti per il “soil washing” (MF-05 e MF-10) sono stati comunque scelti per la fase sperimentale del progetto, in base alla diversa mineralogia e ubicazione (prossimità dei centri abitati). Il campione MF-05 contiene quarzo, calcite e minerali del gruppo delle miche in quantità confrontabili mentre MF-10 non ha calcite e più bassi valori di CEC, materiale organico ed indice di plasticità.

La seconda fase del progetto si è concentrata sullo sviluppo e la messa a punto della procedura di lavaggio in laboratorio seguendo la metodologia proposta e descritta da Urum et al. (2014). Tale procedura è stata in seguito modificata in modo da prendere in considerazione un diverso contaminante ed un differente metodo analitico. Sono state valutate tutte le fasi della procedura di lavaggio e di estrazione del residuo di idrocarburi. Il “setting” procedurale finale è consistito nella contaminazione artificiale dei campioni di terreno con il 15% in peso di diesel, seguita da un lavaggio a bagnomaria a temperatura controllata per 30 minuti con soluzioni di lavaggio a base di tensioattivi in un rapporto di 4 a 1. In seguito, i campioni sono stati sciacquati con acqua deionizzata ed asciugati

in forno a 60°C. Il diesel rimanente è infine stato estratto usando n-esano ed analizzato mediante GC-MS (Gas Cromatografia in Spettrometria di Massa). Negli esperimenti sono stati utilizzati due tensioattivi: SDS (anionico) e TWEEN80 (non ionico).

Gli esperimenti sono stati condotti a due temperature di lavaggio (30°C e 40°C) e con tre concentrazioni di tensioattivo, una al di sotto e due al di sopra della concentrazione micellare critica (CMC). Gli esperimenti con acqua deionizzata come liquido di lavaggio sono stati usati come base di confronto. Per il campione MF-05, il lavaggio con soluzioni di lavaggio SDS ha avuto scarso effetto a concentrazioni inferiori alla CMC, migliorando invece drasticamente al di sopra di essa. Nel campione MF-10 l'efficienza di lavaggio aumenta proporzionalmente alla concentrazione di SDS ma in maniera nettamente migliore per concentrazioni inferiori alla CMC. Superata la CMC l’aumento di efficienza del lavaggio all’aumentare della concentrazione del tensioattivo è molto meno significativa. Il ritardo iniziale nel miglioramento dell'efficienza di lavaggio nel campione MF-05 è probabilmente dovuto all'adsorbimento delle molecole di tensioattivo (caricate negativamente), sulle superfici della calcite (assente nel campione MF-10) caratterizzate da carica positiva. Per entrambi i campioni, il lavaggio con soluzioni TWEEN80 ha messo in evidenza una maggiore efficienza a concentrazioni inferiori alla CMC, con un miglioramento meno marcato a concentrazioni intermedie e una riduzione dell'efficienza alle concentrazioni più elevate. Le prestazioni simili delle soluzioni di lavaggio TWEEN80 nei campioni MF-05 e MF-10 sono coerenti con la sua carica neutra. La temperatura non ha infine prodotto differenze significative nelle prestazioni dei tensioattivi. Prevedibilmente, il tensioattivo SDS ha delle “performance” leggermente superiori rispetto al TWEEN80, ed entrambi mostrano un’efficienza migliore nell'estrarre gli n-alcani dal campione MF-10 rispetto al suolo MF-05. La riduzione dell'efficienza di TWEEN80 alle concentrazioni più elevate potrebbe essere dovuta ad un cambio di forma o a una perdita di stabilita delle micelle.

Acknowledgments

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Table of Contents

Chapter 1

Background and literature review

1.1 Prevalence and remediation strategies of contaminated sites.

As the impact of humanity on the planet’s environment becomes increasingly apparent, there has been a growing movement of awareness and global responsibility that has seen governments take increasingly stringent actions to moderate the damage being done to the environment and to remediate damage already done. Countries of the European Union and beyond have been passing legislature limiting environmental impact of our activities and setting out procedures for environmental clean-up projects.

1.1.1 The European Union

In the 28 European Union member states, as of 2018, there were 650,000 registered sites where polluting activities are taking place or took place in the past. Of these, about 19% will require some degree of remediation. However, because many sites are yet to be registered and/or identified, the actual number of contaminated sites estimated based on artificial surfaces is likely to be about 2.8 million [1]. Compared to 2014, the number of registered contaminated sites has grown by 76,000 and the number of sites being remediated has grown by 5,000. Across the European Union, 65,500 sites have successfully been remediated: 8,500 in the last five years. Although, parameters used to classify contaminated sites and the techniques utilized vary from country to country, these numbers are a clear illustrations of the European Union’s increasing commitment to soil reclamation.

The main soil contaminants across the EU are chlorinated hydrocarbons (CHC), mineral oil, polycyclic aromatic hydrocarbons (PAH), heavy metals, and aromatic hydrocarbons (BTEX) [2], **Figure 1.1**. The main sources of these contaminants are the waste disposal and industrial/commercial activities, which account for about two thirds of reported contamination. Smaller contributions are made by storage, transport spills, military and nuclear, **Figure 1.2**. Within the service sector, which is included in the industrial/commercial activities category, the most common source of contamination reported across Europe is gas stations, accounting for 15% of all contaminated sites [2]. The most common method of treating contaminated sites continues to be landfilling, although recently, increasing restrictions on landfilling and availability of alternative methods have resulted in a rise in the use of other *in situ* and *ex situ* treatments methods, such as soil washing [2].

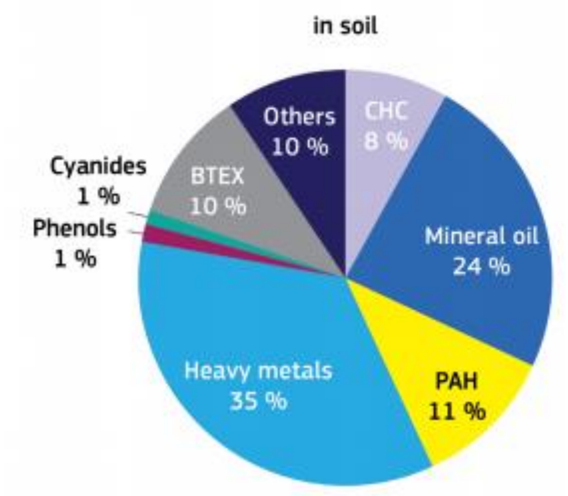

Figure 1.1 The main contaminants found in the soils of EU member states. (Source [2])

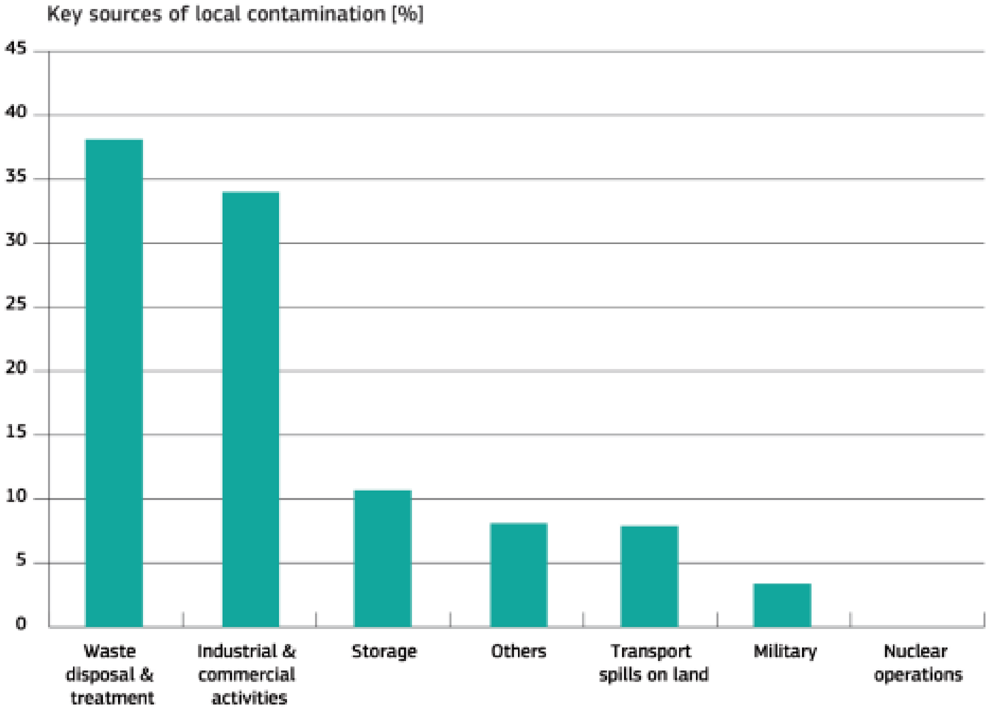

Figure 1.2 The main sources of contamination in the EU (Source [2]).

1.1.2 Italy

According to a survey carried out by the European Commission in 2018, there are 22,100 registered potentially contaminated sites in Italy. However, this is an underestimate since, in Italy, the identification and registration of such sites is the responsibility of each individual region, and only 17 regions and one autonomous province have provided information to the effect. A complete map of potentially contaminated sites (called *Siti di Interesse Nazionale*, Sites of National Interest, in Italy) is presented in **Figure 1.3** [3]. Of these sites, 6,754 still need to be characterized, 1,710 are being evaluated, 5,521 have been deemed not to require remediation and 2,600 require remediation. Remediation efforts are underway at 2,054 site and have been successfully completed at 2,904 [1].

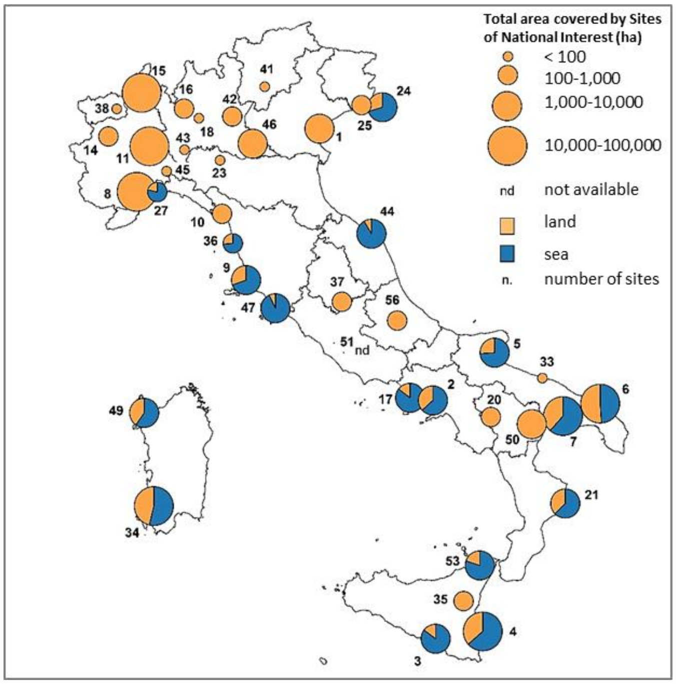

Figure 1.3 The total number and area covered by potentially contaminated sites in Italy, by region. Modified after [3].

The primary soil contaminants in Italy are heavy metals (40%), mineral oils (20%), PAHs (15%), chlorinated hydrocarbons (10%), and aromatic hydrocarbons (10%). Similarly to the rest of Europe, the main sources of this contamination in Italy are industrial and commercial activities and waste disposal at 52% and 40%, respectively [2]. Within the industrial and commercial activities category, the production sector accounts for 75% of potentially contaminated sites, while the services and mining sectors account for 20% and 5%, respectively. In the production sector, the major contamination contributors include the chemical industry (30%), the oil industry (20%), energy production (15%) and the metal working industry (5%). Among the services sector, gas stations account for all 20% of reported contamination in Italy [2]. The most commonly used remediation techniques utilized in Italy include physical and chemical separation (soil washing), biopiling, landfilling, thermal treatment, air/water stripping, activated coal adsorption, filtration/precipitation and biofiltering [4].

1.1.3 The Marche Region

In the Marche Region, as of 2018, there were 1,008 potentially contaminated sites. Of these, 530 were waiting to be characterized, being characterized, undergoing remediation or post-remediation monitoring. The remaining 478 sites have either been successfully remediated or were found not to require remediation under the regulations in force [5]. The four main types of contaminated sites present in the region are industrial sites (35.78%), gas stations (28.44%), waste disposal sites (2.84%) and other (such as fuel spills linked to traffic accidents and underground storage tank leaks located on private land; 32.94%), **Figure 1.4**. With gas stations representing almost one third of contaminated sites in the Marche Region, understanding the best way to tackle this type of contamination in reference to the soils present in the Region is of paramount importance.

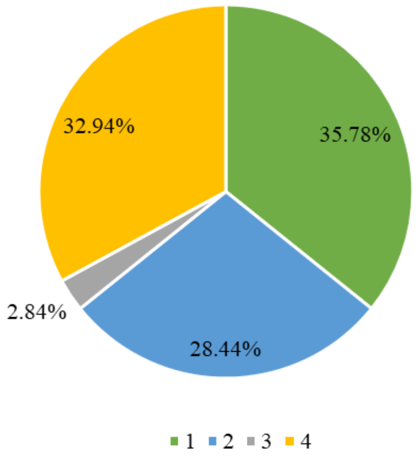

Figure 1.4 The contribution to the overall number of contaminated sites in the Marche Region of (1) industrial sites, (2) gas stations, (3) waste disposal sites and other (4). (Source [5])

1.2 Italian environmental legislation

Italy's first comprehensive attempt at a nationwide legislation governing the identification, characterization, management and remediation of contaminated sites was made in 1999 with the passing of Ministerial Decree 471/99. This law included a list of limit values for the concentration of about 100 contaminants to be used to define the goal of each individual remediation project. Due to unique characteristics of some sites and contaminants, this protocol proved difficult to implement. This decree also introduced the Polluter Pays Principle, which states that if the concentrations of a pollutant at a site exceed the limit values laid out in Ministerial Decree 471/99, the owner of the site is required to submit a remediation plan and finance the clean-up efforts [6]. In 2006, this decree was revised and included into Legislative Decree 152/06-Environmental Code. The main goal of the Italian Environmental Code, which is in force to this day, was to integrate Directive 2004/35/EC into previously stipulated Italian legislation. Title 5 of Section IV of this Environmental Code includes five annexes addressing risk assessments, remediation technologies and soil and groundwater screening values. In this decree, each of the nineteen Italian regions are delegated the task of compiling Regional Remediation Plans (*Piano Regionale di Bonifica*) and communicating them to the Italian Ministry of the Environment. This legislation introduced the concepts of Contamination Threshold Concentrations (*Concentrazioni Soglia di Contaminazione*, CSC) and Risk Threshold Concentrations (*Concentrazioni Soglia di Rischio*, CSR), values that became an integral part of a two-tier site evaluation process. In the first step the Contamination Threshold Values (equivalent to the limit values laid out in Ministerial Decree 471/99) would be used to evaluate the need for further assessment of a site. If any of the listed substances are found to exceed these threshold values, a site-specific risk assessment for soils and groundwater would follow. The goal of the risk assessments is to define site-specific Risk Threshold Values for the site. If the contaminant concentrations are found to exceed these values, the site owner is required to put together and finance a remediation plan; if these values are not exceeded, a monitoring plan must be put together. In both cases, the plans must be submitted to the Italian Ministry of the Environment [7].

Unlike other contaminants, petroleum derivatives, which are a common soil contaminant found at a wide range of sites including airports, industrial areas, refineries and even gas stations, display a high degree of compositional variability. This has made establishing threshold values of this contaminant particularly tricky. To evaluate the total hydrocarbon contamination of a site, the concentrations of the following compounds must be determined: aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), cancer-causing and non cancer-causing chlorinated aliphatic hydrocarbons (CAHs), and cancer-causing halogenated aliphatic hydrocarbons, as well as light (C≤12) and heavy (C>12) hydrocarbons. In addition, the Italian Environmental Code also distinguishes contamination threshold levels based on land use. Two land use categories are specified: residential and industrial. The contamination threshold values for hydrocarbon compounds for the two land use categories set out in the Italian Environmental Code can be seen in **Table 1.1**.

Table 1.1 Contamination threshold values for aliphatic hydrocarbon compounds. (From [7])

	Private and Public Residential Areas	**Commericial and Industrial Areas**
	(ppm)	(ppm)
Hydrocarbons		
Light Hydrocarbons (C≤12)	10	250
Heavy Hydrocarbons (C>12)	50	750

1.3. Hydrocarbon contaminants: gasoline and diesel

1.3.1 Composition and toxicity

The two contaminants most often found in the vicinity of gas stations are diesel and gasoline. Gasoline is a petroleum fraction that distills at 40°C to 180°C. Gasoline is a mixture of aliphatic (59%; of which about 47% are isoparaffins and 12% alkanes) and aromatic hydrocarbon compounds (about 28%) [8]. Specifically, it includes C4 to C12 straight-chained alkanes (also known as paraffins) and branch-chained isoparaffins; alkenes, or olefins (unsaturated linear and branch-chained compounds); and naphthenics (saturated cyclic hydrocarbons). Aromatic compounds (principally benzene, toluene, ethylbenzene, and xylene) are also generally present in gasoline [9].

Diesel fuel is the fraction of petroleum that distills after kerosene, at 200°C to 400°C. Because of differences in feed stock, refining methods and blending practices, the composition of commercially available diesel is also quite variable, although it generally contains predominantly C10 to C19 hydrocarbons of which approximately 64% are aliphatic and 35% aromatic compounds. Additives for ranging from ignition improvers, combustion catalysts, antioxidants, cold flow improvers, metal deactivators and detergents may also be added [10].

Exposure to diesel and gasoline can cause a series health effects ranging from mild eye and lung irritation to kidney damage, increased blood pressure, reduction in the blood's ability to clot, cancer and death. The type and severity of health effects is a function of the duration, dose, exposure pathway and personal characteristics (ex. age and health) [10, 11]. In addition, the release of these hydrocarbon mixtures into the environment can have long lasting effects on the local plant and animal life as well as on soil quality.

1.3.2 Behavior in soils

In a soil-water system, hydrocarbon compounds tend to adsorb to mineral surfaces. The strength with which the hydrocarbon compounds are bonded to the surface is a function of the mineral surface charge and age of the soil. Silica has a net negative surface charge. This creates a repulsive force between the negative charges on the silica surface and the negative charges distributed along the surface of oil droplets. This repulsion results in a beading effect. Calcite found in limestone, on the other hand, has a net positive charge. This results in an attraction between calcite grain surfaces and the surfactants molecules naturally present in oil. This attraction causes the droplets to spread out along the surfaces. Both of these effects, if excessive, can make removal of oil from mineral surfaces more difficult and highlight the importance of characterizing the mineralogy of contaminated soils before formulating a remediation strategy [12]

1.4 Remediation technologies: soil washing

Several soil remediation techniques are currently being utilized to remove petroleum derivatives from soils. They can be divided into non-biological methods, including soil washing, solvent extraction, soil vapor extraction (SVE), air sparging, dual phase extraction, solidification/stabilization, thermal desorption and incineration; and biological methods, including bioventing, biosparging, natural attenuation, landfarming, biopiles, bioslurry, microbiological barriers and so on. Despite their high efficiency and lower environmental impact of the biological technologies, their elevated costs and implementation times have meant that non-biological methods, such as landfilling and soil washing, have remained the remediation technologies of choice.

1.4.1 Historical note

Soil washing is an ex-situ water-based remediation technology that utilizes a combination of physical processes to concentrate the contaminants in a smaller soil volume and chemical processes to extract them. This technology, although not yet known as "soil washing", was first developed in the early 1980's in the Netherlands as a way to treat contaminated beach sands [13, 14]. Since then, it has been used extensively, first in Europe and later in the United States, for the treatment of excavated soils and dredged sediments contaminated with a broad range of organic, inorganic and radioactive contaminants [13,15-16]. The contaminant classes successfully removed by this process include petroleum and fuel residues, radionuclides, heavy metals, PCBs (polychlorinated biphenyls), PCP (pentachlorophenol), pesticides, cyanides, creosote, semivolatiles and volatiles [15, 16]. Soil washing can be used both as a stand-alone soil treatment and as a pretreatment method of reducing the volume of contaminated material prior to treatment with a different method, thus improving cost efficiency of remediation. Currently, the efficiency of soil washing installations allows the recovery of about 75% of contaminated material but it has been shown that recoveries of up to 90-95% can be achieved for heavy metal and hydrocarbon contaminants when heat and chemical compounds (such as surfactants and chelating agents) are added [15].

1.4.2 The procedure

A soil washing plant is not a single installation but rather an arrangement of modules the order and combination of which can be customized to fit the specific requirements of the contaminant/soil system. Generally speaking, a soil washing plant, which can be either static or mobile, will include three modules: a soil pre-treatment module, a washing module and a post-treatment module, **Figure 1.5,** [13, 18, 19]. Once at the plant, the contaminated material is pre-screened, extracting over-sized debris, organic materials and metals. The resulting feed soil is then disaggregated, homogenized and if necessary crushed using a variety of techniques including water sprays, tumbling scrubbers, centrifugal acceleration and vibration. The result of this stage is a slurry with grain size diameters of <2mm. This feed soil now passes to the heart of the plant: the washing module.

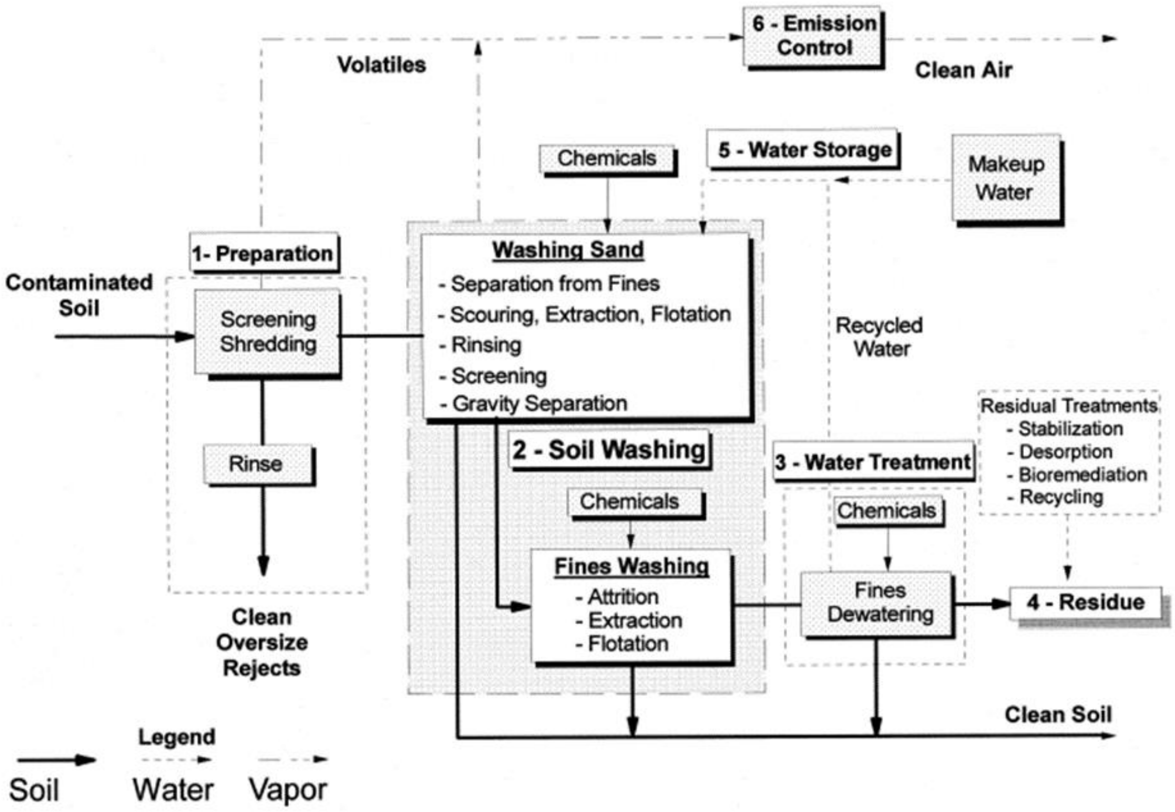

Figure 1.5. Flow chart of a generic soil washing system. (Taken from [18])

This module consists of a combination of hydrocyclones, scrubbing units, gravity separators and flotation tanks in numbers and configurations best suited to the soil type and contaminant being treated. The goal of this stage in the process is twofold: to separate the sand fraction of the soil (>63µm and <2mm) from the fines fraction (<63µm) and to treat these two fractions using methods uniquely suitable to each [18, 19]. This is the stage in the process at which additives, most commonly acids/bases, chelating agents and surfactants, are added to the washing solution to facilitate the transfer of the contaminant from the soil into the aqueous phase [14]. During this stage the soils are separated into the sand and fines fractions which are in turn washed using units suitable to their grain sizes. For example, for the coarser sand fraction, froth flotation or gravitational separation may be used [19]. Depending on the type of contaminant, the silt and clay fractions may also be treated with technologies such as flotation and hydrosizing before proceeding to post-treatment. Other specialized units may be added for certain types of contaminants. For example, to separate lead or mercury, jigs and gravity tables may be used, taking advantage of the contaminants' higher densities. Magnetic separation, on the other hand, may be used to remove certain metals [18].

The third and final module consists of all the units dealing with post-treatment. These include dewatering units, wastewater treatment units, and emissions control units [18, 19]. The dry output of the process includes a clean coarse fraction consisting of sands and gravels (>63µ) and a contaminated fine fraction of silts and clays that is typically sent on for further treatment (such as thermal destruction and bioremediation) and/or disposal. The treated wastewater is usually recycled back into the system.

1.4.3 Applicability and limitations

Despite the great adaptability of soil washing plants, the technology has limitations associated with the physical and chemical characteristics of the soils and the type(s) of the contaminant [15, 16]. Consequently, a detailed investigation of the chemical and physical soil properties, their variation with depth and the contaminant mixture are a pre-requisite for any soil washing project.

The two most important physical parameters that must be evaluated are the soil grain size distribution and cation exchange capacity [15, 16]. In **Figure 1.6** two grain size distribution ranges within which soil washing is a viable remediation solution are shown [15]. Some contaminants tend to preferentially bind to clay surfaces hence the treatment of soils with clay contents greater than 30% is generally not cost effective [15, 16].

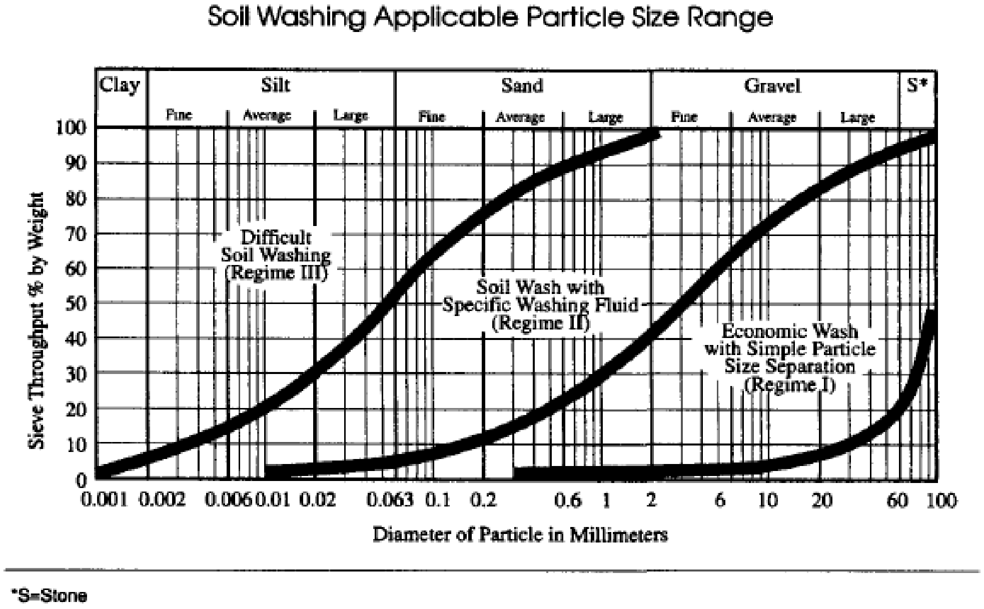

Figure 1.6 Soil washing applicability grain size distribution ranges. (Taken from [15])

Cation exchange capacity is a measure of the soil's ability to exchange cations. The higher the cation exchange capacity, the more tightly the soil will tend to bind pollutants, making removal progressively more difficult. Another important parameter is organic contents, as many contaminants tend to form progressively stronger bonds with organic matter as weathering processes take hold. In order for soil washing to be a viable option, organic contents should be below 2 wt% [15].

In addition, complex contaminant mixtures may require a combination of soil washing additives and/or a sequential multistep washing design. This can significantly reduce the cost-effectiveness of the technology [15, 16]. Soil washing is most effective in non-complex soils with at least 50% sand. As the clay and silt percentages of the soil increase, so does the difficulty in removing contaminants.

1.5 Surfactants in soil washing

During the washing stage of a typical soil washing procedure washing solutions containing chelating agents, surfactants, acids or bases are often added to facilitate the transfer of the contaminant from the solid to the liquid phase. The compositions and concentrations of these solutions are tailored to the contaminant/soil system being treated. The primary additives used in the treatment of soils contaminated with hydrocarbons are surfactants [20, 21].

Surfactants are compounds that are amphiphilic, meaning they contain both hydrophobic (tail groups) and hydrophilic moieties (head groups). This structure makes surfactants particularly efficient at increasing the solubility of certain contaminants in water, particularly of hydrophobic organic compounds [22-24]. When added to a solution they preferentially position themselves along interfaces found in the system (ex. water-oil, water-soil) in the form of monomers, orienting themselves such that their hydrophilic heads are in the water. As concentration increases, the monomers continue to accumulate along the interfaces resulting in a decrease in the polarity of the aqueous phase and a reduction in interfacial and surface tension. As these interfaces fill up, and the surfactant monomers are pushed into solution, their hydrophobic heads tend to clump together forming agglomerates, called micelles, **Figure 1.7a**. The surfactant concentration at which micelles first begin to form is called the Critical Micelle Concentration (CMC) [22, 23]. Micelles tend to be spherical in shape and 4-10 nm in diameter. As the surfactant concentration is increased further, micelles of different shape may begin to form, **Figure 1.7b**. The new configurations, including cylindrical, hexagonally-packed and lamellar, are a function of the surfactant's chemical and molecular structure as well as the physico-chemical conditions of the solvent [24].

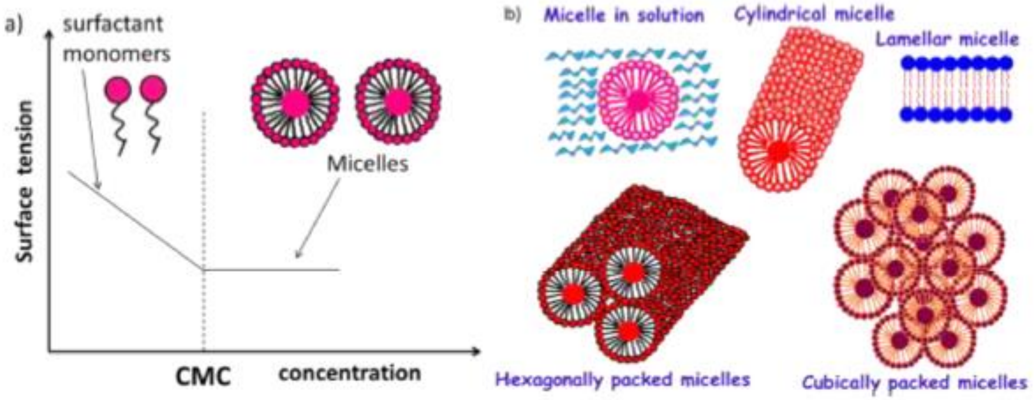

Figure 1.7 (a) CMC and the formation of micelles from single monomers as a function of concentration, (b) different types of micelle structures, (Taken from [21])

1.5.1 Surfactant types and their applications

There is a wide range of surfactants available on the market. They are generally divided into two broad categories based on their origin: synthetic and biologic. Based on the charge of their hydrophilic head group after dissociation in water, synthetic surfactants are further divided into non-ionic, cationic, anionic and zwitterionic. In anionic surfactants, the hydrophilic head group is usually a sulphate, sulfonate or carboxylate group; in cationic surfactants it is usually a quaternary ammonium group, while in non-ionic surfactants it is a polyoxyethylene, sucrose or polypeptide. Zwitterionic surfactants have both an anionic and cationic head group [25]. Of these, non-ionic surfactants have lower toxicity and lower CMC values, which is important in formulating soil washing solutions. However, their lack of charge also makes them less efficient at extracting hydrocarbons. Between the cationic and anionic surfactants, anionic surfactants are used the most because cationic surfactants tend to be attracted to the negatively charged surface of clay particles resulting in substantial active surfactant loss from the washing liquid to adsorption [26].

