DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE FACTORS EFFECTING THE REMEDIATION OF NON-AQUEOUS PHASE LIQUID (NAPL) CONTAMINANTS IN SOILS

by
Gülden GÖK

June, 2012
İZMİR

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"THE FACTORS EFFECTING THE REMEDIATION OF NON-AQUEOUS PHASE LIQUID (NAPL) CONTAMINANTS IN SOILS"** completed by **GÜLDEN GÖK** under supervision of **ASSIST. PROF. DR. GÖRKEM AKINCI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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ABSTRACT

The aim of this thesis is to identify the factors effecting the remediation of NAPLs in the soils. For this purpose, two major types of treatment systems -namely; slurry and fixed bed- were used for the physical and biochemical remediation of soils.

The parameters of initial contaminant concentration, presence of local bacteria, and presence and amount of soil amendments are examined both in slurry systems, and in fixed bed systems, as well as the specific parameters related with the remediation technique. Solid waste compost was used as soil amendment and four different types of soil were used to examine their treatability. Diesel oil was used as a contaminant well represents the NAPLs. The treatment performances were followed by observing the TPHs and PAHs levels in the soils. The systems were also operated with sterile soils to define the extent of volatilization losses of NAPLs during the remediation.

The major findings of the study are as follows; i) TPHs removal efficiencies are decreasing with increasing initial diesel concentration in systems, ii) the efficiencies of fixed bed systems are higher than the slurry systems, iii) by blocking the intersectional area between the soil and air & water because of high concentration of diesel contamination in the soil, treatment efficiencies are decreasing in fixed bed systems, iv) thermal volatilization is the dominant process to remove NAPLs from soils, and its efficiency is dependent both on contaminant properties and soil properties, v) the contamination age adversely effect the efficiency of NAPLs removal from the soils, vi) generally the TPHs removal efficiency increases with increasing CO2 production, vii) the removal rates of PAHs are decreasing with increasing number of benzene rings and PAHs removals are strongly correlated both with their water solubility and vapor pressure, which are determining the extent of their bioavailability and volatilities.

Keywords: Soil remediation, non aqueous phase liquids (NAPLs), total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), diesel

TOPRAKDAKİ SUDA ÇÖZÜNMEZ FAZLI SIVI (NAPL) KİRLETİCİLERİN ARITIMINI ETKİLEYEN FAKTÖRLER

ÖZ

Sunulan tezin amacı, topraktaki suda çözünmeyen fazlı sıvı kirleticilerin (NAPL) arıtımını etkileyen faktörleri belirlemektir. Bu amaçla, akışkan ve sabit yataklı sistemlerde temel arıtma metotlarından fiziksel ve biyokimyasal arıtım çalışılmıştır.

Çalışmada, hem akışkan yataklı hem de sabit yataklı sistemler için spesifik olan parametrelerin yanı sıra, başlangıç kirletici konsantrasyonu, bölgesel bakterilerin varlığı, toprak iyileştici maddelerin varlığı ve miktarı gibi parametreler de araştırılmıştır. Toprak iyileştirici madde olarak katı atık kompostu seçilmiş olup, dört farklı toprak örneği kullanılarak arıtma verimleri araştırılmıştır. Deneylerde, suda çözünmeyen sıvı fazlı kirletici madde özelliklerini iyi temsil ettiği için dizel kullanılmıştır. Arıtma performansları, topraktaki toplam petrol hidrokarbonları (TPH) ve poliaromatik hidrokarbon (PAH) seviyeleri ölçülerek değerlendirilmiştir. Arıtma süreci boyunca, kirleticilerin buharlaşma kayıplarını belirlemek amacıyla sistemler temiz steril toprakla da çalıştırılmıştır.

Çalışmanın temel bulguları şunlardır; i) TPH arıtma verimlerinin sistemdeki başlangıç kirletici konsantrasyonunun artmasıyla azaldığı görülmüştür ii) sabit yataklı sistemlerdeki arıtma verimleri, akışkan yataklı sistemdekilere göre daha yüksektir iii) topraktaki yüksek dizel konsantrasyonu yüzünden, toprak ve hava&su arasındaki kesişme alanı bloke edildiğinde, sabit yataklı sistemlerde toprak artma verimleri düşmüştür iv) termal buharlaşma, kirleticilerin topraktan giderilmesinde baskın olan prosestir ve verimi kirleticinin ve toprağın özelliklerine göre değişmektedir v) kirlilik yaşı NAPL nin topraktan arıtılmasını olumsuz yönde etkilemektedir vi) genel olarak, TPH giderim verimleri CO2 oluşumuyla artış göstermektedir vii) PAH arıtma verimleri, artan benzen halkalarıyla artmasıyla azalma göstermektedir. Kirleticinin biyoelverişliliğini ve uçuculuğunun belirleyen faktörler olan suda çözünürlük ve buhar basıncı ile PAH giderim verimi arasında kuvvetli bir korelasyon olduğu tespit edilmiştir.

Anahtar sözcükler: toprak arıtımı, suda çözünmeyen fazlı sıvı kirleticiler (NAPL), toplam petrol hidrokarbonları (TPH), poliaromatik hidrokarbonlar (PAH), dizel

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CHAPTER ONE
INTRODUCTION

Non-Aqueous Phase Liquids (NAPLs) are immiscible (undissolved) hydrocarbons in the subsurface that exhibit different behavior and properties than dissolved contaminant plumes. NAPLs have a tremendous impact on the remediation of contaminated aquifers, as it is very difficult or impossible to remove all of the NAPL from a hazardous waste site once released to the subsurface. Although many NAPL removal technologies are currently being tested, to date there have been few field demonstrations where sufficient NAPL has been successfully removed from the subsurface to restore an aquifer to drinking water quality (EPA, 1992a). The residual NAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved contaminants to ground water, and effectively prevents the restoration of NAPL-affected aquifers for tens or hundreds of years.

NAPLs immiscibility is not a factor to reduce their mobility in soil. Here, the physical and biological methods for the effective remediation of NAPLs will be studied to determine the factors effecting the remediation performance. Limited number of reports is found in the scientific literature that NAPLs -an important group of soil contaminants- are studied alone and few of them are about remediation. By this work, the lack of information in the literature is aimed to be completed.

The chapter consists of three major parts, namely; the investigation of diesel inhibition on studied soil and compost, the investigation of factors effecting the NAPLs remediation in slurry systems, and the investigation of fixed bed remediation systems for the factors effecting the NAPLs remediation. These parts include subtitles related with the investigated factors.

The slurry systems are investigated according to the solid/liquid ratio, initial contaminant concentration, contamination age, soil type, soil particle size, and presence of soil amendments. The fixed bed systems were studied to find the effects of water content, temperature, initial contaminant concentration, contamination age, soil type, and presence of soil amendments. The control sets are also operated for each of the parameters investigated.

CHAPTER TWO

BACKGROUND INFORMATION

2.1 Sources of Soil Contamination

The contamination of soil can be originated essentially from the following activities:

- Industrial operations
- Agricultural activities
- Domestic and urban activities

Some examples of activities within these categories that result in soil contamination are shown in Table 2.1 (Connell, 1997).

Table 2.1 Examples of activities resulting in soil contamination

Industrial operations
Chemical industries, gas and electricity supply, wood preserving, oil refining, service stations, smelters, mining, tanning, dockyards, waste dumps
Agricultural activities
Treatment of crops, handling and storage of agricultural chemicals, use of cattle dips
Domestic and urban activities
Solid waste disposal, sewage sludge disposal, sewage works and farms, motor vehicle discharges, usage of chemicals

Deliberate disposal of industrial waste to land has been a common disposal method. Generally, this has not been carried out in disregard for the environment but through a lack of regulation by government and a lack of understanding of potential adverse consequences. In fact, many of the land disposal operations were approved by governments as the most appropriate disposal operation for hazardous chemical. Trenches and pits have been used in which waste from such industrial operations as tanneries and coal gas plants were disposed. Accidental spills are also a major cause of soil contamination. Accidental spillages have occurred frequently in such operations as wood preserving, petrol stations, fuel depots and similar activities. The operation of smelters giving atmospheric discharge of contaminated particulates that subsequently deposit in soils is another source of contamination that occurs in many areas. Mining wastes have often been disposed of in special dams and other land-based operations, resulting in soil contamination. The broadcast use of pesticides on crops has resulted in widespread contamination of soil in some areas. More intense contamination has often occurred in specific rural areas where pesticides are stored, distributed and loaded onto vehicles. In addition, the use of dips for treatment of cattle has often resulted in contamination of relatively small areas.

Activities in normal domestic and urban situations also result in soil contamination. Perhaps the major source of contamination in this area is the disposal of solid waste to land areas. Sewage sludge disposal can contain high levels of contaminants and also be disposed of to soil. The use of motor vehicles results in discharges of lead and other contaminants in particulate form, which results in soils in the vicinity of busy roads. A range of chemicals is used in domestic situations. For example, pesticides and other chemicals are used in the maintenance of gardens and lawns. The usage of chemicals and the disposal of waste following the usage can result in contamination of soils in urban areas.

A large number of potentially harmful substances may be present on a contaminated site, though in most cases their concentrations are low. Examples of such substances include:

Heavy Metals	cadmium, lead, zinc, copper, nickel
Inorganics	sulphate, asbestos
Organics	oils, tar, chlorinated hydrocarbons, PCBs, dioxins
Gases	landfill gas

The simplified classification tree of the potential environmental contaminants is shown in Figure 2.1 (Suthersan, 1997).

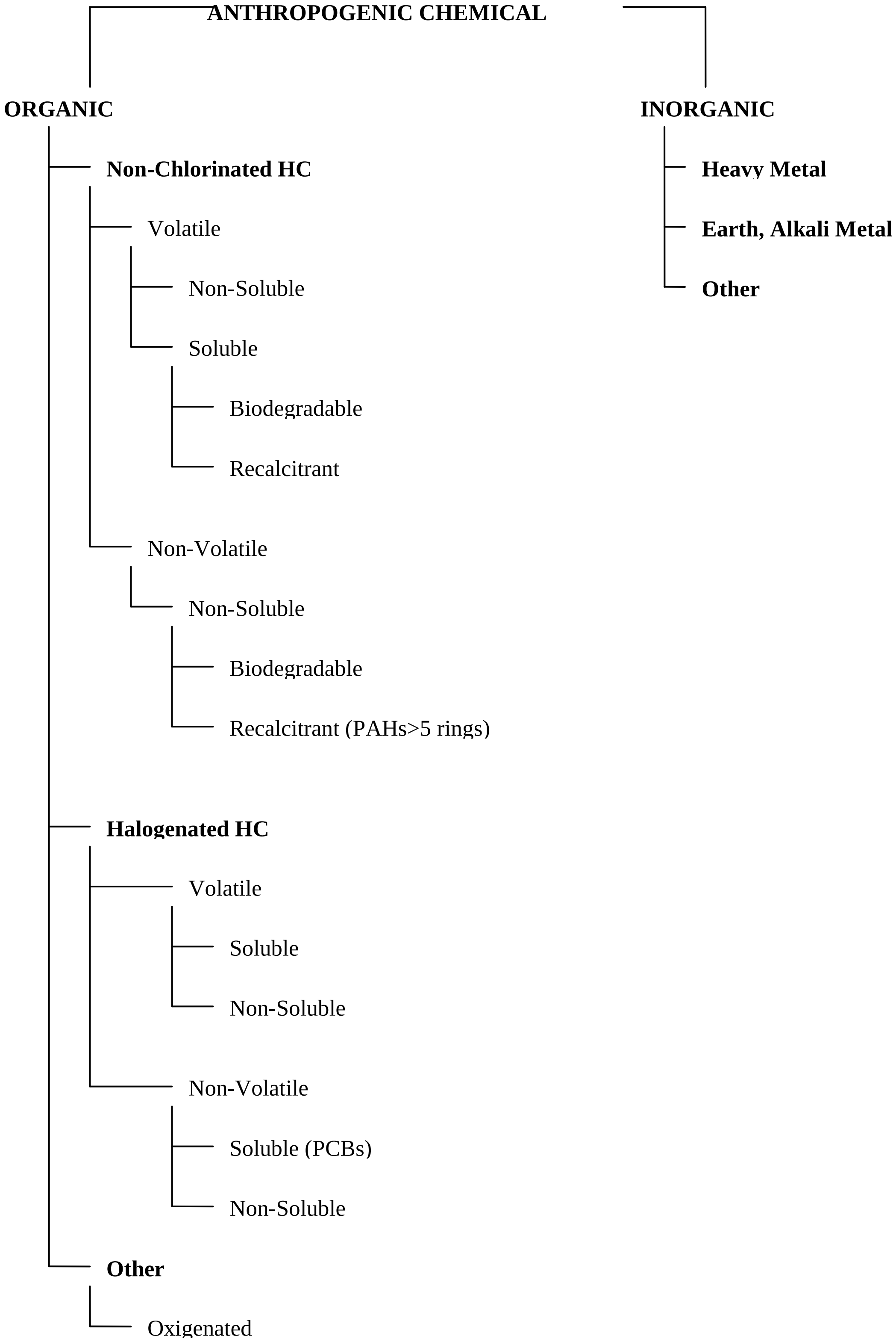


Figure 2.1 Contaminants classification tree

Table 2.2 shows types and sources of soil contamination from 100 sites in The Netherlands (Zoeteman, 1985). Gasworks were the largest source of contamination (45%) followed by waste dump and landfills (26%). The main contaminants identified at these sites were aromatic and halogenated hydrocarbons.

Table 2.2 Classification of types and sources of soil contamination in the netherlands based on the sample 100 cases

Source Contamination	**Type of Contamination**	**Frequency (%)**
Gasworks	Aromatic hydrocarbons, phenols, CN	45
Waste dumps and landfills	Halogenated hydrocarbons, alkyl-benzenes; metals like As, Pb, Cd, Ni, CN; pesticides	26
Chemical production and handling sites (including painting industries and tanneries)	Halogenated hydrocarbons, alkyl-benzenes; metals like Pb, Cr, Zn, As	13
Metal plating and cleaning industries	Tri- and tetrachloroethylene, benzene toluene, Cr, Cd, Zn, CN^-	9
Pesticide manufacturing sites	Pesticides, Hg, As, Cu	4
Automobile service facilities (including gasoline storage tanks)	Hydrocarbons, Pb	3

In 1986, Superfund Amendments and Reauthorization Act were activated in United States. According to this act 35000 suspect sites and 1200 contaminated sites were spotted for necessary clean-up of contaminated land which is called Superfund sites (Cairney, 1993). Palmer et al. (1988) reviewed data on Superfund sites according to the primary hazardous substances detected (Figure 2.2). Sites contaminated by organics made up the largest group, including 136 sites; 78 sites were contaminated by heavy metals. Individual organic compounds frequently singled out as major contaminants include TCE, polychlorinated biphenyls (PCBs), toluene, and phenol. Arsenic and chromium are most frequently identified individual heavy metal contaminants (Boulding, 1995).

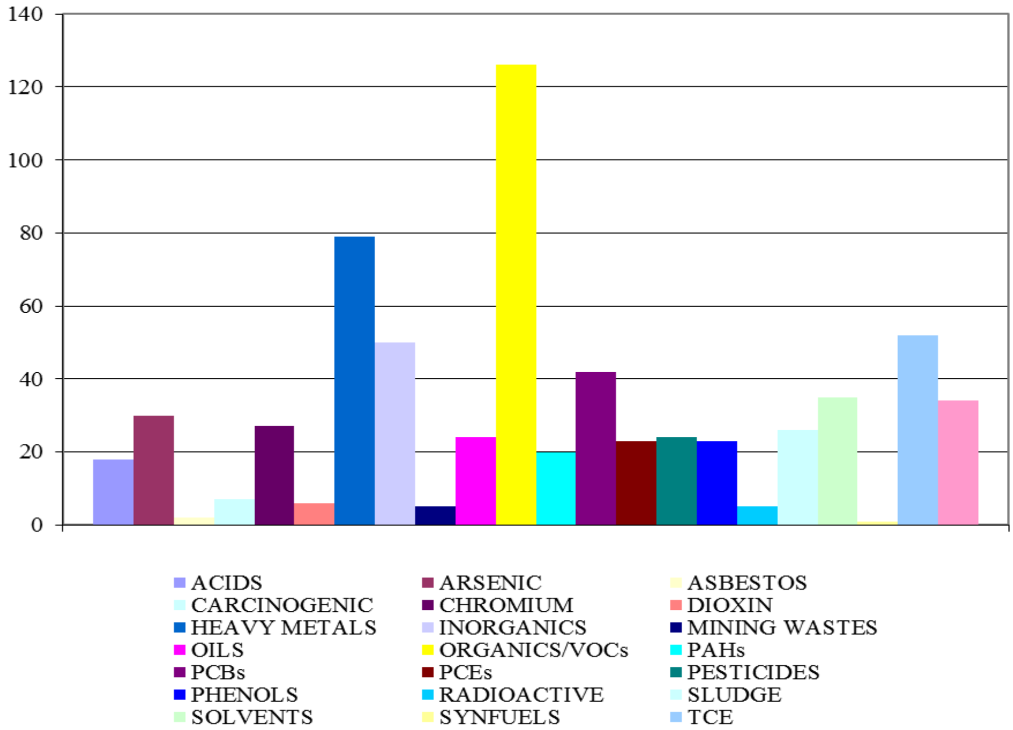


Figure 2.2 Major contaminants at superfund sites

It should be kept in mind that natural soils are not necessarily free of hazardous compounds that may have deleterious biological effects. Of course, compounds that have only originated as a result of synthetic chemical processes would not be present in natural soils. Thus, the synthetic pesticides, such as DDT and dieldrin, as well as industrial chemicals such as the PCBs would not be present in natural soils. The occurrence of these substances would be as a result of human contamination. On the other hand, polycyclic aromatic hydrocarbons (PAHs), polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) are all produced in low concentrations by combustion of organic matter, including natural organic matter such as wood and paper. These substances have been found in low concentrations in natural soils throughout the world. However, there is a tendency for these substances to occur in the vicinity of urban and industrial areas in higher concentration than the natural background levels. Metals such as lead, mercury, and arsenic occur naturally in high concentrations in various geological strata. Where these formations reach the surface, the associated soils can contain relatively high concentrations. Also, there can be the migration of these substances to other areas, which can lead to the contamination of other soils in the vicinity. Thus, natural soils may contain levels of substances that can be considered hazardous to human health and natural ecosystems.

2.1.1 Important Environmental Properties of Soils

Soils are complex mixture of substances that vary in composition from area to area. In dry areas and beaches, the soil consists essentially of silica sand with some calcium carbonate components but very little else. In most agricultural and urban areas, the soil components that affect the environmental properties of contaminants are principally clay and organic matter. Clay consists of various hydrous silicates and oxides that can be characterized by such measures as cation exchange capacity (CEC, mg/100g) and the specific surface area (m^2/g). The specific surface areas of some minerals are as follows; 15-26 m^2/g for Clay, 0.1 m^2/g for Quartz, 0.69 m^2/g for Calcite (Henn et al, 2007). These properties give a measure of how clay affects the behavior of polar organic molecules and metal ions. The cationic exchange capacity is a measure of the capacity of the soil to sorb cations with which it comes in contact. Thus, strongly cationic pesticides such as diquat are strongly sorbed by the clay component in soil. It is interesting to note that diquat is also very soluble in water and thus is highly hydrophilic, as illustrated by the data in Table 2.3. However, the sorption to clay is sufficiently strong to overcome the highly hydrophilic properties of this compound, which would favor its occurrence in water. Glyphosate exhibits somewhat similar properties. The structure of glyphosate is shown in Figure 2.1. It is a molecule with several sites for cationic and anionic effects and in fact exists as zwitter ion. Thus, a hydrogen ion can move internally between ionic groups, depending on the ambient pH. This compound is highly hydrophilic and sorbs strongly to clay minerals in soil.

The organic compounds DDT, dieldrin and benzo(a)pyrene are also strongly sorbed by soil, as indicated by the values of log K_{ow} shown in Table 2.3. The log K_{oc} value is the concentration in soil organic matter/concentration in water at equilibrium, and the K_{oc} values are 63,000 (DDT), 10,000 (dieldrin), and 32,000 (benzo(a)pyrene).

Table 2.3 Properties of some compounds related to their behavior on soils

Compound	**log K_{ow}**	**Water solubility (mg/L)**	**log K_{oc}**	**$t_{1/2}$ (days)**	**VP [a]**	**Mi [b]**
Diquat	-	700,000	Highly sorbed to clay	-	-	-
Glyphosate	-1.7	1200	Highly sorbed to clay	50-70	-	-
Atrazine	2.75	30	2.0	1-8.0	$3x10^{-7}$	-5.4
Malathion	2.36	143	3.3	3-7	$4x10^{-5}$	-2.2
DDT	6.2	0.0032	4.8	700-6000	$2x10^{-7}$	-9.2
Dieldrin	4.3	0.17	4.0	175-1100	$1x10^{-7}$	-7.8
Toluene	2.69	515	3.5	4-22	10	3.16
Benzo(a)pyrene	6.0	0.0004	5.5	57-490	-	-
Benzene	2.24	16.40	3.3	5-16	76	3.9

a Vapor pressure

b Mobility index

2.1.2 Important Environmental Properties of Soil Contaminants

One of the most important properties of contaminants in soil is their persistence. Organic compounds will be degraded by microorganisms as well as by abiotic and other processes. Also, they will be volatilized from the soil and removed by water leaching processes. Of course, metals and organometallic compounds are not susceptible to degradation beyond the elemental state. However, these substances can be removed from soils by transformation to a volatile organic form or organic complex that can result in evaporation into the atmosphere, leaching into groundwater or loss through the action of storm water runoff. Thus, in general, metals would be expected to be more persistent in soils than organic compounds.

Substances removed from soil by environmental processes usually follow first order kinetics. The half-life ($t_{1/2}$) is the characteristic usually used to measure the persistence of a compound in soil. Environmental persistence, in general, is often considered in this phase of the natural environment because soil is a major repository for contaminants in the environment.

A characteristic of particular importance with soils is the moisture content since this exercise a control over potential for growth of microorganisms. Dry soils do not support an actively growing population of microorganisms, whereas moist soils can support large populations of microorganisms. The type of microorganisms present can also influence the degradation processes, as can environmental variables such as temperature and the availability of oxygen. Because of the variability in the composition and population of microorganisms, it would be expected that compounds in soil would exhibit a corresponding variability in persistence measured as the $t_{1/2}$. Some ranges of $t_{1/2}$ values found in soil are shown in Table 2.3. The longest $t_{1/2}$ values are evident with the chlorohydrocarbons, DDT and dieldrin, which have $t_{1/2}$ values from 175 to 6000 days. These substances contain a limited ranged of bond types that are not susceptible to oxidation or hydrolysis, which are common degradation and transformation processes. The hydrocarbons benzene and benzo(a)pyrene exhibit $t_{1/2}$ values from 5 to 490 days, which is less than that of the chlorohydrocarbons. The remaining compounds in Table 2.3 all exhibit shorter $t_{1/2}$ values due their relatively high water solubility, making them more readily available to microorganisms and also to the presence of chemical groups within the molecule, rendering the compound susceptible to attack.

Volatilization is a major process for the removal of contaminants from soil. A diagrammatic illustration of the process of evaporation from soil is indicated in Figure 5. Several processes are illustrated in this figure. First, a compound can partition between the soil particle and the pore water present between the particles (illustrated as $C_s \Leftrightarrow C_w$). Diffusion in the pore water can then occur, and some chemical molecules eventually reach the pore water surface and evaporate together with water molecules as well. Volatilization depends on:

- Inherent properties of a chemical
- Properties of soil

- Environmental conditions

The inherent properties of the molecule are properties such as molecular weight, polarity and other characteristics that govern its vapor pressure and Henry's law constant (water/air distribution coefficient). The properties of the soil that influence the soil/water partition process can be seen as part of the soil volatilization process, as shown in Figure 2.3. Thus, the organic carbon content of the soil influences the volatilization rate. The higher the organic carbon content, the more the lipophilic organic compounds are retained and the lower the evaporation rates. The moisture content of the soil is also a key characteristic. High soil moisture contents give higher evaporation rates. This may be due to higher water content resulting in greater water loss from the soil and with it a greater amount of the contaminant. This effect is often referred to as the Wick effect. These processes are influenced by environmental conditions such as temperature and surface air speeds, with increases in both these factors leading to increased rates of volatilization.

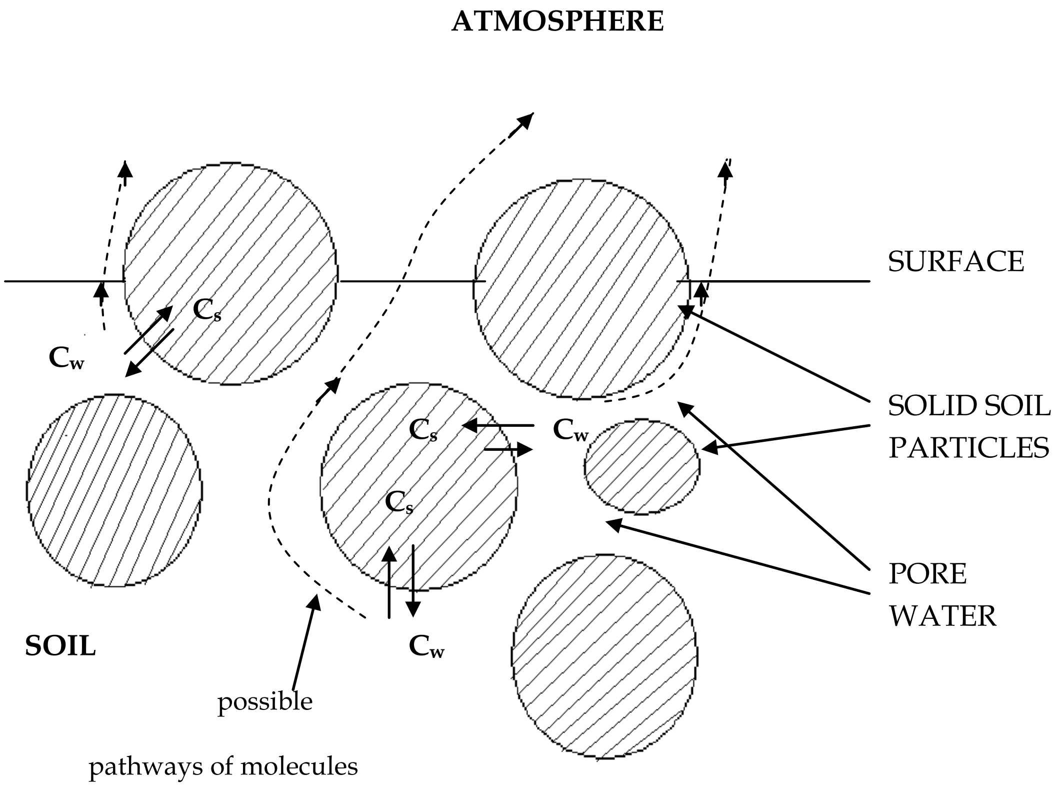


Figure 2.3 Processes involved in the volatilization of a contaminant from soil where C_s is the contaminant in soils and C_w the contamination in water

A variety of expressions have been derived to calculate the loss of a chemical by volatilization. One of the simplest of these applies to a chemical at the surface and is referred to as the Bow Model. The Bow Model can be expressed as follows:

$$t_{1/2} = 1.58x10^{-8}\left(\frac{K_{oc}S}{P}\right)days \qquad \text{Eq. 1}$$

where $t_{1/2}$ is the half-life in days, K_{oc} is the soil water partition coefficient in terms of organic carbon, S is the aqueous solubility (mg/L) and P is the vapor pressure of the compound at the ambient temperature (mmHg). This model is a general model that takes no account of environmental conditions. This means that as K_{oc} and sorption of the chemical to soil particles increases, the rate of loss declines and $t_{1/2}$ increases. Similarly, as solubility in water increases the volatilization of the chemical declines. On the other hand, as the vapor pressure (P) increases, the volatilization increases and $t_{1/2}$ declines.

Often, a chemical can also be removed by leaching. In this process, the pore water is displaced by water movement and in doing so the chemical in the pore water is removed from the soil. Thus, contaminated water from a soil can move to other areas. A simple measure of the leaching capacity of a chemical, R, can be calculated using the following equation:

$$R = \frac{1}{K_D(1-\phi^{2/3})d_s} \qquad \text{Eq. 2}$$

where K_D is the soil/water partition coefficient, ϕ is the pore water fraction of the soil, and d_s is the density of the soil solids. Thus, leachability of a chemical declines as K_D increases and increases as the pore water fraction increases.

Often, an overall measure of mobility of organic compounds in soil is useful. This can be used as a measure of the likely decline in concentration of a soil contaminant due to losses from volatilization and leaching. Soil Mobility Index (MI) can be calculated using the following equation:

$$MI = \log\left[\frac{SV}{K_{oc}}\right] \qquad \text{Eq. 3}$$

where S is water solubility (mg/L), V is vapor pressure at ambient temperature (mm), and K_{oc} is the soil sorption partition coefficient in terms of organic carbon.

Some MI values for different compounds are shown Table 2.3. The meaning of the MI values as measures of mobility is shown in Table 2.4. This indicates that DDT and dieldrin are clearly immobile in soil and have little potential to contaminate surface and groundwater in the water phase. Of course, particles containing sorbed substances may move to contaminate other areas in addition to the water itself, atrazine and malathion are more mobile and move slightly in soils and have some ability to contaminate other environmental phase. Toluene and benzene are very mobile and can readily contaminate surface and groundwater adjacent to the contaminated area (Preslo et al., 1988).

Table 2.4 Interpretation of the relative mobility index

Mobility index	Description
>5.00	Extremely mobile
5.00 to 0.00	Very mobile
0.00 to -5.00	Slightly mobile
-5.00 to -10.00	Immobile
<-10.00	Very immobile

2.2 Distribution of Contaminants in Soil

Mobile chemicals, and even slightly mobile chemicals, in soil can redistribute from soil into various other environmental phases. The major phases influencing the redistribution of soil contaminants are the abiotic phases: the atmosphere, soil solids and pore water. The partition processes involved are illustrated in Figure 2.4.

Chemicals distribute between these phases by sets of two-phase processes. Some of these are illustrated below where C_A, C_W, and C_S are the chemical concentrations in air, water and soil solids, respectively:

$$\begin{tikzcd}
\text{Atmosphere } (C_A) \arrow[d, shift right] \\
\text{Soil solids } (C_S) \arrow[u, shift right] \arrow[d, shift right] \\
\text{Pore water } (C_W) \arrow[u, shift right]
\end{tikzcd}$$

Movement to ground water is a transfer of chemical by actual movement of the water phase. Other mass-transfer processes occur when storm water runs off a contaminated area containing dissolved and particulate sorbed chemicals.

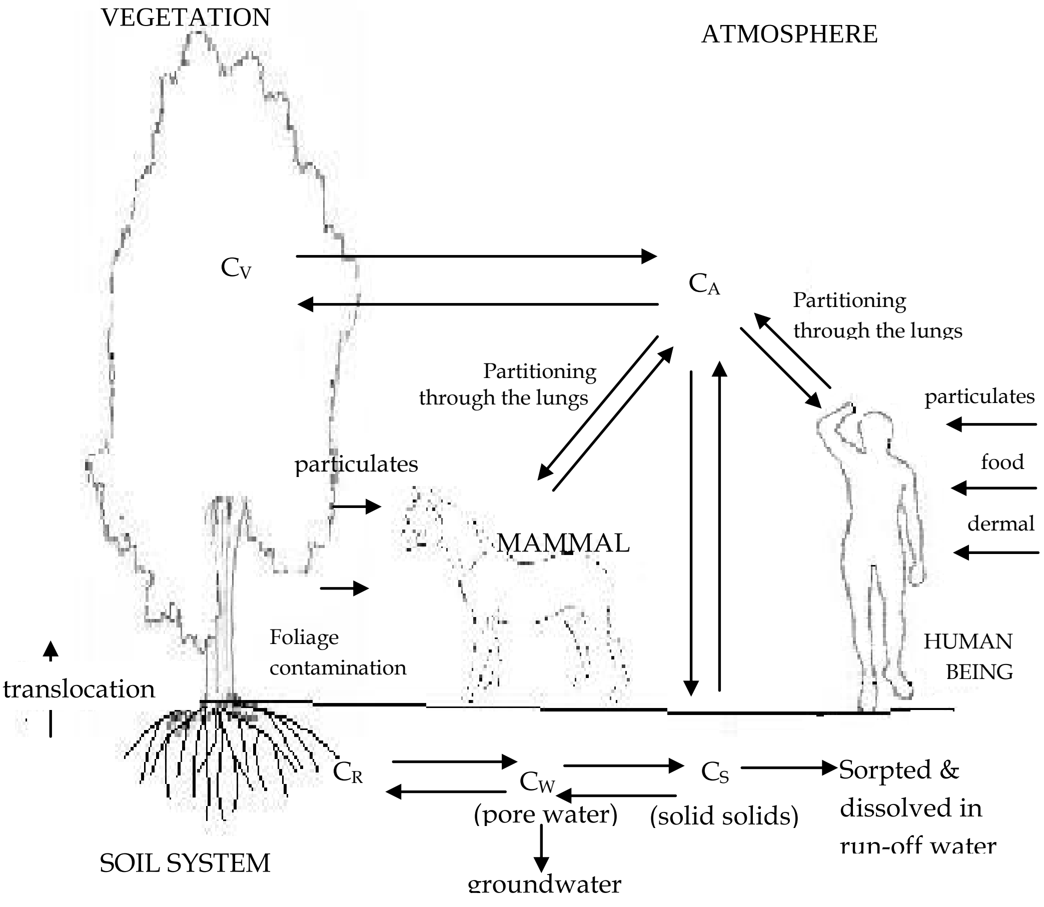


Figure 2.4 Distribution patterns of soil contaminants in soil ecosystems

2.2.1 The Behavior of Organic Contaminants in Soil and Subsurface Materials

Contaminants in soil can be in solid, liquid or gas phase. Contaminants present in any of these forms, particularly gases or liquids, can be mobile. If they migrate beyond the boundaries of contaminated site itself, the contamination can spread to surrounding land. This may have particularly damaging consequences if the underlying groundwater is affected, or if adjoining buildings and structures are put at risk (Cairney, 1993).

Increasingly, organic liquids with limited aqueous solubilities are being released to subsurface environments and threatening groundwater resources. The prominence of organic chemicals among soil and groundwater pollutants has focused particular attention on their adsorption. Partition coefficients for organic chemicals display a large range of values. For example, the low-molecular-weight chlorinated hydrocarbon solvents such as TCE are highly mobile, contaminating aquifers far from the point of discharge. But, there are some high-molecular-weight petroleum hydrocarbons, like tars and asphalts, which are so strongly adsorbed and so insoluble.

In most cases, adsorption of the organics is well approximated by the Freundlich isotherm. That is:

$$x = K_p C \qquad \text{Eq. 4}$$

The equation says the amount of chemical adsorbed is proportional to the concentration in solution and partition coefficient (Devinny et al., 1990). Schwarzenback and Westall (1981) investigated factors controlling the value of K_p. The sorption is dominantly hydrophobic, reflecting the transfer of organics from the aqueous solution to small amounts of organic material in the soil. K_p is proportional to the size of the organic phase, measured as the soil organic fraction. It also reflects the hydrophobicity of each contaminant, which is approximately indicated by the octanol-water partition coefficient of the contaminant. Thus, K_p can be estimated within a factor of two, where the soil organic fraction and the octanol-water partition coefficient have been measured.

This simple relationship breaks down for soils which contain little organic matter. Adsorption is controlled by several different, relatively weak interactions, and contaminants are likely to be mobile. Fu and Luthy (1986) emphasized this relationship. They also found that secondary solvents in the water could cause swelling of the soil organic material, increasing its capacity for adsorption.

Faust (1975) noted that cationic herbicides are strongly held in soils, and Khan (1975) found that the herbicides paraquat and diquat, though they are aromatic hydrocarbons, are adsorbed in soils primarily through ion exchange.

The major processes about the mobilization and fate of NAPLs in soil can be described as follows:

Advection is described as the transport in a fluid. The fluid can be described for such processes as a vector field. The contaminant transported is described as a scalar concentration of substance in the fluid. An example of advection is the transport of silt in a river: the motion of the water carries these impurities downstream. Heat also advects, and the fluid may be water, air, or any other heat carrying fluid material. Any substance or heat can be advected in any fluid.

Dispersion is the process that the phase velocity of a wave depends on its frequency. Dispersion causes the spatial separation of a white light into spectral components of different wavelengths in a prism. Dispersion is often described in light waves sometimes called chromatic dispersion.

Adsorption occurs when a gas or liquid solute accumulates on the surface of a solid forming a molecular or atomic film which is called adsorbate. The term sorption encompasses both adsorption and absorption processes, and desorption is used to define the reverse process.

Volatilisation is the process of vaporization of a compound.

Ion exchange is an exchange of ions between two electrolytes. The term is mostly used to mean the processes of purification, and separation of aqueous and other ion-containing solutions with polymeric or mineral ion exchangers.

Hydrolysis is a chemical reaction or process; a chemical compound is broken down by reaction with water. This is the type of reaction used to break down polymers and water is added.

Precipitation is the condensation of atmospheric water vapor that is deposited on the earth's surface. It occurs when the gaseous phase becomes saturated with water vapour and the water condenses and falls out of solution.

Colloidal dispersion is a type of homogenous mixture. Colloids consist of two separate phases; i) a dispersed phase and ii) a continuous phase. The dispersed phase is made of small particles or droplets that are distributed evenly in the continuous phase. The size of the dispersed-phase particles are between 1 nm and 100 nm.

Metabolism is the chemical reactions occurring in living organisms in order to maintain their life, and allows organisms to grow and reproduce and maintain their structures. Metabolism is divided into two categories; catabolism yields energy (the breakdown of food in cellular respiration) , anabolism uses this energy to construct proteins and nucleic acids.

Table 2.5 gives an expanded list of subsurface processes and corresponding subsurface and contaminant properties influencing these processes (Sabatini and Knox, 1992). The main routes by which contamination can reach targets to create a hazard are given Table 2.6 (Cairney, 1993).

Table 2.5 Subsurface processes and corresponding subsurface and contaminant properties and interactions affecting the fate and transport of contaminants

Process	Subsurface Property	Contaminant Property	Interactions
Hydrodynamic Solute Transport			
Advection	Groundwater gradient, hydroulic conductivity, porosity	Independent of contaminant	
Dispersion	Dispersivity, pore water velocity	Diffusion coefficient	Dispersion coefficient
Preferential Flow	Pore size distribution, fractures, macropores		
Abiotic Solute Transport			
Adsorption	Organic content, clay content, specific surface area	Solubility, octanol-water partition coefficient	
Volatilization	Degree of saturation	Vapor pressure, Henry's constant	
Ion Exchange	Cation exchange capacity, ionic strength, background ions	Valency, dipole moment	
Hydrolysis, Precipitation	pH, competing reactions	Hydrolysis half life	
Dissolution	pH, other metals	Solubility versus pH, speciation reactions	
Cosolvation	Types and fraction of cosolvents present	Solubility, octanol-water partition coefficient	
Redox Colloid	pE, pH	pK_a	
Transport	pH, ionic strength, flow rate, mobile particle size, aquifer and particle surface chemistry	Sorption, reactivity, speciation, solubility	Colloid stability
Biotic			
Metabolism/Cometabolism	Microorganisms, nutrients pH, pE (electron acceptors) trace elements	BOD, COD, degree of halogenation, etc.	
Multiphase Flow			
	Intristic permeability, saturation, porosity	Solubility, volatility, density, viscosity	Relative permeability residual saturation, wettability, surface tension, capillary pressure

Table 2.6 Main routes of contamination

Direct Contact
Presence in surface or foundation zones
Contact with aquifer
Translocation
Disturbance
Seepage of liquids, gases or vapors
Capillary rise
Infiltration
Groundwater movement
Surface drainage
Progressive combustion

2.3 Current Status of Site Contamination, Legal Aspects and Limitations

2.3.1 Site Contamination

2.3.1.1 Status of World

The main sources of soil contamination in Europe are losses of contaminants during industrial and commercial operations, municipal and industrial waste treatment, oil extraction and production and its storage (Figure 2.7) (EEA, 2007). The range of contaminants found in the polluted sites varies according to the country. However, the heavy metals and mineral oil are the main soil contaminants in Europe. These data is based on the frequency of a specific contaminant reported to be the most important in the investigated site. Other contaminants include polycyclic aromatic hydrocarbons (PAHs), aromatic hydrocarbons (BTEX), phenols and chlorinated hydrocarbons (CHC) (Figure 2.8) (EEA, 2007).

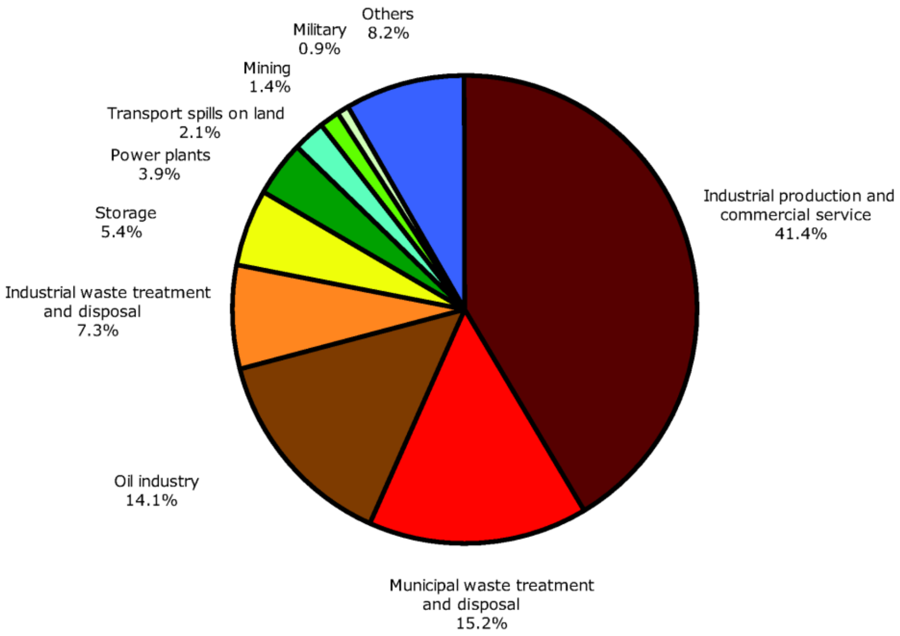


Figure 2.7 Overview of activities causing soil contamination in Europe

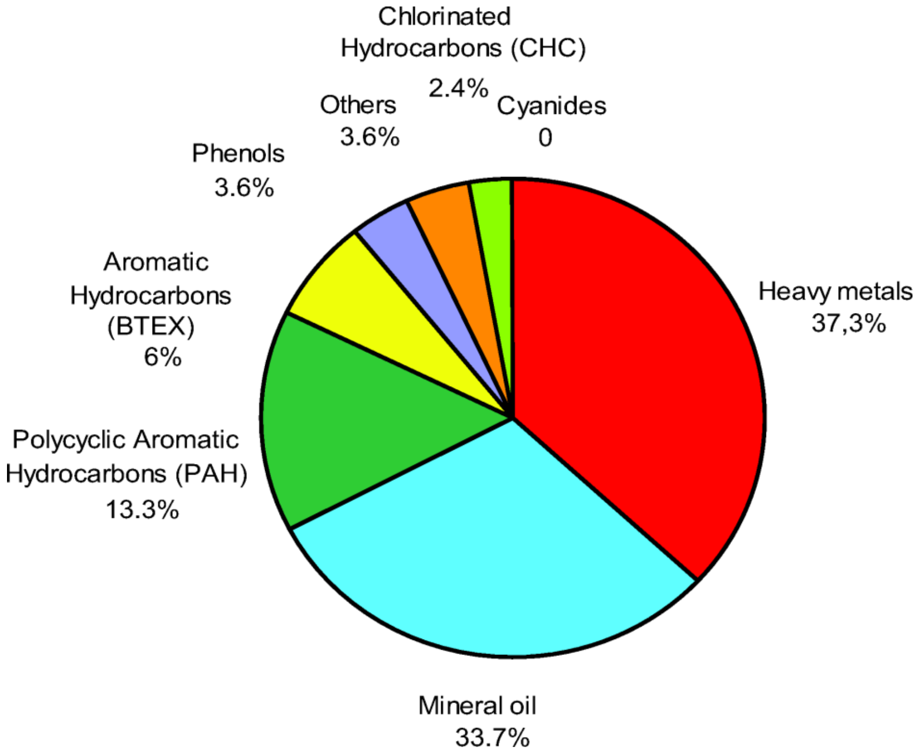
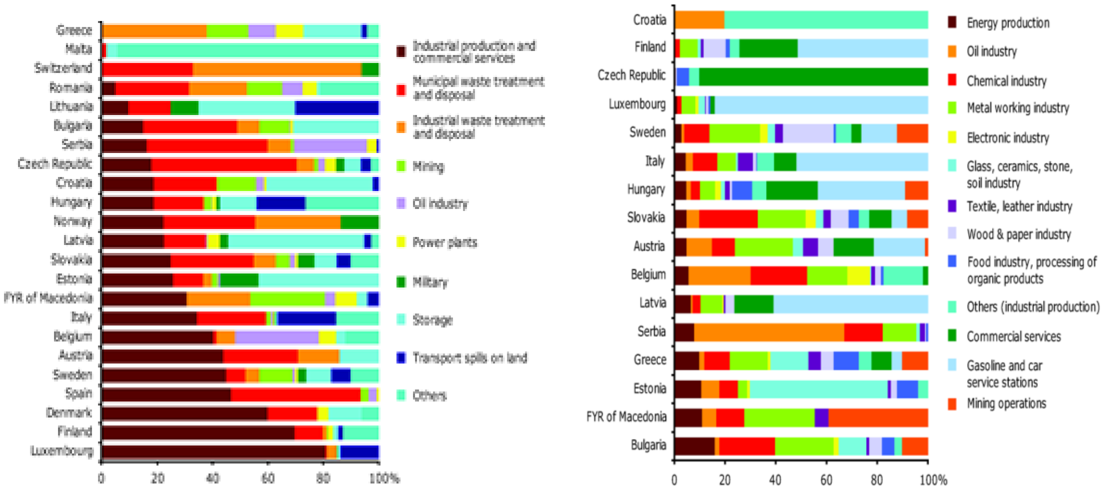


Figure 2.8 Overview of contaminants affecting soil and groundwater in Europe

Contamination from oil storage is relatively important in some countries, such as Latvia, Estonia and Croatia, where it respectively covers 46%, 42% and 36% of all contaminating activities identified. In Bulgaria, the storage of obsolete chemicals covers more than 30% of all activities (Figure 2.9 a) (EEA, 2007).



a) b)

Figure 2.9 a) Breakdown of main activities causing soil contamination by country b) Detailed analysis of industrial and commercial activities causing soil contamination by country-commercial services

At industrial and commercial sites, handling losses, leakages from tanks and pipelines, and accidents are the most frequent sources of soil and groundwater contamination. Industrial sources come mainly from the chemical and metal working industries, energy production and the oil industry. Most of the European countries have relatively high numbers of gasoline stations, their importance in posing significant risks to the environment varies across Europe. This is also reflected in their national legislation. Gasoline and car service stations are reported as most frequent sources of soil contamination in Luxembourg), Latvia (61%), Italy (52%) and Finland (51%).. In other countries, gasoline stations are not included in national.

Figure 2.10 shows remediation technologies applied in the studied countries as percentages of number of sites per type of treatment. Several methods are available for the decreasing of the risks aroused from soil contamination. It is reported that, there is a balance in the application of innovative in situ (on-site) and ex situ (off-site) techniques. A significant high percentage of the most-frequently applied techniques can be defined as traditional (EEA, 2007).

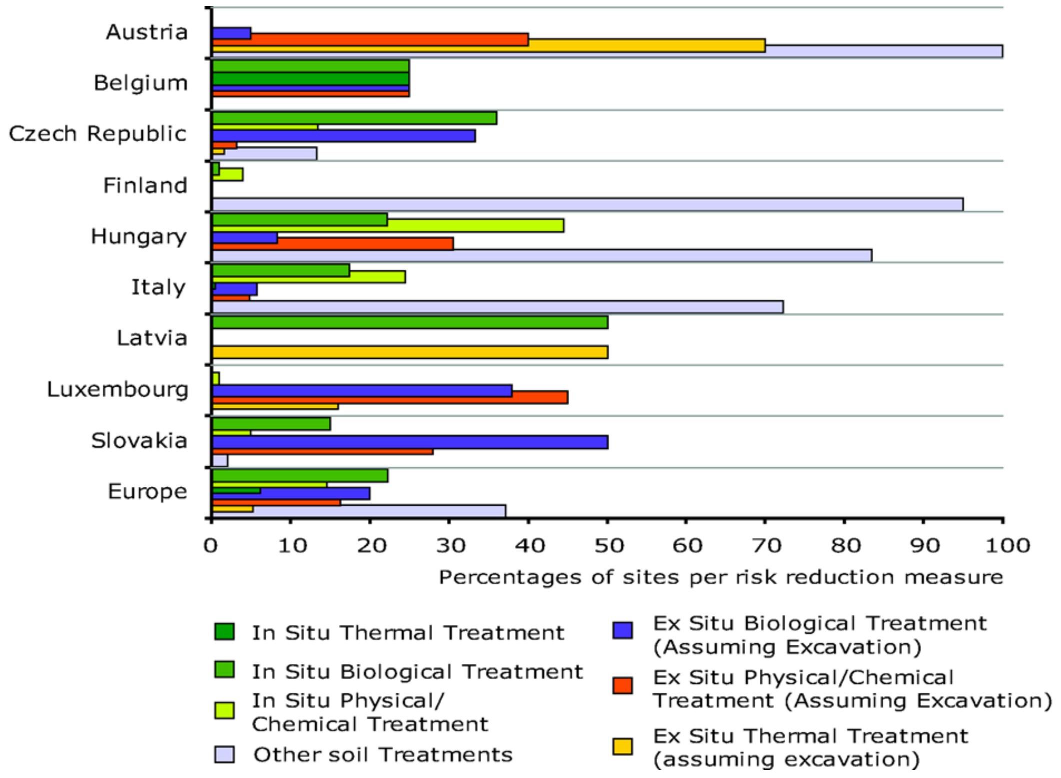


Figure 2.10 Remediation technologies

2.3.1.2 Status of Turkey

Turkey has contaminated soil problems although they do not yet have high priority among other environmental problems. The causes of contaminated soil problems in Turkey may be summarized as follows:

a) Industrialization: In Turkey, industrialization has started in about 1930's. For a long time, no environmental considerations were taken into account. In 1970's environmental pollution control studies have been introduced especially with respect to water and air pollution. Even today, water and air pollution problems are discussed in more detail and soil contamination to a lesser extent. Industrial wastes causing soil contamination also include oil pollution in many cases.

b) Leaking tanks and pipes: In Turkey 40 to 60% of the sewage pipe works needs renewal, in some towns even more than 60% of sewage pipe work is defective. The defective sewage pipes constitute a danger to the subsoil and to the groundwater. Since Turkey is located between Europe and Middle East, transportation of goods is very important. A considerable amount of oil is transported. Thousands of filling stations use buried underground tanks. Many kilometers of underground pipelines carry petroleum products. Although there are no studies about the leakage from these tanks and pipelines, it is known that they start to leak after some time.

c) Accidental spills: 90% of transportation is performed by motorway in Turkey. The number of buses and trucks is equal to total of them in European countries. Accidental spill is an important contamination source for oil because of the occasional tanker trucks accidents.

d) Midnight dumping: During to the application of removal of cesspool contents in some areas, sometimes the wastewaters are discharged to uninhabited areas.