Biosurfactants are typically produced by aerobic microorganisms, such as bacteria or yeasts, in an aqueous media. [25, 27]. Their hydrophobic moieties are composed primarily of proteins, peptides or 10-18 carbon-long chains of fatty acids. The hydrophilic moiety, on the other hand is usually composed of an ester, hydroxy, phosphate, carboxylate group or a sugar [27]. Biosurfactants have several advantages over synthetic surfactants when applied to the remediation of soils. Their simple structure makes them easily biodegradable. Most biosurfactants are anionic or non-ionic. They are easier to produce utilizing renewable raw materials. They also have low toxicity, making the treatment of used washing solutions much simpler [25, 27].

1.5.2 Mechanisms of hydrocarbon compound extraction

Surfactant-enhanced soil washing of hydrocarbons occurs via two distinct mechanisms. Soil roll up, or mobilization, and solubilization. Soil roll-up occurs below the CMC. As the surfactant monomers accumulate along the oil/water interface, the repulsion between the head group and mineral surface results in an increase in the contact angle and a reduction of the capillary force holding the oil to the surface, effectively pushing it off the soil surface. Solubilization, on the other hands, takes place above the CMC and consists of the incorporation of oil droplets into the hydrophobic core of micelles. This mechanism is more effective because the contaminant is less likely to re-adsorb to the surface. Hence it is important to consider the CMC when choosing surfactants.

However, the same process that contributes to the efficiency of soil mobilization can also cause a delay in the improvement of hydrocarbon removal with concentrations above the CMC. The greater the attraction between the surfactant monomers and the mineral surfaces, the greater the amount of surfactant that will be lost to adsorption and hence not participate in solubilization. In line with this reasoning, the adsorption of a cationic surfactants onto soil particles was observed to increase linearly with the cation exchange capacity of the soil, i.e. to be a function of the net negative charge of the mineral surface [22], which makes them more suitable for soils dominated by minerals such as the negatively-charged calcite. For this reason, anionic surfactants are generally the surfactants of choice for sandstone dominated soils [28]. For non-ionic surfactants, it has also been found that sorption loss decreases with increasing soil maturity and is mainly governed by clay contents, as opposed to organics [29]. Furthermore, several studies have shown that although most surfactants show an improvement in hydrocarbon extraction efficiency with increasing concentrations, some, such as saponin and tannin, do not [26, 30, 31]. This behavior has been attributes to the instability of micelle shape in size observed in bulkier surfactants [32]

For this project, two synthetic surfactants were chosen: SDS and TWEEN80. SDS, or sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$), is one of the most popular anionic surfactants on the market, **Figure 1.8a.** Its head moiety is a sulfate group which has been suggested to cause this surfactant to be sensitive to changes in temperature, becoming less efficient at higher temperatures [28]. TWEEN80, polyoxyethylene-(20)-sorbitanmonooleate ($C_{64}H_{124}O_{26}$), is a non-ionic surfactant, **Figure 1.8b**. Compared to other non-ionic surfactants, its relatively low cost and low toxicity to soil microorganisms has made it an attractive choice in remediation of soils contaminated with hydrocarbons [33].

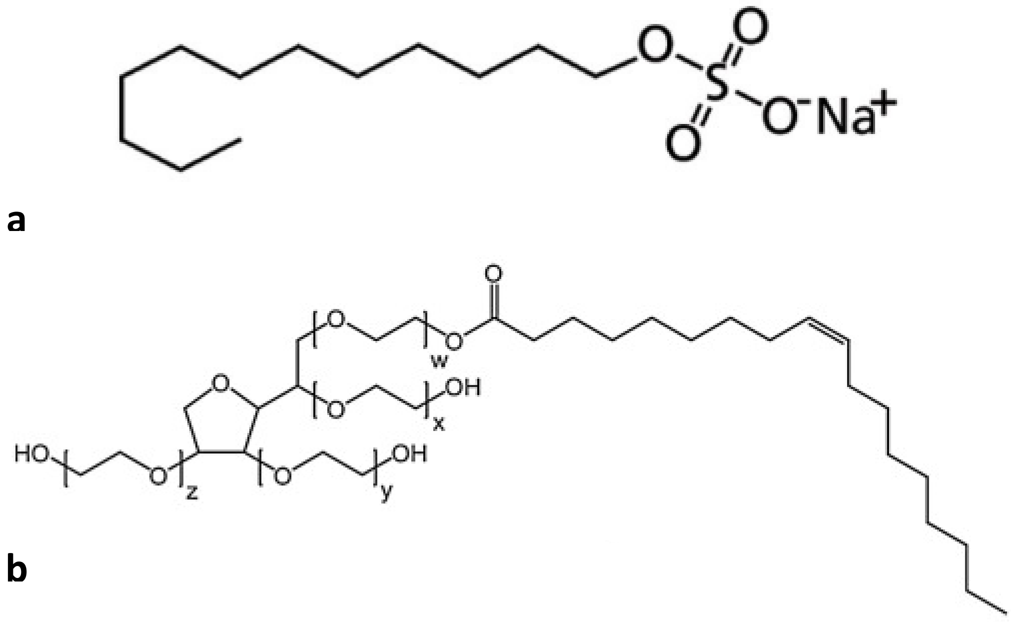

Figure 1.8 Chemical structures of SDS (a) and TWEEN80 (b).

1.6 Previous laboratory soil washing experiments

Since the 1980's, when soil washing first began to be used commercially, there have been many studies evaluating the efficiency of this process. A variety of contaminants and washing solution additives as well as washing conditions have been studied using different approaches. Laboratory scale batch washing studies focusing on efficiency of surfactants in the removal of petroleum hydrocarbons from soils, on the other hand, are not as numerous and few address gasoline/diesel contaminated soils [26, 30, 31, 34-42]. Below is a summary of the batch washing studies of the greatest relevance to the current project.

One of the first studies aiming to evaluate the efficiency of surfactants in the extraction of hydrocarbon compounds in a laboratory setting was carried out by Deshpande et al in 1999 [31]. In this study washing experiments were carried out on three soils of varying physiochemical properties. Two of the soils had been exposed to hydrocarbon contamination for decades: one was from a gas station, the other from an Air Force base, while the third was river alluvium contaminated artificially with representative PAH and Alkane compounds, phenanthrene and decane, respectively. Eight surfactants were evaluated in this study: nonionic surfactants T-Maz 80, T-Maz 20, CA 620 and TerraSurf80; and anionic surfactants Dowfax 8390, SDBS, SDS and Steol 330. Among these were surfactants with food additive status in the US and those previously shown to minimize adsorption and precipitation losses. The washing experiments were performed with a constant 1 to 3 sample to washing solution ratio in 40 ml test tubes shaken for 30 minutes on a wrist shaker at room temperature. The surfactant concentrations were varied by three orders of magnitude (0.25, 4 and 25 times the CMC). The samples were allowed to settle for 24 hours and the washing liquid was then separated using centrifugation. The concentrations of petroleum hydrocarbons in the washing solution were determined using gas chromatography (specifically, the GC/Static Headspace technique). To evaluate the degree of initial contamination, the petroleum hydrocarbons were extracted using methylene chloride and analyzed using gas chromatography. In addition to batch washing studies, surfactant sorption, foaming, turbidity and phase separation studies were also carried out. The study concluded that both the soil rollup and solubilization mechanisms were active and the efficiency of the surfactant-contaminant-soil systems varied widely as a function of both the soil properties (i.e. grain size distribution) and the surfactants susceptibility to sorption. Neither the mineralogy nor the surface charge properties of the soil constituents were considered in this study. [31]

Urum carried out a series of four studies with different collaborators published between 2003 and 2006 [26, 34-36], focusing on the efficiency of different surfactants in the extraction of crude oil from soils contaminated in the lab. In the study published in 2003 [34], the efficiency of six surfactants (aescin, lecithin, rhamnolipid, saponin, tannin and SDS) was tested at different experimental conditions. To this end 2 kg of horticultural grade, lime-free, washed, and graded quartzite grit sand with maximum nominal size of 5 mm were contaminated with North Sea Ekofisk crude oil resulting in crude oil concentrations of 54.4 mg of oil per gram of soil. The contamination was carried out by combining the soil and crude oil in horizontally positioned drum mixer for one hour at 20°C. The contaminated soil was then stored in a hermetically sealed glass container. The washing experiments were carried out by combining 5 g of contaminated soil with a varying amounts of washing solution in a 45 ml centrifugal test tube. The test tubes were positioned horizontally in a water regulated water bath and shaken laterally. During these experiments the following parameters were evaluated: temperature (5°C, 20°C, 35°C and 50°C); concentration of surfactant solutions (0.004, 0.02, 0.1 and 0.5%mass); volume of surfactant solutions (5 ml, 10 ml, 15 ml and 20 ml); shaking speed (80 strokes/min, 120 strokes/min, 160 strokes/min and 200 strokes/min) and washing time (5 min, 10 min, 15 min and 20 min). After washing, the solutions were allowed to settle, the washing liquid was removed, and the remaining soil rinsed with 5 ml of distilled water by shaking laterally for 3 minutes to remove residues of the washing solution. The initial and remaining crude oil was extracted by adding 10 ml of n-hexane to the test tubes, shaking laterally for 5 minutes and removing the resulting n-hexane-crude oil extract. This process was repeated four times. The resulting total extract was brought up to 50 ml with pure n-hexane and centrifuged for 20 minutes at 3000 rpm to remove any suspended particles. The concentration of crude oil in the extract was determined using spectrophotometry. It was found that temperature and surfactant concentrations had the greatest influence on efficiency. The possible influence of soil chemistry on the efficiency of the surfactants under study was not addressed in this study.

In 2004, Urum et al. [35] continued with the washing experiments this time taking a closer look at the influence of soil composition on washing efficiencies of two surfactants: the biosurfactant rhamnolipid and the synthetic SDS. Four soil of variable grain size distributions and cation exchange capacities were used. The mineral composition of the soils was not evaluated. The samples were contaminated with the same crude oil and following the methodology reported in.

In addition, the effect of soil ageing was simulated by placing contaminated soil in an oven set to 50°C for 14 days. The washing experiments were carried out following the procedure and experimental conditions laid out in [34]. It was found that weathering, made the removal of crude oil from all of the soils more difficult. The two surfactants showed similar crude oil removal efficiencies at the same concentrations which makes the more environmentally friendly rhamnolipid a more attractive choice. Although soils with different grain size distributions and cation exchange capacities (CEC) were used in this study, no conclusions about the influence of grain size and CEC are made. From the figures presented, however, it can be concluded that for non-aged samples, CEC had a greater influence on extraction efficiency than the clay content as soil 1, which had the lowest CEC values but the greatest clay contents, shows the best extraction efficiencies for both surfactants evaluated. Temperature, sample to washing solution ratio, shaking speed and washing duration were all shown to enhance extraction efficiency [35].

In the third study of the series, also published in 2004, Urum and Pekdemir [26] evaluated the variation in the efficiency of six surfactants (including SDS and rhamnolipid) in washing soil contaminated with crude oil, linking it to a series properties of the surfactants, including surface tension, interfacial tension, emulsion formation, foaming ability, sorption and solubilization. The soil washing was carried out following the procedure laid out in previous works by the same author. The washing procedure parameters were kept constant: 20 ml of washing solution at 20°C, 20 minute washing duration and 200 strokes per minute washing speed. The only parameters to vary were surfactants concentration. It was found that surfactants with a low CMC and high affinity to soil surfaces are more efficient at removing oil at concentrations far greater than the CMC. Surfactants with shorter, less bulky carbon chains were more efficient at removing oil from soil [26].

Finally, Urum at al [36] evaluated the ability of three surfactants (rhamnolipid, saponin and SDS) to remove individual compounds contained in crude oil before and after artificial weathering. The washing experiment procedure was taken from [26, 35]. This time, the crude oil/n-hexane extract was analyzed non only using a spectrophotometer but also using GC/MS. It was found that rhamnolipid and SDS preferentially removed aliphatic over aromatic hydrocarbons and that different surfactants will preferentially remove some hydrocarbon compounds over others.

In 2009, Chin-Chi Lai et al. [37] performed batch washing experiments evaluating the efficiency of four biosurfactants (Rhamnolipids, surfactin, serrawettin, and a bioemuslifier) and two synthetic surfactants (TWEEN80 and Triton X-100). In the batch studies, 50 grams of oil-contaminated soil from an oil refinery plant was combined with 100 ml of surfactants in 500 ml flasks, which were then shaken at 25 rpm (rotations per minute) in a temperature controlled shaker set to 25°C for 24-168 hours. Soil characterization was limited to grain size distribution, organic content, CEC and total contents of potassium, nitrogen and phosphorus. The total petroleum hydrocarbon in the prewashed soil were determined via extraction using dichloromethane, as described in EPA test method 8015B, followed by GC-FID analysis. It was found that biosurfactants were more effective at extracting hydrocarbon compounds from both low and highly contaminated soils; increasing the washing duration beyond 24 hours did not improve removal percentages; and shaking speeds had to be above 50 rpm before improvements over static incubation were seen [37].

Han et. al. [38] evaluated the efficiency of two non-ionic surfactants 9APG1214 and APG0810 in extracting crude oil from field weathered contaminated soil. In the batch experiments, 10 g of soil were mixed with 50 ml of washing solution in 250 ml glass beakers maintained at 70°C by a temperature-controlled water bath and mechanically agitated for 30 minutes by an electric stirrer. After washing, the slurries were quickly cooled to room temperature, passed through a 0.3 mm sieve and centrifugated for 30 min at 4000 rpm. Next the supernatant was removed, the soils were rinsed with 40 ml of deionized water, allowed to settle for 4 hours, dried at 60°C for 5 hours, ground and stored at 4°C for further study. The residual and initial crude oil compounds were extracted using n-hexane following the procedure described in [4] and analyzed using spectrophotometry and GC-MS. Before GC-MS analysis the extracts were diluted or condensed and filtered through 0.22 µm nylon membranes. The study found optimal washing conditions to be at 80°C, washing time of 30 minutes, solution to soil ratio of 10:1 and agitation speed of 350 rpm. In addition, it was concluded that the addition of inorganic salts greatly reduced the quantity of surfactant needed to achieve the same levels of efficiency [38].

1.7 Scope of the project

Despite a great volume of studies on the topic of surfactant-assisted soil washing, very little research has been done addressing the application of soil washing to the cleaning of soils contaminated with gasoline/diesel, despite the growing demand for viable and cost-effective solutions to soil contamination in vicinity of gas stations.

In addition, although most laboratory batch washing studies include the grain size distribution of the soils being studied, few include values such as organic content and cation exchange capacity, and none take a close look at the mineralogy of the soils being studied. Following and initial listing of the soil characteristics, the influence of these characteristics on the outcome of the experiments is often brushed over. This could result in important mechanisms being overlooked. As shown by Bhandari et al, in 2000 [42], the presence of iron in the form of iron oxide on the surface of sand grains can impact the strength with which a hydrocarbon compound is bonded to the surface and consequently the ease with which it can be removed. These compositional differences are independent of grain size. Rather, they are a function of mineralogy and age of the soil in question.

Consequently, the fundamental aim of this project is to evaluate the efficiency of two commercially available surfactants, SDS and TWEEN80, in the removal of diesel from soils of different mineralogies representative of the Marche Region. Additional parameters that will be evaluated are temperature and surfactant concentration. To overcome the inherent complexity of naturally contaminated soils, clean soils will be sampled and contaminated in the lab. Understanding how the efficiency of surfactants of different characteristics is affected by soil mineralogy at different concentrations and washing conditions is of paramount importance to the formulation of washing solutions during the remediation of contaminated soils.

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Chapter 2

Sample collection, characterization and selection.

2.1 Geological setting of the Marche Region

The geology of the Marche Region is dominated by the Umbria-Marche Apennines, a fold-and-thrust belt formed as a result of differential movements between the African and the European tectonic macroplates. The region's geology reflects three tectonic phases: an extensional phase during the Mesozoic, corresponding to the opening of the Tethys ocean and producing the Umbria-Marche sedimentary succession, which is characterized by carbonates grading upwards into mainly terrigenous sediments; Neogene compression of the latter sedimentary succession, responsible for the folding and thrusting seen; and an extensional phase in the Umbria area from Late Miocene-Pleistocene onwards [1-5].

2.2 Sample collection

The Umbria-Marche Apennines can be divided into the following generalized regions: the external Apennines ridge, consisting of calcareous, marly-calcareous and marly deposits of the Umbria-Marche Succession; siliciclastic turbidite deposits of the Preapennine area, Intra-Apennine basins and the foothills; and the Plio-Pleistocene peri-Adriatic Succession [2].

Fourteen soils distributed among these general areas were selected for sampling. Care was taken to include the most representative and extensive formations of each province. The samples, collected in three field outings, were taken from the following formations/units/sediments: Marnoso-arenacea Formation, Liguride units, Beach deposits, Alluvial terrace deposits, clayey and sandy deposits of the Pio-Pleistocene peri-Adriatic succession, the Laga Formation, minor Intra-Apennine basins, calcareous and marly-calcareous units of the External Apennine Ridge. Samples were taken to an average depth of about 20 cm and stored in plastic bags. The locations of the fourteen sampling sites are shown in **Figure 2.1**.

2.2.1 Marnoso-arenacea Formation

MF-01 was collected from an aerated agricultural field overlying the Marnoso-arenacea Formation, not far from Vocabolo le Ginestre in St. Angelo in Vado, in the Province of Pesaro and Urbino, **Figure 2.2**. The coordinates of the sampling location are 43.6664, 12.3842; and the elevation is 479 meters above sea level. The soil formed large clumps suggesting high clay contents with no visible clasts. Several clumps were taken directly from the surface of the field.

2.2.2 Liguride and Sub-liguride Units (Montefeltro)

MF-02 was collected from an aerated and seeded field along Strada Provinciale 18, not far from Carpegna, in the Province of Pesaro and Urbino, **Figure 2.3**. The coordinates of the sampling location are 43.7812, 12.3514; and the elevation is 654 meters above sea level. Soil was collected to a depth of about 30 cm using a Dutch augur. The soil formed small clumps (suggesting a smaller percentage of clay with respect to sample MF-01) and was rich in pebble-size clasts.

2.2.3 Clayey deposits of the Pio-Pleistocene peri-Adriatic succession

MF-03 was collected along Strada Micaloro in Chiusa di Ginestreto, Province of Pesaro and Urbino, from an aerated field, **Figure 2.4**. The coordinates of the sampling location are 43.8524, 12.8200; and the elevation is 111 meters above sea level. The sample was collected using a small shovel from the surface of the field.

2.2.4 Beach deposits

The Adriatic coast of the Marche Region is densely populated. The large number of gas stations servicing this region makes it particularly vulnerable to contamination. With much of the area covered with beach deposits, which have great potential for suitability for soil washing, it was decided to collect two samples from this area.

MF-04 was collected in a grass covered field in the Province of Pesaro and Urbino, south of Fano, between Via Fratelli Zuccari and the sea using a Dutch augur, **Figure 2.5**. The top layer of the soil containing organic matter was discarded. The coordinates of the sampling site are 43.8375, 13.0395; and the elevation is 7 meters above sea level.

MF-05 was collected in an unpaved parking lot located along SS16 between Pesaro and Fano using a Dutch augur, **Figure 2.6**. The coordinates of the sampling site are 43.8671, 12.982; and the elevation is 7 meters above sea level.

2.2.5 Alluvial terrace deposits

MF-06 was collected near the town Bellocchi (Province of Pesaro and Urbino), along Via Papiria, in the vicinity of Profilglass SpA, from an aerated agricultural field, **Figure 2.7**. The soil is characterized by a great amount of coarse gravel. The coordinates of the sampling location are 43.7893, 13.0142; and the elevation is 26 meters above sea level.

2.2.6 Sandy deposits of the Plio-Pleistocene peri-Adriatic succession

Due to the great extent of these deposits in the Marche Region, three samples from widely spaced locations were collected. MF-07 was collected along Strada Aspio Candia, near the town of Candia, in the Province of Ancona, from an aerated agricultural field. The coordinates of the sampling location are 43.5596, 13.4914; and the elevation is 69 meters above sea level.

MF-08 was collected in a pine grove near Castelfidardo, along Via della Battaglia, Province of Ancona, **Figure 2.8**. The sample was taken using a Dutch augur. The first 5-10 cm were discarded due to a great amount of organic matter. The coordinates of the sampling location are 43.4657, 13.5870; and the elevation is 107 meters above sea level. The sample was loose and dark in color.

MF-09 was sampled in between Pedaso and Campofilone along an unnamed road, from an aerated agricultural field, **Figure 2.10**. The sample was collected from the top 20 cm of soil using a small shovel. The coordinates of the sampling location are 43.0873, 13.8329; and the elevation is 142 meters above sea level.

2.2.7 The Laga Formation

One sample of the Laga Formation was collected near the town of Comunanza (MF-10) in the Province of Fermo, **Figure 2.11**. The sample was taken using a Dutch augur from the top 20 cm of soil, not far from the road, on the edge of a wooded area. The coordinates of the sampling location are 42.9529, 13.3942; and the elevation is 568 meters above sea level.

2.2.8 Minor Intra-Apennine basins

Sample MF-11 was collected along Strada Provinciale 132, in sight of Camerino, Province of Macerata, from an aerated agricultural field overlying the Arenarie di Matelica Formation, **Figure 2.12**. The coordinates of the sampling location are 43.1246, 13.0824; and the elevation is 427 meters above sea level.

2.2.9 External Apennine Ridge: Marly-Calcareous Units

One sample was taken from the Marly-Calcareous Unit of the External Apennine Ridge, MF-12. It was collected along Strada Provinciale delle Cesane, near “Il Caldese” (Urbino), Province of Pesaro and Urbino, using a Dutch augur in a grassy lawn, **Figure 2.13**. The top layer of the soil containing vegetation was discarded. The coordinates of the sampling location are 43.7285, 12.6638; and the elevation is 544 meters above sea level.

2.2.10 Scaglia Rossa Formation (external Apennine Ridge: calcareous units)

Two samples were taken from soils overlying the Scaglia Rossa Formation, outcropping in the Colle Romani locality of the Cesane Mountains, along Strada Provinciale 51, **Figure 2.14**. The two sampling locations were about 50 meters apart not far from a country road. The soil in both locations was poorly developed, ranging in depth from about 5 to 20 centimeters. Samples MF-13a and MF-13b were collected about 20 meters apart at 43.7137, 12.7302; at an elevation of 576 meters above sea level.

2.2.11 Landslide debris

Sample MF-14 was collected from landslide debris overlaying the massive limestone deposits along Via Sant’Anna del Furlo in the Furlo Gorge, Province of Pesaro and Urbino. **Figure 2.15**. The coordinates of the sampling location are 43.6508, 12.7296; and the elevation is 204 meters above sea level. The sample was dark grey in color with little apparent clay content.

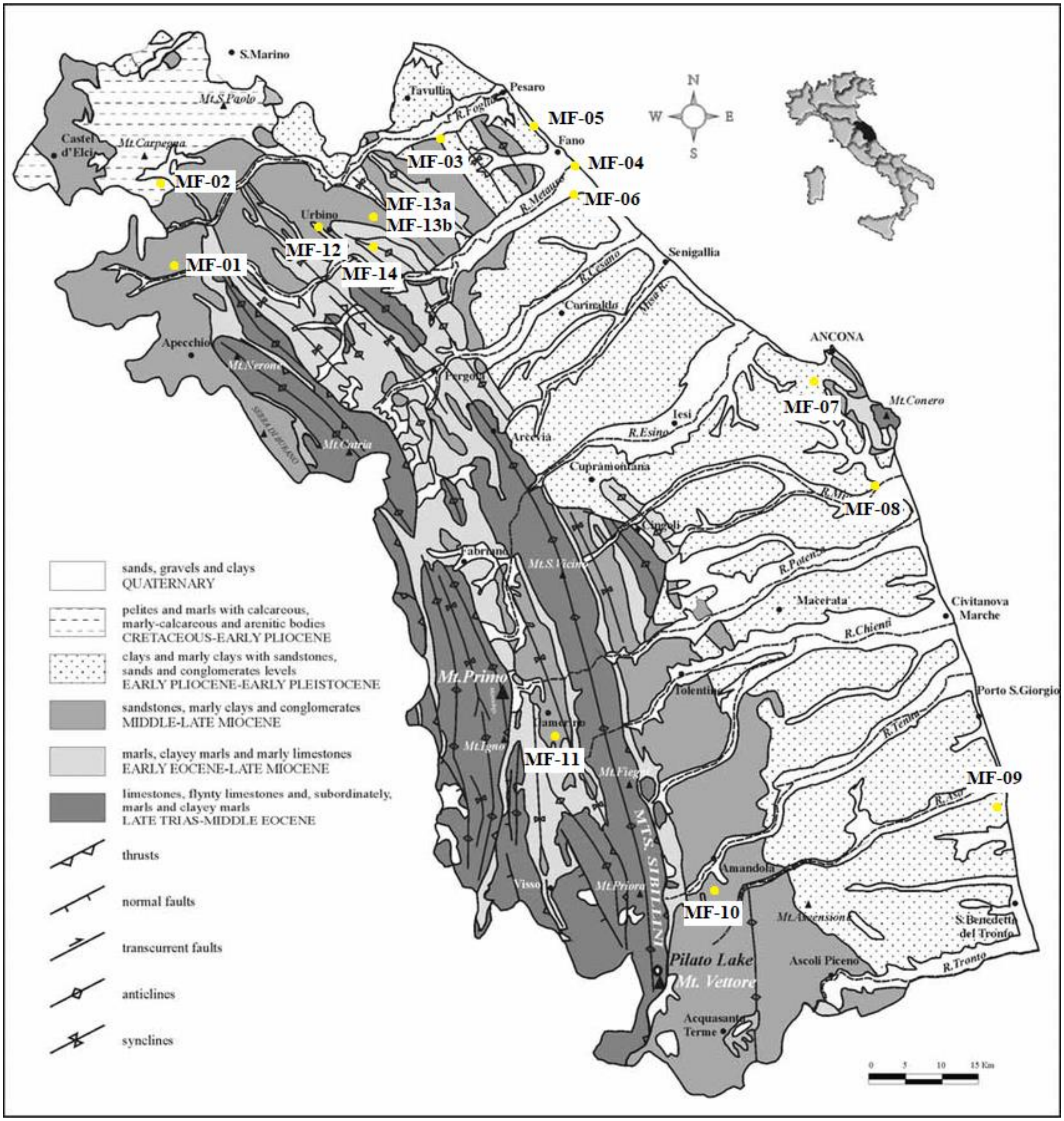

Figure 2.1: The geology of Marche Region and the locations of the fourteen sampling sites (modified after [11]).

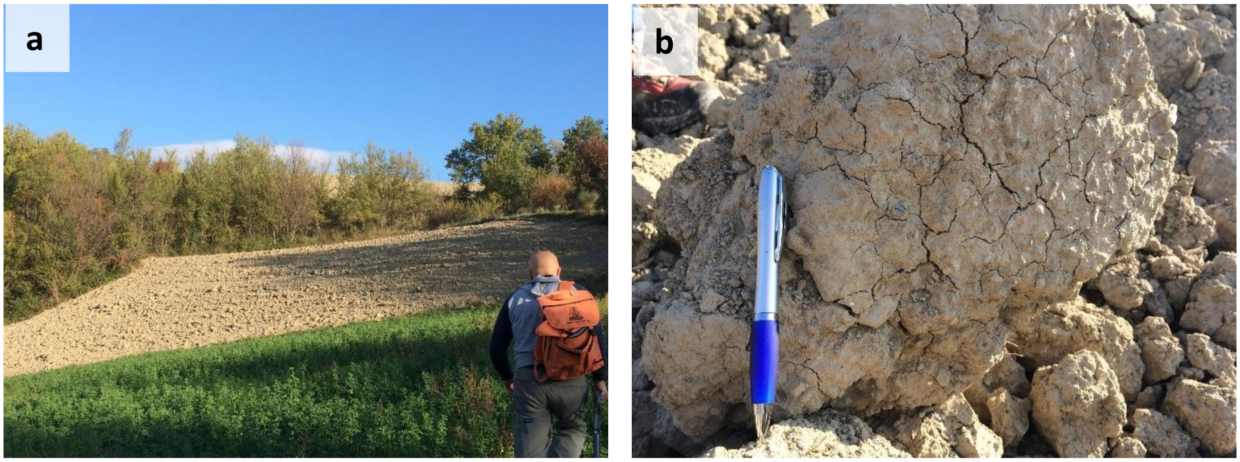

Figure 2.2: A panoramic view (a) and a close up (b) of the sampling location of MF-01.

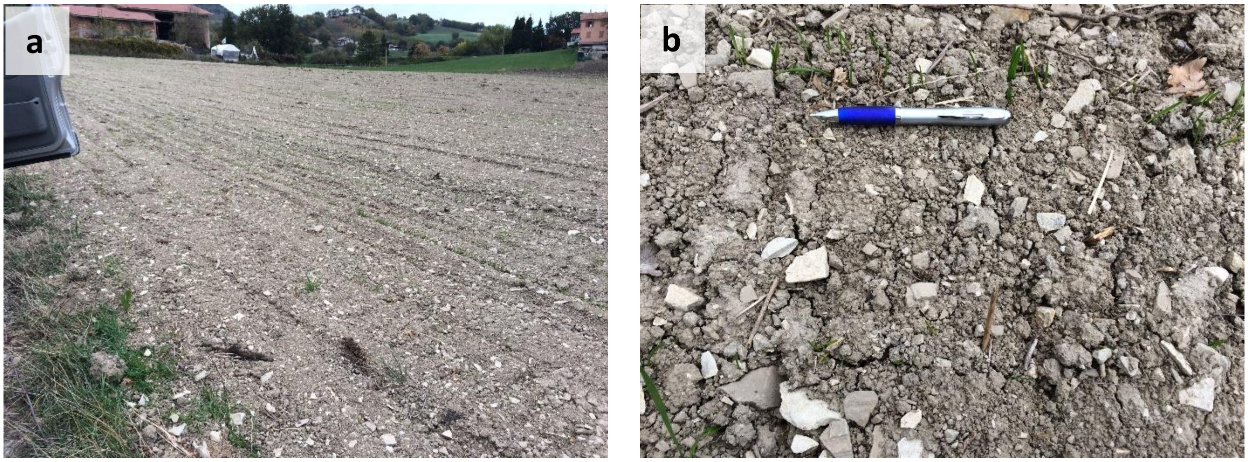

Figure 2.3: A panoramic view (a) and a close up (b) of the sampling location of MF-02.