Contaminated Sites in Turkey

The problem of polluted sites started to emerge especially in heavily industrialized regions of Turkey. However, an inventory of contaminated sites is not maintained (State Planning Organization, 2006b). Currently, identification of any contaminated site is not based on a certain systematic approach. Sites are mostly identified after some potential problems become obvious and public, as a result of the efforts of local authorities or concerned citizens (NATO, 2002). The number of contaminated sites is expected to be in the range of 1000-1500, of which 5-10 % is believed to be sites requiring remediation (Ünlü, 2006).

Soil pollution incidents, which became public, are mostly due to illegal disposal of industrial wastes, oil leakages resulting from accidental spill at oil storage tanks or pipelines, metal leaching from disposed metal ore processing residues and waste disposal sites. Remedial measures were carried out for very few of the contaminated sites. Therefore, some information about the contaminated sites and the remediation techniques used exists officially. However, there is no statistical data about formerly used remedial technologies and methods. Several publicly known soil pollution incidents are given below.

Tuzla Orhanli, Istanbul: The soil pollution incident in Tuzla Orhanli, one of the most publicly known incidents relies on the discovery of 640 toxic barrels in Tuzla Orhanli, a town near Istanbul, in March 2006. Samples taken from the site were analyzed by the Scientific and Technological Research Council of Turkey (TÜBITAK). The barrels, which also included hazardous phenolic compounds, were illegally buried two or three years ago by one or more chemical companies. Some barrels, which were found open on purpose, caused to the contamination of soil. Almost within a month, all 640 barrels and 2000 sacks full with contaminated soil were removed from site very carefully by a team from Izmit Waste Treatment, Incineration and Recyling Co. Inc. (IZAYDAS) and transported with special container trucks to the IZAYDAS hazardous waste treatment and disposal plant. IZAYDAS facilities are the only licensed hazardous waste disposal facility in Turkey. Remediation of contaminated site was mainly based on the incineration of both toxic barrels and highly contaminated soil.

Cayırova Gebze Incident: Cayirova Gebze incident was a subject of the media in the same period of the Tuzla incident. Five barrels, full with asbestos, were found together with some other wastes near a village close to Cayirova Gebze. The Environmental Protection Department of the Kocaeli Greater Municipality took the necessary precautions and the team from IZAYDAS, which were informed, transported the barrels for inspection. BOTAS pipeline incident near Ataturk Dam the leakage of crude oil from the Batman-Yumurtalik pipeline of the Petroleum Pipeline Corporation (BOTAS) near the Ataturk Dam is among the important accidental soil pollution incidents. In April 2005, about 20-25 thousand barrels of crude oil leaked out and caused to pollution in the bay of Yiginak village and shore of Baglica village and surrounding soil, near Sanlıurfa. While the pipeline was repaired, the dispersion of oil in the lake was prevented and afterward collected with the help of barriers. About 500 tons of contaminated soil were removed and transported to a site of 20 acres. The less contaminated soil was cleaned-up with a bioremediation method at the technically arranged site. The highly polluted soil, on the other hand, was transported together with other oily wastes to IZAYDAS incineration plant.

1999 Kocaeli Earthquake Incident: In August 1999, the earthquake, with a magnitude of 7,4 MW, struck the Kocaeli and Sakarya provinces in north western Turkey. The affected region is one of most economically dynamic regions. Industries, which were damaged, were the petrochemical industry, automotive industry and other industrial facilities like paper mills, steel mills, cement, textile and pharmaceutical factories, etc. Among the state-owned petrochemical complexes the heaviest damage occurred at the TUPRAS refinery itself and associated tank farm with crude oil and product jetties. Six tanks of varying sizes in the tank farm of 112 tanks were damaged due to ground shaking and fire. Considering the IGSAS fertilizer factory, ammonia processing and packing units were partially and the administration building extensively damaged. The PETKIM petrochemical facility had limited damage. Besides structural damages at many facilities and factories, other important ones were the silo collapses at the SEKA paper mill, storage rack collapse, toxic releases from mixing chemicals and damaged piping at the Toprak pharmaceutical firm, damaged tanks at the AKSA chemical installation in Yallova, which was associated with leakage of chemicals. Under such catastrophic conditions the contamination of soil and water resources as a result of leakage from storage tanks, pipelines etc is mostly inevitable (Erdik, 2007).

Beykan Oil Field Site: Petroleum hydrocarbon pollution of surface soils, surface and groundwater caused by oil production activities of the Beykan Oil Field is of concern here. The Beykan Oil Field is close to the watershed of a dam and due to the increases in domestic water supply demand, the dam was considered as a potential resource to meet the increasing water demand in the area. A total of 38 oil wells are placed within the protection zones surrounding the dam’s reservoir; 13 of them being in the immediate vicinity, within the first 300 m of the reservoir shore called the “absolute protection zone.” Oil spills at these wells and pipelines connecting wells are considered as pollution sources effecting the reservoir water quality. Spill records revealed that, during the maximum oil production years, 95 tons of yearly average spill occurred, resulting in an average total petroleum hydrocarbons (TPHs) concentration of 20300 ppm in contaminated soils. Contaminant mass leaching to the reservoir from soils contaminated by oil spills is investigated as a primary concern for water quality. In addition to soil and possible water pollution problems, another primary concern at this site is pollution of the Midyat aquifer due to injection of nearly 20 million m3 of formation water between the years of 1971 and 1996. Injected formation water contains high amounts of brine and some emulsified oil (with a concentration of 500 mg/L). The Midyat aquifer overlies the Beykan Oil Field and a primary source of drinking water supply for the nearby community. For this site, studies concerning the assessment of the extent of contamination and appropriate remedial measures are currently underway (NATO, 1998).

Incirlik PCB Contaminated Soils Site: At this site, soil contamination by polychlorinated biphenyls (PCB), oil leaking from storage drums at a military reutilization yard occurred during the operation of the yard between the years of 1970 and 1988. An excavation of 0.5 meters deep was made in October 1991, leaving the excavated soil stored in approximately 300 drums and in a pile. Estimated PCB-contaminated soil volume is 1,600 m^3. Site characterization investigations revealed that site soils are high in clay content (65percent) and potential for groundwater contamination is low. PCB concentrations measured in composite contaminated soil samples range up to 750 ppm. For remediation of contaminated soils, various alternatives are being evaluated including incineration and in situ/ex situ solidification/stabilization (S/S) (NATO, 1998).

Chromium Ore Processing Residue Dump Site: At this site, soil and groundwater contamination by Cr (VI) leaching from chromium ore processing residue (COPR) is of concern. COPR is produced by a chromate production factory providing mostly the needs of leather tanning industry. During the early production years, COPR is dumped at a temporary dump site near factory. The unprocessed row chromites ore ($FeCr_2O_4$) contains nearly 45 percent of chromium oxide (Cr_2O_3). After a roasting process of chromites ore by adding Na_2CO_3 and $CaCO_3$ constituents, COPR contains nearly 25,000 ppm of total chromium. Due to high chromium content, COPR is partly recycled by mixing with chromium ore at a ratio of roughly 1:20. The current chromate production technology used yields approximately three tons of COPR to produce one ton of chromate. Currently, some research work is underway to evaluate soil and groundwater pollution potential of land-disposed COPR and to develop technical guidelines for appropriate management of COPR related wastes and remediation of COPR contaminated soils (NATO, 1998).

Toxic Barrels of Samsun and Sinop: The discovery of 392 barrels at the Black Sea coastline in 1988 is one of the first soil pollution incidents in Turkey. Investigations revealed that the barrels belonged to the Italians. These barrels were thrown into the Black Sea by an Italian Ship, which was carrying about three thousand toxic barrels. About 240 of barrels have been in storage in Alacam near Samsun and the remaining in Soguksu Sinop. Despite the fact that the barrels belonged to Italy, the barrels could not be send back to Italy for 18 years. Finally, it was planned that the toxic barrels are sent to disposal facilities in Germany with a support of the Turkish Cement Manufacturers' Association, which includes Italian companies as well. IZAYDAS, which took the barrels from Samsun and Sinop, transported the barrels to Izmir for further shipment to Europe for their disposal. Unfortunately, about 150 barrels were found empty thus indicating to a contamination of both soil and water resources.

Other Suspected Contaminated Sites: There were some complains about barrels, which were temporary stored by Turkish Petroleum Refineries Corporation (TUPRAS) at a site in Batman for years. These barrels, over hundred pieces, contain chemicals from the petroleum refinery. Competent of TUPRAS stated that the barrels were going to be removed by IZAYDAS. There are many other storage sites, which are accepted as temporary sites, but rather work permanently. According to a hazardous waste management report written by Zanbak and Bayazit Tugal (1997), there is a need for the registration, investigation and rehabilitation of these temporary hazardous wastes disposal sites.

Municipal solid waste dumping sites, especially those used by metropolitan or greater municipalities, cause to significant pollution of soil and groundwater, which is well known. In Turkey, most of the time, commercial and industrial wastes are disposed off together with domestic solid wastes, thus increasing the contamination potential of leachate. Most of the municipal dumping sites do not have a drainage system for leachate collection and a clay layer to prevent leaching into soil and groundwater. When the use of dumping sites is completed, their rehabilitation is carried out. Since measures for the collection and treatment of leachate are generally not taken the contamination of soil and groundwater continues. There are over 3200 municipalities in Turkey, but the number of sanitary landfills and landfills with EIA approval is not over fifty. Under these circumstances it is not difficult to estimate the number of dumping sites suspected as contaminated sites. Some closed or stil operating municipal solid waste dumping sites, well known for conditions are Yakacik (with a capacity of 600 000 m^3), Ümraniye (with a capacity of 2 million m^3) and Halkalı (with a capacity of 10 million m^3) dumping sites of Istanbul (closed), Mamak dumping site of Ankara (operating), Cigli, Uzundere, Buca, Isikkent, Güzelbahçe, and Gaziemir dumping sites of Izmir (closed).

2.3.2 Legal Aspects and Limitations

2.3.2.1 Legal Aspects in the World

To prevent injury to soil, plants, animals, and humans, the council of the European Communities has set criteria limiting the addition of elements to land used for growing food crops (Table 2.7) (European Economic Community, 1986).

Analyses of sewage sludges from 50 publicly owned treatment works by the USE Environmental Protection Agency is shown in Table 2.8 (Fricke et al. 1985).

Table 2.7 Soil limit values determined by the Council of European for the addition of heavy metals from sewage sludge to soil with a pH of 6.0-7.0

Element	Limit values[a] (ppm)
Cadmium	1-3
Copper[b]	50-140
Lead	50-300
Mercury	1-1.5
Nickel[b]	30-75
Zinc[b]	150-300

a "Member States may permit the limit values they Ti to be exceeded in the case of the use of sludge on land which at the time of notification of this Directive is dedicated to the disposal of sludge but on which commercial food crops are being grown exclusively for animal consumption. Member States must inform the Commission of the number arid type of sites concerned. They must also seek to ensure that there is no resulting hazard to human health or the environment."

b "Member States may permit the limit values they fix to be exceeded in respect of these parameters on soil with a pH consistently higher than 7. The maximum authorized concentrations of these heavy metals must in no case exceed those values by more than 50%. Member States must also seek to ensure that there is no resulting hazard to human health or the environment and in particular to groundwater."

According to The Ministry of Environment of the Czech Republic, the limit concentration values of selected elements in soil determine the maximum values of the selected high-risk elements in soil, which, if exceeded, could lead to damage of the soil functions and environmental media (Table 2.9) (Decree 382, 2001).

Table 2.8 Analyses of sewage sludges from 50 publicly owned treatment works by the U.S.A Environmental Protection Agency

Pollutant category	Mean concentration (ppm; dry weight)	Pollutant category	Mean concentration (ppm; dry weight)
Metals and cyanide		**Base neutral compounds**	
Arsenic	5.9	Benzo(a)anthracene	9.1
Berylium	1.2	Benzo(a)pyrene	256.6
Cadmium	32.2	Benzo(b)fluoranthene	1.76
Chromium	427.9	Bis(2-ethylhexy)phthalate	157.6
Copper	562.4	Chrysene	8.3
Cyanide	748.5	Pyrene	6.8
Lead	378.0	3,3'-Dichlorobenzidine	1.64
Mercury	2.8	Hexachlorobenzene	1.25
Nickel	133.9	Hexachlorobutadiene	4.5
Selenium	2.6	n-Nitrosodiphenylamine	0.04
Zinc	1409.2	Phenanthrene	5.9
Volatile compounds		**Pesticides and PCB's**	
Benzene	1.46	Aldrin	ND[a]
Carbon tetrachloride	4.48	Chlordane	ND
Chlorobenzene	1.16	DDD	ND
Chloroform	0.85	DDE	0.06
1,2-Dichloroethane	25.03	DDT	ND
Methylene chloride	8.65	Dieldrin	0.02
Tetrachloroethylene	3.47	Endrin	ND
Toluene	1718.8	Heptachlor	0.02
Trichloroethylene	9.10	Lindane	0.02
Vinyl chloride	35.4	PCB's	ND
		Toxaphene	ND
Acid compounds			
Pentachlorophenol	10.4		
Phenol	19.3		
2,4,6-Trichlorophenol	2.3		

[a] ND=no data

Table2.9 The limit concentration values of selected high-risk elements in soil (indicators for soil evaluation)

The limit concentration values of elements in the extract with aqua regia in mg.kg^{-1} of dry matter in soil								
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Usual soils	20	0.5	90	60	0,3*	50	60	120
Sands, loamy sand, gravel sand	15	0.4	55	45	0,3*	45	55	105

* total content

In recent studies of Cleveland, Ohio, old contamination soils (soils that have been contaminated for decades), heavy metal concentrations far above background were found at brownfields (abandoned manufacturing sites) and commons (public lands such as playgrounds, parks, and city gardens) (Table 2.10).

Table 2.10 Heavy metal background and maximum contamination levels in Cleveland, OH, soils (all values in mg/kg)

Heavy Metal	**Background (OEPA, 1999)**	**Brownfield max. (Jennings et al., 2002a,b)**	**Commons max. (Petersen, 2003)**
Cadmium	1.25	54.3	6
Chromium	22	574	70
Copper	19[a]	22500	360
Nickel	33	837	40
Lead	37	15170	811
Zinc	90	13400	527

[a] Estimated Ohio farm soil background (Logan and Miller, 1983).

2.3.2.2 Legal Aspects in Turkey

In Turkey legal framework for contaminated soil rehabilitation studies have been started recently in 2004. Ministry of Environment has promulgated standards for soil. Soil polluters limit values have been given in Table 2.11 and Table 2.12. Table 2.13 presents maximum heavy metal contents to be allowed in the treatment sludge to be used in agricultural land. Table 2.14 presents heavy metal loads which may be added to the agricultural land annually, based on a 10 year average (Official Gazette, 2001).

Table 2.11 Heavy metal limit values of soil pollutants

Heavy Metal	pH≤ 6 mg/kg oven dry soil	pH≥ 6 mg/kg oven dry soil
Lead	50**	300 **
Cadmium	1**	3 **
Chrome	100**	100 **
Copper	50 **	140 **
Nickel	30 **	75 **
Zinc	150 **	300 **
Mercury	1 **	1,5 **

- If the pH value is bigger than 7, the Ministry can increase the limit values up to 50 %.
- In areas where feed plants are grown, in case it is proven by scientific reports that it does not cause any damage to the environment and human health, those limit values may be allowed to be exceeded.

Table 2.12 Other pollutant parameters in soil

Pollutant Matters	**Limit Values**
Chloride Ion (mg Cl/l) (Total)	25
Sodium (mg Na/l) "	125
Cobalt (Co) (mg/kg oven dry soil)	20
Arsenic (As) "	20
Molibden (Mo) "	10
Tin (Sn) "	20
Barium (Ba) "	200
Floride "	200
Free cyanide (CN) "	1
Complex cyanide (CN) "	5
Sulphite (S) "	2
Brome (Br) "	20
Benzene "	0.05
Butyl benzene "	0.05
Toliol "	0.05
Xylol "	0.05
Phenol "	0.05
Selenium (Se) "	5
Talium (Tl) "	1
Uranium (U) "	5
Polycyclic aromatic hydrocarbon components "	5
Organo Chlorynated compounds "	0.5
Agricultural Struggle Medicines-Individual " Agricultural Struggle Medicines-Total "	0.5 2
PCB Polichlorated biphenils "	0.5
Hexachloro benzol "	0.1
Pentachloro benzol "	0.1
Ψ - HCH (lindan) "	0.1

Table 2.13 Maximum heavy metal contents to be allowed in the treatment sludge to be used in agricultural land

Heavy Metal Contents	**Limit Values (mg/kg oven dry soil)**
Lead	1200
Cadmium	40
Chrome	1200
Copper	1750
Nickel	400
Zinc	4000
Mercury	25

Table 2.14 Heavy metal loads which may be added to the agricultural land annually, based on a 10 year average

Heavy Metal	**Limit Load Value (gr/da/year)**
Lead *	1500
Cadmium	15
Chrome *	1500
Copper *	1200
Nickel *	300
Zinc *	3000
Mercury	10

* If there is at least a 3 month period between the use of treatment sludge on agricultural land and harvesting time, these values may be increased by up to 5 %, excluding mercury and cadmium, through discussions with related institutions.

**These limit values may be allowed to be exceeded in cases when it is scientifically proven that they are not harmful to the environment and human health in the areas where feed plants are grown.

2.4 Conventional Soil Remediation Techniques

Numerous attempts to remediate polluted soils with the use of both in situ and non-in-situ techniques are being made (Table 2.15). None of these is a perfect solution for remediation of contaminated soils and sometimes more than one of the techniques may be required to optimize the cleanup efficiency. The complexity of soils and the presence of multiple contaminants also makes most remediation efforts arduous and costly (Sparks, 2003).

Table 2.15 In situ and non-in-situ techniques used in soil decontamination

Technology	Advantages	Limitations	Relative costs
In situ			
Volatilization (Air Sparging and SVE)	Can remove some compounds resistant to biodegradation	Volatile organic compounds only	Low
Biodegradation	Effective on some nonvolatile compounds	Long-term timeframe	Moderate
Phytoremediation	Effective with a number of inorganic and organic chemicals	Plants are often specific for particular contaminants	Low to medium
Leaching	Could be applicable to wide variety of compounds	Not commonly practiced	Moderate
Vitrification		Developing technology	High
Passive	Lowest cost and simplest to implement	Varying degrees of removal	Low
Isolation/containment	Physically prevents or impedes migration	Compounds not destroyed	Low to moderate
Non-in-situ			
Land treatment	Uses natural degradation processes	Some residuals remain	Moderate
Thermal treatment	Complete destruction possible	Usually requires special features	High
Asphalt incorporation	Use of existing facilities	Incomplete removal of heavier compounds	Moderate
Solidification	Immobilizes compounds	Not commonly practiced for soils	Moderate
Groundwater extraction and treatment	Product recovery, groundwater restoration		Moderate
Chemical extraction		Not commonly practiced	High
Excavation	Removal of soils from site	Long-term liability	Moderate

2.4.1 In Situ Methods

In situ methods are used at the contamination site. Soil does not need to be excavated, and therefore exposure pathways are minimized.

2.4.1.1 Volatilization (Soil Vapor Extraction)

In situ volatilization causes mechanical drawing or air venting of the contaminants from the soil. A draft fan is installed, which creates an air flow through the soil, via a slotted or screened pipe, so that air can flow but entrainment of soil particles is restricted. Activated carbon is used to recover the volatilized contaminant. This technique is limited to volatile organic carbon materials (Sparks, 1993).

2.4.1.2 Biodegradation

In situ biodegradation contains the enhancement of naturally occurring micro-organisms by stimulating their production and activity. The microorganisms are then used in degrading the soil contaminants. A number of soil, environmental, chemical, and management factors affect biodegradation of soil pollutants including moisture content, pH, temperature, the bacteria present, and the bioavailability of nutrients. Biodegradation is facilitated by aerobic soil conditions and soil pH in the range of 5.5 – 8.0, with an optimal pH of about 7 and temperature in the range of 20-43 ºC.

2.4.1.3 Phytoremediation

The use of plants to decontaminate soils and water can be effective. There are hundreds of plants that can detoxify pollutants. For example, sunflowers can absorb uranium, certain ferns have high affinity for As, alpine herbs absorb Zn, cabbage can absorb Cr, mustards can absorb Pb, clovers take up oil, and poplar trees destroy dry-cleaning solvents.

Recently the brake fern (Pteris vittata) was found to be a hyper-accumulator of chromated copper arsenate. Brake ferns extracted 1,442-7,526 mg/kg As from the heavily contaminated soils. The uptake of As into the fern fronds was fast, increasing from 29.4 to 15.9 in two weeks. Almost all of the As present in the plant was inorganic, and there were indications that As (V) was converted to As (III) during translocation from roots to fronds.

2.4.1.4 Leaching

This method involves leaching the on-site soil with water and with a surfactant to treat the contaminants. The leachate is then collected for treatment and/or disposal. The use of this method is limited since large quantities of water are used to remove the pollutants and since the waste stream is large the disposal costs can be high.

The effectiveness of a leaching technique is also depending the properties of the soil, such as: permeability, porosity, homogeneity, texture, and mineralogy. They all affect the release of the contaminant from the soil and the leaching rate of contaminants (Sparks, 1993).

2.4.1.5 Vitrification

In vitrification; the contaminants are solidified with an electric current which result with their immobilization. Vitrification immobilizes the pollutants for as long as 10.000 years. The technique is costly, because a large amount of electricity is necessary.

2.4.1.6 Isolation/Containment

With this method, contaminants are kept in place by supplying subsurface physical barriers such as clay liners and slurry walls to minimize migration. Scientists and engineers have added surfactants to clay minerals to support retention of organic pollutants and to minimize the mobility of pollutants.

2.4.1.7 Passive Remediation

In this method, natural processes such as volatilization, aeration, biodegradation, and photolysis are occurring which may cause decontamination. Passive remediation is easy and not costly and requires only monitoring of the site. Factors that affect this type of remediation include biodegradation, adsorption, volatilization, leaching, photolysis, soil permeability, groundwater depth, infiltration, and the nature of the contaminant.

2.4.2 Non-in-Situ Methods

Non-in-situ methods involve removal of the contaminated soil, usually by excavation, and the soil is then treated on-site, or transported to another location and then treated. With these methods there are obviously concerns about exposure of the contaminants in the moving and hauling process.

2.4.2.1 Land Treatment

In land treatment, the contaminated soil is excavated and placed over land so that natural processes such as biodegradation or photodegradation can occur to decontaminate the soil. The land area is prepared to remove rocks and other debris and the study area is surrounded by barriers to decrease runoff. The soil pH is adjusted to 7.0 to immobilize heavy metals and to enhance the activity and effectiveness of soil microbes. Nutrients are also added for bacterial stimulation. The contaminated soil is then spread on the site and mixed with the other soil to enhance the contact between the contaminant and microbes and to promote aerobic conditions (Sparks, 1993).

2.4.2.2 Thermal Treatment

In thermal treatment, the excavated soil is exposed o high heats using a thermal combuster. The high temperature breaks down the pollutants, and the released volatiles are then collected and moved through an afterburner and combusted or recovered with solvents.

2.4.2.3 Asphalt Incorporation

In this method, contaminated soils are put into hot asphalt mixes. These mixtures are then used in paving. The asphalt and soil are heated while they are mixed. This causes volatilization or decomposition of some of the contaminants. The remaining pollutants are then immobilized in the asphalt.

2.4.2.4 Solidification/Stabilization

This technique involves the addition of an additive to excavated, contaminated soil so that the contaminants are encapsulated. The mixture is then landfilled. Thus, the contaminants are not free to move alone; however, they are not destroyed. This method has been employed to minimize inorganic pollutant contamination.

2.4.2.5 Chemical Extraction

In this treatment the excavated soil is mixed with a solvent, surfactant, or solvent/surfactant mixture to remove the contaminants. The solvent/surfactant and released contaminants are then separated from the soil. The soil is then washed or aerated to remove the solvent/surfactant and the latter is then filtered for fine particles and treated to remove the contaminants. This technique is expensive and is not often used.

2.4.2.6 Excavation

With this method, the contaminated soil is removed and disposed elsewhere (e.g., a landfill). Landfills usually contain liners, such as clay, that diminish the mobility of the contaminants, or the landfills should be located on sites where the soil permeability is low. Landfills require large land areas and often pose hazards for humans. Excavation and disposal costs are high and potential runoff and groundwater contamination problems.

CHAPTER THREE

PROPERTIES OF NON-AQUEOUS PHASE LIQUIDS (NAPLs), THEIR BEHAVIOR IN SOILS AND PREVIOUS STUDIES ON THEIR REMADIATION

3.1 Properties of Non-Aqueous Phase Liquids (NAPLs), Diesel Oil, Polycyclic Aromatic Hydrocarbons (PAHs)

3.1.1 Properties of NAPLs and Their Presence in Soil

Accidental surface release and improper disposal of petroleum products (e.g. jet fuel, refinery wastes, diesel etc.) and volatile organic solvents are recognized as two of the most widespread causes of groundwater contamination by chemical compounds. In subsurface soil-water environments, these contaminants often persist as a separate phase due to their generally low solubility and hence are termed non-aqueous phase liquids (or NAPLs). Non-aqueous phase liquids (NAPL) are organic liquid (or semi-liquid) phases which are not, or very poorly, miscible with water. NAPLs that are less dense than water, including many petroleum products, are termed light non-aqueous phase liquids (LNAPLs) and these commonly collect and pool at, or above, the water table. The other type of NAPL is denser than water (DNAPL) and when spilled, migrates through the unsaturated zone continues on a downward migration through the water table under the influence of gravity into the saturated zone below. Chlorinated solvents used in industrial and manufacturing operations are a common form of this contaminant. A sample showing LNAPL, water, and DNAPL layers are shown in Figure 3.1 (Gavaskar and Chen, 2004).

3.1.1.1 Light Non-Aqueous Phase Liquids (LNAPLs)

Light non-aqueous phase liquids are liquids that are sparingly soluble in water and less dense than water. For example, oil is an LNAPL because it "floats" on top of water and does not mix with water. Hydrocarbons, such as oil and gasoline, are examples of LNAPLs. At LNAPL contamination sites LNAPL can form a pool of

LNAPL in the subsurface on top of the water table. The following diagram is a cross sectional view of a hypothetical LNAPL spill (Figure 3.2) (Delin et al., 1998).

Figure 3.1 A sample showing LNAPL (top), water (middle), and DNAPL (bottom) layers

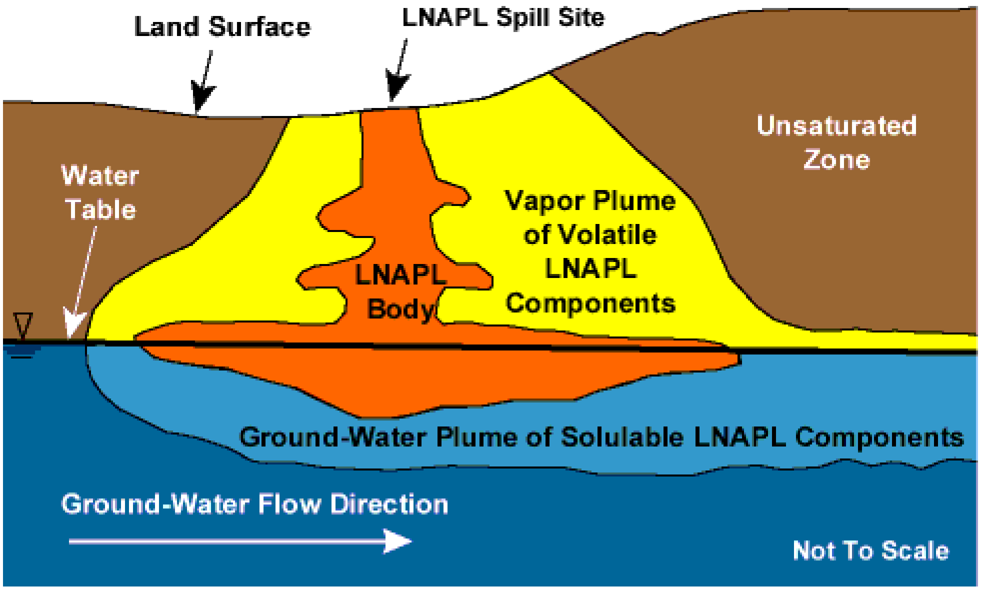


Figure 3.2 A cross sectional view of a hypothetical LNAPL spill

The release of light non-aqueous phase liquids (LNAPLs) into the subsurface is a well-documented environmental concern. Past practices have led to extensive LNAPL groundwater contamination, mostly in the form of petroleum products. Potential for further contamination is also a concern when considering the presence of LNAPL sources in the subsurface (e.g. underground storage tanks and oil/gas pipelines). Surfactant enhanced aquifer remediation, has emerged as one of the most technically effective and cost-competitive technologies for remediation of LNAPL contamination. This technology has applications to filling stations, refineries, and even active well sites. While advances in surfactant chemistry have dramatically improved LNAPL removal efficiencies, the key to further improvements in the economic competitiveness of surfactant-based technologies is to reduce the mass of surfactant needed to recover the free-phase LNAPL. Previous work by the investigators found that some biologically produced surface active agents, biosurfactants, can remove a large percentage of residual hydrocarbon from sand-packed columns at biosurfactant concentrations 10 to 100-fold lower than typically used for surfactant-enhanced LNAPL mobilization. The objective of this research is to assess the relative technical and economic efficiency of synthetic surfactants versus biosurfactants for fear of LNAPL contamination.

Surfactant flushing of contaminated subsurface environments has emerged as one of the most technically effective and cost-competitive technologies for remediation of LNAPL contamination. Surfactants (surface active agents), commonly known as soaps or detergents, are amphiphilic molecules that have both water-like and oil-like regions to their molecule. Because they are amphiphilic, surfactants are surface active molecules, meaning that when they are placed in water-oil or water-air systems, they accumulate at the interface with their water-like region in the polar water phase and their oil-like region in the nonpolar oil or less polar air phase. In this way, both regions of the molecule are in a preferred phase and the free energy of the system is minimized (EPA, 2004).

3.1.1.2 Dense Non-Aqueous Phase Liquids (DNAPLs)

Dense Non-Aqueous Phase Liquid have a specific gravity greater than unity. They're immiscible with water, i.e. they form a separate liquid phase. Their tendency to penetrate the water table and sink into an aquifer where they may slowly dissolve renders them a serious source of groundwater contamination. These proceedings took place in 1979 - a year that heralded the dawn of a huge growth in the awareness of issues surrounding groundwater contamination by DNAPL. In hindsight it seems almost inconceivable that, knowing the toxic nature of common DNAPLs, users were directed to dispose of the product by pouring it onto the ground. This is attributed to a lack of understanding of the DNAPL's physical properties: it certainly appeared that the solvent volatilized very rapidly, and was therefore assumed to evaporate. In actuality, however, a certain amount infiltrated and diffused into the subsurface. The key properties of DNAPL are summarized below;

- Immiscibility with water - they form separate phases, eg. Oil & water.
- Low absolute solubilities - DNAPL can’t dissolve quickly in groundwater: it may persist for decades before dissolving.
- Relatively high densities - DNAPLs are denser than water, and can therefore sink beneath the water table, polluting the full thickness of an aquifer.
- Low viscosities - allows rapid subsurface migration. The low viscosities of chlorinated solvents allow them to migrate rapidly in the subsurface, where mobility is proportional to the density / viscosity ratio.
- High volatility - the property of chlorinated solvents that originally prompted the disastrous disposal practice of pouring spent solvent on dry ground.
- Toxicity - Many DNAPLs are suspected or proven human carcinogens.

DNAPL migration is strongly affected by capillary pressures, dictating which holes the liquid will penetrate, therefore without a comprehensive knowledge of the geometry subsurface fractures, DNAPL migration beneath the water table is very difficult to predict. The dissolved plume however flows normally with the groundwater and therefore has the potential to contaminate abstraction wells. If there is a continuous source of contamination entering moving groundwater, a volume of contaminated groundwater can form – this is called a 'plume'. The combination of moving groundwater and a continuous source of contamination can, therefore, pollute very large quantities of groundwater (Cohen and Mercer, 1993).

Chlorinated Solvent: NAPLs are a serious source of groundwater contamination - these chemicals have been produced in very large quantities for decades and have found use in a wide variety of industries, such that the incidences of solvent spillage are far more widespread. The many uses to which chlorinated solvents are put include metal cleaning and de-greasing, dry-cleaning, leather tanning, pharmaceuticals, dyes and paints, adhesives, aerosols, manufacture of various chemicals. Examples of common chlorinated solvents:

- TCA (1, 1, 1-Trichloroethane) - Metal cleaning, adhesives, aerosols, inks.
- DCM (Methylene Chloride) - Paint stripper, metal cleaning, pharmaceuticals, aerosols.
- TCE (Trichloroethylene) -Metal cleaning, (> 90 of UK use), dry cleaning, extractions.
- PCE (Perchloroethylene) - Dry cleaning, metal cleaning, intermediates in processes.

Chlorinated solvents are found at relatively low concentrations measured in parts per billion (ppb) 1 ppb are equivalent to one second in 31.7 years. Although these ppb concentrations are very low, drinking water limits are set at similarly low concentrations. The concentrations at which chlorinated solvents in groundwater are harmful to human health are extremely low. The drinking water limit for a common chlorinated solvent is 5 mg/L (5ppb), due in part to its carcinogenic nature). The Woburn tragedy was a serious case of a municipal drinking water contamination by chlorinated solvents, which resulted in cases of childhood leukemia between the years 1960-80s. It prompted the major trial which inspired the Jonathan Harry novel 'A Civil Action' and subsequent feature film of the same name.

The source area must be characterized properly for an effective source zone remediation. Due to the difficulty in locating DNAPL, a rule of thumb for assuming the presence of DNAPL is if the concentration of the contaminant in the groundwater is one percent of the saturated aqueous concentration (although 10% aqueous concentrations are used at some sites) (Kram et al. 2001). However, this technique only can be used to indicate whether or not DNAPL is present and not the extent of the contamination. Just one characterization technique cannot accurately assess the extent of the source zone; many tools are needed. The selection of tools for site characterization depends on site conditions, historical site information, and the DNAPL migratory path. Non-geophysical techniques are used for direct and indirect detection of DNAPL. Physical properties are measured by geophysical techniques, which are used to indirectly indicate DNAPL presence (EPA 2004a).

One approach to site characterization, the Triad, incorporates systematic project planning, dynamic work strategies, and real-time measurement technologies to address the heterogeneity encountered at DNAPL sites (EPA 2003). Systematic planning includes laying out clear objectives, optimizing work flow, and focusing on quality control to ensure the data being collected is relevant, accurate, and obtained efficiently. Dynamic work strategies allow flexibility in site characterization; therefore, changes to the location, extent and method of sampling and analysis can be made while still in the field to allow complete characterization in one mobilization. Real-time measurement technologies together with decision support tools allow the conceptual site model to be updated while still in the field, which lets site managers make decisions on site to decide which tools should be used for continued site characterization and where samples should be retrieved in order to obtain an accurate site assessment. The Triad approach usually can result in an accurate site characterization and a reduction in site characterization costs (EPA 2003).

3.1.2 Properties of Diesel Oil

Diesel oil, which contains light and dense hydrocarbons, is selected as the NAPL contaminant which will be used in the study. Diesel oil and gasoline are the major products of the refined crude petroleum. While the oil produced in the world in 1945 was 5 million barrels per day, today this value has reached to the level of 65 million barrels per day. Petroleum diesel, or petrodiesel is produced from petroleum,and is a hydrocarbon mixture, obtained in the fractional distillation of crude oil between 200 °C and 350 °C at atmospheric pressure.

The density of petroleum diesel is about 850 grams per litre whereas petrol (American English: gasoline) has a density of about 720 g/L, about 15% less. When burnt, diesel typically releases about 40.9 megajoules (MJ) per litre, whereas gasoline releases 34.8 MJ/L, about 15% less. Diesel is generally simpler to refine from petroleum than gasoline and often costs less (although price fluctuations sometimes mean that the inverse is true; for example, the cost of diesel traditionally rises during colder months as demand for heating oil, which is refined in much the same way, rises). Also, due to its high level of pollutants, diesel fuel must undergo additional filtration which contributes to a sometimes higher cost. In many parts of the United States and throughout the whole of the UK, diesel is higher priced than petrol.[1] Reasons for higher priced diesel include the shutdown of some refineries in the Gulf of Mexico, and the switch to ultra-low sulfur diesel (ULSD), which causes infrastructural complications (EIA Brochures, 2007).

Diesel-powered cars generally have a better fuel economy than equivalent gasoline engines and produce less greenhouse gas pollution. This greater fuel economy is due to the higher energy per-litre content of diesel fuel and also to the intrinsic efficiency of the diesel engine. While diesel's 15% higher density results in 15% higher greenhouse gas emissions per litre compared to gasoline (EPA, 2005), the 20–40% better fuel economy achieved by modern diesel-engined automobiles offsets the higher-per-liter emissions of greenhouse gases, resulting in significantly lower carbon dioxide emissions per kilometers (BBC News, 2002), (Diesel Technology Forum, 2006).

On the other hand, diesel fuel often contains higher quantities of sulfur. European emission standards and preferential taxation have forced oil refineries to dramatically reduce the level of sulfur in diesel fuels. In contrast, the United States has long had "dirtier" diesel, although more stringent emission standards have been adopted with the transition to ULSD starting in 2006 and becoming mandatory on June 1, 2010 (see also diesel exhaust). U.S. diesel fuel typically also has a lower cetane number (a measure of ignition quality) than European diesel, resulting in worse cold weather performance and some increase in emissions. High levels of sulfur in diesel are harmful for the environment because they prevent the use of catalytic diesel particulate filters to control diesel particulate emissions, as well as more advanced technologies, such as nitrogen oxide (NOx) adsorbers (still under development), to reduce emissions. However, the process for lowering sulfur also reduces the lubricity of the fuel, meaning that additives must be put into the fuel to help lubricate engines. Biodiesel is an effective lubricant.

Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including *n*, *iso*, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) (ATSDR, 1995). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approximately $C_{10}H_{20}$ to $C_{15}H_{28}$. The properties of diesel oil are given in Table 3.1.

3.1.3 Properties of PAHs

Polycyclic aromatic compounds (PAHs) are the organic pollutants that may be originated from food, drink, leather, vegetable oil, soap, chemistry, waste of paint and textile industries. Polycyclic aromatic compounds include different groups of compounds which have two or more benzenoid groups in their structure and various functional groups which may contain several elements. An important group of PAHs which have two or more fused benzonoid rings and no elements other than carbon and hydrogen (Henner et al., 1997). They may be eliminated or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photooxidation. For instance, in some conditions, traces of nitric acid can transform some PAHs into nitro-PAHs (Marce & Borrull, 2000).

Table 3.1 Properties of diesel oil

Property*	
Appearance	Straw-colored to dyed red
Physical State	Liquid
Odor	Characteristic petroleum
pH	unavailable
Vapor Pressure (mm Hg)	0.40
Vapor Density (air=1)	>3
Boiling Point/Range	160-371°C
Freezing/Melting Point	No Data
Solubility in Water	Negligible
Specific Gravity	0.81-0.88 @ 60°F
Percent Volatile	Negligible
Evaporation Rate (nBuAc=1)	<1
Viscosity	32.6-40.0 SUS @ 100°F
Bulk Density	7.08 lbs/gal
Flash Point	>125°F / >52°C
Flammable /Explosive Limits (%)	LEL: 0.3 / UEL: 10.0

*Unless otherwise stated, values are determined at 20°C (68°F) and 760 mm Hg (1atm).

PAHs are organic substances composed of carbon and hydrogen atoms grouped into at least two condensed aromatic ring structures, do not contain heteroatoms or carry substituents . Generally, PAHs are classified into two groups with the numbers of aromatic rings, they are low molecular weight (LMW) PAHs and high molecular weight (HMW) PAHs. naphthalene, anthracene, fluorene, and phenanthrene with two or three rings are included in the LMW PAHs group, whereas pyrene, chrysene, and benzo[a]pyrene with four or more rings are considered HMW PAHs.

The physical properties of PAHs vary with their molecular weight and structure. PAHs have low to extremely low water solubility and also moderate to low vapour pressures. As a general rule, the hydrophobicity increases and the aqueous solubility decreases with an increase in the number of aromatic rings (Manoli and Samara, 1999). The physical properties and chemical structures of the most common PAHs are presented in Figure 3.3.

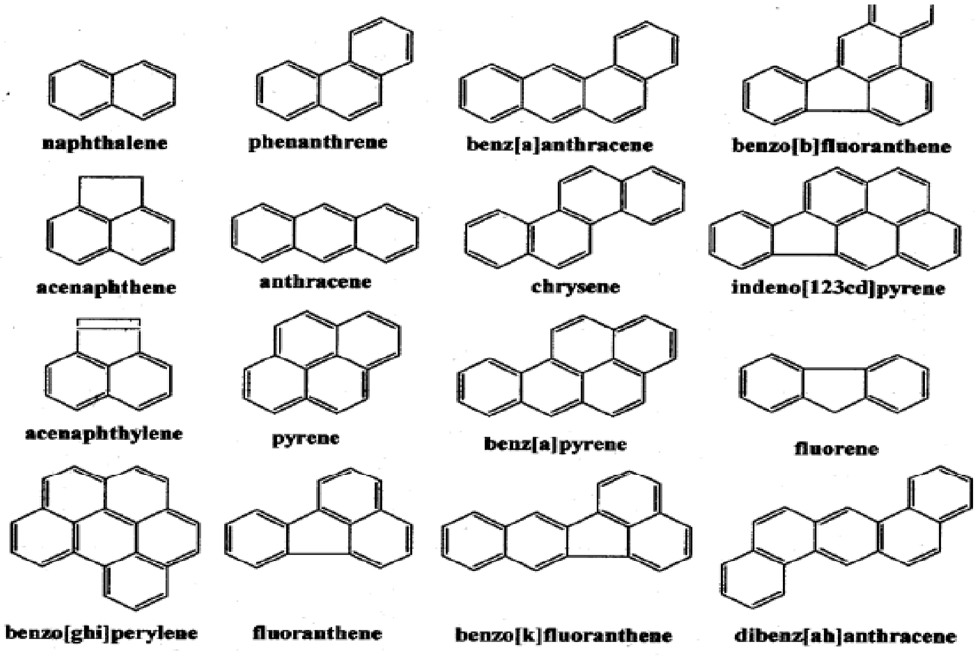


Figure 3.3 The chemical structures of the most common PAHs

The physical and chemical properties of PAHs vary with the number of aromatic rings and the shape (ring linkage pattern) of the individual molecule. Of different physical and chemical properties, solubility and vapor pressure are major factors that control their distribution between the soluble and particle components of atmosphere, hydrosphere and biosphere. The solubility of PAH in water decreases and hydrophobicity increases significantly with increasing molecular sizes, which conforms to its octanol-water partition coefficients (Kow). Their high Kow indicates a relatively high potential for adsorption to suspended particulates in air and in water, and for bioconcentration in organisms. On the other hand, vapour pressures for PAHs are low and decrease with increasing molecular sizes. All completely unsaturated PAHs are solid at room temperature and have relatively high melting and boiling points. Some physical properties and chemical structures of the 16 PAHs defined as priority pollutants by US EPA are listed in Table 3.2 (ATSDR, 1995).

Since the persistent organic toxicants like PAH's are resistant to photocatalitic, chemical and biological treatment, they can be accumulated long term without degradation. The persistence of PAHs in the environment depends on the physical

Table 3.2 Physical and chemical properties of individual PAH

Contaminants	**Chemical Formula**	**Molecular Weight g/mole**	**Boiling Point (°C)**	**Density (g/cm^3)**	**Specific Gravity**	**Water Solubility (mg/L)**	**Log K_{ow}**	**Vapour Pressure (mm Hg)**
Naphthalene	$C_{10}H_8$	128.19	218	1.15	1.14	31.0	3.30	$8.50*10^{-2}$
Acenaphthylene	$C_{12}H_8$	152.20	265-275	-	0.8988	16.1	3.94	$9.12*10^{-4}$
Acenaphthene	$C_{12}H_{10}$	154.21	96.2	1.225	1.0242	3.9	3.92	$2.50*10^{-3}$
Fluorene	$C_{13}H_{10}$	166.2	295	-	1.203	1.89	4.18	$8.42*10^{-3}$
Phenanthrene	$C_{14}H_{10}$	178.2	340	1.063	-	1.15	4.46	$1.12*10^{-4}$
Anthracene	$C_{14}H_{10}$	178.2	342..340	-	1.25	$4.34*10^{-2}$	4.45	$2.67*10^{-6}$
Carbozole	$C_{12}H_9N$	167.21	351.0	1.301		0.721	3.23	$2.66*10^{-4}$
Fluoranthene	$C_{16}H_{10}$	202.26	~375	-	1.252	$2.60*10^{-1}$	5.16	$1.23*10^{-8}$
Pyrene	$C_{16}H_{10}$	202.3	393. 404	1.271	1.271	$1.35*10^{-1}$	4.88	$1.35*10^{-7}$
Benz(a)anthracene	$C_{18}H_{12}$	228.29	158-159	1.274	-	$9.40*10^{-3}$	5.76	$3.05*10^{-8}$
Chrysene	$C_{18}H_{12}$	228.3	448	-	1.274	$2.00x10^{-3}$	5.50	$6.23*10^{-9}$
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.3	168.3	-	-	$1.50*10^{-3}$	5.78	$5.00*10^{-7}$
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.3	550	-	-	$8.00x10^{-4}$	6.11	$9.65*10^{-10}$
Benzo(a)pyrene	$C_{20}H_{12}$	252.3	179-179.3	1.351	-	$1.62x10^{-3}$	5.97	$5.49*10^{-9}$
Dibenz(a,h)anthracene	$C_{22}H_{14}$	278.35	-	1.282	-	$2.49x10^{-6}$	6.75	$1.00*10^{-10}$
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	480	-	-	$2.6x10^{-4}$	6.63	$1.01*10^{-10}$
Indeno(1,2,3-c,d)pyrene	$C_{22}H_{12}$	276.3	530	-	-	$2.20*10^{-5}$	6.70	$1.00*10^{-10}$

and chemical characteristics of the PAH. But biological transformation is probably the prevailing route of PAH loss (Shiaris, 1989). The recalcitrance of PAHs to microbial degradation increases directly with the molecular weight and the octanol-water partition coefficient (log K_{ow}).

The molecular structures of PAHs were shown in Figure 3.3 PAHs are relatively neutral and stable molecules. PAHs have low solubilities and low volatilities except small components like naphthalene. Solubility's of PAHs in water decreases with increasing molecular weight. Their liphophilicity is high, as measured by water octanol partition coefficients (Kow). Due to their hydrophobic nature, the concentrations of dissolved PAHs in water are very low. PAHs show long half-lives in geological media. In anaerobic sediment, for example, half-lives range from three weeks for naphthalene up to 300 weeks for benzo(a)pyrene. PAHs are regarded as persistent organic pollutants (POPs) in the environment. This persistence increases with ring number and condensation degree (Henner et al., 1997).

In natural environments, PAHs are generally found adsorbed on particulates and on humic matter, or solubilized in any oily matter which may contaminate water, sediment and soil. The average estimate of PAH half lives in soil ranges from 24 to 1524 days (Howard et al., 1991).

Polycyclic aromatic hydrocarbons (PAHs) are the widespread contaminants in the different compartments of the environments. Due to their toxic, mutagenic, and carcinogenic characteristics, PAHs are considered to be hazardous to the biota and environments.

3.2 Behavior of NAPLs, Diesel Oil, PAHs in Soil

3.2.1 NAPLs

Adherent or entrapped NAPLs, such as coal tar or creosote, can also function as an important compartment for hydrophobic compounds, which might directly contaminate the soil. In soils directly contaminated by the source materials or by transport of the source materials, PAHs are likely to be associated primarily with NAPLs. A difference between fresh and aged or weathered NAPLs also exists just as for SOM. Diffusion of the hydrophobic compounds within the NAPL phase itself and interfacial mass transfer may be rate-limiting steps for the desorption of these compounds to the aqueous phase. To investigate the desorption mechanism and to model this NAPL compartment, both dissolution kinetics of NAPLs and desorption of the contaminant need to be considered (Zhu, 2008).

3.2.2 Diesel Oil

Two major soil contaminants during the process of exploitation of oil and gas are petroleum hydrocarbons and salts. If not being handled properly, the contaminated sites could cause consequential pollution to the environments and pose high risks to the human health. The crucial problem that needs to be solved for soil remediation within the oil and gas industry is to develop and choose a cost-effective and environmentally responsible method according to the specific situations of different contaminations (Song, 2011).

Diesel fuel contaminated soil is a major environmental concern which is considered as the second most frequently treated contaminant after benzene at the United States Environmental Protection Agency superfund projects and a good typical source is leaking underground storage tanks at service stations. This had led to a demand for further studies in the investigation, assessment, management and remediation of diesel-contaminated sites in the field of petroleum contamination (Ayobamidele, 2005).

3.3.3 PAHs

PAH contamination of environmental systems is a global problem. PAH contamination usually occurs as a complex mixture of compounds and is a result of both the combustion of natural and anthropogenic organic materials and the accidental or improper disposal of industrial materials containing high concentrations of PAHs. Natural sources of PAH contamination include forest fires, volcanic eruptions, and natural oil seeps, but anthropogenic sources remain the primary concern. Anthropogenic sources of PAH contamination include residential fireplace use, high heat cooking practices like grilling with charcoal and wood stove use, cigarette smoke, engine exhaust, coal gasification and other industrial releases.

Airborne PAH contamination is suspected to be the cause for the global distribution of PAHs, with PAH concentrations being the greatest in urban areas. For example, atmospheric benzo[a]pyrene emissions in the US have been estimated to be 3.6 x 106 kg/year. Most of this mass partition onto suspended organic particulates, but the main receptor of atmospheric benzo[a]pyrene is soil or sediment. Particle-associated PAHs can deposit on surfaces and be stripped from the air and from surfaces during rain events. Surface run-off can then lead to contamination of surface water, soil, and sediment. Ultimately, PAHs can bioaccumulate in the food chain and pose a significant risk to human health.

Soil is a dynamic and heterogeneous mixture of minerals, metals, and organic and inorganic material. The soil matrix is composed of aggregates of particles of various sizes resulting in pore spaces that liquids, gases, and microorganisms can permeate. Various depictions of the soil matrix have been published. Soil texture, porosity, pH, oxygen status, moisture content, temperature, and organic carbon content can influence permeability, nutrient distribution, sorption of PAHs to nonaqueous compartments, and the rate of PAH sorption and desorption in the soil matrix. Because of their hydrophobicity, poor aqueous solubility, and low volatility, PAHs associate with NAPLs and mineral and organic surfaces of the soil matrix more than the aqueous or gas phase. This tendency for PAHs to compartmentalize within the soil matrix increases with PAH molecular weight, leads to PAH sequestration in the soil matrix, and contributes to decreased bioavailability and biodegradation, especially over time (Jones, 2010).