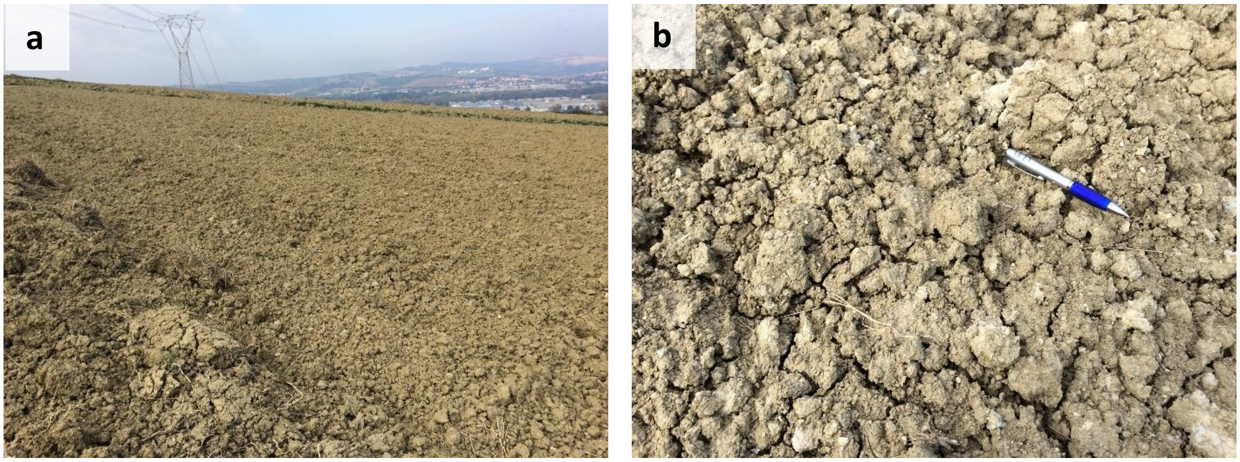

Figure 2.4: A panoramic view (a) and a close up (b) of the sampling location of MF-03.

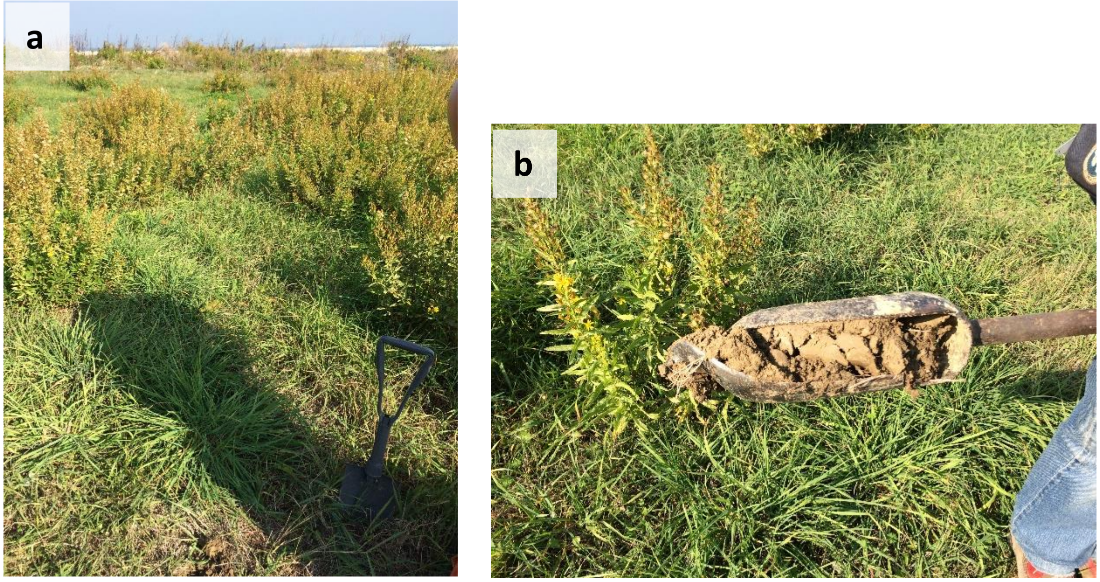

Figure 2.5: A panoramic view (a) of the sampling location and a close up (b) of MF-04.

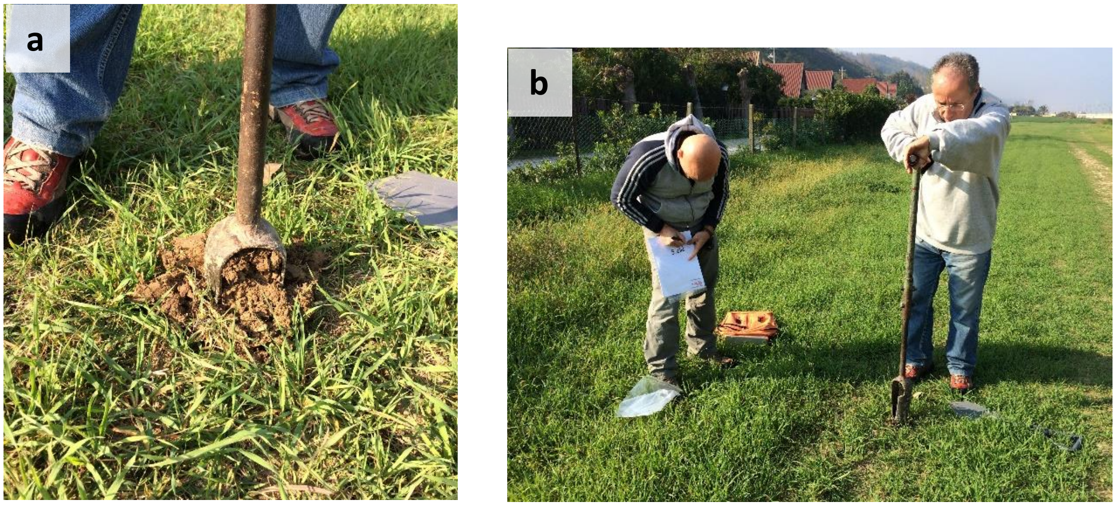

Figure 2.6: A panoramic view (a) and a close up (b) of the sampling location of MF-05.

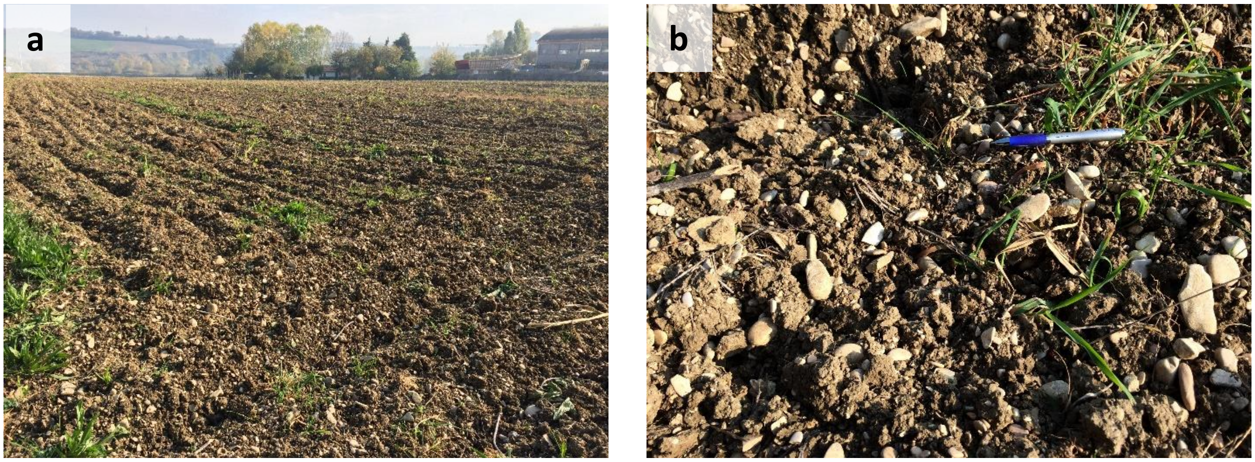

Figure 2.7: A panoramic view (a) and a close up (b) of the sampling location of MF-06.

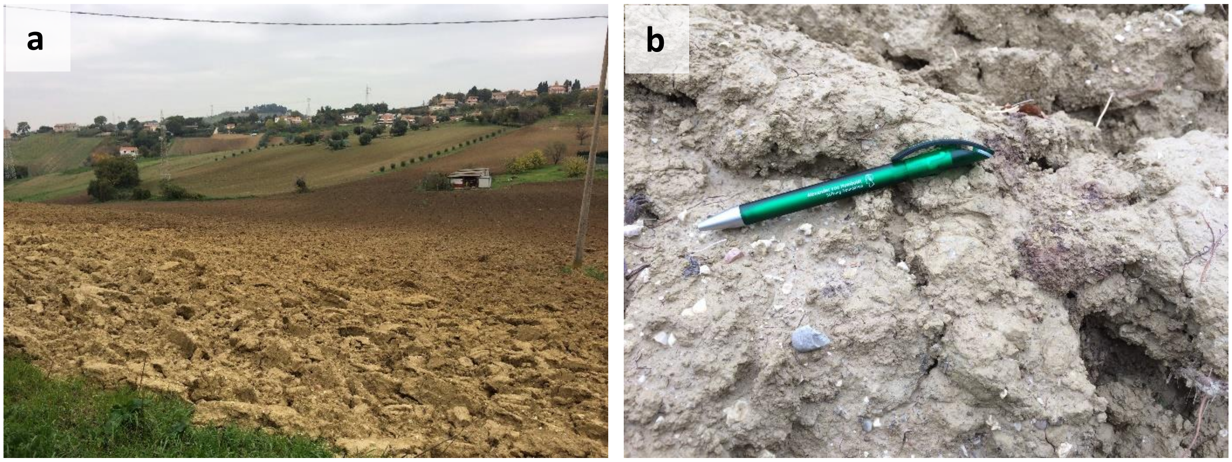

Figure 2.8: A panoramic view (a) and a close up (b) of the sampling location of MF-07.

Figure 2.9: A panoramic view of the sampling location of MF-08.

Figure 2.10: A panoramic view (a) and a close up (b) of the sampling location of MF-09.

Figure 2.11: A panoramic view (a) and a close up (b) of the sampling location of MF-10.

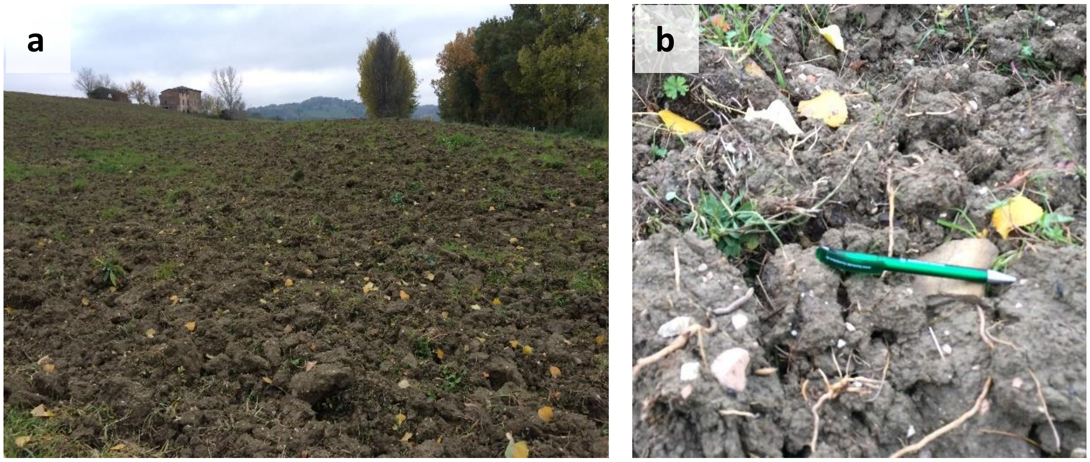

Figure 2.12: A panoramic view (a) and a close up (b) of the sampling location of MF-11.

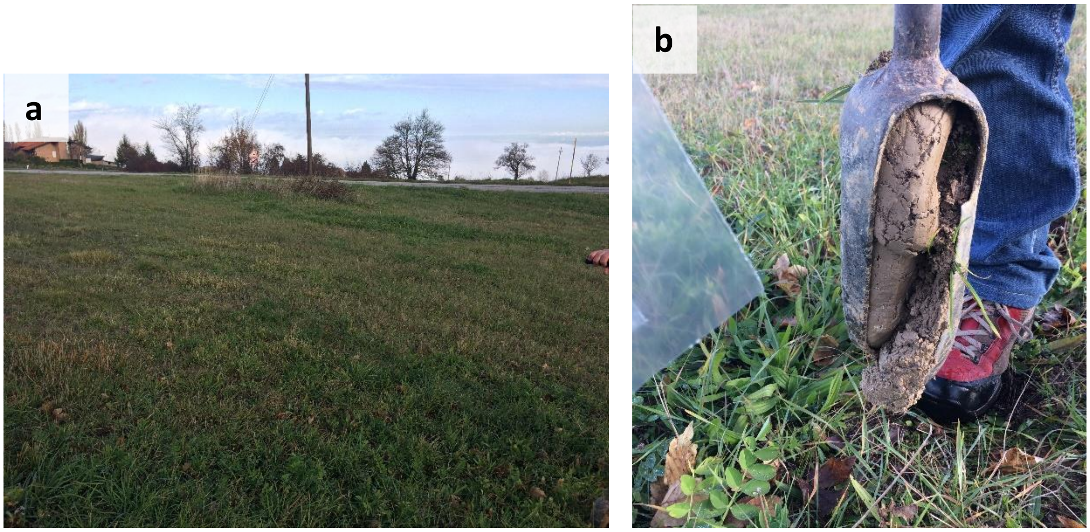

Figure 2.13: A panoramic view (a) of the sampling location and a close up (b) of MF-12.

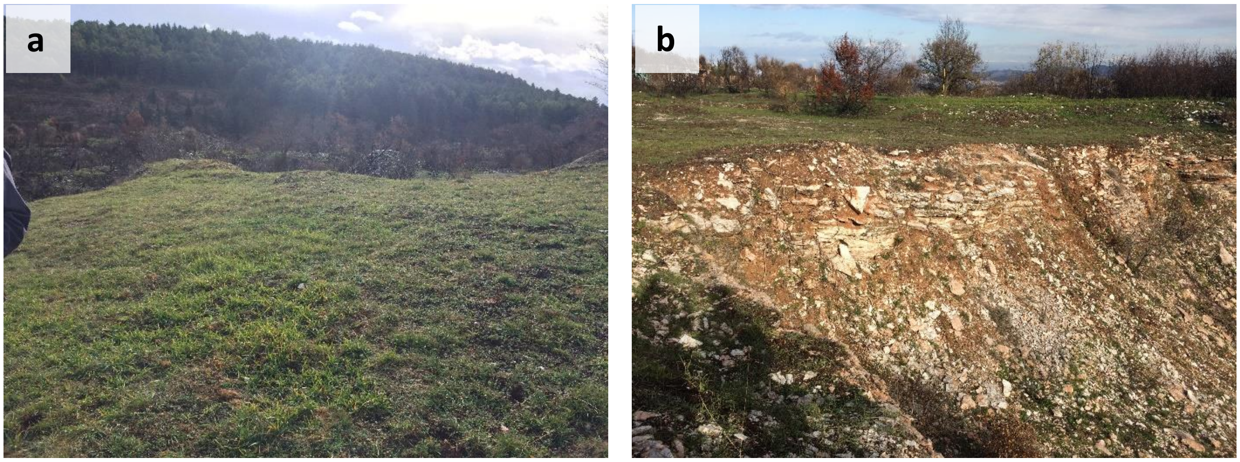

Figure 2.14: A panoramic view (a) and a close up (b) of the sampling location of MF-13a and MF-13b.

Figure 2.15: A panoramic view (a) and a close up (b) of the sampling location of MF-14.

2.3 Sample characterization

2.3.1 Sample preparation and water contents

Immediately following the sampling, the size of each of the samples was reduced using the quartering method to approximately roughly 500 g. Each sample was placed into an aluminum tray and weighed. Following weighing the samples were placed into an oven set to 105°C to dry overnight and then weighed again. The difference in weight was used to calculate the percent water contained in each sample, **Table 2.1**. The water contents of the samples ranged from 4 to 21 percent. In preparation for further characterization the dried samples were gently ground in a ceramic mortar to break up any clumps formed during the drying phase. All analyses, with the exception of the organic content and cation exchange capacity (CEC), were carried out at the University of Urbino "Carlo Bo"

2.3.2 Grain size distribution analysis

2.3.2.1 Methodology

Roughly 150g of each sample were weighed out for grain size distribution analysis. The samples were pre-treated with hydrogen peroxide to remove any organic matter left after initial sieving. The samples were mixed with 500 ml of an 30% solution of hydrogen peroxide added 100ml at a time. Before each addition of H_2O_2, sufficient time was allowed to pass for reactions to seize (**Figure 2.16a**). Samples showing the most violent and prolonged reaction with H_2O_2 were MF-09 and MF-11.

Once the reactions had come to a halt, the samples were wet-sieved to separate the sand fraction from the silt/clay fraction. To this end the samples were transferred into a 62.5 µm sieve suspended over 5 L beakers using a rod, **Figure 2.16b**. The water/sample suspension was stirred manually to facilitate particle movement past each other. Water continued to be added to the sample-filled sieve, until the outflowing water ran clear. The sand fraction left in the sieve was transferred into ceramic bowls and placed into an oven set to 60°C, to dry. The silt/clay fraction suspended in water in 5 L beakers was allowed to settle for the time necessary for the water to become clear, **Figure 2.16c**. As much as possible of the water was then poured out without disturbing the sample. The remaining water was used to facilitate the transfer of the samples from the beaker into ceramic bowls, which were then placed to dry in an oven set to 60°C for the time necessary for complete evaporation of the water.

The sandy fraction of each sample was weighed and separated into progressively finer fractions using a sieve stack consisting of sieves with apertures of 16 mm, 8 mm, 4 mm, 2 mm, 1mm, 500 µm, 250 µm, 125 µm, 62.5 µm. The first two fractions (>16 mm, >8 mm, >4 mm) were obtained manually, while the rest were obtained using a sieve shaker activated for 12 minutes in two 6-minute intervals **Figure 2.17a**. Each grain size fraction obtained was weighed. The grain size distribution of the <63 µ fraction, on the other hand, was determined using a Micromeritics SediGraph particle size analyzer, **Figure 2.17b**. The grain size distribution curves thus obtained are shown in **Figure 2.18**.

Each size fraction was then expressed as a percentage of total weight and the soils classified in line with the tertiary soil classification diagram taken from [6]. The N-values statistical parameters, i.e. mean (Mz) grain size, sorting (σ), skewness (Sk), Kurtosis (Kg), and the median (*d50*) were calculated for each sample in line with procedures described in [7], **Table 2.1**.

2.3.2.2 Results

The soils are mostly poorly sorted clays with variable skewness and kurtosis. Specifically, sample MF-01 is an extremely poorly sorted sandy-gravelly clay with a negatively skewed, mesokurtic grain-size distribution and a median of 8.18; MF-02 is an extremely poorly sorted gravelly-sandy clay with a negatively skewed, platykurtic grain-size distribution and a median of 6.67; MF-03 is a very poorly sorted sandy-gravelly clay with a near symmetrical, platykurtic grain-size distribution and a median of 8.48; MF-04 is an extremely poorly sorted sandy-gravelly clay with a negatively skewed, leptokurtic grain-size distribution and a median of 7.79; MF-05 is an extremely poorly sorted sandy-gravelly clay with a positively skewed, platykurtic grain-size distribution and a median of 6.04; MF-06 is an extremely poorly sorted gravelly-sandy clay with a near symmetrical, very platykurtic grain-size distribution and a median of 4.85; MF-07 is a very poorly sorted sandy-gravelly clay with a near symmetrical, platykurtic grain-size distribution and a median of 8.43; MF-08 is a very poorly sorted sandy gravel with a strongly positively skewed, mesokurtic grain-size distribution and a median of 1.91; MF-09 is a very poorly sorted sandy-gravelly clay with a near symmetrical, platykurtic grain-size distribution and a median of 7.84;

MF-10 is a very poorly sorted sandy clay with a strongly positively skewed, platykurtic grain-size distribution and a median of 4.05; MF-11 is an extremely poorly sorted sandy-gravelly clay with a near symmetrical, mesokurtic grain-size distribution and a median of 7.08; MF-12 is an extremely poorly sorted sandy-gravelly clay with a near symmetrical, platykurtic grain-size distribution and a median of 7.19; MF-13a is an extremely poorly sorted sandy-clayey gravel with a strongly positively skewed, very platykurtic grain-size distribution and a median of 0.51; MF-13b is an extremely poorly sorted gravelly-sandy clay with a negatively skewed, very platykurtic grain-size distribution and a median of 5.88; and MF-14 is an extremely poorly sorted sandy-clayey gravel with a strongly positively skewed, platykurtic grain-size distribution and a median of 0.16.

The grain size distribution histograms of the fifteen samples show a bimodal grain size distribution for about half of the samples (MF-02, MF-04, MF-06, MF-12, MF-13a, MF-13b and MF-14). Six of the samples show a complex pattern of grain size distribution with no apparent peaks (MF-05, MF-07,MF-08, MF-09, MF-10 and MF-11) and two (MF-01 and MF-03) show a clear unimodal distribution, **Figure 2.18**.

When plotted against EPA's [8] grain size distribution ranges of soil washing applicability, **Figure 2.19**, one third of the cumulative grain size distribution curves (MF-02, MF-04, MF-05, MF-11 and MF-12) hug and cross the boundary between regimes I and II, which represent difficult soil washing applicability and soil washing requiring the addition of a custom-formulated washing fluid, respectively. Five samples, MF-06, MF-10, MF-13a, MF-13b and MF-14 are comfortably within the boundaries of regime II and one sample, MF-08, falls into regime III, economic soil washing which may not require chemical additives. Further four samples, MF-01, MF-03, MF-07 and MF-09, fall in Regime I, which makes these soils poor candidates for soil washing.

Table 2.1. Water content, grain size fractions in percentages, grain-size parameters in φ units and soil classification according to Bosellini et al., (1989) for samples MF-01 through MF-14.

Sample Number	water (%)	% gravel	% sand	% silt	% clay	Grain-size parameters				Soil Classification According to Bosellini et al., 1989
		(>2000 µm)	(<2000, >62.5 µm)	(<62.5 µm, >2 µm)	(<2 µm)	Mean, Mz (ϕ)	Sorting, σ (ϕ)	Skewness, Sk (ϕ)	Kurtosis, K_g (ϕ)	
MF-01	4	4	10	49	37	8.18	4.01	-0.11	0.95	sandy-gravelly clay
MF-02	16	18	14	37	31	5.65	5.82	-0.23	0.88	gravelly-sandy clay
MF-03	15	2	7	39	52	8.48	3.59	-0.06	0.84	sandy-gravelly clay
MF-04	16	10	9	47	34	7.72	4.77	-0.19	1.13	sandy-gravelly clay
MF-05	11	4	33	36	26	6.62	4.36	0.12	0.81	sandy-gravelly clay
MF-06	11	33	13	25	30	4.20	6.19	-0.09	0.59	gravelly-sandy clay
MF-07	19	2	8	47	43	8.43	3.46	-0.02	0.76	sandy-gravelly clay
MF-08	5	63	33	2	2	-1.26	2.34	0.43	0.99	sandy gravel
MF-09	14	3	16	36	46	7.86	3.89	-0.03	0.80	sandy-gravelly clay
MF-10	16	1	49	33	17	5.76	3.84	0.58	0.77	sandy clay
MF-11	21	7	21	34	38	7.26	4.55	-0.06	0.93	sandy-gravelly clay
MF-12	17	4	23	38	36	7.21	4.37	-0.05	0.82	sandy-gravelly clay
MF-13a	17	44	14	18	24	2.23	6.20	0.38	0.63	sandy-clayey gravel
MF-13b	17	27	12	25	36	4.83	6.10	-0.18	0.61	gravelly-sandy clay
MF-14	11	41	31	21	8	1.71	5.48	0.42	0.86	sandy-clayey gravel

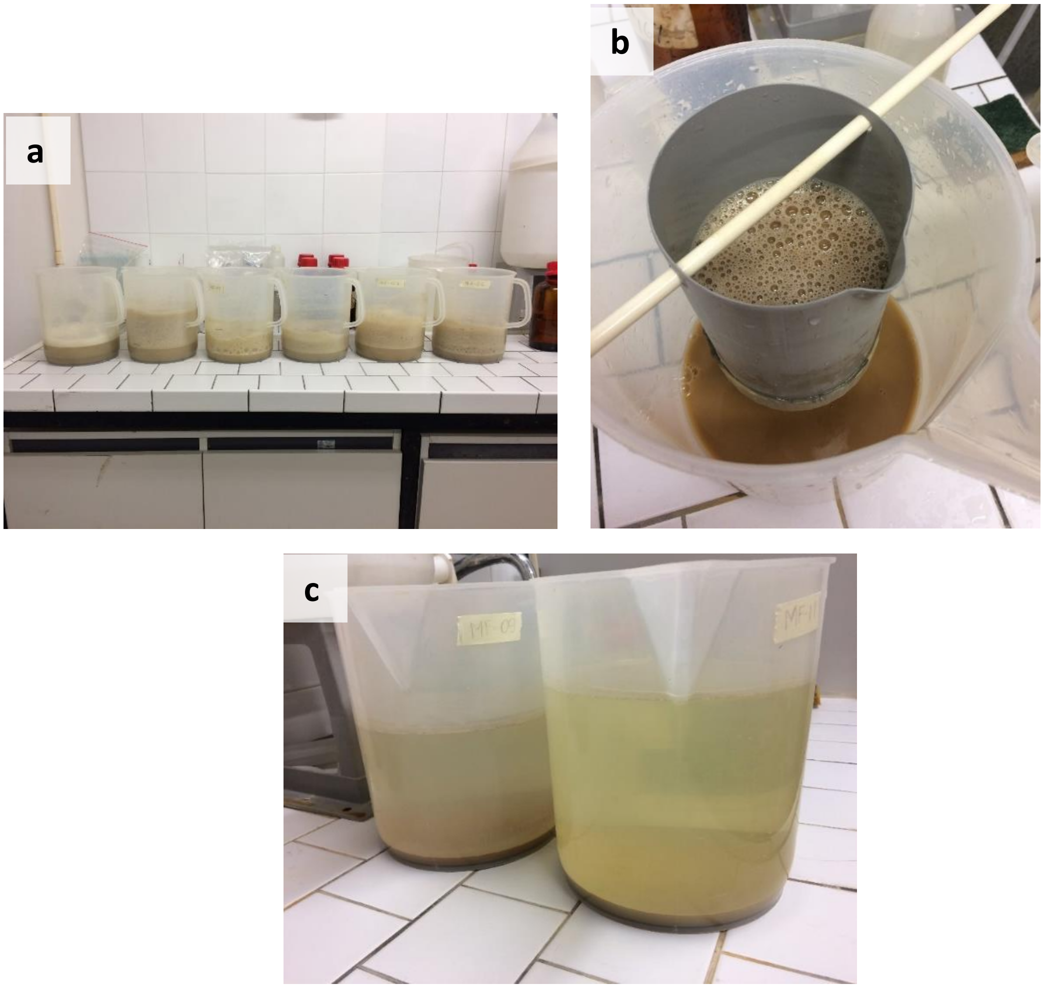

Figure 2.16: (a) Pre-treatment with hydrogen peroxide in 5 L beakers (b) wet-sieving to separate the fines from the sandy fractions (c) The fines fractions of samples MF-09 and MF-11 settling in 5 L beakers.

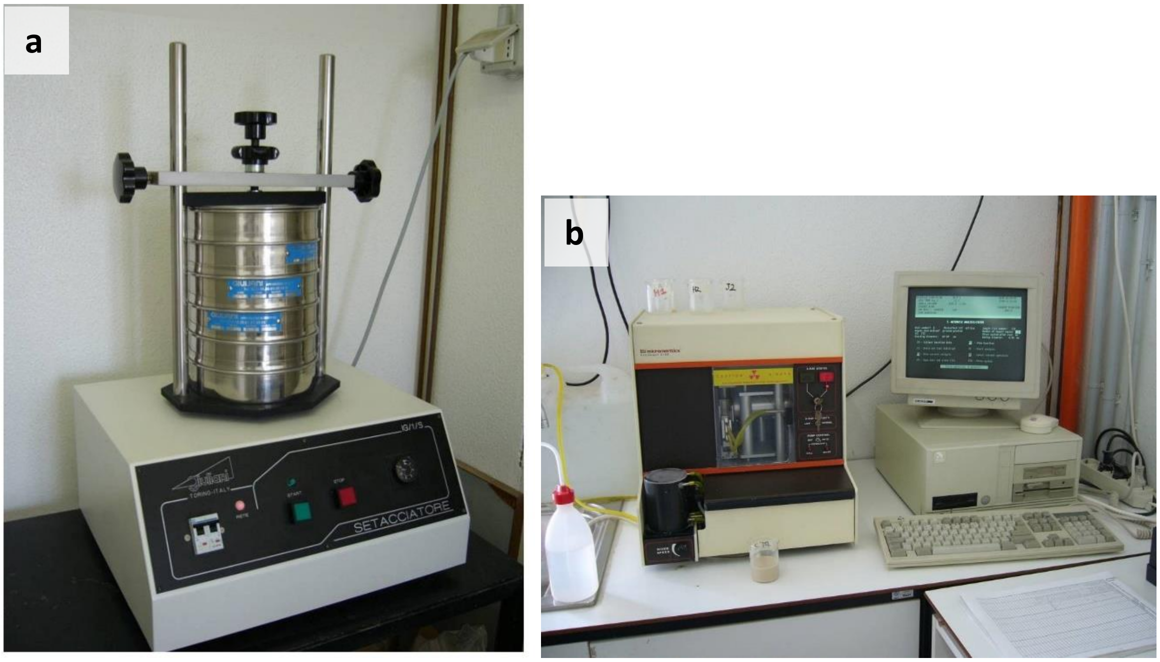

Figure 2.17: (a) The electrical sieve shaker and (b) particle size analyzer used to obtain the grain size distribution of the sand and fines fractions, respectively.

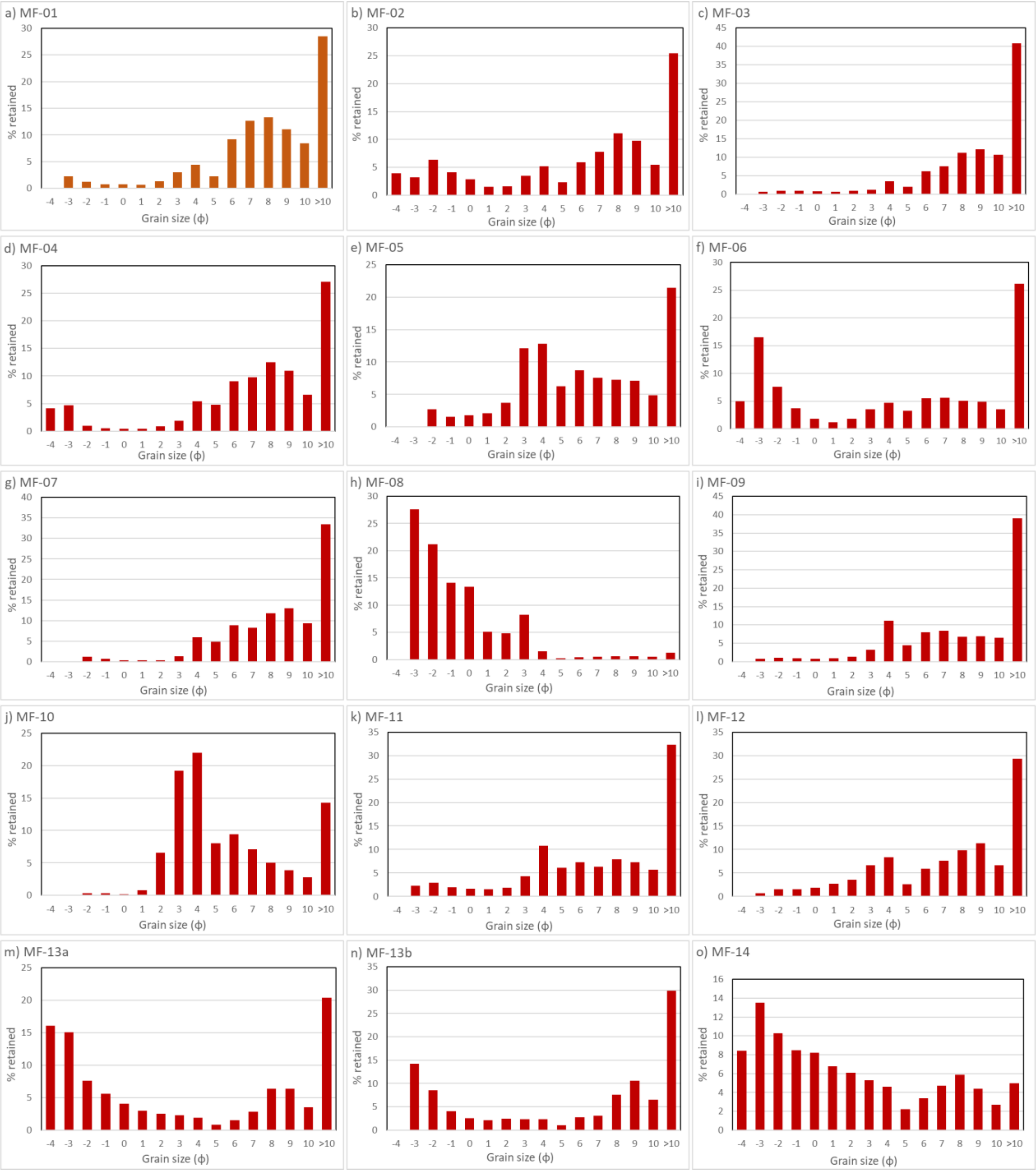

Figure 2.18 Grain size frequency histograms for samples MF-01 through MF-14.