3.3 Previous Studies

A number of studies were reported in literature for the factors affecting the remediation of non-aqueous phase liquid (NAPL) contaminants in soils. Studies found in literature are concentrated on chemical treatment, air sparging/soil vapor extraction (SVE), and bioremediation of NAPL contaminated soils. Major studies may be summarized as follows:

Hupe et al. (1996) shown that the reduction of the diesel fuel contaminants in the soil was independent of the compost age and amounted to approximately 94% of the initial quantity. The addition of biocompost were also enhanced the degradation of real contaminants. After a test period of 162 days in set-ups with compost addition, more than 75% of the lubricating oil contaminants disappeared, while less than 37% of the contaminants disappeared in set-ups without compost addition. Moreover, by the addition of compost, the formation of pellets during the dynamic treatment of soil materials could be reduced.

Márquez-Rocha et al. (2001) research, laboratory and pilot-scale trials have examined the biodegradation of diesel. In both, a fuel-degrading bacterial consortium was carried out using. The enhancement of the microbial activity in hydrocarbon-contaminated soil was being achieved with the combination of stepwise soil inoculation and nutrient additions.

Saponaro (2001) has studied slurry phase bioremediation of PAHs in sandy soil. Biodegradation studies were carried out at 22 ◦C in a slurry system reactor, with a solid to liquid ratio of 10% w/w. Three tests were performed, over a period of 23, 24 and 91 days respectively. In the first test, only soil and water were put into the system. In the second test, microbial activity was inhibited to evaluate the amount of abiotic losses. In the third test, macronutrients were added to the reactor; bioaugmentation was also carried out by an inoculum of autochthonous PAH-degrading microorganisms. Tests showed that high removal efficiency could be obtained following 23 days of treatment for all PAHs, including high molecular weight compounds.23 days of treatment for all PAHs was applied and 63% treatment efficiency was achieved.

The major objective of Namkoong et al. (2002) researched was to find the appropriate mix ratio of organic amendments for enhancing diesel oil degradation during contaminated soil composting. Sewage sludge or compost was added as an amendment for supplementing organic matter for composting of contaminated soil. Sewage sludge or compost was added as an amendment for supplementing organic matter for composting of contaminated soil. The ratios of contaminated soil to organic amendments were 1:0.1, 1:0.3, 1:0.5, and 1:1 as wet weight basis. Target contaminant of this research was diesel oil, which was spiked at 10,000 mg/kg sample on a dry weight basis. Volatilization loss of TPH was only about 2% of initial TPH. Normal alkanes lost by volatilization were mainly by the compounds of C10 to C16. High correlations (r=0.80-0.86) were found among TPH degradation rate, amount of CO2 evolved, and dehydrogenase activity. Treatment efficiency was found >85%.

Mohamed (2002) propesed a novel electro-dialysis based technique has been developed and used to treat a silty clay soil polluted by lead. T The effect of chemical reagents, i.e. tap water at pH 4 (reagent 1) and sodium acetate at pH 5 (reagent 2), on enhancing electro-dialysis extraction of lead from the tested soil was examined. Total lead removal of 80 and 92% was obtained for reagents 1 and 2, respectively. The high removal efficiency was attributed to the separation of electrode reactions from the soil and inclusion of ion selective membranes (ISM), which restrict the movement of counter charged species.

Watts et al. (2002) has studied the mineralization of PAHs in soil in the presence of H_2O_2. Benzo[a]pyrene (BaP) mineralization of 70% to 85% has reached for the different types of soils. The results show that catalyzed H_2O_2 has the ability to rapidly mineralize sorbed/NAPL-phase BaP and that partitioning, which is often the rate-limiting factor in soil remediation, does not appear to limit the rate of vigorous Fenton-like treatment.

Rojas-Avelizapa et al. (2002) studied the bioremediation of TPHs in Clay loam (drilling mud)-polluted sites. Results showed that, after 180 d, total petroleum hydrocarbon (TPH) concentrations decreased from 99300 ± 23 000 mg TPH/kg soil to 5500 ± 770 mg TPH/kg for amended biopiles and to 22900 ± 7800 mg TPH/kg for unamended biopile. An undisturbed soil control showed no change in TPH concentrations. Highest bacterial counts were observed during the first 30 d which correlated with highest TPH removal, whereas fungal count increased at the end of the experimentation period. Results suggested an important role of the straw, nutrient addition and water content in stimulating aerobic microbial activity and thus hydrocarbon removal.

Phenanthrene, pyrene, and benzo(a)pyrene treatment by Fenton oxidation is researched by Reetta Piskonen and Merja Itävaara (2004) with the presence of nonionic sufactants. The surfactants selected for the study were Tween 80, Brij 35, Tergitol NP- 10, and Triton X-100. When surfactant addition was combined with the Fenton oxidation, reduced mineralization rates were obtained when compared with mineralization after Fenton’s treatment alone. The results indicate that the addition of Fenton’s reagent may enhance the mineralization of PAHs in contaminated soil, whereas the addition of surfactants has no significant beneficial effect.

Soil vapor extraction of Toluene is studied in a reactor system by Waduge, et al., (2004). 687 g of toluene is trapped in the sand matrix with a volume of 0.15 m^3. Overall results suggested that it was difficult to achieve the complete remediation of NAPL source due to complex entrapment in heterogeneous soil system.

According to Gavaskar and Chen (2004), Trichloroethene, dichloroethene, methylene chloride, toluene, and oils had identified as NAPLs. Following completion of in situ thermal remediation activities at a 9,900-cubic-meter NAPL contamination area, a sampling program was implemented to verify the success of the remediation. Verification data indicate that the remediation was successful.

According to Schirmera and Butlerb' (2004) report, organic contaminations has been posed a significant threat to groundwater resources. This contaminants are often found as nonaqueous phase liquids (NAPLs) during spills of, for example, gasoline, crude oil, creosote, coal tar or chlorinated solvents. Once released, the liquids seep downward and has dissolve into the groundwater. In many cases, the impacted groundwater has contained a mixture of contaminants, either due to the complexity of the NAPL (e.g. gasoline) or due to co-disposal/co-spillage (e.g. landfill leachates). Many organic contaminants had hazardous to human health and the environment and therefore threaten our potable water resources and natural ecosystems.

Boopathy (2004) studied anaerobic biodegradation of no. 2 diesel fuel in a soil column. Several anaerobic conditions were evaluated in soil columns, including sulfate reducing, nitrate reducing, methanogenic, and mixed electron acceptor conditions. Under mixed electron acceptor condition 81% of diesel fuel was degraded within 310 days. While under sulfate reducing condition 54.5% degradation of diesel fuel was observed for the same period. This study showed evidence for diesel fuel metabolism in a mixed microbial population system similar to any contaminated field sites, where heterogeneous microbial population exists.

Sarkar et al. (2005) investigated two methods of biostimulation were compared in a laboratory incubation study with monitored natural attenuation (MNA) for total petroleum hydrocarbon (TPH) degradation in diesel-contaminated Tarpley clay soil with low carbon content. After 8 weeks of incubation, both biostimulation methods degraded approximately 96% of TPH compared to MNA, which degraded 93.8%. Results suggest that biosolids addition was a more effective soil amendment method for biostimulation than the commonly practiced inorganic fertilizer application, because of the abilities of biosolids to supplement carbon.

Bento et al. (2005) have studied bioremediation of soils contaminated with diesel oil by natural attenuation, biostimulation and bioaugmentation. After 12 weeks of incubation, all three treatments showed differing effects on the degradation of light (C12–C23) and heavy (C23–C40) fractions of TPH in the soil samples.

Bioaugmentation of the Long Beach soil showed the greatest degradation in the light (72.7%) and heavy (75.2%) fractions of TPH. Natural attenuation was more effective than biostimulation (addition of nutrients), most notably in the Hong Kong soil. The greatest microbial activity (dehydrogenase activity) was observed with bioaugmentation of the Long Beach soil (3.3-fold) and upon natural attenuation of the Hong Kong sample (4.0-fold). The number of diesel-degrading microorganisms and heterotrophic population was not influenced by the bioremediation treatments.

Removal of polycyclic aromatic hydrocarbons from aged-contaminated soil using cyclodextrins (CD) has also been studied (Viglianti et al., 2005). β-Cyclodextrin (BCD), hydroxypropyl-β-cyclodextrin (HPCD) and methyl-β-cyclodextrin (MCD) solutions were used for soil flushing in column test to evaluate some influent parameters that can significantly increase the removal efficiency. Results of this work show that CD has a great potential for PAHs extraction on aged-contaminated soils. The use of CDs as a solubility-enhancement agent is effective for PAH compounds. The main mechanism of PAHs extraction from soil to the aqueous phase is the dissolution of NAPL following Raoult's law with or without CD.

According to Ayotamuno et al. (2006), the results of theirs study were indicated that the application of increased concentrations of nutrients (by the application of fertilizers) lead to greater rates of biodegradation of petroleum-polluted agricultural soils. Treatment efficiencies vary between 50-95%.

Antizar-Ladislao et al. (2006) has studied the composting reactors were operated at 18 different operational conditions using a 3-factor factorial design with three temperatures (T, 38 ºC, 55 ºC and 70 ºC), four soil to green waste ratios (S:GW, 0.6:1, 0.7:1, 0.8:1 and 0.9:1 on a dry weight basis) and three moisture contents (MC, 40%, 60% and 80%). PAH losses followed first order kinetics reaching 0.015 day_1 at optimal operational conditions. A factor analysis of the 18 different operational conditions under investigation indicated that the optimal operational conditions for degradation of PAHs occurred at MC 60%, S: GW 0.8:1 and T 38 ºC. Thus, it is recommended to maintain operational conditions during in-vessel composting of PAH-solid waste close to these values.

Alvin-Ferraz et al. (2006) has reported the soil vapour extraction of cyclohexane in beach sand. İncreasing soil water content from 0% to 6% had the following consequences, increased remediation time (1.8–4.9 h, respectively), decreased remediation efficiency (99–97%, respectively) and decreased the amount of contaminant adsorbed onto the soil and in the non-aqueous liquid phase, thus increasing the amount of contaminant in the aqueous and gaseous phases.

Zytner et al. (2006) has used bioremediation of diesel fuel, and individual fuel compounds in silt loam. The results showed that the degradation trend of a compound changed when present in a simple mixture or when degraded in isolation. The presence of the compounds as either an aliphatic or aromatic mixture was not changed the degradation trend. The presence of a mixture also affected the amount of degradation with some compounds degrading to a greater extent when in isolation. Overall, the majority of degradation occurred in the first 10 d, suggesting that the first-order model may not be an appropriate model for degradation periods longer than 10 d when nutrient limited. It was also found that fungal metabolism is important for the degradation of hydrocarbons, particularly for branched species such as pristane as the decay rate increased one order of magnitude when bacteria were inhibited.

Coulon and Delille (2006) has studied biodegration of diesel fuel in soil. A chemical survey conducted during the last 2 years (2002 and 2003) showed that the total extractable hydrocarbons (TPH) content in arid fell field was reduced to £ 50% of their value while it was reduced only to £ 65% in vegetated soil. In addition, the decrease of TPH was always higher in the presence of fertilizer in the arid contaminated area, while fertilizer addition was almost inefficient in the wet contaminated one.

Yu et al. (2007) has been carried out although alkanes have relatively less reactive to chemical oxidation compared to alkenes, the chemical oxidation of alkanes has not been adequately explored in the context of environmental remediation efforts. Laboratory-scale column experiments have been therefore conducted with soil artificially contaminated by diesel fuel as a surrogate for alkanes of environmental relevance. Particular attention has been paid to saturated hydrocarbons refractory to volatilization. The observed removal of diesel range organics (DRO) reached 94% over 14 h of continuous ozone injection.

Another study showed that sparging air at ambient temperature through the contaminated soil can remove NAPLs, however, employing hot air sparging can provide higher contaminant removal efficiency, by about 9% (Mohammed et al., 2007).

Danelle Mohammed, et al. (2007) studied air sparging of NAPLs in fine and medium sands. NAPLs concentration was 16700 mg/kg. This study showed that sparging air at ambient temperature through the contaminated soil can remove NAPLs; however, employing hot air sparging can provide higher contaminant removal efficiency, by about 9%.

Mahanty et al. (2007) have studied biodegradation of pyrene by *Mycobacterium frederiksbergense* in a two-phase partitioning bioreactor system. Degradation rates achieved using *M. frederiksbergense* in TPPB were much higher than the literature reported values for an *ex situ* PAH biodegradation system operated using single and pure microbial species. During the active degradation phase, degradation rate was found to be 82, 139, 230 and 270 mg/L.d for initial concentrations 200, 400, 600 and 1000 mg/L, respectively.

Biodegradation rate of diesel range *n*-alkanes by bacterial cultures *Exiguobacterium aurantiacum* and *Burkholderia cepacia* has studied by Mahanty and Mukherji (2007). The cultures demonstrated good degradation characteristics for diesel range *n*-alkanes (C9–C26) and were also capable of degrading pristane. A significant correlation was observed between maximum decay rate (MTR) of individual *n*-alkane peak area and initial abundance of *n*-alkanes in diesel (r^2=0.79 and 0.97 for *E. aurantiacum* and *B. cepacia*, respectively). Thus, MTR (day^{-1}) was essentially constant, in the range of 0.07–0.20, for *n*-alkanes with a wide range of carbon numbers from C12 to C26.

Schaefer and Juliane (2007) said that the application of additives could not necessarily enhance bioremediation. Despite the high mortality rate, a worm, and therefore trigger the degradation process, the oil contaminated soil improvement medium TPH concentrations apply.

Collina, et al. (2007) has supplied to evaluate influence of two commercial surfactants and inoculum of selected bacteria on biodegradation of diesel fuel in different systems. Tween 80 addition increased the biodegradation rate of hydrocarbons both in liquid and in slurry phase systems.

Jonsson et al. (2007) has studied chemical oxidation with Fenton reagent of PAHs in aged soil samples from various contaminated sites was influenced by soil characteristics and by PAH physico-chemical properties. The results were evaluated using the multivariate statistical tool, partial least squares projections to latent structures (PLS). In general, low molecular weight PAHs were degraded to a greater extent than large, highly hydrophobic variants. Treatment efficiencies vary between 0-72% and overall efficiency was 43.

Adriano Pinto Mariano et al. (2007) investigated the bioremediation processes were applied to a sandy soil with a high level of contamination originated from the leakage of a diesel oil underground storage tank at a petrol station. Efficiency of biodegradation was simultaneously measured by two methods: respirometric (microbial CO2 production) and gas chromatography. Acute toxicity tests with Daphnia similis were applied for examination of the efficiency of the processes in terms of the generation of less toxic products. Results showed that all bioremediation strategies enhanced the natural bioremediation of the contaminated soil and the best results were obtained when treatments had nutritional amendment. Respirometric data indicated a maximum hydrocarbon mineralization of 19.8%, obtained through the combination of the three agents, with a total petroleum hydrocarbons (TPH) removal of 45.5% in 55 days of treatment. At the end of the experiments, two predominant bacteria species were isolated and identified (Staphylococcus hominis and Kocuria palustris).

Arrar et al. (2007) investigated the bioremediation of diesel-oil contaminated soil (40000 mg/kg) was studied in a jet–fluidized reactor by the stimulation of indigenous oil micro-organisms. Removal and biodegradation ratios ranged from 69% to 99%, and 54% to 84%, respectively after 15 days of treatment. The best biodegradation ratio of 84% occurred in the case of an expanded bed with minimum fluidization, operating at a jet velocity of 37 m/s. The diesel-oil biodegradation was governed by first-order kinetics. Important air flows enhanced the efficiency of diesel-oil removal, and abiotic loss and hence decreased the biodegradation ratio.

Hallgren and Jin (2008) investigated petroleum compounds account for the vast majority of contaminants in soils. Bioremediation was a widely accepted strategy in degrading these contaminants. This study was used a solid-phase circulating bioreactor (SCB). In a bench-scale SCB, total petroleum hydrocarbon (TPH) concentration (5000 mg/kg) in soil decreased 92% within 15 days. In a scaled-up SCB system containing 120 kg petroleum-contaminated soil (TPH at 125,000 mg/kg), a degradation rate of 635 mg/kg.d was obtained from the poultry manure-amended treatment during a 200 day period of operation. Treatments with the same amount of nitrogen (as ammonium nitrate) attained a TPH degradation rate of 469 mg/kg.d during the same period.

Salinas-Martinez et al. (2008) was studied the biodegradation with specific cultures of diesel fuel in fine sand. The heap leaching technique was demonstrated good efficiency in the column and pile, decreases lowering the TPH concentration from 61,000 to 1800 mg/kg (98.5%) in 15 d.

Nikakhtari et al. (2008) has tested to using indigenous bacteria enriched from industrial contaminated soil at room temperature, a baffled roller bioreactor was able to biodegrade high diesel oil concentrations at high biodegradation rates.

Grace Liu, et al. (2008) has investigated as the simulated in situ bioremediation for diesel-contaminated soil by a column operation. Several bioremediation approaches had been conducted to examine the feasibility. Several bioremediation approaches were conducted to examine the feasibility. Four lab-scale soil columns were operated specific to the following approaches: nutrient enhancement (NE), bioaugmentation (BA), biostimulation (BS), and sterilized soil (SS). The diesel-degradation efficiency was 67%, 80%, 45%, and 24%, accordingly.

Maliszewska-Kordybach et al. (2008) investigated the content of R16PAHs ranged from 80 to 7264 μg/ kg with a median of 395 μg/ kg and with a dominance of 4–6 rings hydrocarbons (74% of total PAHs). Toprak features found that affects the content of PAH.

Cai et al. (2008) has presented The Chinese regulation and/or other maximum acceptable values for SVOCs were used for the characterization of soils. In general, the compounds that were mostly studied in Chinese soils were organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). According to the studies reviewed here, the most abundant compoundswere phthalic acid esters (PAEs) and PAHs (up to 46 and 28 mg/kg dry weight, respectively); PCBs and OCPs occurred generally at concentrations lower than 100 μg/kg dry weight.

Lin and Mendelssohn (2009) studied the phytoremediation of diesel fuel in salt marsh sediments. Concentration reduction in all categories of hydrocarbons suggested that J. roemerianus effectively phytoremediated the diesel-contaminated wetlands.

Jiang et al. (2009) evaluated that a principal component analysis and PAHs isomeric ratios indicate that PAHs in Shanghai urban soil mainly originated from combustion. The toxic assessment suggested that soil PAHs exposure was medium carcinogenic at present level.

Tsai and Kao, 2009 has evaluated the contamination of subsurface soils with petroleum hydrocarbons. The studied controlling factors that affect the removal efficiency of petroleum hydrocarbons included concentrations of H_2O_2, basic oxygen furnace slag (BOF slag) dosages, types of petroleum hydrocarbons (e.g., fuel oil and diesel), and types of iron mineral. Approximately 76% and 96% of fuel oil and diesel removal were observed (initial total petroleum hydrocarbon (TPH) concentration = 10,000 mg/kg), respectively, with the addition of 15% of H_2O_2 and 100 g/ kg of BOF slag after 40 h of reaction. Results demonstrate that Fenton-like oxidation catalyzed by BOF slag is a potential method to be able to remediate petroleum-hydrocarbon contaminated soils efficiently and effectively.

Maliszewska-Kordybach et al. (2009) has investigated that the concentrations 16PAHs compounds were determined in agricultural soils in Poland. The samples (n=216) were collected from the upper layer of arable land in the year 2005. Half of the samples represented typical rural areas, while the rest derived from the territories potentially subjected to the urban/industrial pressure of various intensity. The mean (geometric) content of individual compounds varied from 1 μg/kg for acenaphtylene to 55 μg/kg for fluoranthene with the highest contributions (11.6%–12.9%) of phenanthrene, fluoranthene and pyrene. Higher molecular weight PAHs (4 rings) were strongly linked mutually and with the total 16PAHs. They contributed substantially (73%) to the overall content of PAHs, which implies domination of anthropogenic sources. The most pronounced effect of spatial parameters corresponded to PAHs (4 rings), while lower molecular weight compounds showed more homogeneous concentration through the country.

Serrano et al. (2009) evaluated the soil biological activity and phytotoxicity to garden cress (Lepidium sativum L.) in a soil polluted with diesel fuel. The germination activity of the soil was seen to recover 200 days after the spill.

Peng et al. (2009) has concluded that phytoremediation of soils contaminated by organic chemicals was a challenging problem in environmental science and engineering. On the basis of identifying remediation plants from ornamentals, the remediation capability of Mirabilis Jalapa L. to treat petroleum contaminated soil from the Shengli Oil Field in Dongying City, Shandong Province, China was further investigated using a field plot experiment carried out in a greenhouse. The results showed that the average efficiency of removing total petroleum hydrocarbons (TPHs) by M. jalapa over the 127-day culture period was high, up to 41.61–63.20%, when the removal rate by natural attenuation was only 19.75–37.92%.

Lina et al. (2010) tried to an innovative bioremediation method. This study presented an innovative bioremediation method, the Systematic Environmental Molecular Bioremediation Technology (SEMBT), for biopiles by combining bioaugmentation and biostimulation with the reseeding strategy. The diesel-contamination was efficiently removed to about 70 by bioremediation of biopiles over a period of 28 days. A Field experimental result has showed that the residual TPH concentration in the complex biopile was reduced to less than 500mg TPH/ kg dry soil.

Tang et al. (2010) investigated the levels and sources of heavy metals (Cu, Cr, Cd, Pb, Zn, Hg and As) and persistent organic compounds including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in soils taken from Wenling, an emerging e-waste recycling city in Taizhou, China. The results suggested that most heavy metals exceeded the respective Grade II value of soil quality standards from State Environmental Protection Administration of China and also exceeded the Dutch optimum values.

Another study showed that the effects of two grass species (Festuca arundinacea Schreb. and Festuca pratensis Huds.), infected (E+) and non-infected (E-) by endophytic fungi (Neotyphodium coenophialum and Neotyphodium uncinatum, respectively) on the degradation of petroleum hydrocarbons in an aged petroleum contaminated soil has been investigated (Soleimani et al., 2010). The results was demonstrated that E+ plants contained more root and shoot biomass than E- plants and created higher levels of water-soluble phenols and dehydrogenase activity in the soil, while there was no significant difference in bacterial counts of planted soils. their results show that TPHs in retention time range of n-alkanes with C10–C25 chain lengths and TPH were more degraded in the rhizosphere of E+ plants compared to E- ones. Thus, grasses infected with endophytic fungi could be more efficient for removal of TPH from oil-contaminated soils.

In a study by Liu et al. (2010) PAHs in soil samples were collected in Beijing urban area. Soil samples taken from urban area of cultural education field samples, classical garden, business area, residential area, the roadside area and public green space. PAHs in roadside areas determined traffic emission properties. PAHs in the field of culture education was determined that the burning of coal. PAHs in other land uses came from mixed sources. Coal combustion and vehicle emission contributed about 46.0% and 54.0% to PAHs in Beijing’s urban soils, respectively. Risk assessment based on the Canadian soil criterion indicated a low contamination level of PAHs. However, higher contents in some sensitive land uses such as CEA and CG should draw enough attention.

Tang et al. (2011) investigated TPH contaminated soil samples collected from Shengli Oilfield of China. Toxicity analysis was carried out based on earthworm acute toxicity, plant growth experiment and luminescent bacteria test. The soil was contaminated bypetroleum hydrogcarbons with TPH concentration of 10.57%. From the experiment result, it was concluded that TPH content of 1.5% is considered to be a critical value for plant growth and living of earthworm and 0.5% will affect the activity of luminescent bacteria.

Thavamani et al. (2011) has been studied underpins the science and importance of metal bioavailability and speciation based site characterisation in mixed contaminated sites. A detailed elemental chemistry of the gas works site soils were discussed using different methods.

Park et al. (2011) that the use of humic acid (HA) to enhance the efficiency of phytodegradation of petroleum hydrocarbons in soil contaminated with diesel fuel was evaluated. The results suggested that humic acid (HA) could act as an enhancing agent for phytodegradation of petroleum hydrocarbons in soil contaminated with diesel fuel and heavy metals.

Taccari et al. (2012) evaluated the bioremediation of diesel-contaminated soil. Used laboratory scale bioreactors were investigated for 120 days. Results showed that the addition of compost plus a bacterial consortium caused a progressive increase in both heterotrophic cultivable aerobic bacteria and presumptive Pseudomonas.

Santos et al. (2012) was investigated that soil microcosms contaminated with crude oil with or without chromium and copper were monitored over a period of 90 days for microbial respiration, biomass, and for dehydrogenase, lipase, acid phosphatase, and arylsulfatase activities. A significant difference was observed for biochemical activities and microbial community structures between the microcosms comprised of uncontaminated soil, soil contaminated with crude oil and soil contaminated with crude oil and heavy metals.

Gong (2012) has studied the remediation of weathered crude oil-contaminated soil by biostimulation of indigenous microbes through addition of peanut hull as bulking agent was conducted in laboratory. The results showed that, after bioremediation for 20 weeks, reduction of total petroleum hydrocarbons (TPHs) by 88.9% was observed in the combined treatment compared with 55.1% in the biological treatment alone.

Balachandran et al. (2012), degrading Streptomyces sp. isolate ERI-CPDA-1 was been shown recovered from oil contaminated soil in Chennai, India. The degradation efficiencies were examined by GC-FID and the results showed that the isolate could remove 98.25% diesel oil, 99.14% naphthalene and 17.5% phenanthrene in 7 days at 30 º C (0.1%).

Zhang et al. (2012) has investigated that a phytoremediation potential of emergent wetland species may be influenced by co-contamination by metals and polynuclear aromatic hydrocarbons (PAHs) in soils. The results have indicated that it is feasible to use wetland species for phytoremediation of soil cocontaminated with Cd and PAHs, but further work in naturally have contaminated soils under field conditions is needed.

CHAPTER FOUR
ANALYTICAL METHODS AND EXPERIMENTAL SET UP

The sampling procedures for the soils, materials used for the study, the methods of the analysis, and the properties of the experimental setup are described in this chapter.

4.1 Analytical Methods Preparation Sampling of Soil Samples

Agricultural soils obtained for the study are analyzed for the characterization studies. Approximately 300 kg of agricultural clean soil is obtained from a 60 year old olive plantation close to Kaynaklar Village, Buca in Summer, 2008. It is informed that the olive plantation is a belonging of a family for more than 3 generations and none of the soil conditioners, fertilizers, or pesticides have been applied to neither the soil nor the trees for last 4 decades. The soil was collected from the top 20 cm of the soil and it is stored in plastic bags at room temperature until it is prepared for the further use and analysis.

In this study, the other different soil type samples are used. Kütahya soil obtained for the study is analyzed for the characterization studies. Example of a stream, river sand that was Turgutlu in İzmir. Other examples of sand taken from Ayvalık Sarımsaklı of the beach in Balkesir. Examples washed and eliminated. Sand samples obtained for the study are analyzed for the characterization studies.

At the laboratory, the samples were placed in zip lock plastic bags after they are dried at 65 ºC, screened through a 2 mm sieve to remove larger fraction, and homogenized. In the table below, the laboratory works and analysis completed in soil are listed in order.

4.1.1 Analysis Techniques

4.1.1.1 General Characterization Studies of Soil Samples

4.1.1.1.1 pH. The pH values of the soil samples were determined by using wet samples according to the EPA Method 9045 C (USEPA, 1995). 20 g of soil samples was vigorously mixed with 20mL of distilled water for 5 minutes and centrifuged at 4000 rpm for 10 minutes. Then, the pH value of the supernatant was measured. NUVE NF 815 centrifuge and HANNAH HI 8314 pH meter was used for the experiments.

4.1.1.1.2 Water Content. Soil water content was determined via gravimetric analysis by drying the wet soil samples overnight at 105ºC. MEMMERT Loading Modell 100-800 drying oven was used for this process. The moisture content of the sample was determined gravimetrically by using the difference between the weight of wet and dry samples.

4.1.1.1.3 Organic Matter Content. The determination of organic matter content of the soil samples were conducted according to the Standard Methods (Franson et al., 1992). The dried samples were combusted at 500±50ºC for 2 hours and differences between the initial and final weights were used to determine the organic matter content of dry portion. MEMMERT LM 100-800 furnace was used for the experiments.

4.1.1.1.4 Total Petroleum Hydrocarbon (TPH) Analysis. Eluate: According to the EPA Method 1310, 160 ml of distilled water was added to 10 grams of dry material sediments. The pH of the mixture was decreased to 5±0.2 by adding 0.5 N glacial acetic acid. The mixture was agitated for 24 hours and analyzes were done in the filtered and centrifuged supernatant.

EPA Method 3550 is modified for total Petroleum Hydrocarbons determinations. EPA Methods 3550 is a procedure for extracting nonvolatile and semi volatile organic compounds from solids such as soils, sludges, and wastes and it is a gravimetric method. Sample is extracted with hexane in an ultrasonic extractor according to EPA 3550B. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. Here, the described procedure is modified to allow fast measurements. A 5 g of sample was mixed with 5 g of Na_2SO_4, and extracted with 20 mL of hexane in an ultrasonic bath (84 Watt) for 10 minutes at 20ºC. After the extraction, 10 mL extract is transferred into a crucible and evaporated in a water bath (50ºC) under fume hood and the recovery rate is determined by gravimetric method.

4.1.1.1.5 Method of Soil Microorganisms. Nutrient Agar (Merck 1.05450). Multi-purpose general medium. Broth: 28.0 g/L is heated to be dissolved in distilled water is sterilized by autoclaving at 121 ° C. The sterile Petri dishes for 15 minutes 12.5 ml, poured into the other. The broth is clear and colorless, yellowish be stored in refrigerator for 2 months.

Standard Plate Count Method was used. Calculate the number of bacteria (CFU) per gram of sample by dividing the number of colonies by the dilution factor multiplied by the amount of specimen added to liquefied agar.

4.1.1.2 Particle Size Distribution, Specific Gravity, Porosity and Specific Bulk Density of the Soil Samples

4.1.1.2.1 Particle Size Distribution. The grain size distributions of the soil samples were determined by wet sieving using 4 sieves with different hole sizes. Particles larger than 2000µm were eliminated since they are counted as rock and gravels. Soil Samples were poured on the top of the sieve set and sieves were rocked to collect the fractions under the tap water (pH 7.8-8.2). Particles accumulated on the sieves were dried in the oven at 65ºC and dry soil samples with different size fractions were obtained on the sieves. Dry soil samples on the sieves were than swept and weight. The humidity of the sediment size fractions are considered in the following analysis. The detected size fractions are given with Table 4.1.

Table 4.1 Fractions used to determine grain size distribution

Fraction	**Soil Type**
2000 µm>F_A>300 µm	sand
600 µm>F_B>300 µm	sand
300 µm>F_C>90 µm	sand
90 µm>F_D>45 µm	sand + silt
45 µm>F_E	silt + clay

4.1.1.2.2 Specific Gravity. C128-07a Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate (ASTM C 128) was used.

4.1.1.2.3 Porosity. ASTM F1815 - 11 Standard Test Methods for Saturated Hydraulic Conductivity, Water Retention, Porosity, and Bulk Density of Athletic Field Rootzones was used for porosity analysis.

4.1.1.2.4 Specific Bulk Density. Bulk density is an indicator of soil compaction. It is calculated as the dry weight of soil divided by its volume. This volume includes the volume of soil particles and the volume of pores among soil particles. Bulk density is typically expressed in g/cm^3. ASTM D7263 - 09 Standard Test Methods for Laboratory Determination of Density (Unit Weight) of Soil Specimens was used.

4.1.1.2.5 Hydrometer. Hydrometer analysis is the procedure generally adopted for determination of the particle size distribution in a soil for the fraction that is finer than No.200 sieve size (0.0075 mm). The lower limit of particle-size determined by this procedure is about 0.001 mm (ASTM D 422).

4.1.1.2.6 Field Capacity. The amount of water held by soil was determined by saturating the soil until the added water starts to leak. By this way, the amount of water that the soil particles can hold against gravity can be determined.

4.1.1.3 XRF, XRD, and BET Results

*4.1.1.3.1 XRF (X-ray fluorescence).***Samples preparation of multi-element analysis by PEDXRF;** The samples were sun-dried and then ground into fine powder in an agate mortar. The samples were sieved to pass through of 200 μm, and then pressed into thick pellets of 32 mm diameter. USGS standards, GEOL, GBW 7109 and GBW-7309 equally pressed into pellets in a similar manner as the samples, and these used for quality assurance (Timothy and La, 1989; Johnson et al., 1999).

PEDXRF measurements; Multi-element concentration was determined by using polarized energy dispersive XRF. The spectrometer used in this study was Spectro XLAB 2000 PEDXRF spectrometer which was equipped with a Rh anode X-ray tube, 0.5 mm Be side window. The detector of spectrometer is Si (Li) by liquid N_2 cooled with resolution of < 150eV at Mn Kα, 5000 cps. Total analysis time for each addition element was 30 min. The sample measurements by PEDXRF mainly done by three types of targets (Stephens and Calder, 2004):

i. Light element targets of high density designed for efficient scattering and polarization of polychromatic source radiation. This target is suitable for the excitation of elements with Z > 22 and this target named as Barkla target.

ii. The second target is oriented crystal target, mosaic and single crystals; this will generate very intense source radiation of more specific energies. This target is suitable for light elements up to Z = 22 and can be named as Bragg targets.

iii. The last target is pure metal target, generate very intense near monochromatic X-ray sources, include unpolarized and polarized radiation scattered from the X-ray tube. This target is suitable for specific elements or small groups of adjacent elements. In addition this target is useful for generating Compton scatter peaks which can be used for matrix correction.

4.1.1.3.2 XRD (X-ray Diffraction). The XRD analysis of the samples was completed in Ankara University Department of Geological Engineering. The samples were, first powdered to 200 mesh (20 μm) and the analysis was done by using Inel -

Equinox 1000. Co-Ka1 tube producing a wave length of ג=1.788970 ◌̊A was used as X-Ray source. The peaks observed were evaluated with Search Match software program.

4.1.1.3.3 BET. The specific surface areas of the grain fractions were detected by multi point BET method. For surface area detection, the samples were degassed overnight at a temperature of 300°C in a vacuum oven prior to the analysis. Surface area analyses were carried out by the multi-point BET method by using N_2 adsorption with a Quantochrome NovaWin 2.

4.1.2 Soil Spiking with Diesel Oil

Typical diesel oil concentrations in contaminated soil have been reported in the range of 5000-15000 mg total petroleum hydrocarbons (TPH) (kg soil^{-1}) (Berry and Burton, 1997; Demque et al., 1997).

Target contaminant of this study was diesel oil, which was spiked at 10000 mg/kg sample on a dry basis. 12.5 ml diesel oil is dissolved in 150 ml petroleum ether and 1000 g of clean soil is soaked into the solution. The soil than mixed gently to obtain a homogeneous distribution of contaminant and placed in a tray under the fume hood to evaporate petroleum ether at room temperature for 12 hours.

To obtain the initial concentrations of 10000 ppm, 25000 ppm, and 100000 ppm diesel oil in the soil, it was added to the clean soil after dissolving the required amount of contaminant in petroleum ether. The solvent was, then, evaporated under the fume hood. It is foreseen that negligible amount of contaminant removed from the soil during evaporation period.

4.1.3 Soil Extraction & Pre-Concentration Methods

4.1.3.1 Ultrasonic Extraction

Sonication involves the use of sound waves to agitate a sample immersed in an organic solvent. The preferred approach is to use a sonic probe, although a sonic bath can also be used (Figure 4.1). The sample is placed in a suitable glass container and enough organic solvent is then added to cover the sample. The system is then sonicated for a short time-period, typically 3 min, using the sonic bath or probe. After extraction, the solvent containing the analyte is separated by centrifugation and/or filtration and fresh solvent added. The whole process is repeated three times and all of the solvent extracts are then combined (Dean, 2003). A typical procedure used for ultrasonic extraction is shown in Figure 4.2.

Figure 4.1 The Ultrasonic extraction system

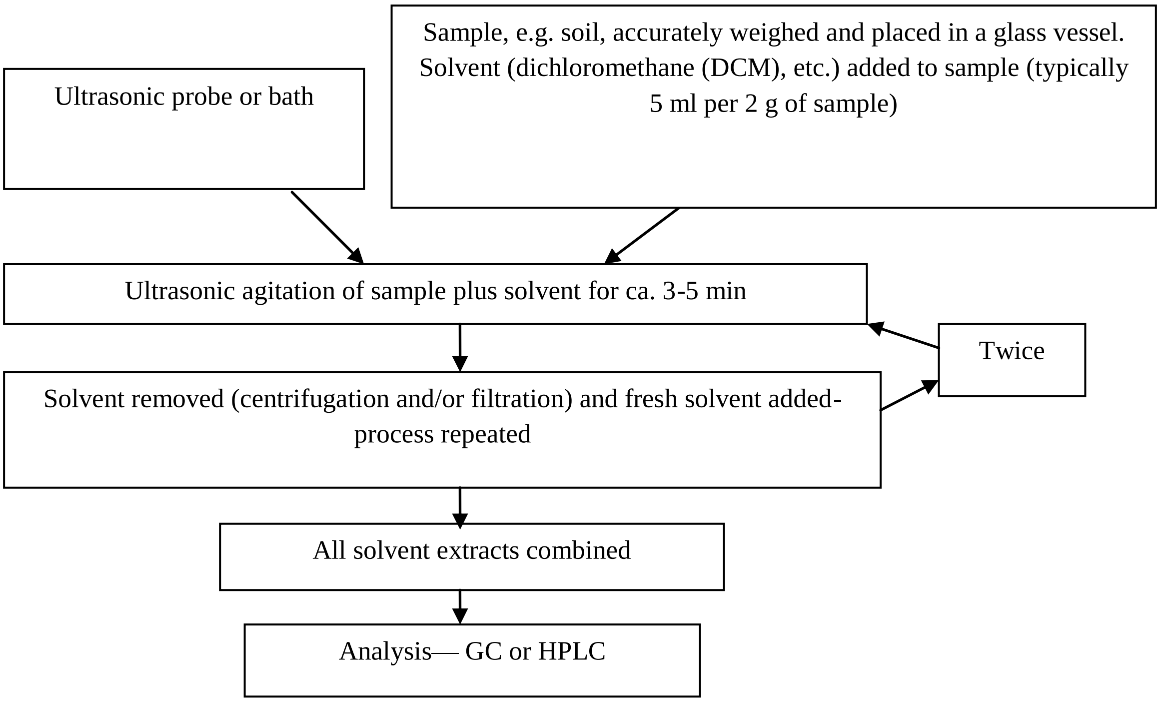


Figure 4.2 Typical procedure used for the ultrasonic extraction of solids

Extraction Conditions are as follows;
Sample: 2 g contaminated soil plus 2 g anhydrous sodium sulfate
Solvent: 5 ml dichloromethane (DCM)
Extraction time: 5 min.
Extraction power: 84 Watt
Extraction Temperature: 20°C
The analyze is duplicated.

4.1.3.2 Kuderna-Danish Evaporative Concentration

The Kuderna-danish evaporative condenser was developed in the laboratories of Julius Hyman and Company, Denver, Colorado, USA. This consists of an evaporation flask (500 ml) connected at one end to a Snyder column and the other end to a concentrator tube (10 ml) (Figure 4.3). The sample-containing organic solvent (200-300 ml) is placed in the apparatus, together with one or two boiling chips, and heated with a water bath. The temperature of the water bath should be maintained at 15-20 ºC above the boiling point of the organic solvent. The positioning of the apparatus should allow partial immersion of the concentrator tube in the water bath but also allow the entire lower part of the evaporation flaks to be bathed with hot vapour (steam). Solvent vapours then rise and condense within the Snyder column. Each section of this column consists of a narrow opening covered by a loose-fitting glass insert. Sufficient pressure needs to be generated by the solvent vapours to force their way through the column. Initially, a large amount of condensation of these vapours returns to the bottom of the Kuderna-Danish apparatus. In addition to continually washing the organics from the sides of the evaporation flask, the returning condensate also contacts the rising vapours and assists in the process of recondensing volatile organics. This process of solvent distillation concentrates the sample to approximately 1-3 ml in 10-20 min. Escaping solvent vapours are recovered by using a condenser and collection device. The major disadvantage of this method is that violent solvent eruptions can occur in the apparatus, thus leading to sample losses. ‘Micro-Snyder’ column systems can be used to reduce the solvent volume still further.

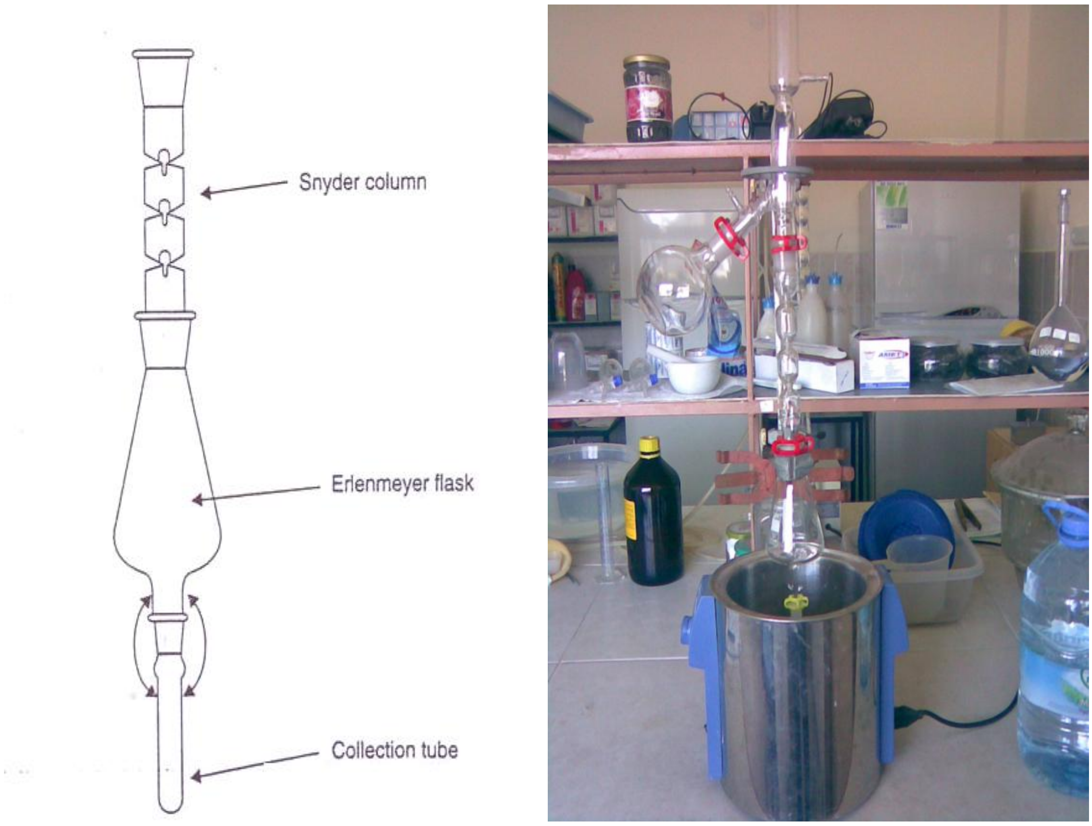


Figure 4.3 Schematic diagram of the Kuderna-Danish evaporative concentration condenser system

4.1.4 Total Petroleum Hydrocarbons (TPHs)

Water TPHs

The total petroleum hydrocarbons (TPH) in water samples were determined according to the Oil Grease Analysis in Standard Methods (5-41).

Modified EPA Method 3550B for TPHs determinations

EPA Method 3550 is a procedure for extracting nonvolatile and semi volatile organic compounds from solids such as soils, sludges, and wastes and it is a gravimetric method. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. Here, the described procedure is simplified to allow fast measurements. In our method, the soil is spiked with diesel oil as described in part 2.3.1, mixed with 5 g of Na_2SO_4, and extracted with 20 ml of hexane in an ultrasonic bath (84 Watt) for 10 minutes at 20°C. This step is repeated after the hexane is removed, and the solvents from first and second steps of the extraction are then combined. After the extraction, the solvent containing dissolved contaminant is allowed to be evaporated in a water bath (50ºC) under the fume hood and the TPHs is determined by gravimetric method.

4.1.5 Polycyclic Aromatic Hydrocarbons Analysis (PAHs)

For GC-MS analysis of PAHs, soil extractions are completed according to the Ultrasonic Extraction.

The first step of cleanup procedure is the addition of 0.5 ml “Internal Standard Mix (ISM) solution” into the extracts obtained from the extraction procedures and also into the solutions prepared.

> *Standard mix is obtained from AccuStandard (Internal Standard Mix Z-014J) and contains 4mg/ml each of the Acenaphthene-d10, Chrysene-d12, 1,4 Dichlorobenzene-d4, Naphthalene-d8, Perylene-d12, and Phenanthrene-d10*

> *in DCM. "ISM solution" is prepared by diluting 1 ml ISM with hexane to 250 ml volume.*

Since internal standards are passed all steps of the clean up procedure thoroughly, the concentrations of each chemical in the final volume are the same and equal to 1600 ng/ml.

The cleanup column is prepared according to the EPA Method 3610B.

> *Cleanup column contains 2 g of Na_2SO_4, 2 g of Alumina humidified with 120 µl of deionized water, 3 g of Siliclylic acid humidified with 100 µl of deionized water, and glass wool from top to the bottom.*

The cleanup column is flushed with 20 ml DCM and 20 ml petroleum ether prior to the new cleanup and the solvent collected from the bottom part is wasted. <u>2 ml</u> <u>of extract</u> (containing ISM solution) is added to the cleanup column (Figure 4.4).

Figure 4.4 A cleanup column

When the cleanup starts, first 20 ml petroleum ether is filtered through the column and the strain (that contains PCBs) is collected in a 40 ml vial. Then, 20 ml DCM is added to the column and the strain containing PAHs is collected in another 40 ml vial. This strain is transferred into the Kuderna-Danish Apparatus (water temperature 65°C, DCM boiling point: 40°C) and the volume of the extract reduced to 10 ml. 10 ml hexane was added to the system once more and the volume is reduced to 5 ml final volume by arranging the water bath to 65°C until the first 10 ml collected (for DCM collection) and then by arranging it to 95°C (Hexane boiling point: 69°C) for hexane collection. 1 ml of final volume is placed in a 1.8 ml glass vial and used for GC-MS analysis.

All extracts were analyzed for 15 PAHs including acenaphthylene, acenaphthene (ACT), fluorine (FLN), phenanthrene (PHE), anthracene (ANT), carbozole (CRB), fuoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BahiP) with a gas chromatograph (GC) (Agilent 7890A) equipped with a mass selective detector (Agilent 5975C inert MSD). A capillary column (HP5-ms, 30 m, 0.25 mm, 0.25µm) was used. The initial oven temperature was held at 50ºC for 1 min, was raised to 200ºC at 25 ºC min^{-1}and from 200 to 300 ºC at 8 ºC min^{-1}, and was held for 5.5 min. the injector, ion source, and quadrupole temperatures were 295, 300, and 180 ºC, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 mL min^{-1}, 45 cm s^{-1} linear velocity). The MSD was run in selected ion monitoring mode. Compounds were identified on the basis of their retention times; target and qualifier ions quantified using the internal calibration procedure.

4.1.6 Soil Amendments (Compost)

Compost sample were taken from Solid Waste Recycling and Composting Facility in Istanbul. The characterization of compost is determined. The results are given in Chapter 5.

CO_2 productions in the slurry reactors are also measured by titrating NaOH(0.1 M) solutions with HCl(0.1 M) after each sampling.

4.2 Experimental Set Up

4.2.1 Inhibition of Diesel Oil on Soil and Compost Bacteria

The effect of diesel oil contamination on soil and compost bacteria was investigated. First, the initial bacteria counts of clean Kaynaklar soil, compost used in the experiments and the compost-soil mixture (1/10) were detected, as well as the Kaynaklar soil and compost-soil mixture (1/10) contaminated with different diesel concentrations. Soil diesel concentrations of 2500 ppm, 5000 ppm, 10000 ppm, 25000 ppm, and 100000 ppm were studied. The bacteria amounts of clean and contaminated soil, compost, compost soil mixtures were counted after 48 96, 192, and 384 hours of incubation at 28°C. Standard Plate Count of Soil Bacteria was used. By this time the colony was read. Calculate the number of bacteria (CFU) per gram of sample by dividing the number of colonies by the dilution factor multiplied by the amount of specimen added to liquefied agar.

4.2.2 Slurry System Remediation

Flotation is a common physical method for the treatment of oily wastewaters. Mostly, the system is agitated by dispersed air to stimulate the oil molecules to come together to form oil droplets. Additionally, air helps these droplets to move upwards and floating on the surface of the water. The method can also be used to separate the LNAPLs that attach on to the soil particles and fill the pores, especially for high concentrations are considered.

Here, the system was operated in glass flasks equipped with Teflon caps (Figure 4.5). And the agitation was obtained by an orbital shaker.

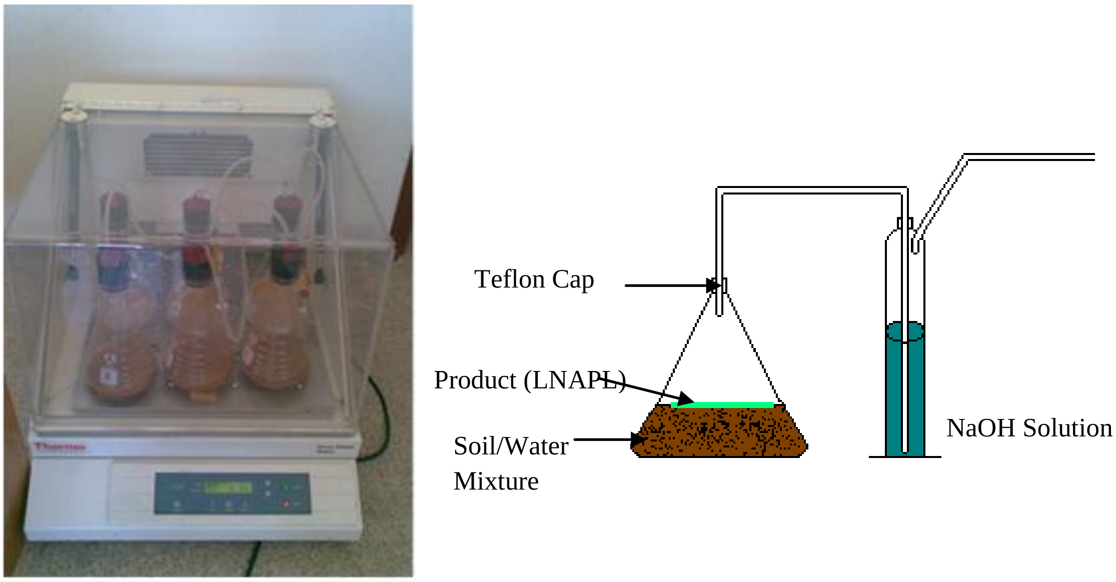


Figure 4.5 The slurry reactor system used for the study

The initial and final concentrations of NAPLs in the soil were used to determine the flotation efficiency of the system. The soil was extracted with dichloromethane and contaminants were detected in the extract by GC-MS. The total petroleum hydrocarbons in the water phase were determined gravimetrically by liquid/liquid extraction of supernatant with hexane.

The system was tested for the initial NAPLs concentrations, contact time of contaminant with soil, different solid/liquid ratios, pH, and the presence or absence of microorganisms. The absence of soil bacteria was obtained by adding 3000 ppm $HgCl_2$ to the soil and supplying bacterial inhibition.

4.2.2.1 Slurry System without Soil Amendment

In that case, aeration will not be an available agitation way for the system, because of high volatilities of the contaminants.