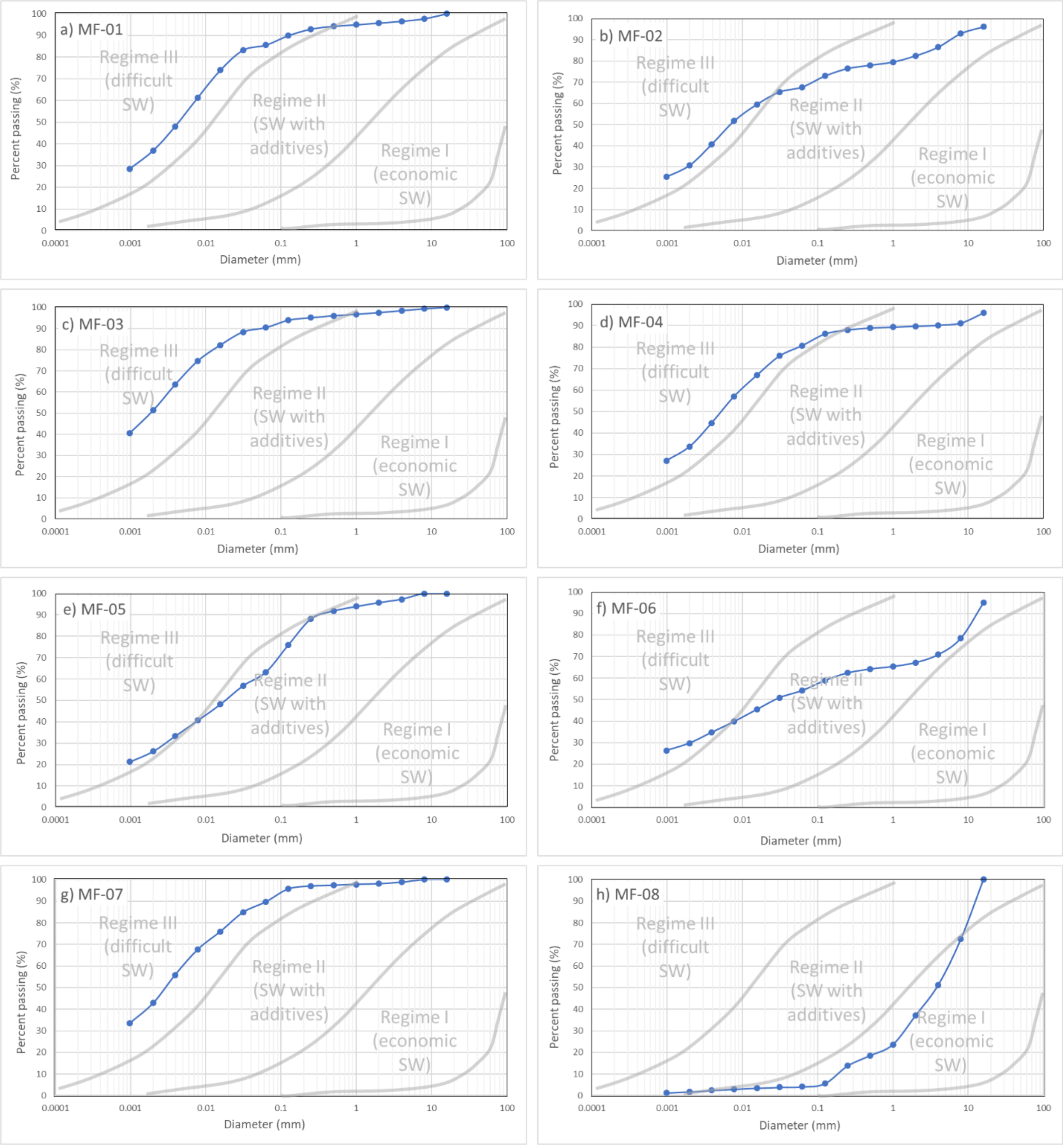

Figure 2.19: (a-h) Cumulative grain-size distribution curves for samples MF-01 through MF-14.

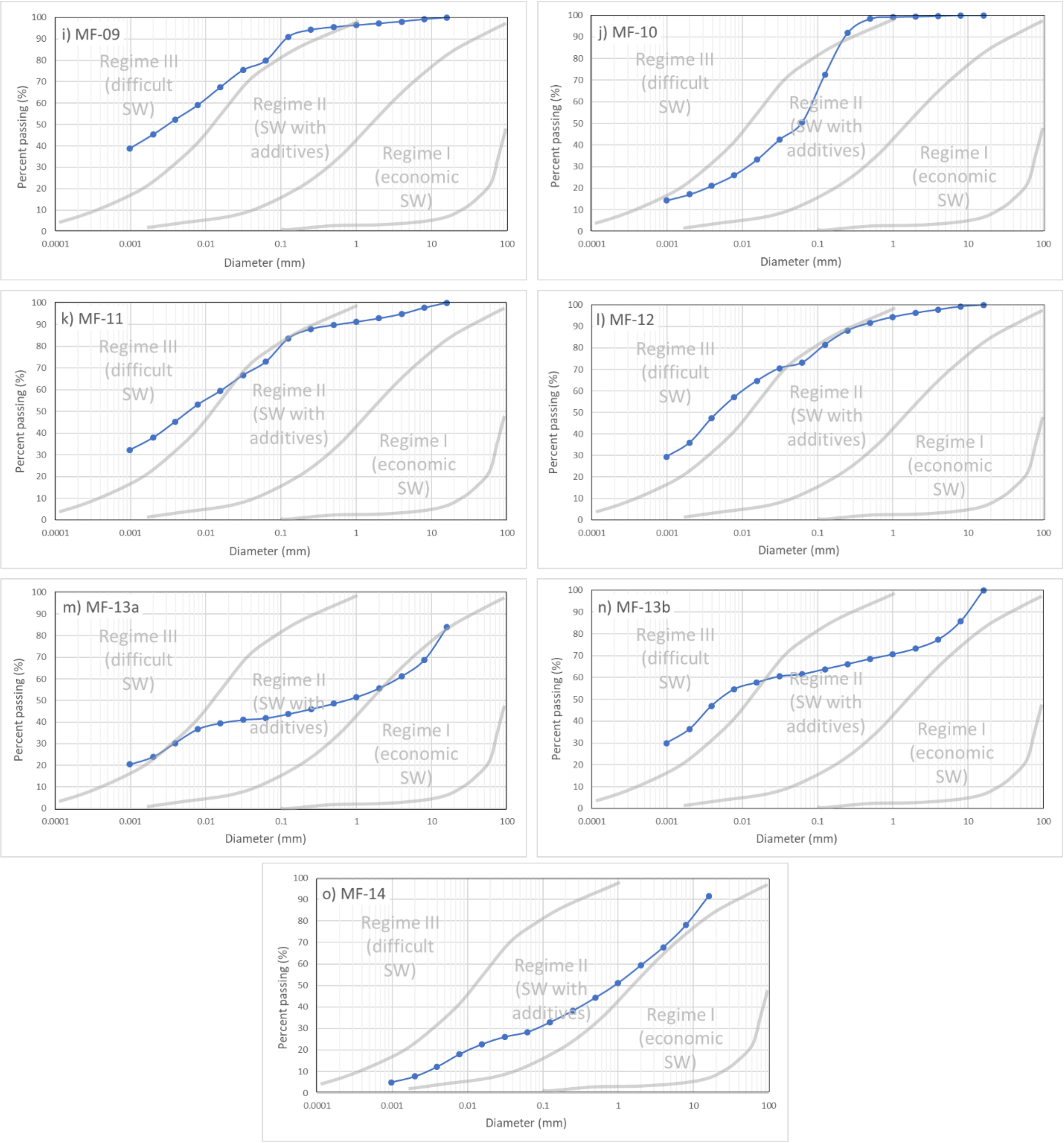

Figure 2.19 cont. (i-o) Cumulative grain size distribution curves for samples MF-01 through MF-14.

2.3.3 pH measurements

2.3.3.1 Methodology

The soil pH was determined for the fines (sand+silt) fractions (<2 mm) of all 15 samples. This fraction was chosen because this was the fraction that would be used in the washing experiments. The procedures from two organizations were used to determine the pH: EPA method 9045D [9] and the Australian Soil and Land Survey test pHW [10].

Following the EPA procedure, 20 grams of each sample was mixed with 40 ml of deionized water obtaining 2:1 soil suspensions. Each suspension was mixed at room temperature using a magnetic stirrer for 15 minutes at 600-800 rpm. The suspensions were allowed to settle for 45 minutes after which, the pH of the suspending liquid was measured using a TRACER PockeTester field pH meter. The measurements were taken three times to confirm repeatability.

Following the Australian Soil and Land Survey (ASLS) procedure, 10 grams of each sample were weighed out using an analytical balance and transferred into 50 ml glass beakers along with 50 ml of deionized water, obtaining 5:1 soil suspensions. The suspensions thus obtained were mechanically mixed using a magnetic stirrer turning at speeds between 200-600 rpm for one hour. The stirring speed was selected as a function of the density of the suspension in question. The pH of the suspensions was then measured using a TRACER PockeTester field pH meter. The measurements were repeated 3-5 times to ensure repeatability.

2.3.3.2 Results

A summary of the results is presented in **Table 2.2** and **Figure 2.20**. The pH of the sampled soils is mildly alkaline, ranging from 8.0 to 8.8. As can be seen in **Figure 2.20**, the samples have mildly alkaline pH with values that vary between the two procedures by as much as 0.8 pH units. Because of the apparently high clay contents of some of the samples, which resulted in large amounts of water being absorbed with the subsequent increasing thickness of the suspensions, it is thought that the ASLS procedure, characterized by a higher water to soil ratio, is the more reliable in this case.

Table 2.2: pH measurements of the 15 soil samples following EPA and ASLS soil pH measurement procedures.

	EPA-based Procedure							ASLS-based Procedure					
Sample Number	Weight (g)	Water (ml)	Stirring		Settling time (min)	Temp (°C)	Average pH	Weight (g)	Water (ml)	Stirring			Average pH
			Velocity (rpm)	Time (min)						Velocity (rpm)	Time (min)	Temp (°C)	
MF-01	20.1	40	800	15	45	22	**8.2**	10	50	500	65	25	**8.5**
MF-02	20	40	600	15	45	22	**8.1**	10	50	400	58	28	**8.4**
MF-03	20	40	600	15	45	22.4	**8.3**	10	50	200	67	26	**8.5**
MF-04	20	40	800	15	45	22.7	**8.5**	10	50	200	60	27.7	**8.8**
MF-05	20	40	600	15	45	23.6	**8.5**	10.01	50	400	60	28	**8.7**
MF-06	20	40	600	15	45	23.3	**8.2**	10	50	200	60	28.6	**8.5**
MF-07	20.1	40	600	15	45	19.7	**8.0**	10	50	400	60	29.7	**8.8**
MF-08	19.9	40	600	15	45	19.9	**8.2**	10	50	500	60	29.7	**8.5**
MF-09	20	40	800	15	45	20	**8.3**	10	50	600	62	23	**8.7**
MF-10	20	40	600	15	45	20.1	**8.5**	10	50	500	61	25	**8.3**
MF-11	20	40	600	15	45	20.8	**8.1**	10	50	600	60	27.8	**8.3**
MF-12	20	40	600	15	45	21	**8.3**	10	50	500	61	26.7	**8.6**
MF-13a	20	40	800	15	45	20.8	**8.0**	10	50	600	60	29.5	**8.3**
MF-13b	20	40	600	15	45	19.2	**8.6**	10	50	500	60	28.4	**8.4**
MF-14	20	40	600	15	45	21.4	**8.7**	10	50	600	62	30	**8.7**

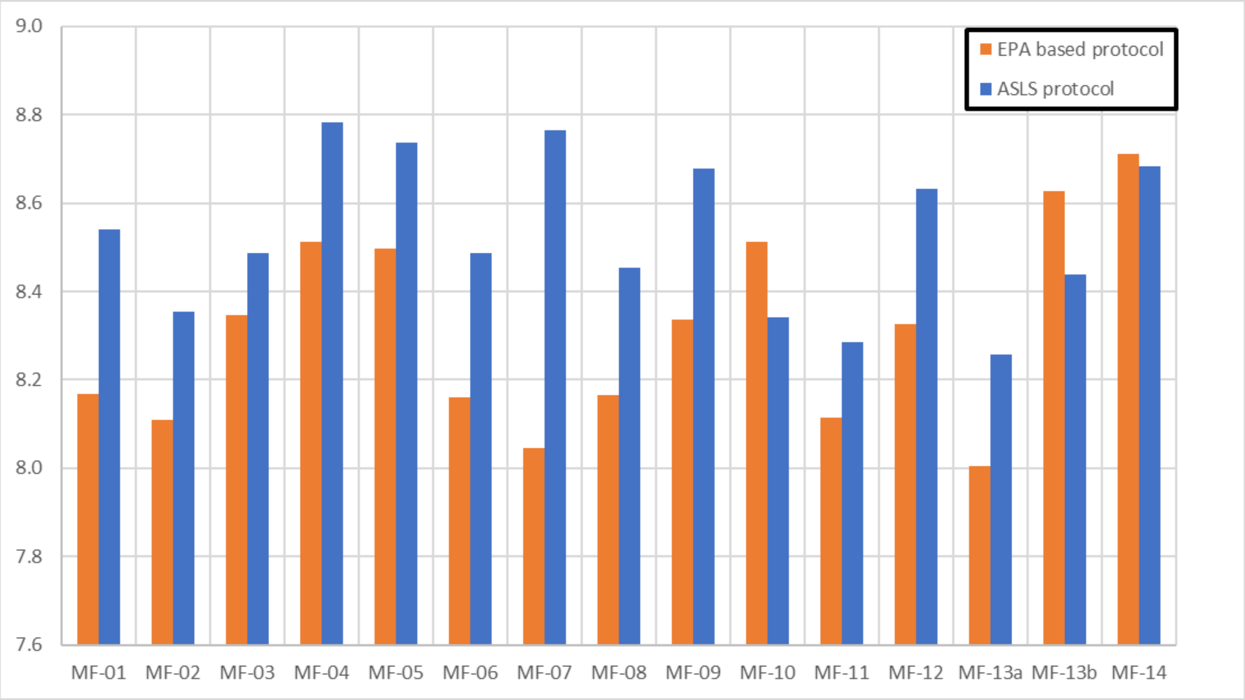

Figure 2.20: A comparison of pH measurements obtained using the two methodologies.

2.3.4 Atterberg limits

The Atterberg Limits, i.e. the Liquid and the Plastic Limits of a soil representing the moisture content, expressed as percent water, at which the consistency of a soil changes from liquid to plastic and from plastic to semi-solid, respectively. Knowing these parameters allows to distinguish silts from clays and to assess the expansion potential of a soil. For the purposes of this study, the limits where used to assess the probability of absorption of the water solution by the soil during washing. The Atterberg limits were determined for soil fractions passing through a sieve with a 0.425 mm aperture. All samples had previously been oven dried and gently crushed in a ceramic mortar to break up any clumps, removing as much of the organic material as possible (mainly sticks, grass, roots and snail shells).

2.3.4.1 Methodology

The Liquid Limits were determined utilizing the Casagrande apparatus. First, some of the sample to be analyzed was combined with tap water in a ceramic bowl. The water was added a little at a time to allow time for absorption. The mixture was then kneaded and stirred until it had the consistency of a paste. This paste was then transferred into the bowl of the Casagrande apparatus with a spatula, filling it about 2/3 of the way and smoothing out its surface with as few strokes as possible to avoid air entrapment. A grooving tool was then used to incise a clean, vertical groove across the centerline of the soil mixture exposing about 2 mm of the bowl’s bottom and dividing the sample in two halves, **Figure 2.21**. Next, the crank of the apparatus was turned, lifting and dropping the bowl until the two halves of the sample flowed together, closing the groove for a length of 10-14 mm. The number of drops required to achieve this were recorded and a small amount of the paste was then transferred into a metal dish, weighed and placed into an oven set to 105°C for at least 6 hours to dry. Once dried the sample was weighed again to determine the moisture content. Next, the sample was placed onto a glass sheet and kneaded to facilitate evaporation before being placed back into the Casagrande apparatus. The procedure described above was then repeated at least two more times. The object being to obtain moisture content values corresponding to drop amounts ranging from 15 to 35. The resulting moisture contents were plotted on a semi-logarithmic scale. The curve thus obtained was used to determine the water content corresponding to 25 drops, which is by definition the Liquid Limit.

The Plastic Limits of the samples were determined utilizing the pastes prepared during the Liquid Limit tests. Each paste was rolled out into three threads with a diameter of 3 mm. The threads were then in turn rolled on a textured glass plate to gradually remove moisture until they began to crack. At this stage they were placed in an aluminum dish, weighed and set in an oven at 105°C to dry for at least 6 hours after which they were weighed once more to permit the calculation of the moisture content. The moisture contents at the plastic limit obtained for all three threads were then averaged to obtain the final value of the plastic limit.

The values of the liquid and plastic limits of all 15 samples thus obtained were then used to calculate the plasticity index using the following formula:

PI=FL-PP

Where, PI is the plasticity index, FL is the fluid limit and PL is the plastic limit. The values of the Atterberg parameters for all soil samples are listed in **Table 2.3**.

2.3.4.2 Results

The liquid limits of the samples range from 24 to 50, while the plastic limits range from 21 to 31. For four of the samples, MF-08. MF-13a, MF-13b and MF-14, neither the liquid nor the plastic limit could be determined, while for sample MF-03 only the plastic limit could not be determined. Hence, these samples can be classified as exhibiting non-plastic behavior. Of the remaining ten samples two, MF-05 and MF-10, can be classified as having low plasticity, with plasticity index values falling between 5 and 10; seven, MF-01, MF-02, MF-04, MF-06, MF-09, MF-11, MF-12, can be classified as having medium plasticity, with values falling between 10 and 20; and just one, MF-07, can be classified as having high plasticity with a plasticity index that falls between 20 and 30 **Table 2.3**.

2.3.5 Cation Exchange Capacity (CEC) and organic content

The cation exchange capacity (CEC) and the organic content of the fifteen samples were determined at ALS Global in the Czech Republic. The cation exchange capacity was determined using the barium chloride method (S-CECBACL2), while the total organic content was determined via the combustion method using IR (S-TOC1-IR). The results are reported in **Table 2.3**. The organic contents of the samples range from 0.21 to as high as 6.37% of dry weight. The cation exchange capacity values, on the other hand, vary from 7.18 to 35 cmol/kg.

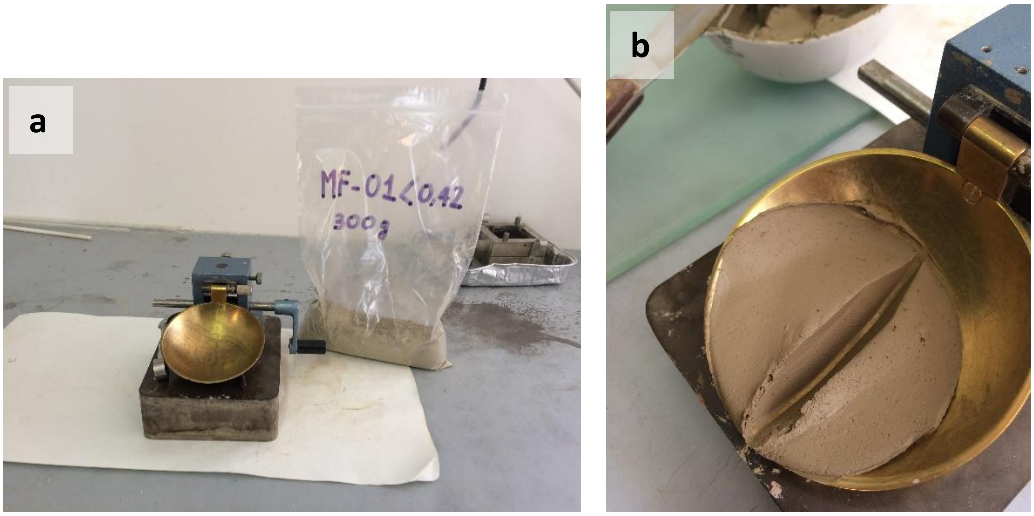

Figure 2.21: The Casagrande apparatus (a) and a sample divided in half ready for the lift and drop phase (b).

Table 2.3. Organic carbon, cation exchange capacity (CEC) and Atterberg Limits of the fifteen soil samples.

Sample Number	Organic Carbon	CEC (cmol+/kg)	Liquid Limit (%W)	Plastic Limit (%W)	Plasticity Index
MF-01	0.95	15.6	40.1	24.6	15.5
MF-02	1.81	24.5	47.2	30.7	16.5
MF-03	0.71	23.2	47.6	0	NP*
MF-04	1.13	19.7	41	27.7	13.3
MF-05	1.05	12.6	30.2	23.5	6.7
MF-06	1.58	19.3	42.4	24.2	18.2
MF-07	0.21	18.4	50	25.2	24.8
MF-08	5.96	7.18	0	0	NP*
MF-09	0.83	19	38.7	23.6	15.1
MF-10	0.26	8.28	24.2	21.7	2.5
MF-11	1.58	21.1	48.6	31.4	17.2
MF-12	0.81	20.7	46.6	30.9	15.7
MF-13a	6.37	31.2	0	0	NP*
MF-13b	4.32	35	0	0	NP*
MF-14	4.17	18.1	0	0	NP*

*** NP stands for non-plastic**

2.3.6 X-ray diffraction (XRD) characterization

2.3.6.1 Methodology and instrument settings

The mineralogic characterization of the samples was carried out using X-ray Diffraction analysis. Two grain size fractions of each of the fifteen samples were analyzed: <62.5 µm and between 62.5 µm and 2000 µm. Each of the thirty samples thus obtained were gently crushed into a fine powder in a marble mortar. The powders were then tightly packed in an aluminum holder specially designed to maximize peak resolution in mixed mineral samples, **Figure 2.22**. The samples were analyzed with a Phillips X'Change PW3710 X-ray powder diffractometer equipped with a Cu x-ray tube and using Bragg-Brentano geometry. The analytical conditions were set at 35 kV and 30 mA. The scanning was carried out across an angle range of 2-65° with a step size of 0.01°. As an example, the diffraction patterns of the sand and fines fractions of sample MF-05 are shown in **Figure 2.23**. The peaks identified in the diffraction patterns of each powder sample were then compared to reference patterns to identify the dominant phases present in the samples. Once the phases were identified, a qualitative analysis of their relative abundances was performed by comparing the heights of the main peaks of each phase present in a given diffraction pattern.

2.3.6.2 Results

The samples consist of variable amounts of quartz, calcite, mica-type minerals and clay minerals, with occasional plagioclase and alkali feldspar. The mineral phase compositions and their relative abundances are shown in **Table 2.4**.

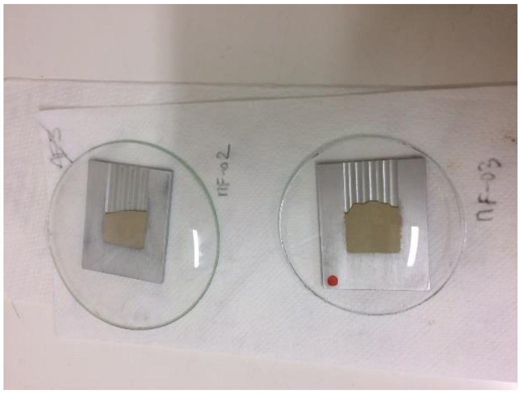

Figure 2.22: XRD sample holders with samples MF-02 and MF-03 ready for analysis. The holders were specially designed to minimize background signal and maximize peak resolution.

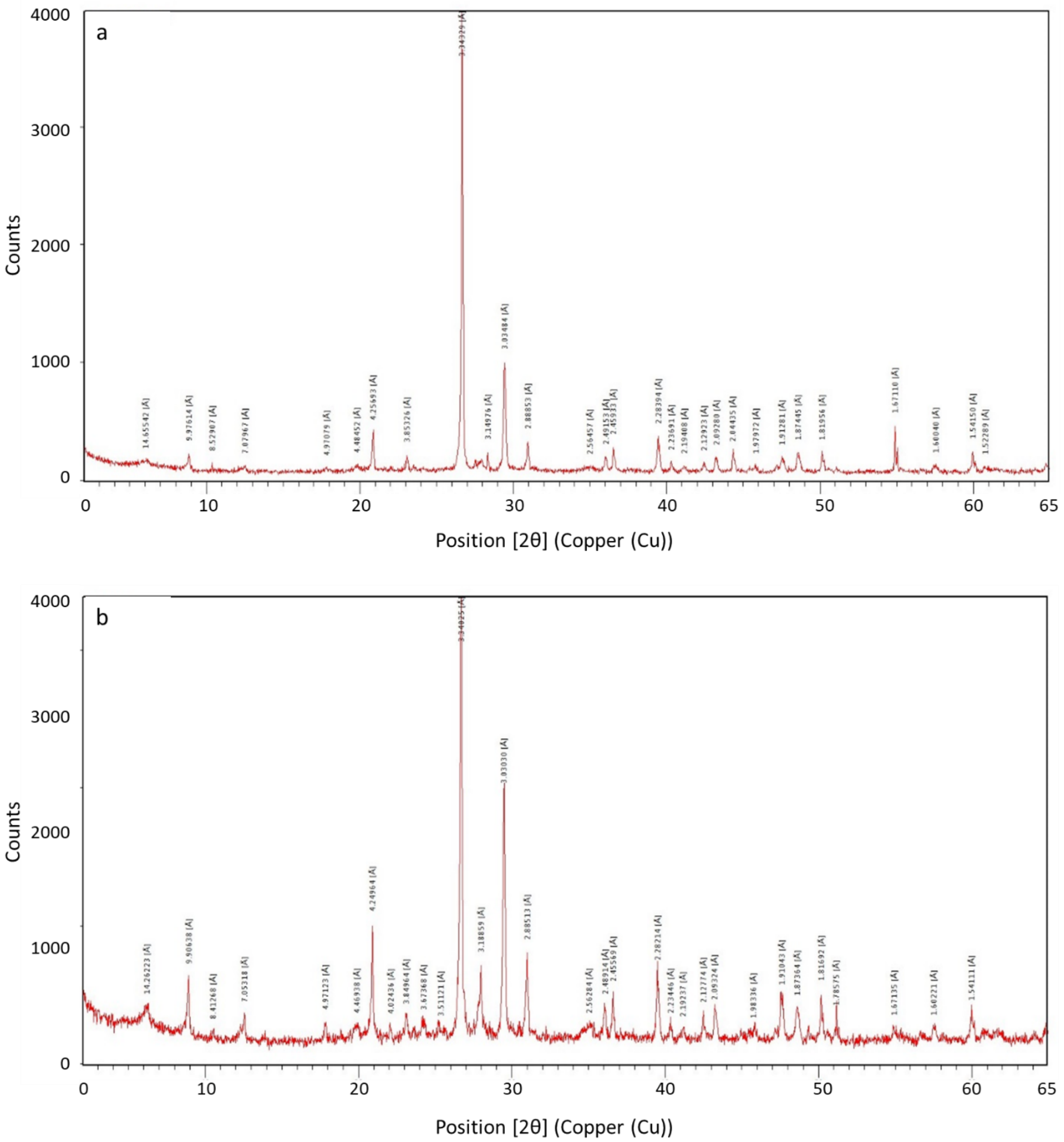

Figure 2.23. X-ray powder diffraction scans of the sand (a) and fines (b) fractions of MF-05.

Table 2.4. Major mineral phases and their abundances in percepts obtained using X-ray powder diffraction.

Sample Nome	sand fraction						fines fraction (<62.5 µm)						sand+fines fraction (<2000 µm, >62.5 µm)						
	quartz %	calcite %	mica %	clays %	plagioclase %	feldspar %	quartz %	calcite %	mica %	clays %	plagioclase %	feldspar %	quartz %	calcite %	mica %	clays %	plagioclase %	feldspar %	Total %
MF-01	19	18	51	7	5		21	23	40	8	7		20.8	22.5	41.1	7.9	6.8	0.0	99
MF-02	18	40	32	8	3		12	48	30	7	3		13.0	46.6	30.3	7.2	3.0	0.0	100
MF-03	20	23	42	9	5		23	30	32	9	6		22.8	29.5	32.7	9.0	5.9	0.0	100
MF-04	24	36	27	5	7		23	38	27	4	7		23.1	37.8	27.0	4.1	7.0	0.0	99
MF-05	26	23	38	8	5		33	36	31				30.6	31.5	33.4	2.8	1.7	0.0	100
MF-06	24	32	28	5	11		28	36	20	7	9		27.2	35.2	21.5	6.6	9.4	0.0	100
MF-07	19	58	18	5			17	39	37	4	3		17.2	40.6	35.4	4.1	2.8	0.0	100
MF-08	16	79			4		59	36			5		20.6	74.4	0.0	0.0	4.1	0.0	99
MF-09	31	23	35		11		28	20	41		11		28.5	20.5	40.0	0.0	11.0	0.0	100
MF-10	18		63	5	14		62			9	17	11	40.2	0.0	31.2	7.0	15.5	5.6	99
MF-11	27	31	23	11	8		25	43	23	9			25.5	40.3	23.0	9.5	1.8	0.0	100
MF-12	14	48	20	14	5		16	59		20	5		15.5	56.4	4.7	18.6	5.0	0.0	100
MF-13a	20	73		7			12	82		6			14.0	79.8	0.0	6.3	0.0	0.0	100
MF-13b	13	76		11			6	84		9			7.2	82.7	0.0	9.3	0.0	0.0	99
MF-14	3	97					5	95					4.0	96.0	0.0	0.0	0.0	0.0	100

2.4 Selection of samples for washing experiments

The selection of soil samples for use in laboratory soil washing experiments was carried out in two steps. First, soils meeting the minimum requirements for successful soil washing had to be identified. Specifically, the cation exchange capacity, organic content and clay percentage of the soils, which should be below 5-10 cmol/kg, 2 wt% and 30 wt% respectively. In addition, soils with lower plasticity index values where given preference since a low plasticity index is another indicator of low clay content. Second, since one of the goals of this study is to evaluate the efficiency of certain surfactants in washing soils of different mineral compositions, the mineral phase abundances had to be considered. In addition, the locations of the sampling sites were kept in mind to ensure that areas and soils at greatest risk of future contamination were included in the study. Hence, soils sampled from areas with the greatest population density also had to be given preference.

During the first stage of the evaluation, sample MF-01 was taken out of consideration due to its high clay contents (49%); samples MF-08, MF-13a, MF-13b and MF-14 were excluded due to high organic contents (5.96, 6.37, 4.32 and 4.17 % dry wt., respectively); while samples MF-02, MF-03, MF-11 and MF-12 where removed from consideration because of high CEC values (24.5, 23.2, 21.1 and 20.7 cmol/kg, respectively). Of the remaining six soils, five (MF-04, MF-05, MF-06 and MF-07) had calcite as their dominant phase, with quartz being the second most abundant, while samples MF-09 and MF-10 had quartz and mica-type minerals as the most abundant phases, with calcite being present in MF-09 in smaller amounts and absent in MF-10. From the first group, MF-05 had the lowest plasticity index and was sampled along the Adriatic coast, in one of the most densely populated areas of the Marche Region. In the second group, the much lower clay content, lower CEC and plasticity index, as well as the lack of calcite of sample MF-10 made it the best candidate for soil washing efficiency comparisons with MF-05.

2.5 References

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Chapter 3

Fine-tuning of the experimental protocol with gasoline as the contaminant.

3.1 Analytical phase

3.1.1 Gas Chromatography-Mass Spectrometry (GS-MS) settings

All GS-MS analyses were carried out at the Liquid Chromatography and Mass Spectrometry Laboratory of the University of Urbino's DiSPeA Department utilizing an Agilent Technologies 6890 Series gas chromatographer, **Figure 3.1**, equipped with an Agilent Technologies 7683B automatic sampler and correlated with an Agilent Technologies 5976C Series inert XL MSD mass spectrometer equipped with a triple-axis detector. The analytes were separated in an Agilent Technologies HP-5 MS column with a length of 30 m, internal diameter of 0.25 mm and stationary phase thickness of 0.25 µm. The column was brought up to temperature according to the following program: two minutes at 75°C, then up to 245°C at a rate of 25°C/min. and then to 320°C at a rate of 6°C/min. for a total run time of 25 minutes. The carrier gas (He) flow rate was set at 1 ml/min. The injector was operating in splitless mode, which ensured maximum sensitivity, at a temperature of 300°C and an injection volume of 1µl. The transfer line temperature was set at 280°C. The mass spectrometer source and quadrupole temperatures were set at 280°C and 150°C, respectively. Data collection was carried out in the Selected Ion Monitoring (SIM) mode with an acquisition window of 5-24 min. Mass spectra of n-Alkanes are marked by a characteristic fragmentation where the m/z 57 ion is one of the most stable. Hence, this was the ion monitored in this work for n-Alkanes. A list of all n-Alkanes characterized is given in **Table 3.1**. The ions monitored for the non-deuterated and deuterated pairs of PAH compounds of interest are listed in **Table 3.2**

Figure 3.1. Agilent Technologies 6890 Series gas chromatographer and Agilent Technologies 5976C Series inert XL MSD mass spectrometer.

Table 3.1. A list of all n-Alkanes analyzed.

Carbon N.	n-Alkane	Carbon N.	n-Alkane
C10	**n-Decane**	C23	**n-Tricosane**
C11	**n-Undecane**	C24	**n-Tetracosane**
C12	**n-Dodecane**	C25	**n-Pentacosane**
C13	**n-Tridecane**	C26	**n-Hexacosane**
C14	**n-Tetradecane**	C27	**n-Heptacosane**
C15	**n-Pentadecane**	C28	**n-Octacosane**
C16	**n-Hexadecane**	C29	**n-Nonacosane**
C17	**n-Heptadecane**	C30	**n-Triacontane**
C18	**n-Ocatadecane**	C31	**n-Hentriacontane**
C19	**n-Nonadecane**	C32	**n-Dotriavontane**
C20	**n-Eicosane**	C33	**n-Triatriacontane**
C21	**n-Heneicosane**	C34	**n-Tetriacontane**
C22	**n-Docosane**	C35	**n-Pentatriacontane**

Table 3.2.A list of the 16 PAH compounds analyzed as well as their corresponding deuterated compounds and their characteristic ions.

PAH	Ion (m/z)	Deuterated PAH	Ion (m/z)
Naphthalene	128	Naphthalene D8	136
Acenaphthylene	152	Acenaphthylene D8	160
Acenaphthene	153	Acenaphthene D10	164
Fluorene	166	Fluorene D10	176
Phenanthrene	178	Phenanthrene D10	188
Anthracene	178	Anthracene D10	188
Fluoranthene	202	Fluoranthene D10	212
Pyrene	202	Pyrene D10	212
Benz[a]anthracene	228	Benz[a]anthracene D12	240
Chrysene	228	Chrysene D12	240
Benzo[b]fluoranthene	252	Benzo[b]fluoranthene D12	264
Benzo[k]fluoranthene	252	Benzo[k]fluoranthene D12	264
Benzo[a]pyrene	252	Benzo[a]pyrene D12	264
Indeno(1,2,3-c,d)pyrene	276	Indeno(1,2,3-c,d)pyrene D12	288
Dibenz[a,h]anthracene	278	Dibenz[a,h]anthracene D14	292
Benzo[g,h,i]perylene	276	Benzo[g,h,i]perylene D12	288

3.1.2 Calibration curves for n-Alkanes

The calibration curves for the n-Alkanes were initially prepared using LGC-Dr. Ehrenstorfer DRO1 Mixture 1 (1000 ng/µl in n-Hexane) containing alkanes ranging from n-Decane (C10) to n-Pentacosane (C25). For later analysis, LGC-Dr. Ehrenstorfer Alkanes-Mix 10 (500 ng/µl in Toluene) containing alkanes ranging from n-Decane (C10) to n-Pentatriacontane (C35) was used primarily because the larger amounts of heavier alkanes present in diesel with respect to gasoline. In all cases the two lighter alkanes, n-Decane and n-Undecane, were not taken into consideration because they were often masked by elevated levels of background noise characteristic of the initial few minutes of the runs. The n-Alkane concentrations used for the calibration curves were 0.1 ppm 0.2 ppm, 0.5 ppm, 1 ppm, 5 ppm and 10 ppm, with 0.1 ppm and 10 ppm being set as the lower and upper quantification limits for the analyses. Each of the chosen concentrations was prepared by the progressive dilution method. Each sample was analyzed three times to check for instrumental repeatability. Chromatograms of m/z 57 ion were extracted and the areas under the peaks located at retention times corresponding to each n-Alkane calculated using the software provided with the instrument. The average areas under each peak were then plotted against the known concentrations of the analyzed solutions to obtain a linear curve (ex. **Figure 3.2a**). A list of correlation equation parameters, coefficients and corresponding relative standard deviations for each standard concentration are given in **Table 3.3.** Only curves with correlation coefficients greater than 0.99 were utilized. No deuterated standard for n-Alkanes is currently available hence, an internal standard could not be used for their quantification. In order to account for any changes in instrument response, new calibration curves were prepared for all n-Alkanes of interest once a month.

3.1.3 Calibration curves for PAH compounds

Calibration curves for PAH compounds were prepared using LGC-Dr. Ehrenstorfer PAH Mix 9 (100 ppm in cyclohexane) and LGC-Dr. Ehrenstorfer PAH Mix 9 Deuterated (100 ppm in cyclohexane). Six standard solutions were prepared using the progressive dilution method containing 1 ppm of deuterated PAHs and non-deuterated PAH compounds in the following concentrations: 0.1 ppm, 0.5 ppm, 1 ppm, 5 ppm and 10 ppm. Each solution was analyzed three times to ensure instrumental repeatability. Chromatograms of ions corresponding to each individual PAH compound (deuterated and non-deuterated) were extracted and the area under the main peaks calculated. The ratios of the average areas for each concentration of each non-deuterated compound and the average areas of the corresponding deuterated compounds were calculated. The resulting ratio values were then plotted against the known concentrations of the non-deuterated PAH compounds in the analyzed solutions to determine the limits of linearity of the calibration curves for each compound (**ex. in Figure 3.2b**). A list of correlation equation parameters, coefficients and corresponding relative standard deviations for each standard concentration are given in **Table 3.4.** Only curves with correlation coefficients greater than 0.99 were utilized. Subsequently, 1 ppm of the PAH deuterated standard was added to all samples before analyses. This use of an internal standard improves accuracy of the quantification as it allows for the deuterated and non-deuterated PAH concentrations measured at exactly the same analytical conditions to be compared.

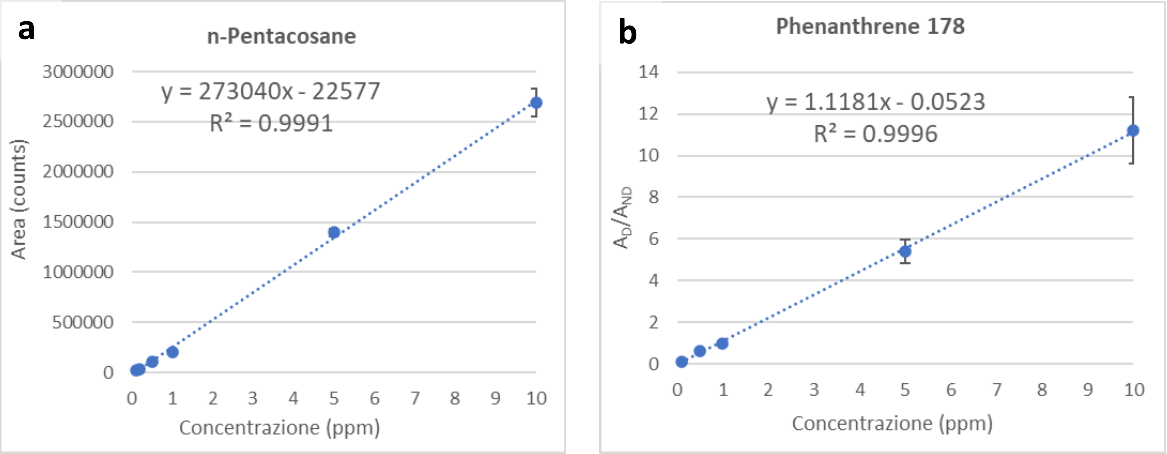


Figure 3.2. Examples of calibration curves: (a) n-Pentacosane and (b) Phenanthrene. Error bars reflect Relative Standard Deviation (n=3) of the instrument.

Table 3.3 A list of regression equations and the associated correlations coefficients (n=3) as well as the average areas and associated %RSD values for the six standard concentrations used in the last set of n-Alkane calibration curves.

n-Alkanes	slope	y-intersept	Corr. Coef.	Average Areas and %RSD Values (n=3)					
			(R2)	0.1 ppm	0.2 ppm	0.5 ppm	1 ppm	5 ppm	10 ppm
n-Dodecane (C12)	292553	7428	0.9976	29741 (1.99)	47820 (4.10)	156552 (1.87)	263580 (4.80)	1579560 (1.86)	2882201 (4.32)
n-Tridecane (C13)	298514	5189	0.9978	28084 (0.87)	47355 (3.58)	156188 (2.37)	268357 (3.67)	1606221 (1.62)	2939970 (4.22)
n-Tetradecane (C14)	293251	12424	0.9968	31912 (2.75)	49323 (2.17)	162657 (2.09)	265493 (5.04)	1606263 (2.05)	2885514 (4.15)
n-Pentadecane (C15)	295379	14203	0.9970	32313 (2.09)	50883 (3.36)	161874 (2.35)	277246 (3.38)	1615863 (2.08)	2909408 (4.99)
n-Hexadecane (C16)	276636	16841	0.9968	29651 (2.80)	48013 (2.26)	152678 (2.94)	270757 (4.74)	1522379 (1.95)	2725044 (3.79)
n-Heptadecane (C17)	279945	13529	0.9967	28766 (2.66)	46584 (2.54)	156120 (3.36)	260689 (3.72)	1537499 (1.60)	2754586 (4.90)
n-Ocatadecane (C18)	275476	8094	0.9975	27442 (3.87)	45308 (1.87)	148134 (3.07)	255981 (3.96)	1507063 (2.32)	2743033 (4.35)
n-Nonadecane (C19)	278485	4459	0.9979	27534 (2.31)	44604 (1.90)	142429 (2.08)	251785 (4.28)	1495323 (1.58)	2743629 (4.86)
n-Eicosane (C20)	279810	-611	0.9983	25510 (2.66)	41943 (1.40)	138819 (3.09)	247207 (4.14)	1486892 (2.54)	2756778 (4.46)
n-Heneicosane (C21)	275052	-2585	0.9981	23992 (3.18)	39077 (2.42)	132569 (3.17)	239419 (4.37)	1464664 (2.71)	2705634 (4.42)
n-Docosane (C22)	278689	-10242	0.9988	23475 (3.78)	38370 (1.51)	127895 (3.28)	231810 (5.13)	1453830 (3.10)	2745139 (4.48)
n-Tricosane (C23)	277652	-13674	0.9988	22084 (3.47)	36118 (1.34)	122958 (3.67)	224458 (5.16)	1445309 (3.10)	2731580 (4.59)
n-Tetracosane (C24)	278684	-22171	0.9993	20857 (2.37)	34481 (1.64)	116437 (3.71)	215618 (5.59)	1414437 (2.90)	2747025 (4.83)
n-Pentacosane (C25)	273040	-22577	0.9991	19925 (3.19)	33298 (0.60)	110079 (3.60)	207064 (6.17)	1395508 (2.98)	2685732 (5.16)
n-Hexacosane (C26)	276891	-29023	0.9994	19189 (3.37)	32001 (1.38)	106987 (3.71)	202350 (6.41)	1390290 (3.14)	2726814 (5.24)
n-Heptacosane (C27)	272419	-32445	0.9993	17586 (3.72)	30314 (1.04)	100334 (4.08)	192630 (6.70)	1360051 (3.26)	2681061 (4.90)
n-Octacosane (C28)	270635	-34065	0.9992	16827 (2.37)	29448 (1.30)	96223 (3.57)	186990 (7.47)	1352333 (3.04)	2660452 (5.08)
n-Nonacosane (C29)	265946	-35371	0.9992	16002 (3.05)	28261 (1.39)	91839 (3.21)	180436 (8.06)	1326029 (2.86)	2613101 (4.92)
n-Triacontane (C30)	271928	-42184	0.9992	15066 (3.81)	27052 (1.13)	87553 (3.06)	173582 (8.40)	1341758 (3.13)	2670275 (4.77)
n-Hentriacontane (C31)	271117	-42065	0.9990	14207 (2.87)	26872 (4.02)	84617 (2.39)	170391 (6.82)	1349397 (2.85)	2656891 (5.01)
n-Dotriavontane (C32)	261294	-40782	0.9987	13438 (2.92)	24927 (2.19)	78599 (2.46)	161103 (7.00)	1312052 (2.75)	2554934 (4.47)
n-Triatriacontane (C33)	260080	-43476	0.9986	12477 (2.17)	23925 (2.09)	75713 (1.64)	153887 (8.20)	1300987 (2.22)	2541501 (3.77)
n-Tetriacontane (C34)	255095	-43728	0.9984	11630 (0.64)	22490 (1.65)	72761 (2.19)	146218 (8.70)	1281139 (1.68)	2488994 (3.42)
n-Pentatriacontane (C35)	240055	-43767	0.9983	10273 (1.71)	20931 (4.48)	64301 (1.66)	132689 (7.57)	1201532 (1.01)	2340592 (3.50)

Table 3.4 A list of regression equations and the associated correlation coefficients (n=3) for the calibration curves of sixteen PAH compounds. The ratios of the non-deuterated PAH compounds at five concentrations to 1 ppm of their deuterated pairs used to obtain the curves and associated %RSD values are also included.

PAH	**slope**	**y-intersept**	**Corr. Coef.**	**A_{ND}/A_D and %RSD Values (n=3)**				
			(R2)	**0.1 ppm**	**0.5 ppm**	**1 ppm**	**5 ppm**	**10 ppm**
Naphthalene (m/z 128)	0.9836	0.0345	0.9996	0.11 (2.27)	0.49 (0.34)	0.97 (0.40)	5.07 (0.19)	9.76 (0.44)
Acenaphthylene (m/z 152)	0.9131	0.0884	0.9986	0.12 (6.11)	0.49 (0.30)	0.97 (0.29)	4.95 (0.53)	9.11 (0.78)
Acenaphthene (m/z 153)	1.1384	0.0404	0.9990	0.14 (0.34)	0.59 (0.70)	1.13 (0.32)	5.98 (0.25)	11.29 (0.36)
Fluorene (m/z 166)	1.0485	0.0591	0.9985	0.13 (0.22)	0.54 (0.08)	1.07 (0.39)	5.56 (0.03)	10.36 (0.34)
Phenanthrene (m/z 178)	1.1181	-0.0523	0.9996	0.13 (5.66)	0.62 (1.24)	1.00 (2.92)	5.38 (10.41)	11.20 (14.15)
Anthracene (m/z 178)	1.0195	0.0351	0.9985	0.13 (2.68)	0.45 (1.08)	1.10 (1.68)	5.44 (7.03)	10.13 (3.92)
Fluoranthene (m/z 202)	0.9460	0.0792	0.9982	0.12 (0.36)	0.51 (0.12)	1.01 (0.42)	5.07 (0.27)	9.41 (0.28)
Pyrene (m/z 202)	0.9343	0.0782	0.9986	0.12 (0.16)	0.51 (0.29)	1.01 (0.37)	5.04 (0.24)	9.26 (0.53)
Benz[a]anthracene (m/z 228)	1.0421	0.0801	0.9992	0.13 (0.35)	0.55 (0.32)	1.08 (0.48)	5.49 (1.02)	10.44 (1.16)
Chrysene (m/z 228)	1.1384	0.0404	0.9990	0.13 (0.31)	0.56 (0.11)	1.11 (0.08)	6.01 (0.19)	11.27 (0.85)
Benzo[b]fluoranthene (m/z 252)	0.9741	0.1461	0.9970	0.13 (5.46)	0.62 (3.38)	1.08 (10.8)	5.45 (5.62)	9.72 (3.78)
Benzo[k]fluoranthene (m/z 252)	1.1407	-0.0073	1.0000	0.13 (2.81)	0.57 (1.79)	1.11 (1.47)	5.75 (0.69)	11.42 (1.45)
Benzo[a]pyrene(m/z 252)	1.0953	0.1037	0.9983	0.14 (0.12)	0.58 (0.30)	1.15 (0.24)	5.93 (0.14)	10.94 (0.41)
Indeno(1,2,3-c,d)pyrene (m/z 276)	1.1236	-0.0303	1.0000	0.11 (6.51)	0.54 (3.64)	1.08 (2.90)	5.56 (3.19)	11.17 (3.70)
Dibenz[a,h]anthracene (m/z 278)	1.2173	-0.0415	0.9997	0.14 (3.06)	0.58 (0.86)	1.16 (0.11)	5.93 (6.89)	12.17 (1.98)
Benzo[g,h,i]perylene (m/z 276)	1.0227	0.1048	0.9958	0.13 (2.97)	0.53 (0.26)	1.06 (0.18)	5.66 (6.37)	10.14 (1.76)

3.1.4 Calculation of hydrocarbon concentrations in the analytes

Each of the solutions subsequently prepared where analyzed using the procedure described in section 3.1.1. The areas under the characteristic peaks of each n-Alkane and PAH compound under investigation were calculated in manual setting. This was necessary due to the "noisiness" of the gathered chromatograms. This noisiness is the result of interference from unknown compounds, as is to be expected when carrying out experiments on natural soil samples contaminated with commercially available gasoline and diesel.

For the n-Alkanes, the areas thus obtained were substituted into the correlation equations of the calibration curves to determine the concentrations in ppm of each compound of interest. If necessary, the concentrations were then corrected for dilution. Each analyte was analyzed in triplicates. The areas thus obtained were averaged and their relative standard deviation, representative of instrumental error, calculated.

3.2 Setting a benchmark

3.2.1 Gasoline and diesel compositions

Two contaminants were used during this project: gasoline and diesel. Gasoline, the more refined petroleum product, and diesel. Gasoline was used during the phase of experimental procedure modification in order to protect the instrumentation for as long as possible from contamination by the heavier hydrocarbon compounds contained in diesel. The gasoline was purchased at an IP gas station and the diesel at a Chevron gas station, both in the Province of Pesaro and Urbino. The gasoline was stored initially in a plastic gas can and later in a 1L brown borosilicate glass bottle. The diesel was stored in a 1L brown borosilicate glass bottle for the entire duration of the project.

GC-MS analyses of both gasoline and diesel were carried out to establish proportions of the n-Alkanes and PAHs of interest. Gasoline generally has very small amounts of the heavier n-Alkanes and PAHs. Consequently, the initial analysis of gasoline was carried out on a sample diluted with n-Hexane to a ratio of 1:10. The GC-MS chromatograms of gasoline were characterized by elevated amounts of Naphthalene and Phthalate. The presence of Phthalate is likely the result of contamination from the Polyethylene gas can, in which the gasoline was initially stored. In order to quantify Naphthalene, the gasoline was then diluted with n-Hexane in three additional rations 1:40, 1:100 and 1:200. Gasoline was also analyzed undiluted, in order to ensure that the concentrations of as many as possible of the n-Alkane and PAH compounds fell within the linearity limits of the calibration curves and could therefore be quantified. A chromatogram of extracted m/z 57 ion obtained by analyzing pure gasoline showing the locations and relative peak heights of the n-Alkanes present is shown in **Figure 3.3a**. Diesel, which generally contains much higher percentages of the n-Alkanes with carbon chain lengths above C12 was diluted 200 and 2000 times with n-Hexane to ensure as many of the n-Alkanes and PAH compounds as possible could be quantified using the calibration curves. A chromatogram of extracted m/z 57 ion obtained by analyzing diesel diluted 200 times showing the locations and relative peak heights of the n-Alkanes present is shown in **Figure 3.3b**.

The chromatogram of C12 to C35 n-Alkanes in both gasoline and diesel shows a characteristic bell-shaped distribution curve. However, as expected, the concentrations are several orders of magnitude lower in gasoline, **Table 3.5**. The most abundant n-Alkanes in gasoline are n-

Tetradecane and n-Octadecane at 17.12 and 18.6 ppm, respectively. The most abundant n-Alkane in the diesel on the other hand is n-Tridecane at 10,781 ppm.

In contrast, the concentrations of PAH compounds are low in both gasoline and diesel with many not quantifiable, **Table 3.6**. In the gasoline the most abundant PAH compound is Phenanthrene at 10.5 ppm. All of the others, with a notable exception of Naphthalene, have concentrations below 10 ppm and most below 2 ppm. Naphthalene stands out for its extremely high concentrations: over 800 ppm. In diesel, only seven of the sixteen PAHs analyzed were found to have concentrations that could be quantified. Three of these, Naphthalene, Fluorene and Phenanthrene, have concentrations ranging from 30 to 200 ppm, several orders of magnitude lower than the concentrations of n-Alkanes. Such a drastic difference in concentrations will render the analysis of residual hydrocarbons in samples after washing experiments complicated as it would require two separate dilutions to ensure both the n-Alkanes and PAHs fall in the linearity range of the calibration curves. Consequently, it was decided not to focus on the PAH compounds any further.

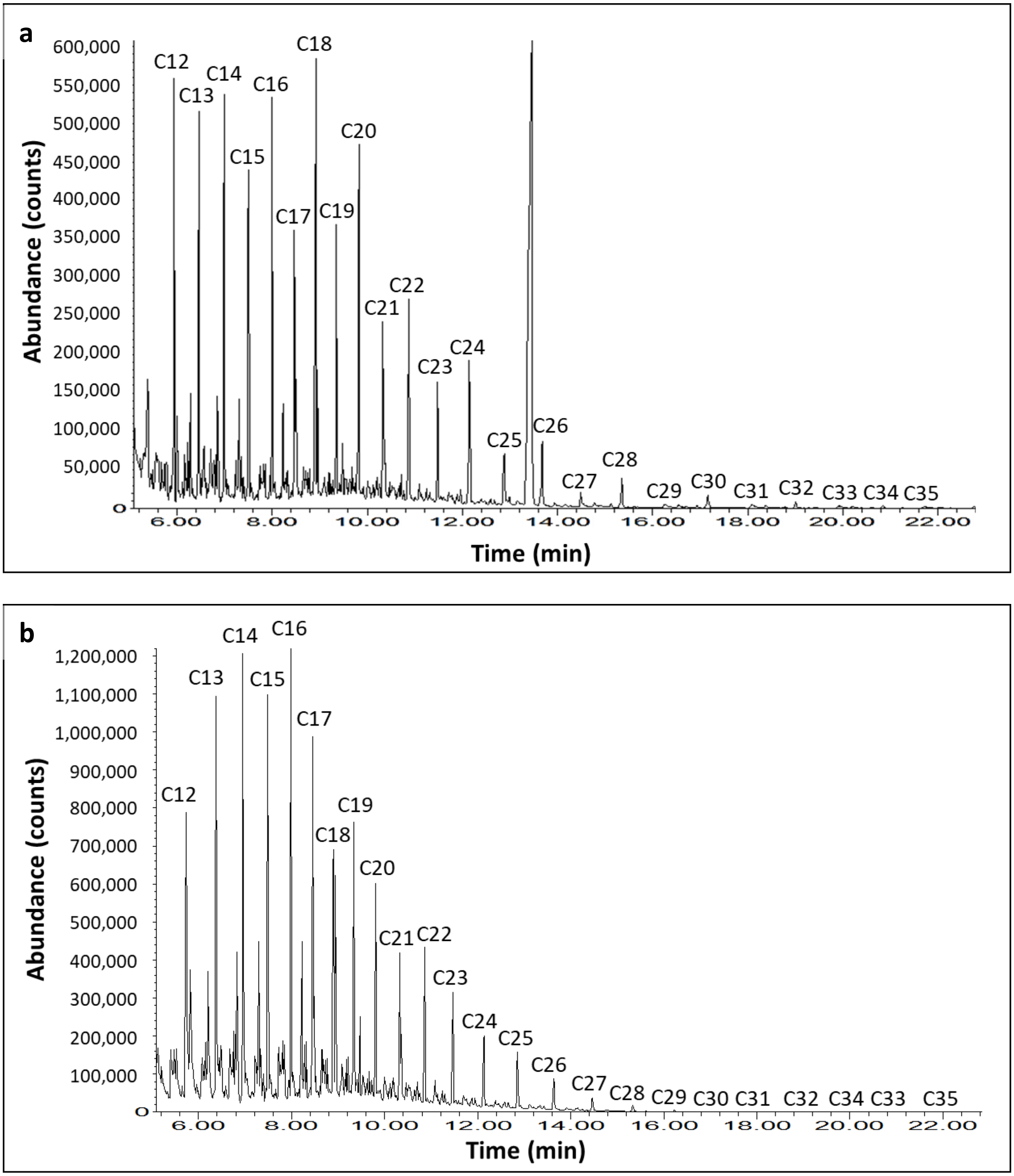


Figure 3.3 Chromatogram of extracted ion m/z 57 showing the locations of the n-Alkanes compounds present in undiluted gasoline (a) and diesel diluted 200 times with n-Hexane (b).

Table 3.5 The concentrations of n-Alkanes in the two contaminants: gasoline and diesel fuel.

n-Alkane	Gasoline Concentration (ppm)	Diesel Concentration (ppm)	n-Alkane	Gasoline Concentration (ppm)	Diesel Concentration (ppm)
n-Dodecane	0.16	10414	n-Tetracosane	6.29	2359
n-Tridecane	15.88	10781	n-Pentacosane	2.74	1544
n-Tetradecane	17.12	9193	n-Hexacosane	2.67	1224
n-Pentadecane	16.27	8651	n-Heptacosane	0.69	526
n-Hexadecane	16.37	7801	n-Octacosane	1.15	261
n-Heptadecane	15.66	8633	n-Nonacosane	0.38	97
n-Ocatadecane	18.60	8182	n-Triacontane	0.56	61
n-Nonadecane	6.89	5184	n-Hentriacontane	0.45	48
n-Eicosane	16.32	5075	n-Dotriavontane	0.32	48
n-Heneicosane	6.63	3426	n-Triatriacontane	0.28	49
n-Docosane	8.16	3125	n-Tetriacontane	0.22	0
n-Tricosane	4.51	2717	n-Pentatriacontane	0.33	0

Table 3.6 The concentrations of PAH compounds in the two contaminants, gasoline and diesel.

PAHs	Gasoline Concentration (ppm)	Diesel Concentration (ppm)
Naphthalene	840.65	185.23
Acenaphthylene	-	-
Acenaphthene	2.44	1.36
Fluorene	7.42	39.84
Phenanthrene	10.47	30.52
Anthracene	2.76	-
Fluoranthene	2.02	-
Pyrene	3.37	-
Benz[a]anthracene	0.28	9.19
Chrysene	0.12	-
Benzo[b]fluoranthene + Benzo[k]fluoranthene	-	3.98
Benzo[a]pyrene	-	-
Indeno(1,2,3-c,d)pyrene	-	-
Dibenz[a,h]anthracene	-	-
Benzo[g,h,i]perylene	0.31	1.42

3.2.2 Determination of background contamination

Because both sample MF-05 and MF-10 were collected in close vicinity to public roads, before proceeding with contamination and washing experiments, the presence of background contamination with hydrocarbons, if any, had to be assessed. The samples were mixed manually and three 5 g, maximally spaced subsamples were taken from each sample. This was done to assess and eliminate any bias arising from a lack of sample homogeneity. The possible presence of background contamination was assessed using a hydrocarbon extraction procedure modified after Urum et. al. 2004 [1]. The subsamples were mixed with 10 ml of n-Hexane in 40 ml borosilicate glass test tubes and manually agitated for 5 minutes. The subsamples were then allowed to settle, and the n-Hexane supernatant was transferred into clean 40 ml borosilicate glass test tubes. This procedure was repeated three additional times. In the last step, the sub-samples were centrifugated in an ALC 4225 centrifuge at 3000 rpm for 5 minutes before supernatant transfer. The sum of the supernatants of each subsample were then centrifuged for an additional 20 minutes at 3000 rpm to ensure any fines inadvertently transferred with the supernatant were taken out of suspension. The extracts were then analyzed using GC-MS at settings described above. The mean values of the three analysis of each subsample extract were used to calculate the percent relative standard deviation of the extraction method.

The initial analysis showed variable background contamination among different subsamples of the same sample, **Table 3.7.** For sample MF-05, the first subsample analyzed had the highest amounts of n-Alkane contamination with C20 to C25 chain n-Alkanes present in maximum concentrations of over 55.6 ppm (n-Tetracosane). The second and third subsamples of MF-05 showed markedly lower values of background contamination with C22 to C25 compounds detected in concentrations that do not exceed 12 ppm. Background contamination in sample MF-10 was highest in the second subsample, with n-Alkane compounds from C17 to C25 detected at concentrations that reached 93.7 ppm for n-Tetracosane (C24). The third subsample had slightly lower background contamination with compounds from C19 to C25 detected at concentrations that reached a maximum of 28.2 ppm for n-Tetracosane (C24). The first subsample of MF-10 showed the lowest concentrations of background contamination with C22 to C25 compounds detected in concentrations that did not exceed 12 ppm.

In order to eliminate the observed heterogeneity in background contamination, the samples were gently ground in a ceramic mortar to eliminate any residual clumping and thoroughly mixed, then the extraction was repeated. As a result of this additional homogenization the background contamination was redistributed throughout the sample such that the resulting concentrations were below the instrumental detection limits. Hence, the samples can be considered free of background contamination.