4.2.2.1.1 The Effect of Solid/Liquid Ratio on Soil Remediation in Slurry Systems. The slurry reactors with different solid/liquid ratios were used and as 1/5, 1/10 and 1/20 solid/liquid ratios was established in the sets (Table 4.2). The contaminated Kaynaklar soil that has 100000 mg/kg diesel was used with 1/5, 1/10, and 1/20 solid/liquid ratios in slurry systems. The experiments were conducted by using sterilized soil to eliminate the possible effect of bacterial degradation on the remediation of NAPLs.

Table 4.2. Mass balance and solid/liquid ratios in the experimental sets

Solid/Liquid Ratios	Solid, mL	Liquid, mL	Total volume, mL
1/5	50	250	300
1/10	27	270	300
1/20	14	286	300

The soil microbial mass was inhibited by using 3000 mg/kg $HgCl_2$ and autoclaving prior to the diesel spiking, and the contaminated soils were immediately placed in to the remediation systems after spiking. Additionally, used soil in this set was autoclaved for 15 minutes at 121°C.

The slurry phase experiments were carried out in 1000 ml flasks with 300 ml reaction volume. The slurry phase experiments were conducted in shaking incubator (Thermo Electron 420) at 100 rpm to avoid death volumes and settling of soil particles. Temperature was maintained at 25 °C during the experiments.

All slurry reactors were operated for 8 hours. 10 mL samples were taken from the mixture in the slurry reactors at the end of the each two hours and the parameters of TPHs, pH and PAHs are analyzed in the soils. Each analysis is duplicated and the mean values are given in Chapter 6.

4.2.2.1.2 The Effect of Presence of Light, the Soil Properties, and the Presence of Local Bacteria on Soil Remediation in Slurry Systems. Here, it is aimed to investigate and discuss the effects of soil type, presence of light, and presence of local bacteria on the efficiency of slurry soil remediation systems. The contaminated Kaynaklar soil and Beach sand having 25000 mg/kg diesel was used with a 1/5 solid/liquid ratio in the slurry systems studied in this part. The experiments were conducted by using soil with local bacteria with a control of sterilized soil under the light and dark medium (Table 4.3). Target contaminant of this research was diesel oil, which were spiked at the levels of 10000 and 25000 mg/kg to the samples on a dry basis. The microbial activities in soil samples were completed in three different sets as follows: i) Natural soil microbial activities, ii) The soil which $HgCl_2$ added to inhibit microbial activities and autoclaved.

Table 4.3 Mass balance and solid/liquid ratio in the experimental sets

		Solid/Liquid Ratios	Solid, ml	Liquid, ml	Total volume, ml
Microorganisms (Natural)	Beach sand (Light)	1/5	50	250	300
	Beach sand (Dark)	1/5	50	250	300
	Kaynaklar soil (Light)	1/5	50	250	300
	Kaynaklar soil (Dark)	1/5	50	250	300
Microorganisms (Inhibited+Autoclaved)	Beach sand (Light)	1/5	50	250	300
	Beach sand (Dark)	1/5	50	250	300
	Kaynaklar soil (Light)	1/5	50	250	300
	Kaynaklar soil (Dark)	1/5	50	250	300

The soil microbial mass was inhibited by using 3000 mg/kg $HgCl_2$ and autoclaving prior to the diesel spiking, and the contaminated soils were immediately placed in to the remediation systems after spiking.

The slurry phase experiments were carried out in 1000 ml flasks with 300 ml reaction volume and were conducted in a shaking incubator (Thermo Electron 420) at 90 rpm to avoid death volumes and settling of soil and sand particles. Temperature was maintained at 25 °C during the experiments.

All slurry reactors were operated for 168 hours (7 days). 10 mL samples were taken from the mixture in the slurry reactors at 8 and 168 hours and the parameters of TPHs, number of microorganisms, and pH are analyzed in the soils. CO_2 productions in the slurry reactors are also measured by titrating NaOH (0.1 M) solutions with HCl (0.1 M) after each sampling. Each analysis is duplicated and the mean values are given in Chapter 6.

4.2.2.1.3 The effect of Soil Particle Size on Soil Remediation in Slurry Systems. The systems were operated by using coarse particles (2000-300 μm), medium particles (300-45 μm), and fine particles (<45μm) as well as bulk soil. The contaminated Kaynaklar soil having 100000 mg/kg diesel was used with a 1/1 solid/liquid ratio in the slurry systems studied here. The experiments were conducted by using soil with local bacteria with a control of sterilized soil in dark environment. The number of bacteria in the soils was detected throughout the remediation period and reported, as well as produced CO_2 from the reactors. The systems were operated for 60 days. Soils were sampled from the reactors 15, 30, 45, and 60 days. The parameters of water content, pH, TPHs, and number of microorganisms are analyzed in the soils. CO_2 productions in the reactors are also measured by titrating final NaOH solutions with HCl. Each analysis is duplicated and the mean values are given in next section.

4.2.2.2 Slurry System Remediation with Soil Amendment

4.2.2.2.1 The effect of Initial Contaminant Concentration and Compost to Soil Ratio on Slurry Bioremediation of Diesel Contaminated Soils. The Kaynaklar soil used in the slurry systems are contaminated with 25000 ppm and 100000 ppm diesel. The soil amount in the systems 100 g, and three different compost amounts were applied as compost-soil ratio; 30g compost/100g soil, 20g compost/100g soil, and 10g compost/100g soil (Table 4.4). For keeping the mass of solids constant in the systems, 10 and 20 grams of glass beads were substituted to the systems with 20 g and 10 g of compost content, respectively. The control sets with soils having local bacteria and sterilized soils were operated only with 30g of glass beads substitution instead of compost.

For operating the reactors as remediation systems, the survival of local microorganisms is allowed. Control Reactors were operated as a thermal volatilization system and 3000 mg/kg $HgCl_2$ was applied to the soil before it was placed into the reactor, to inhibit microbial activity. Additionally, the blanks were autoclaved for 45 minutes at 121°C before contaminated. The reactors were operated for each set to investigate the process by opening each of them 15 days apart.

Table 4.4 Mass balance and solid/liquid ratio in the experimental sets

The concentration of pollution	**Details**
25000 ppm	100 g of the contaminated soil + 30 g of compost+ 100 ml of water
25000 ppm	100 g of the contaminated soil + 20 g of compost+ 10 g of glass beads (3-4 mm) + 100 ml of water
25000 ppm	100 g of the contaminated soil + 10 g of compost+ 20 g of glass beads (3-4 mm) + 100 ml of water
25000 ppm	100 g of the contaminated soil + 30 g of glass beads (3-4 mm) + 100 ml of water
25000 ppm	100 g of the contaminated soil sterilized+ 100 ml of water
100000 ppm	100 g of the contaminated soil + 30 g of compost+ 100 ml of water
100000 ppm	100 g of the contaminated soil + 20 g of compost+ 10 g of glass beads (3-4 mm) + 100 ml of water
100000 ppm	100 g of the contaminated soil + 10 g of compost+ 20 g of glass beads (3-4 mm) + 100 ml of water
100000 ppm	100 g of the contaminated soil + 30 g of glass beads (3-4 mm) + 100 ml of water
100000 ppm	100 g of the contaminated soil sterilized+ 100 ml of water

Each of the reactors was operated for 60 days. Soils were sampled from the reactors 15, 30, 45, and 60 days. The parameters of water content, pH, TPHs, and number of microorganisms are analyzed in the soils. CO_2 productions in the reactors are also measured by titrating final NaOH solutions with HCl. Each analysis is duplicated and the mean values are given in next section.

4.2.2.2.2 The effect of Contamination Age on Soil Remediation in Slurry Systems with Soil Amendment. 10000 ppm and 25000 ppm diesel spiked and two years- aged Kaynaklar soils with soil- liquid ratio of 1/1 and compost-soil ratio (C/S) of 10g compost/100g soil were used in slurry systems. The systems were aerated and operated for 60 days. The controls with aged sterilized soil and the aged soil with local bacteria were also operated. pH, CO_2 production, bacterial counts, TPHs and

PAHs are followed during the treatment period and the results are analyzed in the soils.

4.2.3 Fix Bed Bioremediation

In this part of the thesis three different sets were studied. The details of the used Fixed Bed Systems were given in Figure 4.6.

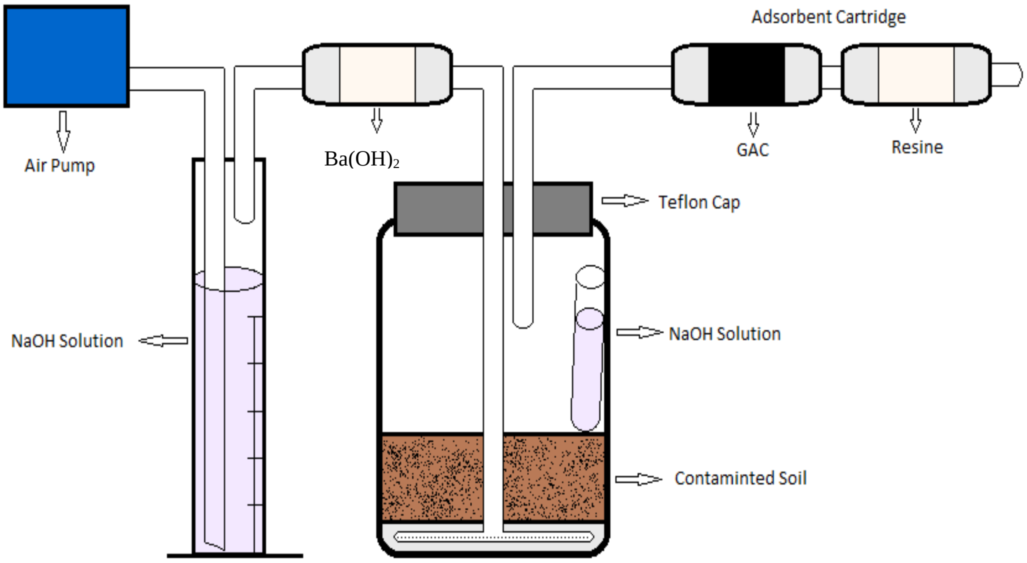


Figure 4.6 The details of the reactor systems

The experiments were conducted in 1 L reactors under 25°C or 40°C where the temperature was kept constant in an incubator. Each system has a reactor body with a 200 g soil volume and it is installed with an aeration trench. A glasswool bottom line was used to distribute air evenly to the soil matrix. Inlet air obtained by a pump is passed through NaOH to strip the including CO_2. A 0.5 M NaOH solution in a 10 mL test tube to trap CO_2 produced by microbial activities was placed in to the flasks. Finally, outlet air from the reactor was passed through GAC and Resin cartridges, respectively, to collect the degradation products.

System performance was determined by the difference between the initial and final TPHs concentration in the soil. Solid/liquid extraction with dichloromethane solvent was completed and GC/MS analysis of the extract was done for finding the PAHs remediation efficiency.

For determining the decomposition products, GAC and Resin cartridges were flushed by dichloromethane and the extract was analyzed by using GC/MS. Produced CO_2 by the microbial mass were determined by the titration of NaOH solution with HCl at the end of the treatment period.

In this section were conducted with whether the existence of soil native bacteria are allowed or not, as well as the presence of additional substrate and bacteria obtained by compost addition. By this way, the effects of soil water content, initial contaminant concentration, temperature, contamination age, and soil type on thermal volatilization and bioremediation are investigated.

4.2.3.1 Fixed Bed Soil Remediation by Thermal Volatilization

The efficiency of thermal volatilization on NAPLs treatment from the soil was investigated. For this purpose the soil native bacteria was inhibited by autoclaving and $HgCl_2$ addition to detect the net volatilization of NAPLs. Parallel sets without aeration (blanks) were executed for comparing the results. An aeration rate of 0,025 L/min (200 L/min.m^3 of soil) was obtained for each of the reactors.

4.2.3.1.1 The effect of Water Content, Initial Contaminant Concentration, and Temperature on Soil Remediation by Thermal Volatilization in Time. Target contaminant of this research was diesel oil, which were spiked at 10000, 25000 and 100000 mg/kg samples on a dry basis. Experimental apparatus was placed in an incubator in which temperature was maintained at 25 °C and 40°C to minimize the effect of exterior temperature variation. The field capacity of the Kaynaklar soil used for the experiments is (27%). For remediation studies, two different level of water content (as 20% and 40%) was applied to the soil to observe the effect of water content on the treatment efficiency. Each reactor was loaded with 200 g of humidified soil which was contaminated to obtain 10000 or 25000 ppm diesel oil on dry basis.

For operating the reactor as a bioremediation system, the survival of local microorganisms is allowed. Control Reactor was operated as a thermal volatilization system and 3000 mg/kg $HgCl_2$ was applied to the soil before it was placed into the reactor, to inhibit microbial activity.

Each of the reactors was operated for 60 days. Soils were sampled from the reactors 15., 30., 45., and 60. days and the parameters of water content, pH, TPHs, and PAHs and are analyzed in the soils. Each analysis is duplicated.

4.2.3.1.2 The effect of Soil Properties. Target contaminant of this research was diesel oil, which was spiked at 25000 mg/kg samples (Kutahya soil, and River sand) on a dry basis. Experimental apparatus was placed in an incubator in which temperature was maintained at 25 °C to minimize the effect of exterior temperature variation. The field capacities of the Kutahya soil, and River sand, used for the experiments are 46%, and 21% respectively. For bioremediation studies, two different level of water content (as 20% and 40%) was applied to the soil to observe the effect of water content on the treatment efficiency. Each reactor was loaded with 200 g of humidified samples which was contaminated to obtain 25000 ppm diesel oil on dry basis. An aeration rate of 0,025 L/min (200 L/min m^3 of soil) was obtained for each of the reactors.

Control Reactors were operated as a thermal volatilization system and 3000 mg/kg $HgCl_2$ was applied to the soil before it was placed into the reactor, to inhibit microbial activity. Additionally, the blanks were autoclaved for 45 minutes at 121°C before contaminated. The reactors were operated for each set to investigate the process by opening each of them 15 days apart.

Each of the reactors was operated for 60 days. Soils were sampled parameters of water content, pH, and TPHs are analyzed in the soils.

4.2.3.1.3 The effect of Contamination Age. The investigation of the effect of contamination age on the thermal volatilization of NAPLs from the soils, 1 L reactors was used in an incubator at 25°C. The initial Kaynaklar soil diesel concentrations of 10000 ppm, 25000 ppm, and 100000 ppm were examined with initial water content of 40%. Water content, pH, and change in TPHs levels in the soils were followed during the operational period of 60 days.

4.2.3.2 Fixed Bed Soil Bioremediation

The efficiency of bioremediation on NAPLs treatment from the soil was investigated. For this purpose the soil having native bacteria was used by addition of compost (1/10 of compost/soil ratio on dry basis) as soil amendment. Parallel sets with sterilized soils and the soils with local bacteria were also executed for comparing the results. The field capacity of the soil used for the experiments is (27%). For bioremediation studies, two different level of water content (as 20% and 40%) was applied to the soil to observe the effect of water content on the treatment efficiency. An aeration rate of 0,025 L/min (200 L/min.m^3 of soil) was obtained for each of the reactors.

4.2.3.2.1 The Effect of Water Content, Initial Contaminant Concentration, Temperature, and Presence of Soil Amendment in Bioremediation of NAPLs Contaminated Soils. The experiments were conducted in 1 L reactors under 25°C or 40°C where the temperature was kept constant in an incubator. The initial soil diesel concentrations of 10000 ppm, 25000 ppm, and 100000 ppm were examined as well as initial water contents of 20% and 40%. The TPHs and PAHs removal from the soils were observed with local bacteria as well as compost amendment. Water content, pH, CO2 generation, bacterial counts, changes in TPHs and PAHs concentration in the systems were followed during the operational period of 60 days. The system with 100000 ppm IDC was operated only with 40% water content and the PAHs were measured only in the system with 25000 ppm IDC. The compost amendment was supplied with a compost-soil ratio of 1/10.

Target contaminant of this research was diesel oil, which were spiked at 10000, 25000 and 100000 mg/kg samples (Kaynaklar soil) on a dry basis. In this set compost addition to the soil was applied as the total mass of soil/compost mixture will be the same (200 g). The compost/soil ratio was decided as 1/10. The water content, organic matter content, and the pH level of the compost used were 25.7%, 35.45% dw, and 8.06, respectively. Experimental apparatus was placed in an incubator in which temperature was maintained at 25 °C and 40°C to minimize the effect of exterior temperature variation. The field capacity of the soil used for the experiments is (27%). For bioremediation studies, two different level of water content (as 20% and 40%) was applied to the soil to observe the effect of water content on the treatment efficiency. An aeration rate of 0,025 L/min (200 L/min m^3 of soil) was obtained for each of the reactors.

For operating the reactors as bioremediation systems, the survival of local microorganisms is allowed. Control Reactors were operated as a thermal volatilization system and 3000 mg/kg $HgCl_2$ was applied to the soil before it was placed into the reactor, to inhibit microbial activity. Additionally, the blanks were autoclaved for 45 minutes at 121°C before contaminated. The reactors were operated for each set to investigate the process by opening each of them 15 days apart.

Each of the reactors was operated for 60 days. Soils were sampled from the reactors 15., 30., 45., and 60. days and the parameters of water content, pH, TPHs, and number of microorganisms are analyzed in the soils. CO_2 productions in the reactors are also measured by titrating final NaOH solutions with HCl. Each analysis is duplicated and the mean values are given in section 3.

4.2.3.2.2 The effect of Soil Properties on the Remediation of NAPLs in Fixed Bed Bioremediation Systems with Compost Amendment. Target contaminant of this research was diesel oil, which was spiked at 25000 mg/kg samples (Kutahya soil, and River sand) on a dry basis. In this set compost addition to the soil was applied as the total mass of sample/compost mixture will be the same (200 g). The compost/sample ratio was decided as 1/10. The water content, organic matter content, and the pH level of the compost used were 25.7%, 35.45% dw, and 8.06, respectively. Experimental apparatus was placed in an incubator in which temperature was maintained at 25 °C to minimize the effect of exterior temperature variation. The field capacities of the Kutahya soil, and River sand, used for the experiments are 46%, and 21% respectively. For bioremediation studies, two different level of water content (as 20% and 40%) was applied to the soil to observe the effect of water content on the treatment efficiency. Each reactor was loaded with 200 g of humidified samples which was contaminated to obtain 25000 ppm diesel oil on dry basis. An aeration rate of 0,025 L/min (200 L/min m^3 of soil) was obtained for each of the reactors.

For operating the reactors as bioremediation systems, the survival of local microorganisms is allowed. Control Reactors were operated as a thermal volatilization system and 3000 mg/kg $HgCl_2$ was applied to the soil before it was placed into the reactor, to inhibit microbial activity. Additionally, the blanks were autoclaved for 45 minutes at 121°C before contaminated. The reactors were operated for each set to investigate the process by opening each of them 15 days apart.

Each of the reactors was operated for 60 days. Soils were sampled from the reactors 15., 30., 45., and 60. days and the parameters of water content, pH, TPHs, and number of microorganisms are analyzed in the soils. CO_2 productions in the reactors are also measured by titrating final NaOH solutions with HCl. Each analysis is duplicated and the mean values are given in section 3.

4.2.3.2.3The effect of Contamination Age on NAPLs Remediation in Fixed Bed Bioremediation Systems with Compost Amendment. In this part of the study, for investigating the soil type effect on bioremediation, two other types of soils namely; Kutahya soil and River sand were used with compost amendment. The initial soil diesel concentration of 25000 ppm was applied with 20% and 40% soil initial water content at 25°C. The systems were aerated as described in Chapter 4. Water content, pH, CO2 production, bacterial counts, TPHs and PAHs levels were followed during the 60 days of operation time.

CHAPTER FIVE

PROPERTIES OF THE SOILS AND COMPOST USED IN THE STUDY

In this chapter, the initial properties of the soils and compost used in the content of the thesis were presented.

5.1 The Initial Properties of Soil Samples

Four different types of soil samples were used during the studies. The soils were collected from an agricultural area in Kaynaklar-Izmir, another agricultural area in Kutahya, from a river bed in Torbali (sand), and from Sarmisakli beach in Ayvalik (sand). Soil samples were sieved from 2 mm, and particles smaller than 2 mm were used for the analysis, except water content. pH, organic matter content (OM), and total petroleum hydrocarbons (TPH's), parameters were determined in dry samples, initially. The particle size distribution curves of the samples were also formed to define soils' texture according to the hydrometer analysis, as well as their specific gravities, porosity and bulk density. Field capacities of the soils were also determined. In addition, the bulk chemical composition of the soils and the contained elemental levels were detected by XRF analysis, the mineral compositions of the soils were identified and quantified by XRD method, and the specific surface areas of the soils were specified by BET analysis.

5.1.1 General Properties of Soil Samples

General properties of soil samples used in the study are given in Table 5.1.

Table 5.1 General properties of the soils used in the study

Soil Name	pH	WC, %	OM, % dw	Background TPH's, ppm	Number of microorganisms, 10^{14}/g soil
Kaynaklar Soil	6.76	1.00	4.98	565.66	273
Kutahya Soil	8.20	16.75	13.93	240.23	45
Beach Sand	7.73	0.10	0.55	80.08	50
River Sand	7.76	3.02	0.95	164.98	98

d*Dissolvable- EPA 1310

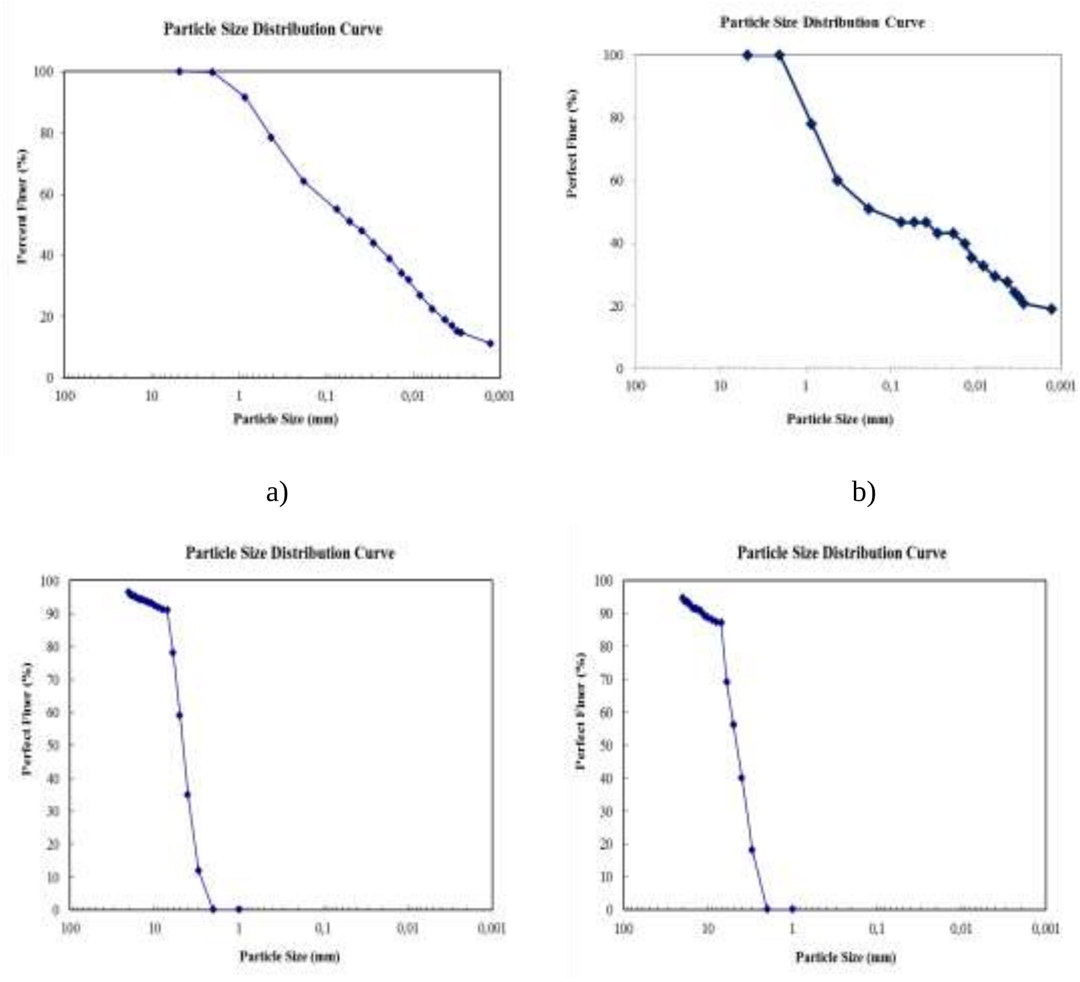
The pH levels of the samples are in neutral interval except Kutahya soil which express alkaline character. This may be related with its higher organic matter content (13.93% dw) linked with the residues from legumes grown in this soil for decades. Kaynaklar soil has 4.98% dw organic content, which is relatively higher than sand (0.55 % for beach sand and 0.95 for river sand) samples. In this area, olive has been grown at least for last 60 years. The background TPHs levels detected in samples may be related with the intensity of the mechanical agricultural activities in the land and the surrounding industrialization.

The initial bacterial populations in the soils were also detected. It was found that Kaynaklar soil has the largest microbial population ($273*10^{14}$/g), and it is followed by River sand ($98*10^{14}$/g). The number of bacteria found in Kutahya soil ($50*10^{14}$/g) and Beach sand ($45*10^{14}$/g) are similar to each other.

5.1.2 Particle Size Distribution, Specific Gravity, Porosity and Specific Bulk Density of the Soil Samples

The results of the hydrometer analyses completed for the soil samples are given in Figure 5.1.