Table 3.7. Background concentrations of n-Alkanes in samples MF-05 and MF-10.

n-Alkane	MF-05							MF-10						
	Background contamination						Background after homogenization	Background contamination						Background after homogenization
	Repeat 1		Repeat 2		Repeat 3			Repeat 1		Repeat 2		Repeat 3		
	ppm	%RSD (n=3)	ppm	%RSD (n=3)	ppm	%RSD (n=3)	ppm	ppm	%RSD (n=3)	ppm	%RSD (n=3)	ppm	%RSD (n=3)	ppm
n-Dodecane (C12)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Tridecane (C13)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Tetradecane (C14)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Pentadecane (C15)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Hexadecane (C16)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Heptadecane (C17)	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.20	0.58	ND	ND	ND
n-Ocatadecane (C18)	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.05	1.89	ND	ND	ND
n-Nonadecane (C19)	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.34	0.71	0.026	0.33	ND
n-Eicosane (C20)	6.70	0.48	ND	ND	ND	ND	ND	ND	ND	8.12	1.65	0.06	0.97	ND
n-Heneicosane (C21)	7.86	1.93	ND	ND	ND	ND	ND	ND	ND	13.08	3.75	0.03	0.60	ND
n-Docosane (C22)	29.22	1.52	11.72	0.64	11.82	0.16	ND	11.98	0.06	44.94	3.82	0.16	0.84	ND
n-Tricosane (C23)	41.68	1.60	6.87	1.00	7.39	0.71	ND	6.68	0.19	71.34	4.46	0.25	1.14	ND
n-Tetracosane (C24)	54.60	1.97	6.83	1.93	7.83	1.37	ND	6.22	0.34	93.67	4.72	0.42	1.48	ND
n-Pentacosane (C25)	51.69	1.70	6.59	4.14	7.75	1.98	ND	5.98	0.80	88.23	4.53	0.50	1.79	ND
n-Hexacosane (C26)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Heptacosane (C27)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Octacosane (C28)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Nonacosane (C29)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Triacontane (C30)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Hentriacontane (C31)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Dotriavontane (C32)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Triatriacontane (C33)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Tetriacontane (C34)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND
n-Pentatriacontane (C35)	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	ND

NA: not analyzed
ND: not detected

3.2.3 Establishing contamination procedure

Several contamination procedures were considered when choosing the most suitable for this project. Urum et al. [1-3] used a horizontally positioned drum mixer to contaminate their soil samples in bulk directly, with no use of a carrier fluid. In other studies, an emulsion of water and hydrocarbon contaminant was used to ensure a homogeneous distribution of contaminant throughout the sample. To assure a similar initial degree of loss of the more volatile hydrocarbon compounds, it was decided to spike the samples shortly before each washing experiment instead of bulk contamination.

Next, a series of tests was carried out to determine the wt% of the contaminant that would result in the most homogeneous distribution within the soil samples. 5 grams of each sample were weighed out into 100 ml borosilicate glass beakers and spiked with 15, 20 and 30 wt% gasoline and diesel. The test showed that although spiking with 30 wt% (which would bring the samples close to their liquid limits) gasoline/diesel ensured complete saturation of the sample, tapping on the container containing the samples spiked with 15 wt% was sufficient to ensure homogeneous contamination of both MF-05 and MF-10. Hence, 15 wt% was chosen as the spiking amount to use in all experiments.

3.2.4 Recovery experiments on gasoline and diesel

Before proceeding to the contamination and washing of the soil samples, the efficiency of the hydrocarbon extraction protocol (adopted from [1]) had to be evaluated and the percent recovery determined for both sample MF-05 and MF-10. To do this, 5 g of the soils were weighed out into 50 ml borosilicate test tubes and contaminated with 15 wt% gasoline or diesel. The test tubes were left open for about 30 minutes, until their weight stabilized. Each test was carried out in triplicates to access procedural repeatability. The contaminants were then extracted with n-Hexane as described in Section 3.2.2. The extracts were analyzed in triplicates using GC-MS and the concentrations of the n-Alkanes calculated using the most recent calibration curves. The concentrations thus obtained where then compared with the concentrations added to the soils to obtain a percent recovery value of the extraction protocol and the instrumental as well as experimental percent relative standard deviations calculated.

The percent recovery values and the percent experimental standard deviation values for n-Alkanes in gasoline and diesel thus obtained are listed in **Table 3.8**. The percent recovery values for gasoline range from 72 to 95% for sample MF-05 and between 61 and 101% for sample MF-10 with percent experimental relative standard deviation ranges of 3.4 to 10.8 and 4.4 to 27.5, respectively. Compounds with carbon chains longer than C26 (n-Hexacosane) were not analyzed in gasoline. The present recovery values for diesel are range from 43 to 108% for sample MF-05 and 50 to 95% for sample MF-10 with percent experimental relative standard deviation ranges of 3.3 to 9.2 and .5 to 4.5, respectively. For both samples, recovery values below 60% were obtained for the heaviest of the quantifiable compounds, i.e. C27-C28. N-Alkane compounds with carbon chains longer than C29 (n-Octacosane) were present in quantities too low to be quantified. For these reasons, n-Alkanes beyond C26 will not be considered further in this study.

Table 3.8. Percent recovery values and experimental standard residual errors of n-Alkanes for samples MF-05 and MF-10.

n-Alkane	MF-05				n-Alkane	MF-10			
	Gasoline		Diesel			Gasoline		Diesel	
	% Recovery	%RSD (n=3)	% Recovery	%RSD (n=3)		% Recovery	%RSD (n=3)	% Recovery	%RSD (n=3)
n-Dodecane	72.2	6.00	78.4	5.85	n-Dodecane	61.7	6.10	70.0	0.54
n-Tridecane	72.5	6.80	73.2	6.23	n-Tridecane	62.3	5.30	63.7	4.09
n-Tetradecane	76.1	6.30	83.6	5.77	n-Tetradecane	61.4	9.70	77.7	0.78
n-Pentadecane	77.9	4.70	81.0	5.79	n-Pentadecane	67.6	6.10	76.6	2.80
n-Hexadecane	81.5	4.10	81.3	6.36	n-Hexadecane	63.1	6.00	77.3	1.27
n-Heptadecane	77.9	10.00	74.1	6.98	n-Heptadecane	72.8	4.40	64.9	5.17
n-Ocatadecane	95.1	10.80	71.0	5.23	n-Ocatadecane	101.1	12.40	68.1	1.88
n-Nonadecane	77.3	3.80	92.1	4.29	n-Nonadecane	68.9	9.00	86.5	1.59
n-Eicosane	84.6	4.00	77.6	3.39	n-Eicosane	84.2	15.80	71.9	2.35
n-Heneicosane	83.5	5.80	107.9	9.18	n-Heneicosane	80.8	17.00	94.8	4.45
n-Docosane	84.3	3.40	88.6	4.64	n-Docosane	87.7	20.80	82.9	3.29
n-Tricosane	74.7	6.70	80.0	4.79	n-Tricosane	77.7	27.50	72.8	2.31
n-Tetracosane	80.1	5.00	79.4	4.33	n-Tetracosane	83.7	22.50	73.8	1.98
n-Pentacosane	80.3	7.70	81.9	5.02	n-Pentacosane	81.3	20.00	75.6	2.49
n-Hexacosane	84	7.20	73.2	4.90	n-Hexacosane	86.4	20.30	69.2	2.92
n-Heptacosane	NA	-	53.0	3.29	n-Heptacosane	NA	-	50.4	0.52
n-Octacosane	NA	-	47.1	4.44	n-Octacosane	NA	-	45.4	1.91
n-Nonacosane	NA	-	ND	-	n-Nonacosane	NA	-	ND	-
n-Triacontane	NA	-	ND	-	n-Triacontane	NA	-	ND	-
n-Hentriacontane	NA	-	ND	-	n-Hentriacontane	NA	-	ND	-
n-Dotriavontane	NA	-	ND	-	n-Dotriavontane	NA	-	ND	-
n-Triatriacontane	NA	-	ND	-	n-Triatriacontane	NA	-	ND	-
n-Tetriacontane	NA	-	ND	-	n-Tetriacontane	NA	-	ND	-
n-Pentatriacontane	NA	-	ND	-	n-Pentatriacontane	NA	-	ND	-
ND: not detectable									
NA: not analysed									

3.3 Testing of the laboratory soil washing procedure

The laboratory washing experiments in this study were modeled after those described in [1] and [2]. Specifically, the original procedure involved washing 5 g of contaminated soil with 20 ml of washing solution by agitating 45 ml test tubes placed horizontally in a shaking water bath set to the temperature desired and to 200 oscillations per minute (opm) for 30 minutes. After washing, the samples were centrifuged, and the washing solution removed. The remaining sample would be rinsed with 5 ml of distilled water by shaking the test tube laterally. The sample was then allowed to settle, and the water removed. The residual contaminants where then extracted from the soil samples using n-Hexane. Due to differences in the chosen analytical method, contaminant used and available laboratory equipment, every step of this procedure had to be verified and modified where necessary before washing experiments could begin. Since variable interaction of the surfactants with the samples could complicate the interpretation of results a washing solution consisting of just distilled water and no surfactants (a blank washing solution) was used.

3.3.1 Washing phase: identifying the ideal containers for adequate agitation

The first step in the evaluation of the procedure was to establish the best containers for the washing phase. In the protocol of Urum et al. [1], 45 ml test tubes were positioned horizontally in a shaking water bath set to 200 strokes per minute. Such a set-up proved unfeasible for this study, as the only centrifuge-suitable borosilicate glass test tubes available had screw caps that did not provide a sufficient seal. Three other washing containers where tested: 250 ml borosilicate bottles, 250 ml borosilicate Erlenmeyer flasks and 500 ml Erlenmeyer flasks. Soil washing tests with 5 g of each sample and 20 ml of distilled water were carried out in a PBI international temperature-regulated water bath shaker set to 30 °C and 250 opm (oscillations per minute) to ascertain which container allowed for maximum sample agitation, ensuring constant circulation of the washing solution throughout the sample. Because the washing experiments would have to be carried out in three different labs (Biomolecular Laboratory headed by Prof. Antonella Penna, Geotechnical Laboratory headed by Gianluigi Tonelli, and Liquid Chromatography and Mass Spectrometry Laboratory headed by Prof. Achille Cappiello), borosilicate bottles, which could be properly sealed when necessary, were the containers of choice. However, they proved too heavy and of insufficient base diameter to ensure adequate agitation of the sample during washing. The 250 ml Erlenmeyer flasks, although sufficiently light, also proved to have insufficient base diameter to ensure adequate sample agitation. The 500 ml Erlenmeyer flasks, although heavier than their 250 ml counterparts, had sufficient base diameter to allow continuous movement of the entire soil sample in the washing solution. To avoid damage to the rubber stoppers supplied with the Erlenmeyer flasks by evaporating hydrocarbons, the flasks were covered with aluminum foil secured with parafilm during the washing stage and transfer between labs. The flasks and their arrangement in the water bath are shown in **Figure 3.4**.

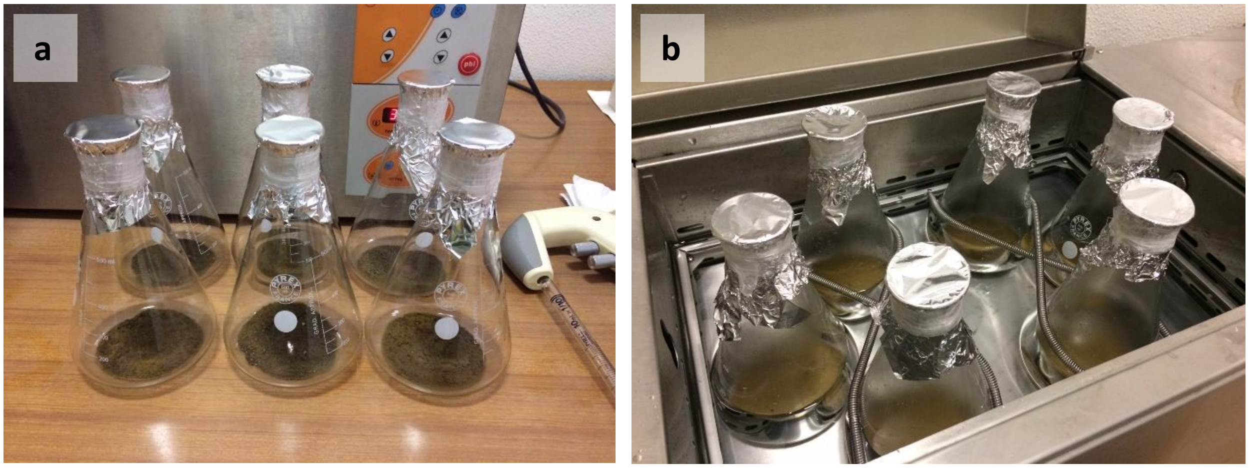


Figure 3.4. 500 ml Erlenmeyer flasks used in the experiments and their arrangement in the regulated temperature water bath shaker.

3.3.2 Drying stage: testing drying temperature, duration and containers

The use of GC-MS for analyzing the residual hydrocarbon contents of contaminated soils meant that a drying step following washing had to be added to the procedure. In choosing the most appropriate drying procedure to use, a balance between the temperature and drying duration had to be found that would minimize the potential for additional loss of hydrocarbon compounds from the samples prior to extraction and analysis. To find such a balance, a set of six 5 g samples (three for MF- and three for MF-10) were contaminated with 15% gasoline, washed with 20 ml of the blank washing solution (just distilled water and no surfactants) in a temperature controlled water bath set to 30 °C and 250 opm for 30 minutes. The samples were then transferred into borosilicate glass test tubes, centrifuged at 2000 rpm for 15 minutes. The water was decanted, and the remaining samples rinsed with 10 ml of distilled water by manually agitating for 5 minutes. The samples were then centrifuged once more and the water decanted. At this point the samples were ready for drying. Four drying stage set-ups were tested. Drying in glass test tubes at 30 °C, in glass test tubes at °60C, in glass dishes at 30 °C and in glass dishes at 60 °C. Drying the samples in test tubes at 30 °C was not successful. Over a week after being placed in the oven, the samples were still not dry enough to proceed with extraction. Raising the temperature of the oven to 60 °C reduced the drying times to 1 night. For the next test, the samples were transferred from the glass test tubes into glass dishes after rinsing and placed into an oven set to 30 °C. The larger surface area for sample/air contact afforded by the glass dishes reduced the drying time to 5 days, which however, was still too long for our purposes. When the temperature was raised to 60 °C, the drying time of the samples in glass plates was reduced to 3 hours.

The residual concentrations of n-Alkanes in samples dried in dishes at 30 °C and 60 °C (**Figure 3.5**) were analyzed to assess which of the two parameters, drying time or drying temperature, had a greater effect on loss of n-Alkanes. It was found that for both samples MF-05 and MF-10, higher temperature resulted in a greater loss of the two lightest n-Alkanes (C12 and C13). For all the other n-Alkanes loss was greater for samples dried overnight despite the lower temperature settings, **Figure 3.6a** and **b**. Consequently, the latter of the four set-ups, drying in dishes at 60 °C, was chosen as the most suitable for the purposes of this study.

Figure 3.5. Washed soil samples placed to dry in an oven in Petri dishes.

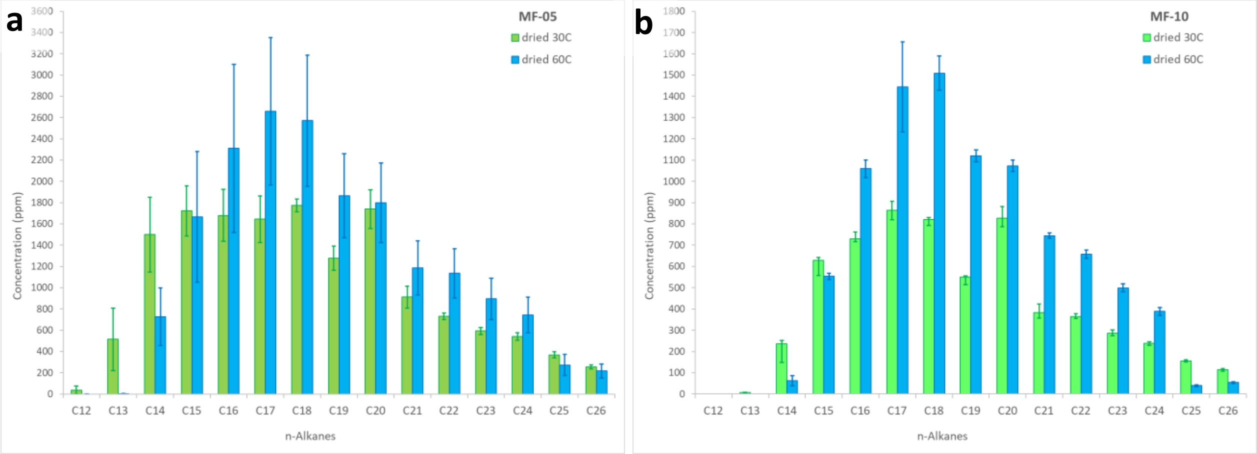


Figure 3.6 A comparison of residual n-Alkanes extracted from soil samples MF-05 (a) and MF-10 (b) contaminated with 15 wt% diesel, washed with distilled water and dried in borosilicate glass dishes overnight at 30 °C and for three hours at 60 °C. Error bars represent experimental relative standard deviation with n=3.

3.3.3 Evaluating the influence of the drying stage on contaminant concentrations

Once the procedure of the drying stage was established, the actual effect of adding this step on the residual hydrocarbon concentrations had to be assessed. This time diesel, the hydrocarbon derivative to be used in washing experiments, was used as the contaminant. Three sets of 6 samples (3 for MF-05 and 3 for MF-10) were contaminated with the same amounts of diesel (15 wt%). For the first of these, extraction with n-Hexane was carried out within 30 minutes of contamination. The second set of samples was first placed in an oven set to 60 °C for 3 hours to simulate the drying stage, then the hydrocarbon compounds were extracted and analyzed. Each of the third and last set of samples was washed with 20 ml of distilled water and then placed in an oven set to 60 °C to dry for 3 hours. The residual n-Alkanes in these samples, once dry, where then extracted with n-Hexane and analyzed using GC-MS. **Figure 3.7a and b** shows the n-Alkane concentrations in these three sets of experiments. With the exception of the two lightest n-Alkanes (C12 and C13), the loss of hydrocarbon compounds due to the drying stage was found to be minimal compared to amounts removed during washing. Because of the excessive loss of the two lightest n-Alkanes, n-Dodecane (C12) and n-Tridecane (C13), it was decided to exclude them from further consideration.

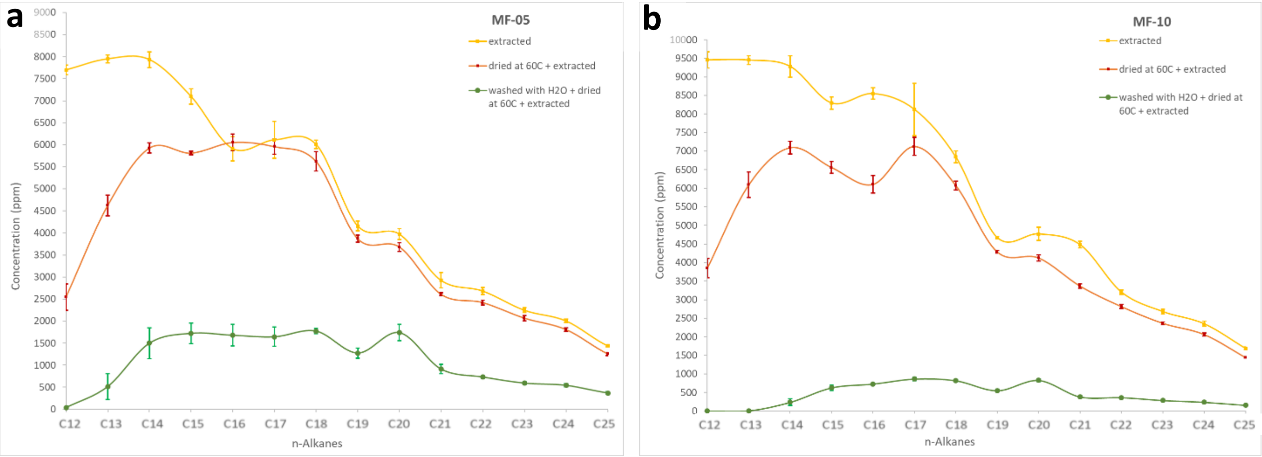


Figure 3.7. A comparison of n-Alkane concentrations extracted with n-Hexane from samples MF-05 (a) and MF-10 (b) immediately after contamination, after drying at 60 °C, and after washing with distilled water and drying.

3.4 Final methodology

3.4.1 The scope of this procedure

The object of this procedure is to facilitate the formulation of optimized washing solutions targeting soils contaminated with hydrocarbon derivatives by simulating the process of soil washing on artificially contaminated soils in a laboratory setting.

3.4.2 Materials and equipment

Glassware: 500 ml Erlenmeyer flasks, graduated pipettes, heavy duty centrifuge test tubes, Pasteur pipettes, Petri dishes, 2 ml GC-MS sample vials.

Other materials and equipment: analytical balance, shaking water bath, centrifuge, vortex, automatic pipettes, aluminum foil and Parafilm, mortar and pestle, spatulas, GC-MS.

3.4.3 Procedure

3.4.3.1 Sample preparation and contamination

1) Weigh 5 g of the sample and transfer into corresponding Erlenmeyer flask. Repeat two more times.

2) Calculate the required amount of hydrocarbon contaminant for each sample using the following equation:

$$V_{hc} = W_s \text{ x } 1/D_{hc} \text{ x } P$$

where V_{hc} is the volume of contaminant in ml, W_s is the weight of the sample in grams, D_{hc} is the density of the hydrocarbon contaminant in g/ml and P is the percent contamination expressed as a decimal.

3) Add the corresponding volume of contaminant to each sample making sure to distribute it evenly across the entire sample using an automatic pipette. Tap the side of the Erlenmeyer flask to homogenize the sample.

4) Allow about half an hour for lighter hydrocarbons to evaporate and the weight of the sample to stabilize.

3.4.3.2 Washing

5) Add 20 ml of the washing solution using a volumetric pipette to each sample.

6) Cover the flasks with aluminum foil and secure with parafilm.

7) Place the flasks into shaking water bath previously brought up to the desired temperature (30 °C and 40 °C in this study, see Chapter 4) making sure to secure them well and shake at 250 opm.

8) After 30 minutes, take the flasks out of the bath and transfer the samples and the washing solutions into borosilicate glass, heavy duty, centrifuge-safe test tubes. Add 10 ml of distilled water to the flask with a graduated pipette, washing away as much of the sample from the walls as possible.

9) Centrifuge at 2000 rpm for 20 minutes.

10) Use the glass Pasteur pipettes to remove as much of the washing solution from the samples as possible. Discard the washing solution.

3.4.3.3 Rinsing

11) Add 10 ml of distilled water to the test tubes and vortex to break up the sample.

12) Manually agitate the test tubes for 5 minutes to mobilize any residual washing solution.

13) Centrifuge for 20 more minutes a 2000 rpm.

14) Remove the rinsing liquid with a Pasteur pipette and discard.

15) Add 5 ml of distilled water and vortex to break up the sample.

16) Transfer into glass dishes.

17) Use a Pasteur pipette with distilled water to wash any remaining sample from the walls of the test tube.

3.4.3.4 Drying

18) Place the dishes into an oven set to 60 °C for about 3 hours, or as long as it takes for the samples to fully dry.

19) Take the samples out of the oven and allow them to cool.

20) Transfer into a mortar using a spatula to break up and detach the sample from the walls of the dish.

21) Carefully crush any clumps formed as a result of drying and transfer the samples back into the glass test tubes.

22) Weigh each sample on an analytical balance.

3.4.3.5 Extraction

23) Add 10 ml of n-Hexane to each sample using a graduated pipette.

24) Manually agitate the test tubes for 5 minutes.

25) Allow the samples to settle and transfer the n-Hexane into a clean test tube with a Pasteur pipette being careful to avoid the sample.

26) Repeat three more times stopping short of step 25 on the last repetition.

27) Centrifuge the samples with the last dose of n-Hexane at 2000 rpm for 10 minutes.

28) Transfer the n-Hexane extract to the test tube containing the previous doses.

29) Centrifuge the test tube containing the n-Hexane supernatants for 10 minutes at 2000 rpm.

3.4.3.6 Analysis

The resulting concentrations of residual hydrocarbon compounds have a dilution ratio with n-Hexane of 1:40. Additional dilution may be required in order for the concentrations to fall within the range of the calibration curve. All analysis should be repeated three times to check instrumental repeatability.

3.5 References

[1] Urum, K., et al., 2004, Surfactant treatment of crude oil contaminated soils, Journal of Colloids and Interface Science, Vol., 276, pp. 456-464

[2] Urum, K., Pekdemir, T., and Gopur, M., 2003, Optimum conditions for washing of crude oil-contaminated soil with biosurfactant solutions, Transactions of the Institution of Chemical Engineers, Vol. 81, Part B, pp. 203-209

[3] Urum, K., et. al., 2006, A comparison of the efficiency of different surfactants for removal of crude oil from contaminated soils, Chemosphere, Vol. 62, pp. 1403-1410

Chapter 4

Assessing the influence of mineralogy on the efficiency of SDS and TWEEN80 washing solutions of diesel contaminated soil.

4.1 Experimental plan

In order to assess the potential influence of mineralogy on washing efficiency, the samples were washed with washing solutions containing two surfactants: Sodium dodecyl sulfate (SDS) and TWEEN80. SDS is an anionic surfactant while TWEEN80 is a non-ionic surfactant. The negative charge of the hydrophilic end of SDS makes it more effective at removing petroleum derivatives compared to TWEEN80 but it also makes it less ecologically friendly and subject to adsorption to positively charged mineral surfaces. In addition, the much higher critical micelle concentration (CMC) of SDS means that a much larger concentration of the surfactant is needed to achieve the same effect as TWEEN80, as it has been shown that washing efficiency is highest at concentrations above the CMC [1].

To establish a baseline for comparison, samples MF-05 and MF-10 were first washed with a washing solution containing only deionized water (i.e. a surfactant concentration of 0 mM). Then, each sample was washed with three solutions of increasing concentrations of either SDS or TWEEN80. The concentrations were 0.25, 1.5 and 2 times the CMC for each surfactant: SDS – 1.75mM, 10.5mM and 14 mM; TWEEN80 – 0.003mM, 0.024mM and 0.18mM. In addition to varying surfactant concentration, each series of experiments was carried at two washing temperatures, 30 °C and 40 °C. This was done to assess the combined influence of surfactant concentration and washing temperature on the degree of cleaning that could be achieved for soils with different mineralogical compositions. A summary table of all the experiments carried out and their experimental conditions can be seen in **Table 4.1.** Stock solutions of both SDS and TWEEN80 were prepared and used to obtain all three concentrations of each surfactant via dilution. Experiments were carried out following the methodology described in Section 3.4 of the previous chapter. All experiments were performed in triplicates and analyzed three times to ensure experimental and instrumental repeatability.

Table 4.1. A summary of the experimental conditions of washing experiments carried out in this study.

	MF-05		MF-10	
	Washing Temperature		Washing Temperature	
Washing Solution	30°C	40°C	30°C	40°C
Distilled water				
	Exp 2	Exp 3	Exp 2	Exp 3
SDS				
1.75 mM (0.25 CMC)	Exp 5	Exp 4	Exp 5	Exp 4
10.5 mM (1.5 CMC)	Exp 9	Exp 8	Exp 9	Exp 8
14mM (2 CMC)	Exp 6	Exp 7	Exp 6	Exp 7
TWEEN80				
0.003 mM (0.25 CMC)	Exp 10	Exp 11	Exp 10	Exp 11
0.018 mM (1.5 CMC)	Exp 14	Exp 15	Exp 14	Exp 15
0.024 mM (2 CMC)	Exp 13	Exp 12	Exp 13	Exp 12

4.2. Results

4.2.1 Soil washing tests with SDS-based washing solutions

For sample MF-05 washed at 30 °C, washing with SDS-based washing solutions resulted in only a slight increase in efficiency of the washing solution over water at concentrations below the CMC of SDS followed by dramatic improvement at concentrations above the CMC. Washing with 1.75 Mm SDS solutions (0.25 times the CMC) resulted in an overall 4.5% improvement in washing efficiency compared to washing with water. The greatest improvement in efficiency was seen in n-Alkanes with chain lengths of C22 and longer (18-37%). Notably, the two lightest n-Alkanes considered, with carbon chain lengths of C14 and C15, did not show any improvement over water. Increasing the SDS concentrations in the washing solutions to concentrations above its CMC (7 mM) produced an even better improvement in washing efficiency. Washing solutions of 10.5 mM (1.5 times the CMC) resulted in a washing efficiency improvement of 85% over deionized water. The greatest improvement in efficiency was seen in middle length n-Alkanes (C17-C20) with 86 to 87% greater removal of n-Alkanes with respect to water. Further increase in SDS concentration in the washing solution (2 times the CMC) did not improve washing efficiency; in contrast, the overall efficiency decreased slightly from 85% to 81% improvement over water. Specifically, the decrease in efficiency improvement over water gradually increases with increasing size of n-Alkanes, passing from 1% (for C26) to 14% (for C25). However, once the negative correlation between n-Alkane concentrations in the diesel used in soil contamination and their carbon chain lengths is taken into account, the greatest decrease in efficiency is seen in n-Alkanes C17 to C20. Only the two lightest n-Alkanes (C14 and C15) showed a progressive improvement in efficiency with increasing SDS concentrations in the washing solution.

For sample MF-10 washed at 30 °C, the addition of SDS to the washing solution resulted in an immediate substantial improvement in washing efficiency followed by a flattening out at concentrations above the CMC and even a slight decrease in efficiency for the most concentrated washing liquid. Washing experiments with 1.75 mM SDS (0.25 times the CMC) resulted in an overall improvement in washing efficiency of 72% with respect to experiments using deionized water as the washing solution. As with sample MF-05, the two lightest n-Alkane compounds showed the lowest improvements in efficiency, which increased with increasing carbon chain lengths of the compounds. Further increasing the concentration of SDS in the washing solution resulted in continued improvement in efficiency, with an overall further improvement of 10%, which however was seen mainly in the two lightest n-Alkanes and n-Alkane compounds with carbon chain lengths of C17-C20. Interestingly, the heaviest compounds (C23-C26) display a decrease in efficiency at SDS concentrations above the CMC. At the highest concentrations of SDS in the washing solutions, all but the C15 n-Alkane show a decrease in washing efficiency, with an overall drop in efficiency of 2%.

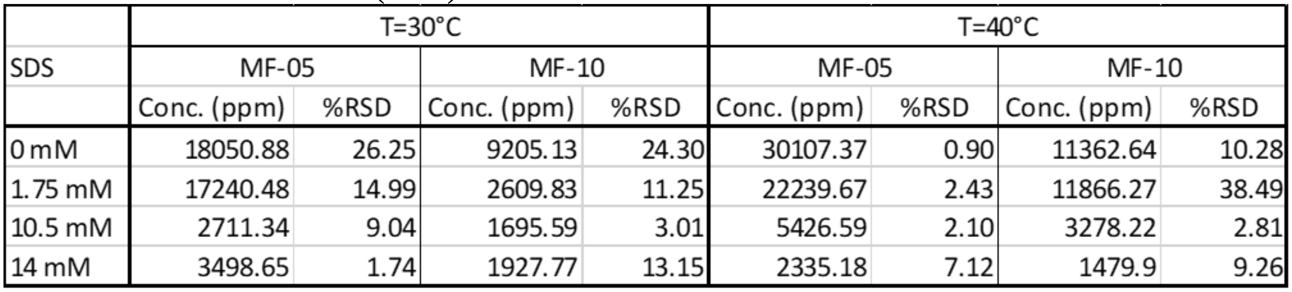
The variation in total residual n-Alkanes with increasing SDS concentrations is shown in **Table 4.2**. The percent improvements in the extraction of each n-Alkane considered compared to washing experiments with deionized water at 30 °C of samples MF-05 and MF-10 are listed in **Table 4.3**. Histograms of the changes in residual n-Alkane concentrations with increasing concentrations of SDS in the washing solutions for samples MF-05 and MF-10 washed at 30 °C can be seen in **Figure 4.1**.

Increasing the washing temperature to 40 °C resulted in an increase in the washing efficiency of sample MF-05 at all three concentrations of SDS and an evening out of the improvement trend. At the lowest SDS concentrations (1.75 mM), the overall improvement in washing efficiency compared to deionized water is of 26% with all n-Alkane compounds seeing equal improvement. As the SDS concentration in the washing solution exceeds CMC, the overall efficiency relative to water jumps to 82% with none of the n-Alkanes being affected more than its neighbors. At the highest SDS concentration (14 mM), the overall efficiency improvement rises further to 92%. However, this additional improvement affects the longer-chained n-Alkanes to a greater degree.

For sample MF-10, increasing the washing temperature to 40 °C has also resulted in an overall improvement in washing efficiency relative to deionized water, although less pronounced than in sample MF-05. The overall improvement trend has evened out, showing a steady increase with concentration. At the lowest concentrations of SDS in the washing solutions (1.75 mM), the improvement in the removal of individual n-Alkanes is variable, with C17 and C21 n-Alkanes being most affected. At the two SDS concentrations above the CMC, the improvement in washing efficiency is exhibited above all by n-Alkanes with carbon chains of C15 to C18. For the two heaviest n-Alkanes, there is no detectible difference in washing efficiency compared to water, likely due to the low initial concentrations of said n-Alkanes in the contaminant.

The variation in total residual n-Alkanes with increasing SDS concentrations is shown for samples MF-05 and MF-10 washed at 40 °C in **Table 4.2**. The percent improvements in the extraction of each n-Alkane considered compared to washing experiments with deionized water at 40 °C of samples MF-05 and MF-10 are listed in **Table 4.4**. Histograms of the changes in residual n-Alkane concentrations with increasing concentrations of SDS in the washing solutions of samples MF-05 and MF-10 washed at 40 °C can be seen in **Figure 4.2**.

Table 4.2 Total residual concentrations of n-Alkanes C14 through C26 in samples MF-05 and MF-10 washed with SDS-based washing solutions at 30 °C and 40°C. Percent experimental Relative Standard Deviation (RSD) is for n=3.



	T=30°C				T=40°C			
SDS	MF-05		MF-10		MF-05		MF-10	
	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD
0 mM	18050.88	26.25	9205.13	24.30	30107.37	0.90	11362.64	10.28
1.75 mM	17240.48	14.99	2609.83	11.25	22239.67	2.43	11866.27	38.49
10.5 mM	2711.34	9.04	1695.59	3.01	5426.59	2.10	3278.22	2.81
14 mM	3498.65	1.74	1927.77	13.15	2335.18	7.12	1479.9	9.26

Table 4.3 Percent improvement in n-Alkane extraction efficiency at 30 °C for each n-Alkane considered in the two samples (MF-05 and MF-10) at different SDS concentrations compared to extraction efficiency of a surfactant-free washing solution, i.e. deionized water.

SDS	Improvement in extraction relative to water (%)					
T=30°C	MF-05			MF-10		
	1.75 mM	**10.5 mM**	**14 mM**	**1.75 mM**	**10.5 mM**	**14 mM**
C14	-86.94	79.08	80.93	-191.05	-109.63	-12.76
C15	-31.04	85.18	85.71	31.72	67.20	72.15
C16	10.72	85.84	84.72	70.12	78.98	78.22
C17	6.08	86.82	82.16	71.42	84.75	81.17
C18	2.33	86.08	80.90	69.34	86.66	83.50
C19	15.62	86.14	80.87	75.55	87.08	83.50
C20	19.51	86.12	80.01	76.34	86.58	83.19
C21	10.38	84.87	79.64	79.57	85.04	78.99
C22	20.52	84.78	78.39	84.63	84.94	80.93
C23	18.36	83.67	77.21	89.70	83.12	78.38
C24	21.79	83.30	75.32	93.79	81.53	76.45
C25	37.43	68.53	54.06	100.00	-24.00	-56.36
C26	29.95	72.75	60.21	100.00	38.22	21.41
Total	4.49	84.98	80.62	71.65	81.58	79.06

Table 4.4 Percent improvement in n-Alkane extraction efficiency at 40 °C for each n-Alkane considered in the two samples (MF-05 and MF-10) at different SDS concentrations compared to extraction efficiency of a surfactant-free washing solution, i.e. deionized water.

SDS	Improvement in extraction relative to water (%)					
T=40°C	MF-05			MF-10		
	1.75 mM	**10.5 mM**	**14 mM**	**1.75 mM***	**10.5 mM**	**14 mM**
C14	17.90	86.89	91.84	-54.07	83.23	81.89
C15	24.66	83.70	93.04	-24.90	73.59	86.32
C16	35.16	84.12	93.04	6.28	79.68	86.52
C17	34.13	84.88	93.10	10.90	79.25	88.27
C18	15.97	82.14	92.68	-4.57	76.07	89.70
C19	24.00	82.15	92.29	4.25	74.24	88.90
C20	23.19	81.30	92.14	0.59	72.15	88.60
C21	33.86	83.78	91.39	10.09	71.81	88.88
C22	22.32	79.70	91.47	1.36	65.83	87.24
C23	23.55	78.90	91.35	1.46	60.10	86.46
C24	24.63	74.36	90.86	2.95	45.22	85.41
C25	33.95	55.83	85.87	-191.87	-480.32	-31.66
C26	31.78	43.84	87.29	-36.78	-201.19	55.81
Total	26.13	81.98	92.24	-4.43	71.15	86.98

* Experimental RSD values for this experiment are very high, i.e. 38.5% overall

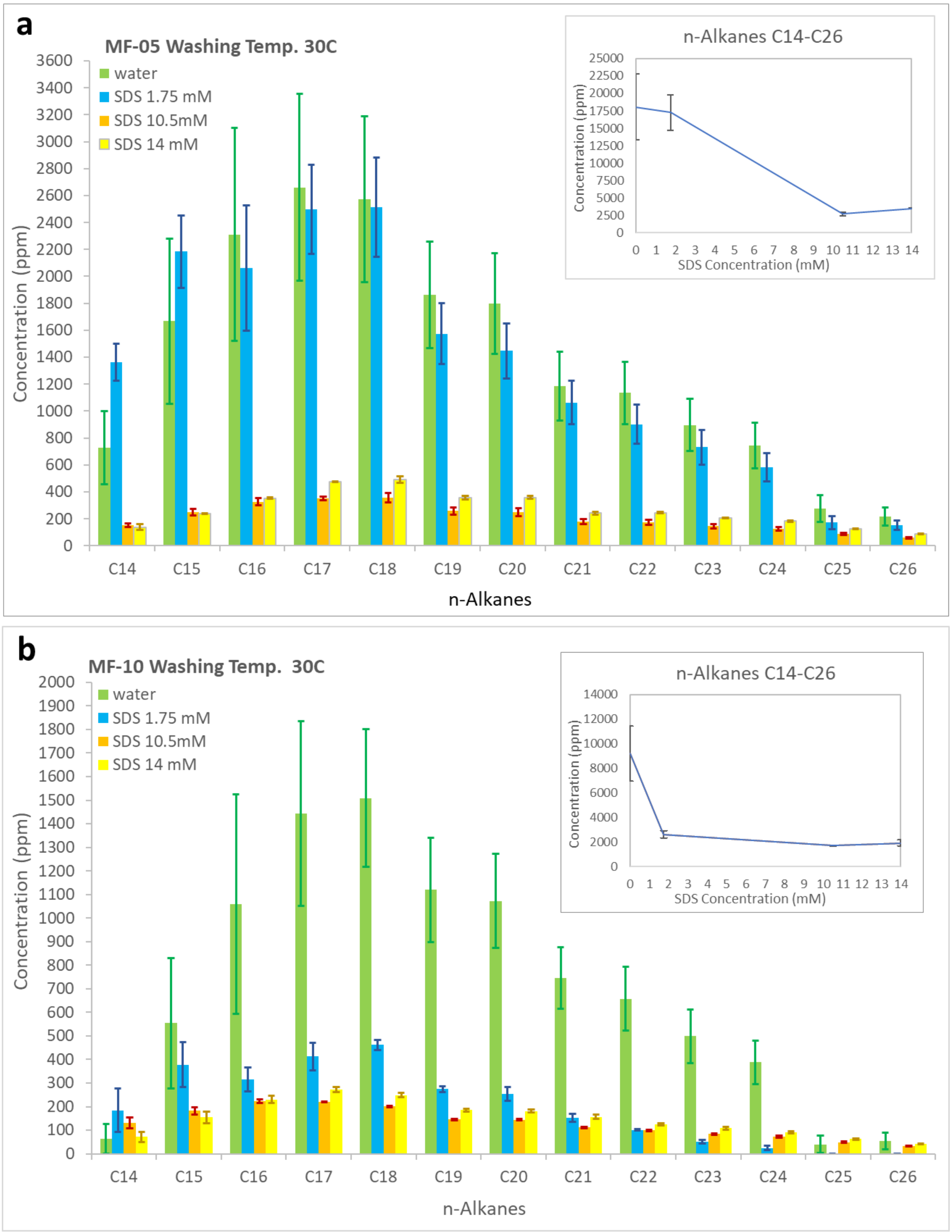


Figure 4.1 A histogram of the residual concentrations of n-Alkanes with carbon chain lengths of C14 to C26 in samples MF-05 (a) and MF-10 (b) after washing with washing solutions of increasing SDS concentrations at 30°C. Insets show the variation of residual concentrations of n-Alkanes C14-C26 with increasing concentrations of SDS. Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

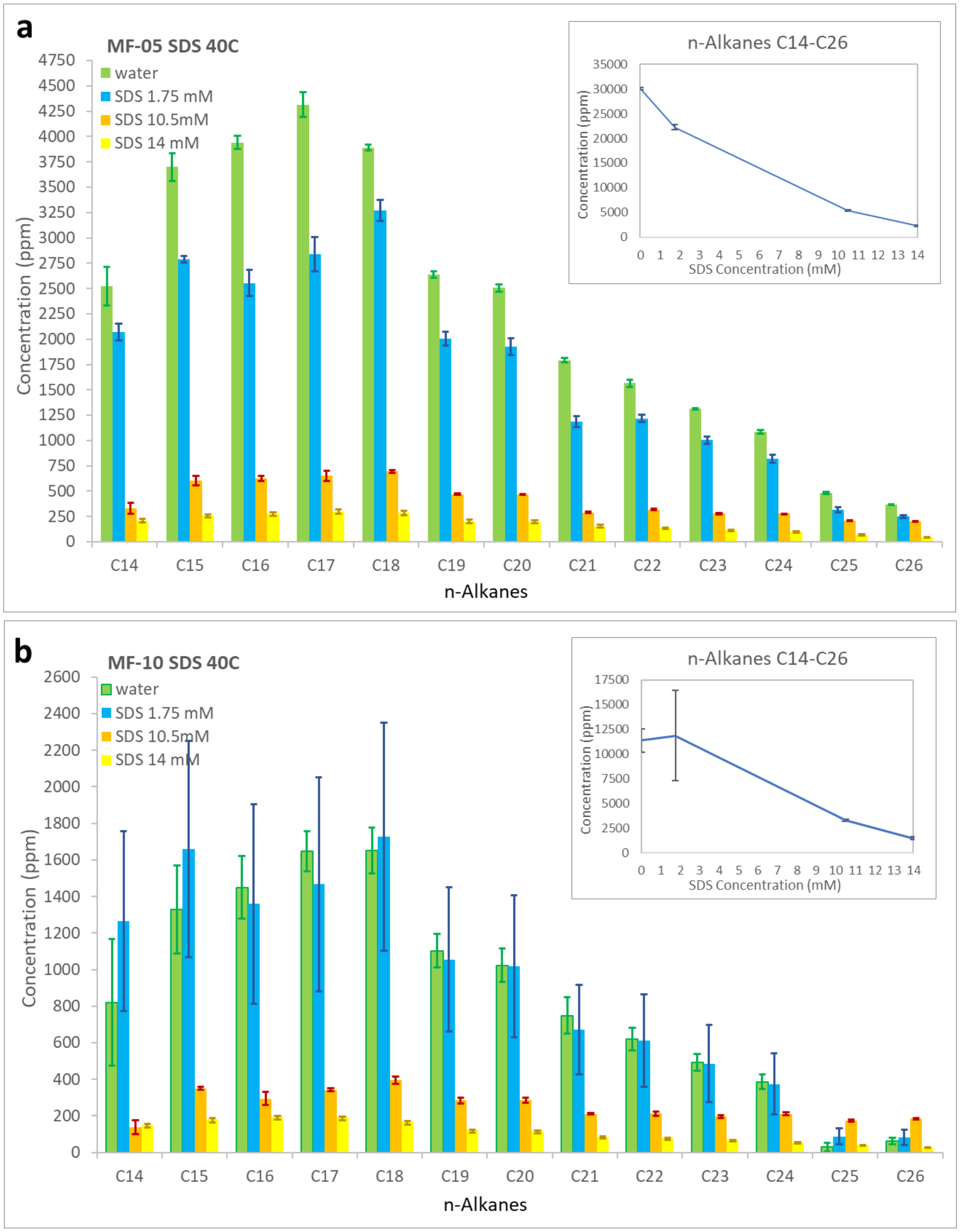


Figure 4.2 A histogram of the residual concentrations of n-Alkanes with carbon chain lengths of C14 to C26 in samples MF-05 (a) and MF-10 (b) after washing with washing solutions of increasing SDS concentrations at 40°C. Insets show the variation of residual concentrations of n-Alkanes C14-C26 with increasing concentrations of SDS. Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

4.2.2 Soil washing tests with TWEEN80-based washing solutions

For sample MF-05, washed at 30°C, the overall improvement in washing efficiency of the least concentrated TWEEN80 washing solution (0.003 mM; 0.25 CMC) with respect to water was 55%. Individual n-Alkane compounds showed variable improvements in washing efficiency. The greatest improvements are seen in n-Alkanes with carbon chain lengths of C17-C20, tapering towards both the longer chain and shorter chain n-Alkanes.

Increasing the concentrations of TWEEN80 in the washing solutions to concentrations above the CMC resulted in an initial improvement in washing efficiencies relative to water, which rose to 78%, followed by a drop off at concentrations two times the CMC, with overall improvements with respect to water calculated to be at just 47%. For individual n-Alkanes, washing efficiency improved dramatically for the shortest chain n-Alkanes (88% for C14) and tapered towards the longer chain compounds (47% for C25) at concentrations 1.5 times above the CMC of TWEEN80 (0.018 mM). At TWEEN80 concentrations twice the CMC, the improvement in efficiency was greatest for the C19 n-Alkane (57%).

For sample MF-10, washed at 30°C, the overall improvement in washing efficiency with respect to water was 51% at TWEEN80 concentrations below the CMC (0.003 mM). C18 to C20 n-Alkanes showed the greatest improvement in washing efficiency, which then tapered off towards the shorter and longer n-Alkanes. Increasing the TWEEN80 concentrations above the CMC resulted in an initial improvement in overall washing efficiency, with percent removal relative to water rising to 67%, only to drop off substantially at concentrations twice the CMC (23%). The greatest improvement in efficiency among the individual n-Alkanes was observed for the C18 and C19 n-Alkanes at both TWEEN80 concentrations.

For sample MF-05, increasing the washing temperatures to 40 °C resulted in an overall improvement in washing efficiency at all concentrations, rising to 77.5%, 82.5% and 65%, respectively. The drop off in efficiency at TWEEN80 washing solution concentrations twice the CMC, observed at 30°C, was still evident at 40°C. At all three surfactant concentrations, the greatest improvement in washing efficiency was observed for shortest chain n-Alkanes, gradually decreasing with carbon chain length.

In sample MF-10, on the other hand, no apparent improvement in washing efficiency was observed at any of the concentrations. However, when the residual n-Alkane concentrations are compared to those of DI water at the same temperature, some improvements do become apparent. For the washing solutions containing TWEEN80 in concentrations 1.5 times the CMC, increasing temperature did not produce any further improvement in washing efficiency. However, for TWEEN80 concentrations below and twice the CMC, some overall improvement compared to DI water is visible. For the individual n-Alkanes, at washing solution concentrations below the CMC, the greatest improvement was seen in C17-C19 compounds (61-64%). Similarly, at TWEEN80 concentrations twice the CMC, the greatest improvement in efficiency was seen in n-Alkanes with carbon chains of C17, C18 (43% and 46%) and the two lightest n-Alkanes (52% and 47%).

The variation in total residual n-Alkanes with increasing TWEEN80 concentrations is presented for samples MF-05 and MF-10 washed at both 30 °C and 40 °C in **Table 4.5**. The percent improvements in the extraction of each n-Alkane compared to washing experiments with deionized water at 30 °C and 40 °C of samples MF-05 and MF-10 are listed in **Tables 4.6** and **4.7**, respectively. Histograms of the changes in residual n-Alkane concentrations with increasing concentrations of TWEEN80 in the washing solutions for samples MF-05 and MF-10 washed at 30 °C and 40 °C can be seen in **Figures 4.3** and **4.4**.

Table 4.5 Residual concentrations of n-Alkanes C14 through C26 in samples MF-05 and MF-10 washed with TWEEN80-based washing solutions at 30 °C and 40°C. Percent experimental Relative Standard Deviation is for n=3.

TWEEN80	T=30°C				T=40°C			
	MF-05		MF-10		MF-05		MF-10	
	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD
0 mM	18050.88	26.25	9205.13	24.30	30107.37	0.90	11362.64	10.28
0.003 mM	8101.00	2.34	4501.37	6.96	6753.28	3.39	4830.71	3.92
0.018 mM	4036.23	2.21	3028.92	5.32	5249.42	4.11	4185.95	7.39
0.021 mM	9489.39	3.65	7044.87	6.21	10617.42	0.66	7318.88	4.73

Table 4.6 Percent improvement in n-Alkane extraction efficiency at 30 °C for each n-Alkane considered in the two samples (MF-05 and MF-10) at different TWEEN80 concentrations compared to extraction efficiency of a surfactant-free washing solution, i.e. deionized water.

TWEEN80	**Improvement in extraction relative to water (%)**					
T=30°C	**MF-05**			**MF-10**		
	0.003 mM	**0.018 mM**	**0.021 mM**	**0.003 mM**	**0.018 mM**	**0.021 mM**
C14	29.24	88.59	17.72	-367.94	70.60	-666.41
C15	56.10	84.13	41.54	30.63	78.70	-25.88
C16	55.93	80.84	45.38	49.35	72.12	12.62
C17	60.10	78.80	54.75	59.78	71.43	29.96
C18	59.80	77.84	53.29	63.47	71.65	44.02
C19	65.24	76.98	57.52	67.91	71.69	49.12
C20	57.75	76.70	54.14	61.74	68.50	40.57
C21	55.28	75.93	44.10	57.23	63.23	37.37
C22	54.81	74.87	47.34	56.18	63.77	33.71
C23	52.00	73.92	46.27	50.30	58.90	29.70
C24	47.44	71.42	42.99	41.11	54.22	22.64
C25	2.28	46.88	-2.80	-314.24	-207.81	-397.84
C26	7.47	53.19	14.79	-152.25	-56.49	-130.35
Total	55.12	77.64	47.43	51.10	67.10	23.47

Table 4.7 Percent improvement in n-Alkane extraction efficiency at 40 °C for each n-Alkane considered in the two samples (MF-05 and MF-10) at different TWEEN80 concentrations compared to extraction efficiency of a surfactant-free washing solution, i.e. deionized water.

TWEEN80	**Improvement in extraction relative to water (%)**					
T=40°C	**MF-05**			**MF-10**		
	0.003 mM	**0.018 mM**	**0.021 mM**	**0.003 mM**	**0.018 mM**	**0.021 mM**
C14	80.11	89.47	77.57	58.23	71.24	52.68
C15	83.28	87.30	71.57	65.56	72.79	47.10
C16	78.44	85.01	65.20	63.19	67.58	33.32
C17	79.50	83.12	66.52	61.20	65.02	37.44
C18	77.51	82.73	64.30	62.41	68.59	43.40
C19	78.94	81.64	66.03	64.01	70.03	46.03
C20	76.02	80.49	61.84	58.12	61.84	35.34
C21	77.71	80.27	60.33	55.36	56.03	27.69
C22	73.89	78.55	56.08	54.21	54.78	28.59
C23	73.61	77.71	58.73	48.19	51.31	24.18
C24	70.48	75.94	56.12	39.75	45.87	15.11
C25	53.60	62.25	33.66	-463.79	-385.07	-623.69
C26	53.15	65.39	42.75	-123.24	-61.44	-123.32
Total	77.57	82.56	64.73	57.49	63.16	35.59

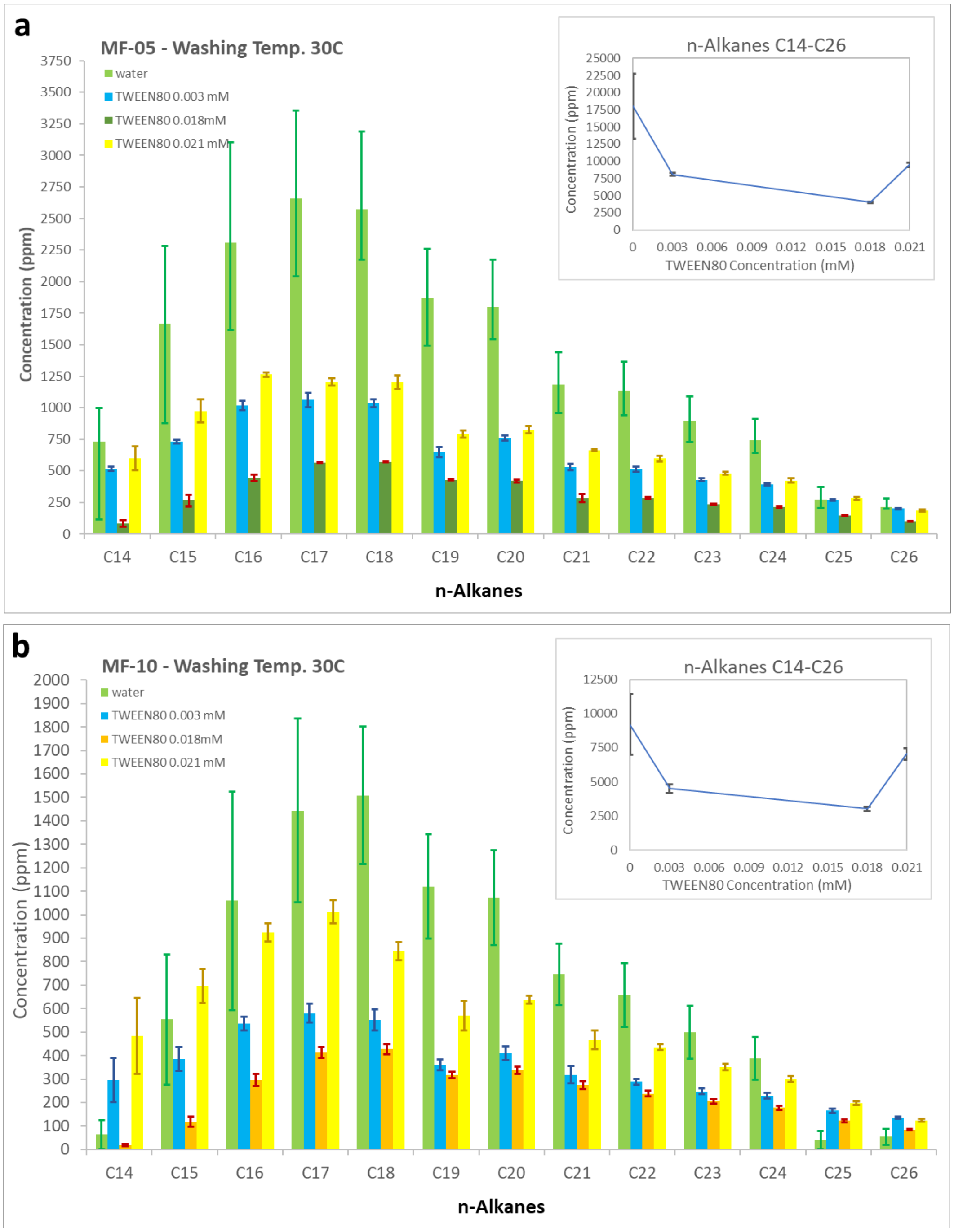


Figure 4.3 A histogram of the residual concentrations of n-Alkanes with carbon chain lengths of C14 to C26 in samples MF-05 (a) and MF-10 (b) after washing with washing solutions of increasing SDS concentrations at 30°C. Insets show the variation of residual concentrations of n-Alkanes C14-C26 with increasing concentrations of TWEEN80. Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

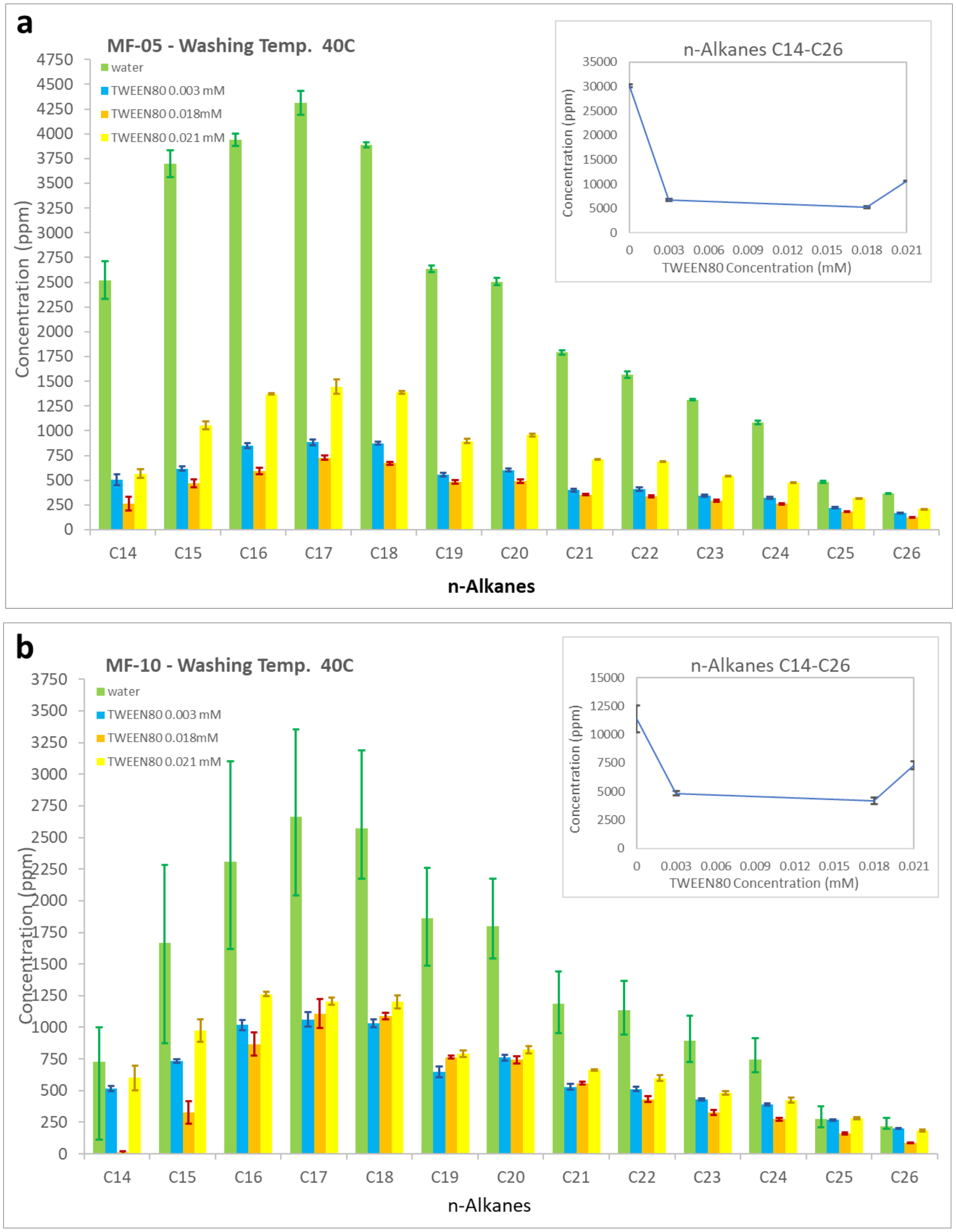


Figure 4.4 A histogram of the residual concentrations of n-Alkanes with carbon chain lengths of C14 to C26 in samples MF-05 (a) and MF-10 (b) after washing with washing solutions of increasing SDS concentrations at 40°C. Insets show the variation of residual concentrations of n-Alkanes C14-C26 with increasing concentrations of TWEEN80. Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

4.3. Discussion

4.3.1 Variation in washing efficiency with temperature

Increasing the temperature of SDS-based washing solutions when washing sample MF-05 results in a decrease in washing efficiency at concentrations 0.25 times the CMC (1.75 mM), **Figure 4.5a**. However, when compared to the extraction efficiency of water, the overall n-Alkane extraction efficiency improves by about 20%. As the concentration of the washing solution is increased above the CMC (10.5 mM SDS), the decrease in washing efficiency with increasing temperature becomes less marked, **Figure 4.5b**. The overall percent extraction efficiency relative to water decreases by 3%, reflecting this drop. Surprisingly, increasing the concentration of the washing solution to twice the CMC (14 mM SDS) reverses this trend, **Figure 4.5c**. This is reflected by a 12% improvement in the overall washing efficiency of this solution relative to water at 40°C.

For sample MF-10, increasing the temperature of the SDS-based washing solution to 40 °C results in a substantial drop in washing efficiency, **Figure 4.5d.** In fact, the drop is so great, that the efficiency is now lower than that of deionized water, as seen from the negative values of percent improvement relative to water. This, however, may be in part an artifact of the high errors associated with this particular experiment. At SDS concentrations above the CMC (10.5 mM SDS), the washing efficiency is substantially higher, **Figure 4.5e**. However, it is still less than that of deionized water at the same temperature. As the concentration of SDS in the washing solution is increased to twice the CMC (14mM) this trend reverses: the washing efficiency improves by about 10% relative to that at 30 °C and by a further 16% compared to deionized water at 40°C, **Figure 4.5f**.

Increasing the temperature of TWEEN80 washing solutions improved slightly the washing efficiency of sample MF-05 at concentrations below the CMC, **Figure 4.6a**. Relative to 40 °C surfactant-free washing solution the overall percent improvement was on the order of 20%, with the shorter length n-Alkanes being most affected. At TWEEN80 concentrations above the CMC (0.018mM and 0.021mM), increasing the temperature slightly decreased the washing efficiency, **Figure 4.6b** and **c**. However, when compared to washing efficiencies of deionized water at the same temperature, the percent improvement is actually greater at 40 °C than at 30 °C for both TWEEN80 concentrations.

For MF-10, increasing the temperature of the TWEEN80 washing solution to 40 °C results in a slight decrease in washing efficiency at all concentrations, **Figures 4.6d, e** and **f**. However, when the washing efficiencies are compared to those of DI water at 30 °C and 40°C, a slight improvement in overall efficiency is observed below the CMC (about 6%) and at concentrations twice the CMC (about 12%). However, these values may be somewhat skewed by the extremely poor performance of TWEEN80 compared to DI water for the two heaviest n-Alkanes analyzed. A result that may, in turn, be partly an artifact of the low concentrations of the heavier alkanes in the diesel contaminant, making the obtainment of reliable concentration values more difficult.

See **Tables 4.3** and **4.4** for the changes in the n-Alkane removal efficiencies compared to water.

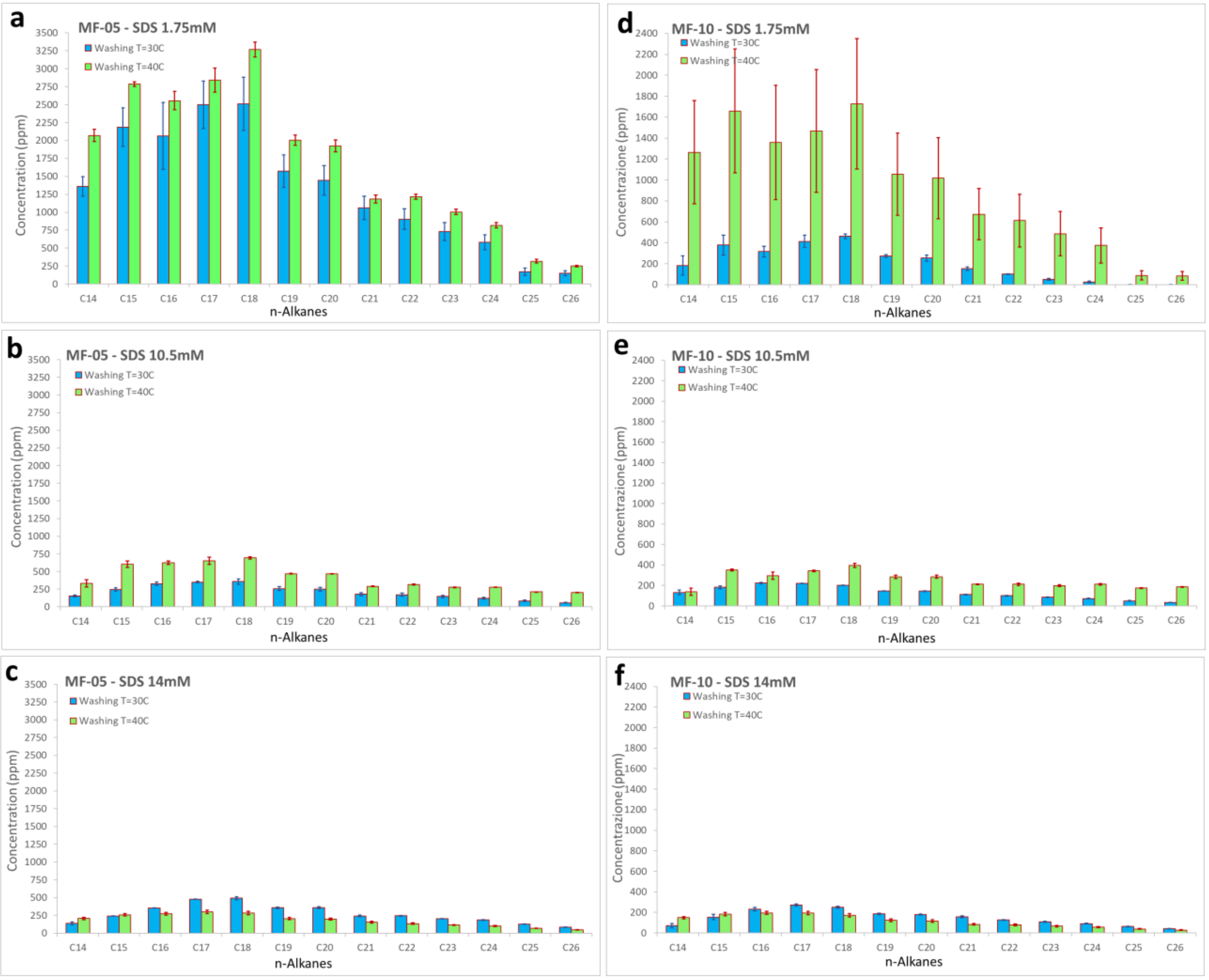


Figure 4.5 A comparison of residual n-Alkane concentrations in sample MF-05 (a-c) and MF-10 (d-f) washed with different concentrations of SDS at the two washing temperatures. Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

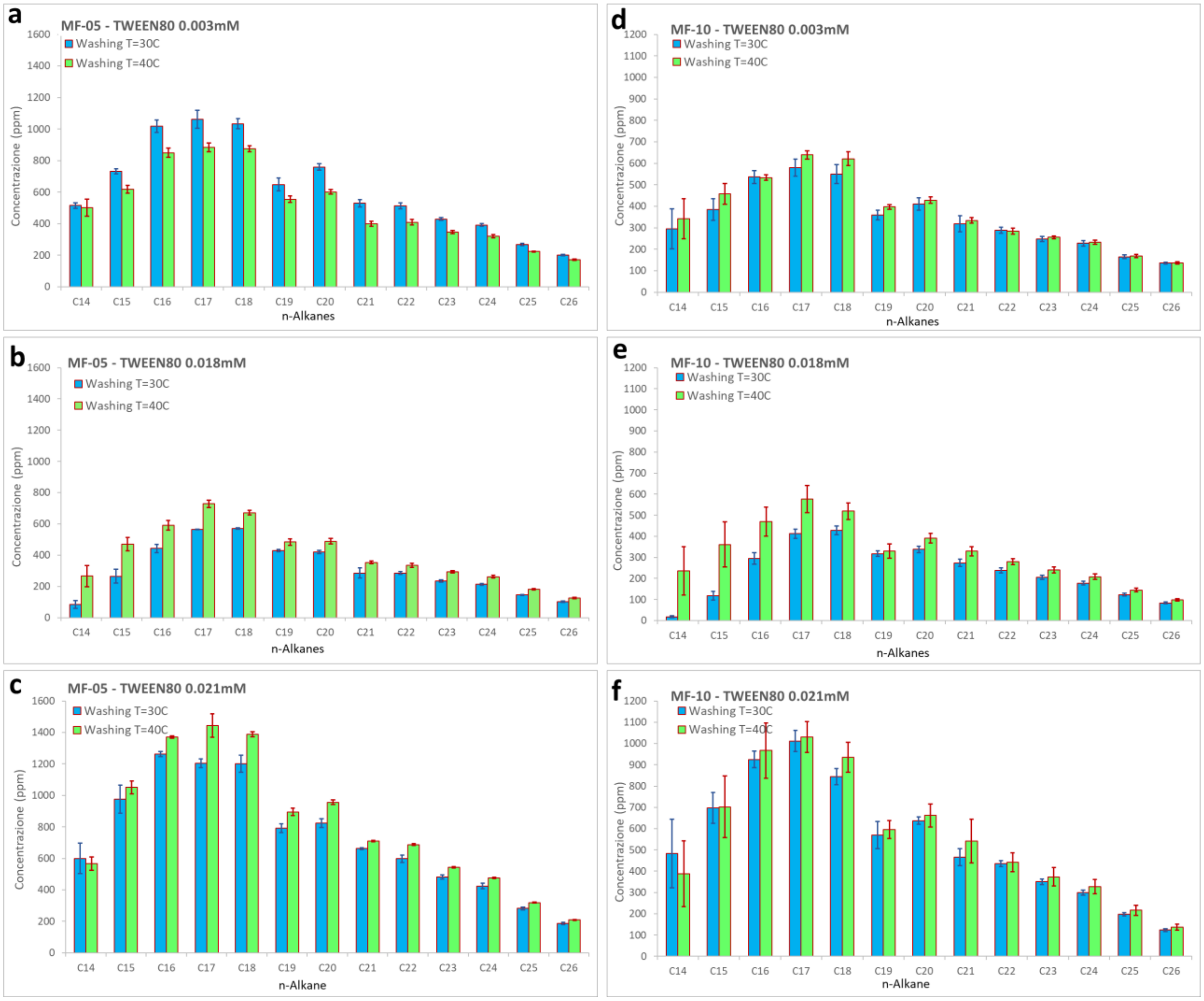


Figure 4.6 A comparison of residual n-Alkane concentrations in sample MF-05 (a-c) and MF-10 (d-f) washed with different concentrations of TWEEN80 at the two washing temperatures. Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

4.3.2 Comparison of washing efficiency of the two surfactants used

For sample MF-05, at surfactant concentrations below the CMC, there is a substantial improvement in the overall washing efficiency with TWEEN80 and a less pronounced improvement in the washing efficiency of SDS at both 30 °C and 40°C, **Figure 4.7a**. At 30°C, the greatest improvement in washing efficiency relative to DI water was seen in the longer-chained n-Alkanes for SDS (maximum improvement of 37% for C25), and for medium length n-Alkanes for TWEEN80 (maximum improvement of 65% for C19), **Figure 4.8a** and **b**. At 40°C, there is a further ~20% improvement in efficiency for both surfactants relative to water of the same temperature, with maximum overall values reaching 35% and 83% for SDS and TWEEN80, respectively. The greatest improvements are seen in the lighter n-Alkanes for both surfactants, **Figure 4.8b**.

Increasing the concentrations of the surfactants to 1.5 times the CMC, produces a substantial improvement in the overall washing efficiency of sample MF-05 with SDS at both 30 °C and 40 °C and a less pronounced improvement in the washing efficiency of TWEEN80 at 40°C, **Figure 4.7a**. This reversal of the improvement trend results in similar values of washing efficiencies of sample MF-05 for both surfactants at these concentrations. When compared to washing with DI water, improvements in efficiency are very high for both surfactants at both temperatures (on the order of 80%) with slight drop off towards the heavier n-Alkanes, **Figure 4.8c** and **d**. However, it is important to note that for SDS-based washing solutions, increasing the concentrations to above the CMC resulted an additional improvement in efficiency relative to water of 55% and 80% at 30 °C and 40°C, respectively; while for the TWEEN80-based washing solutions, the additional improvement in efficiency attributable to the increase in surfactant concentration is of just 20% and 6% at 30 °C and 40°C, respectively.

A further increase in surfactant concentrations proved ineffective in further improving the washing efficiency of either surfactant. For SDS-based washing solutions, increasing the concentration from 1.5 to 2 times the CMC resulted in a slight additional decrease in residual n-Alkane concentrations at 40 °C and an increase in residual n-Alkane concentrations at 30 °C, **Figure 4.7a**. Compared to washing with pure DI water, the washing efficiency decreased by 5% at 30 °C and increased by 10% at 40 °C, with longer-chained n-Alkanes being more effected in both cases, **Figure 4.8e**. The concentrations of residual n-Alkanes after washing with TWEEN80-

based solutions at concentration 2 times the CMC at both 30 °C and 40 °C were not only greater than those following washing with solutions at concentrations 1.5 times the CMC, but even greater than the residual concentrations following washing at concentrations below the CMC **Figure 4.7a**. The overall increase in washing efficiency relative to DI water dropped by 30% and 18% at 30 °C and 40 °C, respectively, **Figure 4.8f**. The lag in washing efficiency improvement observed for SDS-based washing solution below the CMC relative to TWEEN80 is most likely due to the interactions of the negatively charged SDS head groups with the positively charged surfaces of calcite contained in sample MF-05.

For sample MF-10, at concentrations below the CMC, a significant drop in residual n-Alkane concentration is observed for TWEEN80-based washing solution at both 30 °C and 40 °C but only at 30 °C for the SDS-based solution, **Figure 4.7**. At 40 °C no improvement in n-Alkane removal with respect to water can be seen for the SDS-based washing solution. This difference in response is likely, at least in part, to be an artifact of the high standard deviation errors observed for the latter experiment. The overall washing efficiency of the solutions has improved by 72% and 51% with respect to DI water for SDS and TWEEN80 solutions at 30°C, respectively, with medium-length n-Alkanes showing the greatest improvements for TWEEN80-based solutions and longer-chained n-Alkanes for SDS-based solutions, **Figure 4.9a**. At 40°C, the overall washing efficiency with respect to DI water of the TWEEN80-based solutions has improved by 57% with the greatest improvements seen in middle-length n-Alkanes (C17-C19), **Figure 4.9b.** Overall washing efficiency of the SDS-based solution on the other hand has decreased by 5%.

When the surfactant concentrations were increased above the CMC, both SDS and TWEEN80-based washing solutions, at both 30 °C and 40°C, proved moderately more effective at removing n-Alkanes, **Figure 4.7b**. When compared to DI water, the overall efficiency of the surfactant-based solutions at concentrations above the CMC improved by 80% and 70% for the SDS-based solution at 30 °C and 40°C, respectively, and by 67% and 63% for the TWEEN80-based solution at 30 °C and 40°C, respectively. In all but the 40 °C SDS-based solution, this translated into an additional improvement in efficiency of about 10%. The greatest improvements in efficiency were seen for the medium-length n-Alkanes for all solutions except TWEEN-80 at 40°C, for which the greatest improvements were seen for the lightest n-Alkanes, progressively decreasing with increasing n-Alkane length, **Figure 4.9c** and **d**.

Further increasing the concentration of the surfactants in the washing solutions resulted in a substantial decrease in the efficiency of TWEEN80 at both 30 °C and 40 °C and a slight decrease in the efficiency of SDS at 30°C. The only solution to produce an additional improvement in extraction efficiency was SDS at 40°C, **Figure 4.7b**. When compared to DI water, overall, the SDS-based solution is still substantially more effective, with 79% and 87% improvement at 30 °C and 40°C, respectively, **Figure 4.9e**. The TWEEN80 solution on the other hand is now just 23% and 47% more effective than DI water at 30 °C and 40°C, respectively, **Figure 4.9f**. The trend observed for higher concentrations of TWEEN80 could be the result of changes in the shape of micelles observed at higher surfactants concentrations which can lead to loss of stability [2]. The likelihood of this occurring increases with increasing bulkiness of the surfactant molecule, a fact consistent with the greater size of TWEEN80 molecules relative to those of SDS.

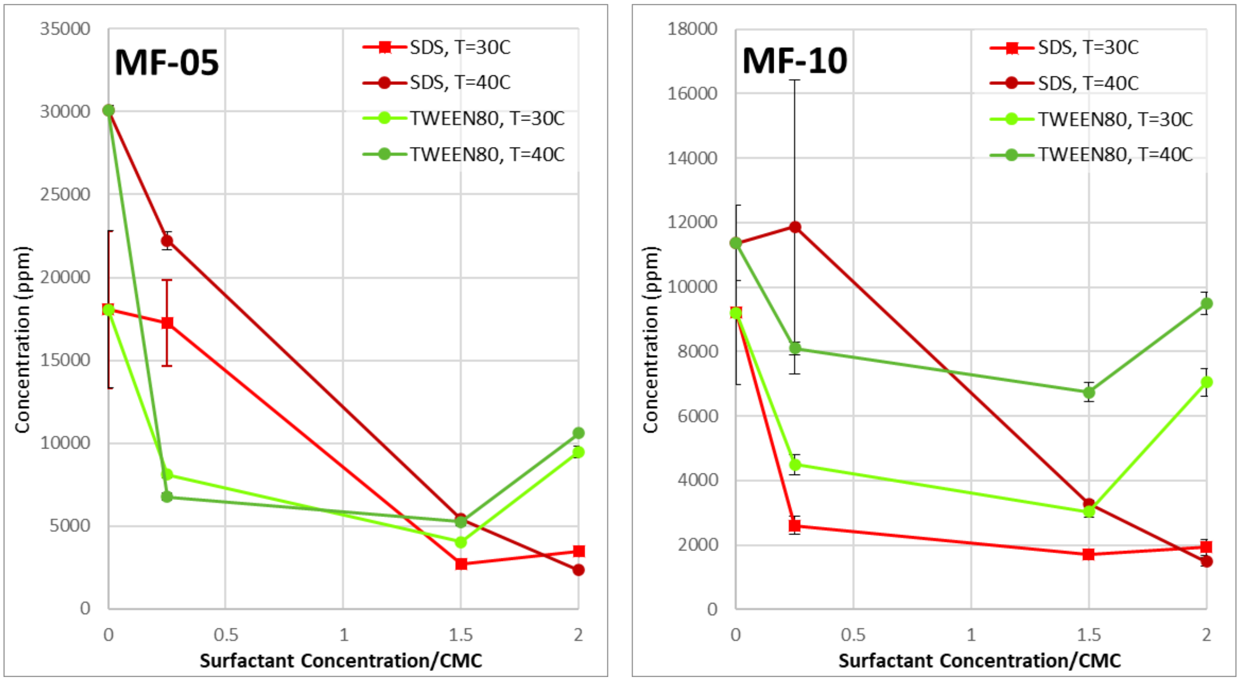


Figure 4.7 Plots of residual n-Alkane concentrations versus the ratio of surfactant concentrations to CMC for MF-05 (a) and MF-10 (b). Error bars represent Relative Standard Deviation of the experimental method (n=3).

Figure 4.8 Histograms of percent improvement in washing efficiency relative to DI water at 30°C and 40°C for sample MF-05 at the three surfactant concentrations.

4.3.3 Variation in washing efficiency with mineralogy

The difference in the washing efficiencies is apparent even before the surfactants are added to the washing solutions. Pure DI water is twice as effective at removing n-Alkanes from sample MF-10 than sample MF-05. This is most likely the result of the combined effect of the higher clay and organic contents found in the latter, which strongly absorb petroleum compounds, making extraction more difficult [3]. The addition of SDS and TWEEN80 to the washing solution succeeds only in slightly modifying the gap in the washing efficiency between the two samples. **Figure 4.10** compares the variation in total residual n-Alkane concentrations with surfactant concentrations and washing temperatures for the two samples.

For SDS the greatest differences in efficiency between the two samples is seen at concentrations below the CMC, with MF-10 showing lower residual n-Alkane concentrations than MF-05. As the SDS concentration in the washing solution is increased, the washing efficiencies for the two samples tend to converge towards similar overall values**.** This trend could be the result of interactions between the negatively charged SDS molecules and positively charged mineral surfaces contained in the samples. This interaction results in the adsorption of the surfactant molecules onto mineral surfaces, effectively taking them out of solution and consequently, lowering the concentration of SDS available for n-Alkane removal. The presence of calcite, a mineral with positively charged mineral surfaces (as reflected in the higher CEC values), in sample MF-05 has determined the observed lower washing efficiencies for this sample **Tables 2.3** and **2.4**. For MF-10, with its absence of calcite and lower CEC values, this effect is much less pronounced. As the concentration of SDS in the washing solution is increased, the magnitude of the influence of this effect on the overall efficiency of the washing solution becomes progressively lower, as the overall percent of surfactant molecules lost to adsorption goes down. If individual n-Alkanes are considered, the greatest differences in washing efficiencies of the two samples are observed for C15 to C20 n-Alkanes, **Figure 4.11**.

For TWEEN80, on the other hand, there is little observable variation in the difference in washing efficiency of the two samples with increasing surfactant concentrations. For both samples and both temperatures an immediate increase in washing efficiency is observed after the addition of the surfactant to the washing solution. As the concentration of the surfactant is increased, the efficiency initially slightly increases and then drops off significantly, with the differences in efficiency between samples MF-05 and MF-10, at both temperatures, remaining constant and relatively low. This can be explained by the neutral nature of the TWEEN80 molecule, a property which renders it less efficient at n-Alkane removal but also less subject to variation in efficiency due to mineralogical differences in the soils being treated. Similarly, to SDS-based washing solutions, when individual n-Alkanes are considered, the greatest differences in washing efficiencies of the two samples are observed for C15 to C20 n-Alkanes, **Figure 4.12**.

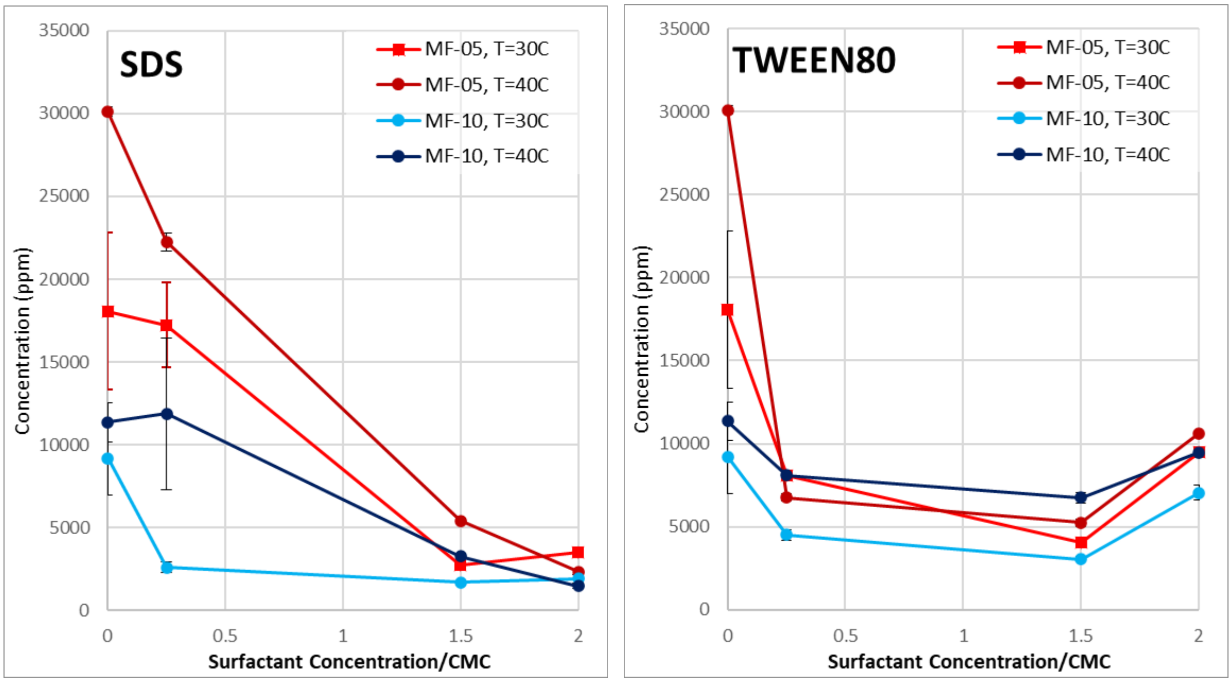


Figure 4.10 Plots of residual n-Alkane concentrations versus the ratio of surfactant concentrations to CMC for SDS (a) and TWEEN80 (b). Error bars represent Relative Standard Deviation of the experimental method (n=3).

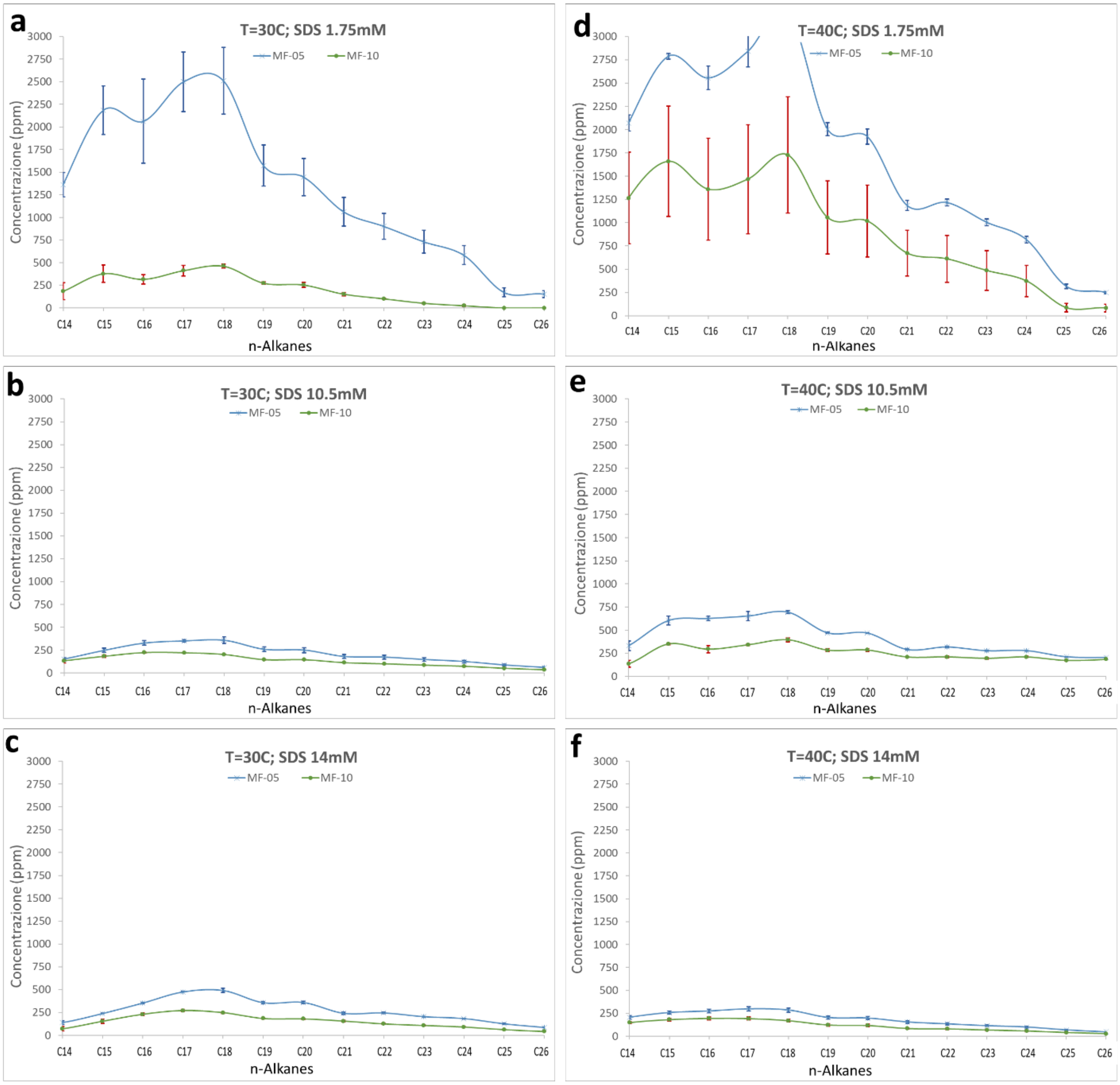


Figure 4.11 Residual concentrations of individual n-Alkanes in samples MF-05 and MF-10 after washing after washing with SDS at 30°C (a, b, c) and 40°C (d, e, f). Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

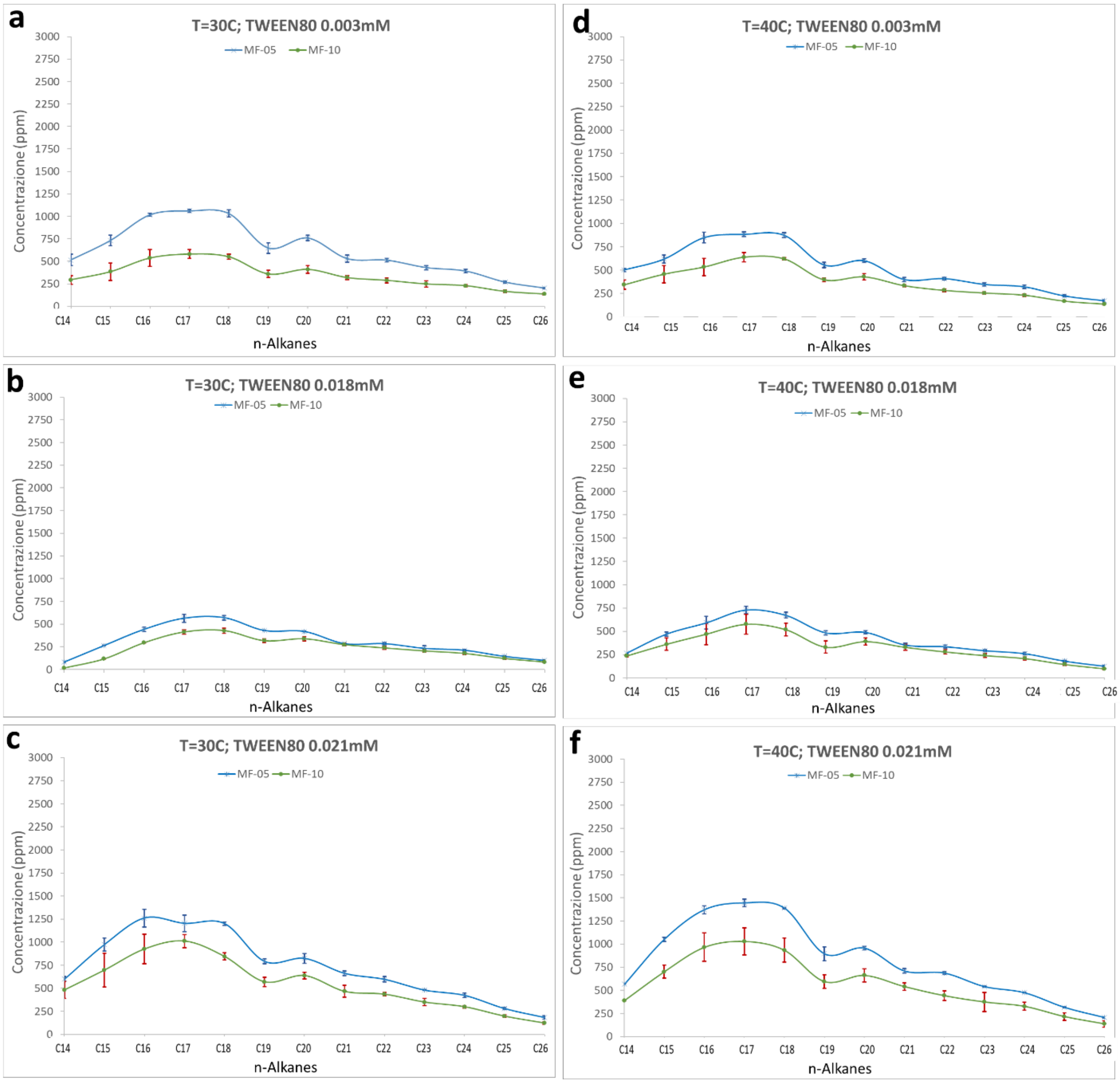


Figure 4.12 Residual concentrations of individual n-Alkanes in samples MF-05 and MF-10 after washing with TWEEN80 at 30°C (a, b, c) and 40°C (d, e, f). Error bars reflect Relative Standard Deviation (n=3) of the experimental method.

4.4 Conclusions

Having completed the sampling, characterization and selection of typical soils of the Marche Region and having fine-tuned a laboratory-scale soil washing simulation procedure, it was possible to pass on to the heart of this PhD project: the comparison of the relative efficiencies of an anionic and non-ionic surfactants, SDS and TWEEN80 respectively, in the removal of diesel from two soils of different physical, mineralogical and chemical properties, MF-05 and MF-10.

It was found that for sample MF-05, TWEEN80 is generally more efficient at removing n-Alkanes at concentrations below the Critical Micelle Concentration (CMC). As the surfactant concentrations are increased above the CMC however, SDS becomes equally effective and then surpasses TWEEN80, which shows a drop off in efficiency at the highest concentration studied. For sample MF-10, SDS and TWEEN80 show similar trends of washing efficiency improvement with increasing surfactant concentrations. The lag in efficiency improvement with increasing surfactant concentration observed for SDS in sample MF-05 is no longer present. SDS is now more effective at extracting n-Alkanes than TWEEN80 of the same temperature for all concentrations. TWEEN80, on the other hand shows an identical trend of washing efficiency variation with increasing surfactant concentration for both samples with a characteristic reversal in efficiency improvement at the highest concentration. Finally, both surfactants are more effective at extracting n-Alkanes from sample MF-10 than sample MF-05.

All of these observations can be explained by taking a closer look at the differences in mineralogic composition of the studied samples and the expected effect these differences will have on interactions with surfactant molecules. SDS is an anionic surfactant containing a negatively charged head group. When it is used to extract n-Alkanes from sample MF-05, which contains 30wt% calcite, the negatively charged surfactant molecules are adsorbed to the surface of calcite crystals effectively taking them out of solutions. This is the source of the poor improvement in extraction efficiency observed for sample MF-05 at SDS concentrations below CMC. Once the calcite surface is saturated and no more surfactant molecules are taken out of solution, the rate of improvement in extraction efficiency with increasing surfactant concentrations rebounds. As expected, for sample MF-10, which consists mostly of quartz (62wt%), a mineral with a negatively charged surface, this trend is not observed. This mineral composition of sample MF-10, along with its slightly lower clay and organic matter contents (which can also result in loss of surfactants to adsorption) are the reason that both surfactants are more effective at removing n-Alkanes from this sample. Unlike SDS, TWEEN80 is a neutral molecule that is not attracted to charged mineral surfaces. Consequently, no difference in the trends in the rate of improvement of extraction efficiency with increasing surfactant concentrations was either expected or observed for samples MF-05 and MF-10. The observed reversal in the extraction efficiency observed at the highest TWEEN80 concentrations analyzed requires further study. A possible explanation is the destabilization of micelles due to a change in their shape linked.

Increasing temperature has had little effect on the efficiency of n-Alkane removal for both MF-05 and MF-10, and for both surfactants. For both samples, increasing the washing temperature from 30 °C to 40 °C for SDS-based washing solutions only improves the washing efficiency at concentrations 2 times the CMC. Although slight, this improvement means that the improvement rate of washing efficiency with increasing concentration no longer flattens out but continues to rise. This means that if temperature and surfactant concentrations are increased concurrently, a continued improvement in washing efficiency can be achieved for SDS. For TWEEN80-based solutions, a slight improvement in efficiency with temperature is observed only for sample MF-05 at surfactant concentrations below the CMC. Consequently, varying the washing temperature by 10°C is either insufficient to result in an improvement or not an effective way of improving washing efficiency for this surfactant.

As illustrated in this study, understanding the mineralogy of the soils in need of remediation is of crucial importance to establishing the correct formulation of washing solutions. In addition to the standard grain size distribution and geochemical analysis, case by case evaluations of the mineralogy of contaminated soils will help maximize efficiency while minimizing costs and mitigating environmental impact.

4.5 References

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