The soil texture obtained from hydrometer analysis and the soil porosities can be summarized as in Table 5.2.



a) b)

c) d)

Figure 5.1 Hydrometer results for soil samples; a) Kaynaklar soil, b) Kutahya soil, c) Beach sand, and d) River sand

Table 5.2 The soil textures according to the hydrometer analysis

Soil Name	Sand/ Sandysilt	Silt	Clay	Porosity, % volume
	% dw			
Kaynaklar Soil	45.1	41.8	13.1	31.0
Kutahya Soil	53.3	27.7	19.98	33.8
Beach Sand	91.0	5.5	3.5	29.6
River Sand	87.0	7.5	5.5	28.6

Kutahya is the soil with the highest clay content (19.98%) according to the particle size distribution, which is followed by Kaynaklar (13.1%). Sand samples clay levels are much lower as it is expected. The porosities of the samples are close to each other with the highest value of 33.8% in Kutahya soil, but since the analysis were completed with disturbed soil samples the porosity of Kutahya soil may be much higher than the detected level.

The specific gravity, bulk density and field capacity of soils are also summarized in Table 5.3.

Table 5.3 The specific gravity, bulk density and field capacity of soils

Soil Name	**Specific gravity**	**Bulk density, g/cm^3**	**Field capacity, %**
Kaynaklar Soil	2.75	1.38	27.0
Kutahya Soil	2.44	1.03	46.0
Beach Sand	2.78	1.43	25.0
River Sand	2.70	1.51	21.0

Because of their high sand content, the sizes of the pores in beach and river sand samples are larger and the field capacities of these samples are much lower than Kaynaklar and Kutahya soil samples. Lower bulk density and specific gravity of Kutahya soil may be because of its high organic content. Here, it can be seen that the increasing bulk densities and specific gravities are directly correlated with decreasing organic content.

5.1.3 The Results from XRF, XRD, and BET Analysis

The “Diffraction Pattern Graphics” from XRD analysis of the soil samples are given in Figures 5.2-5.5. The results showed that, in sand samples, the dominant mineral is quartz with a share of over 60% and they are having minerals from carbonate group as the selector mineral group from other soil samples. The clay

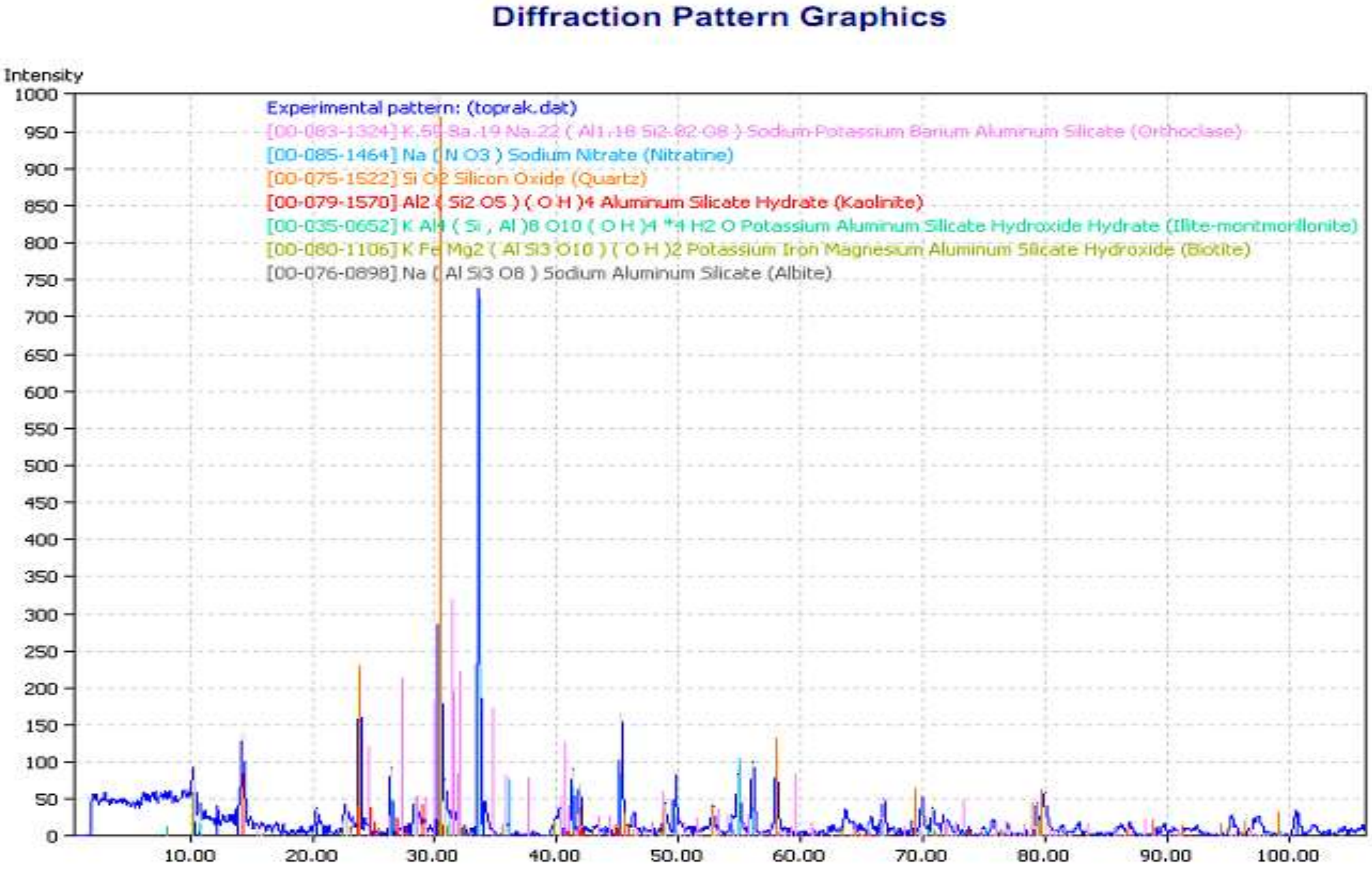


Figure 5.2 XRD Analysis of Kaynaklar Soil

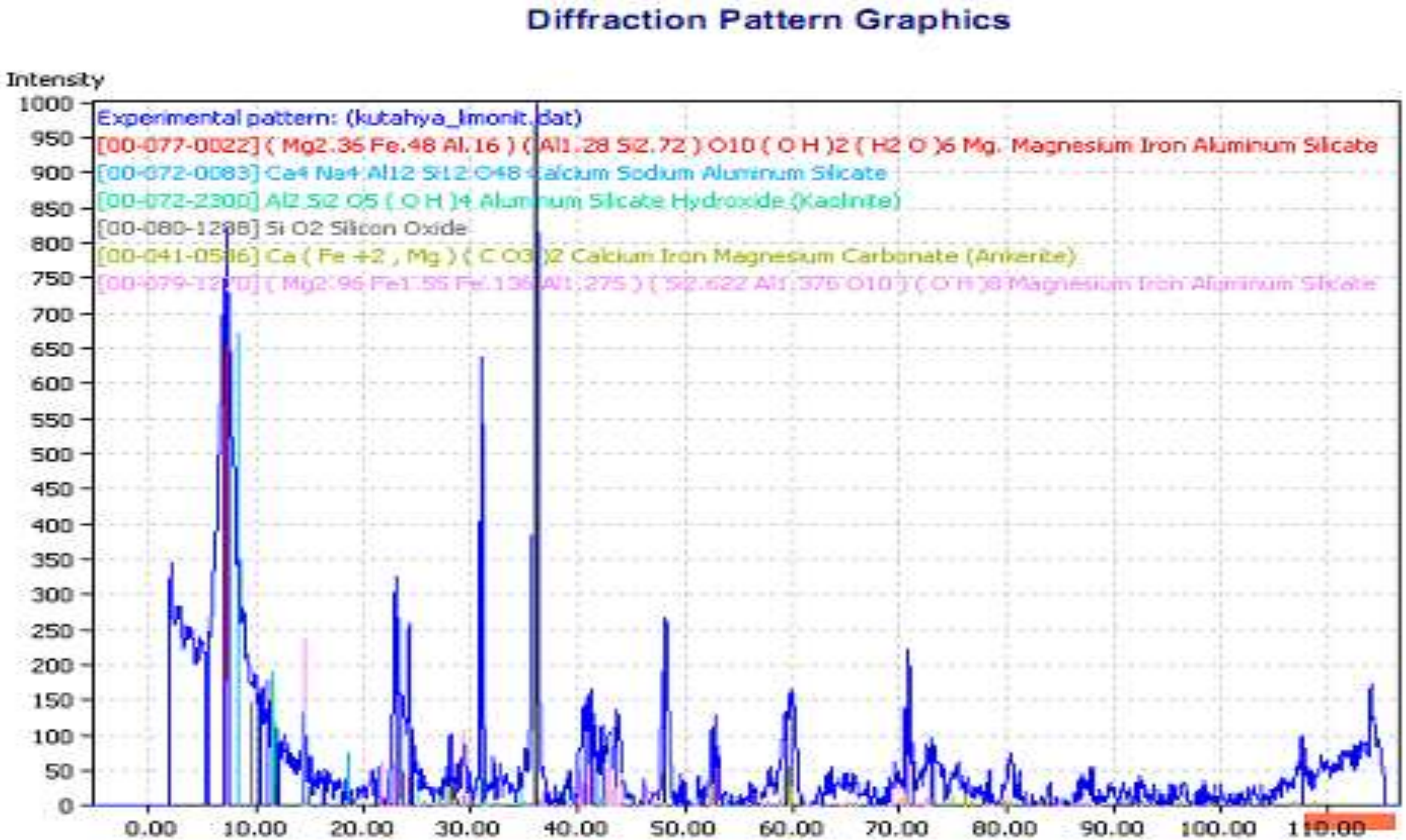


Figure 5.3 XRD Analysis of Kutahya Soil

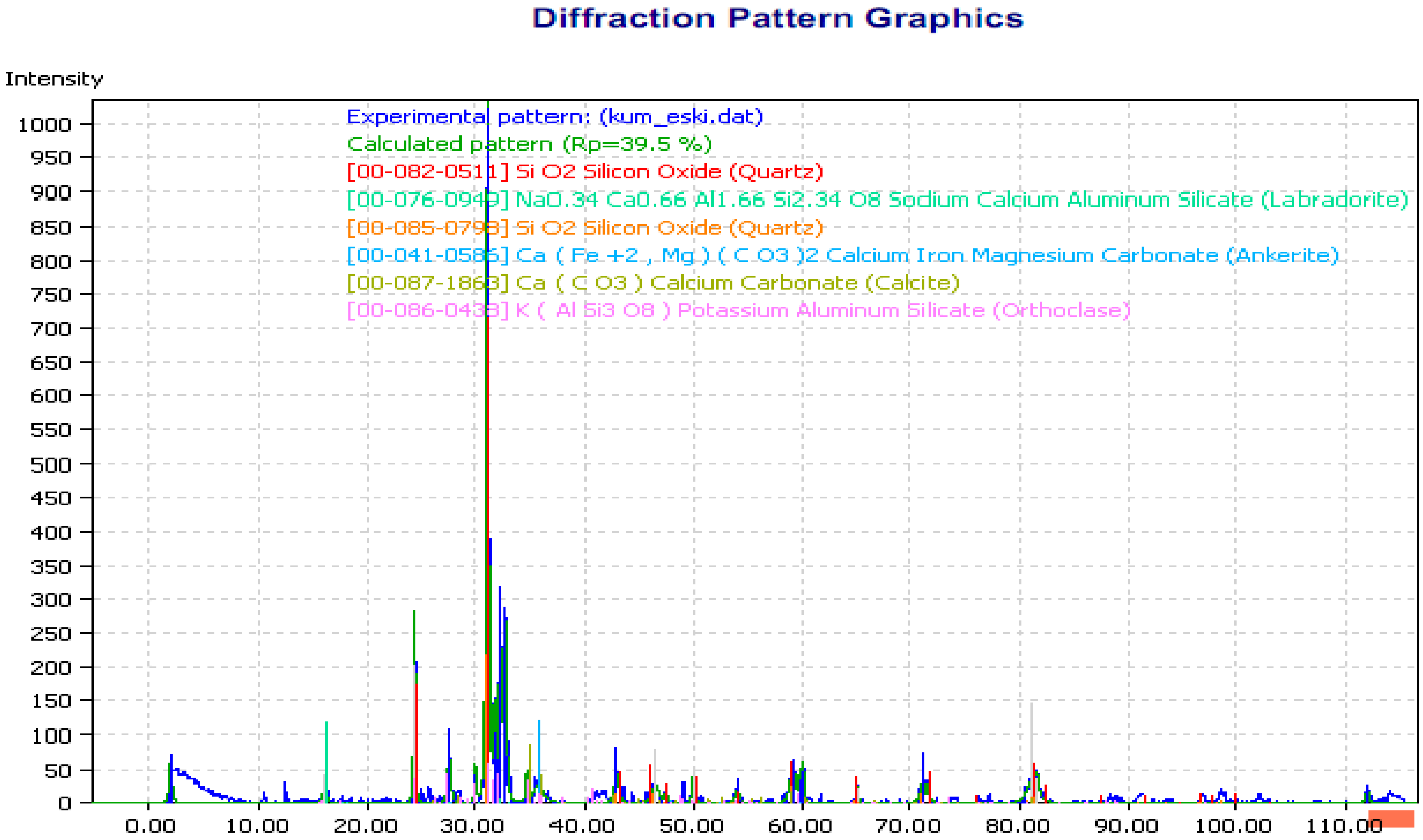


Figure 5.4 XRD Analysis of Beach sand

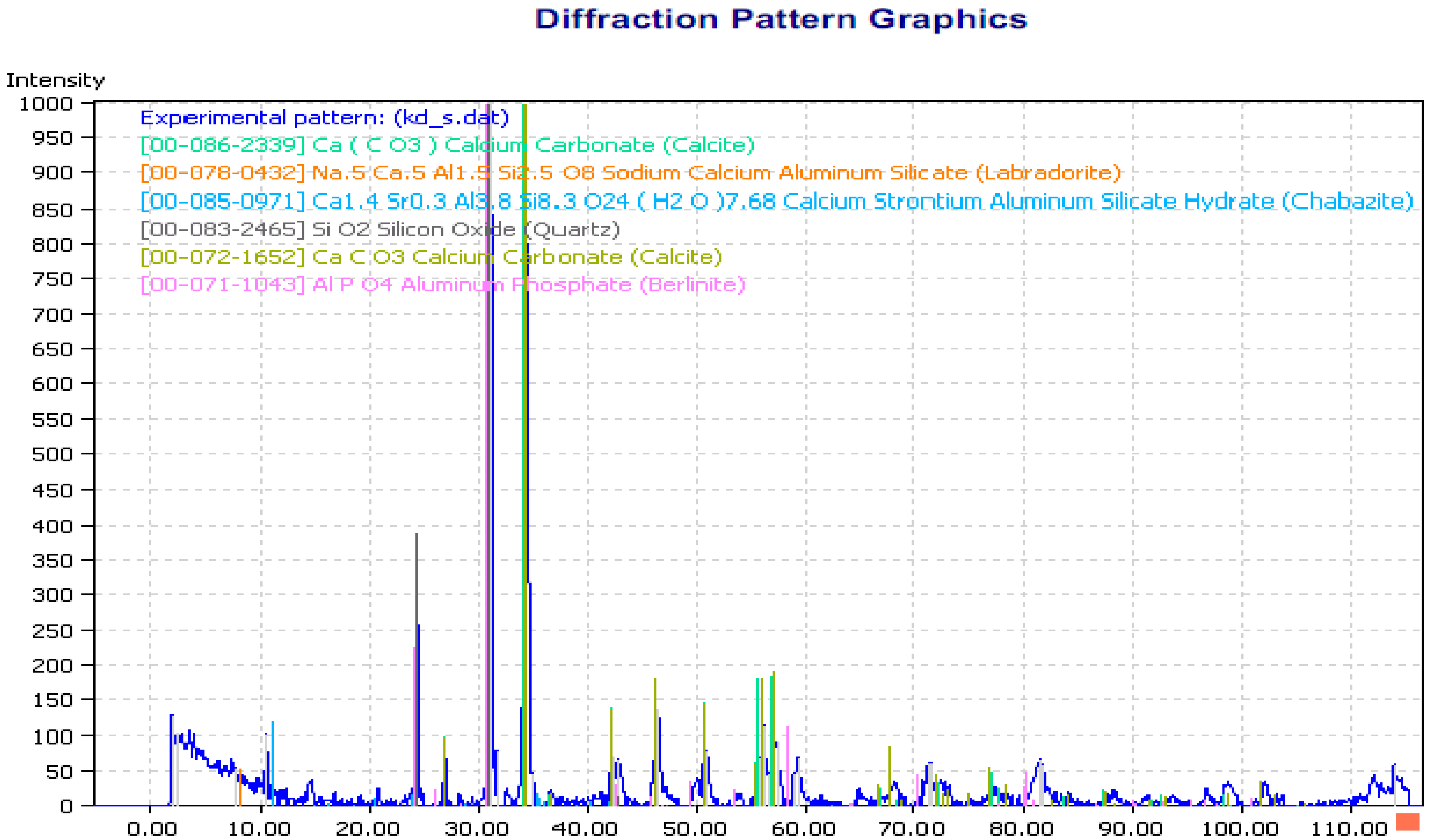


Figure 5.5 XRD Analysis of River sand

minerals are only seen in Kaynaklar and Kutahya soils. The results from Search Match files of XRD analysis are also presented in Table 5.4 with the chemical compositions from XRF analysis and the specific surface area results from BET analysis. In table 5.4, the Fe_2O_3 and Al_2O_3 amounts in chemical composition of Kutahya soil can be easily distinguished from the other samples, which define that Kutahya soil is an example of typical vermiculite and kaolin clay minerals.

According to the results, Kaynaklar soil contains 10.86% clay minerals (6.83% Kaolinite, 4.03% Illite-montmorillonite) where Kutahya soil contains 41.03% clay (4.67 % Vermiculite, 6.71% Kaolinite, and 29.65 % Clinochlore). In addition, the organic matter content of the samples, which is indicated in table 5.4 once more, is well correlated with their clay content.

The contained mineral is the major factor on the specific surface area of the soils. In Table 5.5, the SSAs of some soil minerals are given. As can be seen, clay minerals have larger SSAs than the other silicate groups. The specific surface areas (SSAs) of the soils used in the study are significantly different according to their mineral compositions. Kaynaklar soil (14.176 m^2/g) and Kutahya soil (58.798 m^2/g) have larger SSAs because of their clay contents, Beach sand (2.027 m^2/g) and River sand (0.786 m^2/g) have very small SSAs since they are not carrying any clay minerals, but quartz.

The distribution of the other elements in Kaynaklar soil, Kütahya soil, River sand, and Beach sand measured by XRF analysis are given in Table 5.6.

As can be seen from Table 5.6 the heavy metal concentrations in the soil were much lower than the limit values indicated in Turkish Soil Pollution Control Regulation (Official Gazette, 2001). Furthermore, these values are also much lower than universal soil background heavy metal concentrations (Pais, et al., 1997).

Table 5.4 The elements, minerals, and organic matter contents in clean Kaynaklar Soil, Kutahya Soil, beach sand, and river sand

	Kaynaklar Soil	**Kutahya Soil**	**Beach Sand**	**River Sand**
		Bulk Chemical Composition , % dw		
Na_2O	0.071	0.074	2.309	0.078
MgO	0.931	5.981	0.721	0.698
Al_2O_3	10.578	7.24	10.52	3.03
SiO_2	41.284	34.83	68.41	37.34
P_2O_5	0.121	0.0303	0.0972	0.0492
K_2O	1.795	0.816	4.045	0.530
CaO	19.324	7.84	2.16	28.02
TiO_2	0.610	0.674	0.163	0.199
MnO	0.111	0.266	0.019	0.049
Fe_2O_3	4.773	8.994	1.760	1.967
Others*	0.902	0.4547	0.1258	0.5998
LOI ^{4}	19.5	32.8	9.67	27.44
OMC^5, % dw	4.98	13.93	0.55	0.95
		Identified Minerals According to their Silicate Groups, % dw		
	FWS^1-Silica Minerals: Quartz 26.47 **NS^2-Carbonates:** Nitratine 27.56 **FWS^1-Feldspar Group:** Albite 2.19 Orthoclase 29.56 **SS^3- Mica Group:** Biotite 3.36 **SS^3- Clay Minerals:** Kaolinite 6.83 Illite-montmorillonite 4.03	**FWS^1-Silica Minerals:** Quartz 5.83 **NS^2-Carbonates:** Ankerite 43.08 **FWS^1-Feldspar Group:** Labradorite 10.05 **SS^3- Clay Minerals:** Kaolinite 6.71 Vermiculite 4.67 Clinochlore 29.65	**FWS^1-Silica Minerals:** Quartz 61.64 **NS^2-Carbonates:** Calcite 9.18 Ankerite 8.86 **FWS^1-Feldspar Group:** Labradorite 4.56 Orthoclase 15.76	**FWS^1-Silica Minerals:** Quartz 64.34 **NS^2-Carbonates:** Calcite 24.81 **NS^2-Phosphates:** Berlinite 9.41 **FWS^1-Feldspar Group:** Labradorite 0.12 **FWS^1-Zeolite Group:** Chabazite 1.32
General Chemical Formula of the Identified Minerals	Quartz - SiO_2 Nitratine-$Na(NO_3)$ Albite-$Na(AlSi_3O_8)$ Orthoclase-$K_{.59}Ba_{.19}Na_{.22}(Al_{1.18}Si_{2.82}O_8)$ Biotite-$KFeMg_2(AlSi_3O_{10})(OH)_2$ Kaolinite-$Al_2(Si_2O_5)(OH)_4$ Kaolinite - $Al_4[Si_4O_{10}](OH)_8$ Illite-montmorillonite-$KAL_4(Si,Al)_8O_{10}(OH)_4{*}4H_2O$		Ankerite-$Ca(Fe^{+2},Mg)(CO_3)_2$ Labradorite-$Na_{0.34}Ca_{0.66}Al_{1.66}Si_{2.34}O_8$ Vermiculite-$(Mg,Ca)_{0.6\text{-}0.9}(Mg,Fe^{+3},Al)_{6.0}[(Si,Al)_8O_{20}](OH)_4.nH_2O$ Clinochlore-$(Mg_{2.96}Fe_{1.55}Fe_{.136}Al_{1.275})(Si_{2.622}Al_{1.376}O_{10})(OH)_8$ Calcite - $CaCO_3$ Berlinite-$Al(PO_4)$ Chabazite-$Ca_{1.4}Sr_{0.3}Al_{3.8}Si_{8.3}O_{24}(H_2O)_{7.68}$	
		Specific Surface Area, m^2g^{-1}		
	14.176	58.798	2.027	0.786

1 FWS: Framework Silicates
2 NS: Non-Silicates
3SS: Sheet Silicates

4 at 950°C
5 at 600°C
*Given in Table xx.

Table 5.5 The specific surface areas of some soil minerals

Minerals	Specific Surface Areaof the group numbers, m^2g^{-1}	Grain Size, μm	Sources
Quartz	0.1	106-180	Kenneth and Preet, 1990
Calcite	0.69	<45	Kenneth and Preet, 1990
Dolomite	1.82	NR	Boucif et al., 2010
Feldspar	0.08	180-250	Hodson, 2006
	0.42	10-20	
Mica	5.2	106-180	Kenneth and Preet, 1990
	2	NR	Okada et al., 2002
Clay Minerals			
Chlorite	5-39	NR	Henn et al., 2007
Kaolinite	15-26	NR	Cerato and Luteneggerl, 2002
Smectite	34-97.4	NR	Volker et al., 2005

The specific surface areas of the Kaynaklar soil grain fractions were also determined by BET method, since the content of the study includes the effect of soil particle size on the treatment efficiency of NAPLs. The SSAs of the coarse, medium, and fine fractions were found as 13.750 m^2/g , 14.378 m^2/g, and 15.844 m^2/g, respectively (Table 5.7). The table also includes the results from sieve analysis. The findings indicate that the smaller the particle diameter, the larger the SSA.

Table 5.6 Other elements in Kaynaklar Soil, Kutahya Soil, Beach Sand, and River Sand

	Kaynaklar Soil	Kutahya Soil	Beach Sand	River Sand
	Elemental levels ,ppm dw			
Mn	0.829	1.968	0.1474	0.358
Fe	32.17	60.15	12.15	12.97
Cl	0.235	57.4	359.4	57.3
Cr	0.2027	629	50.4	542
V_2O_5		209	86	124
SO_3		1183	1769	1397
Co	41.1	74.1	23.6	<15
Ni	66.4	517.8	8.6	22.5
Cu	30.1	48.1	2.1	14.6
Zn	68.1	68.7	13.5	21
Ga	13	12.1	11.1	4.2
Ge	0.6	0.9	1.1	0.8
Cd	1.8	<0.9	<0.8	<0.9
Hg	<1.3	<1.3	<1.9	<1.5
Tl	0.8	<1.3	1	<1.3
Pb	23.7	15.7	26.8	7.4
As	10.9	0.8	8.5	14.6
Se	<0.5	0.5	<0.6	<0.5
Br	7	2.7	1.7	0.7
Rb	69.6	47.3	110.6	17.4
Sr	120.9	211.3	419.5	112.5
Y	19.7	19.8	12.8	8.3
Zr	160.6	111	166.2	91.1
Nb	11.6	12.2	10.3	3.3
Mo	4	<3.3	2.5	5.1
Ag	<1.3	<1.0	<0.9	<1.0
Sn	3.5	1.8	2.6	<1.0
Sb	<1.1	<0.9	<1.0	<1.0
Cs	8.7	5.4	8.4	4.5
Ba	211.7	130.6	1317	104.7
La	29	24.8	109.7	17.9
Ce	46.2	38.7	170.4	27.7
Hf	4.4	<6.2	3	5.1
Ta	<5.9	<9.1	3.8	<4.5
W	<4.4	<7.9	110.7	26.1
Au	<3.3	<3.3	<5.2	<3.6
Th	8.7	2.3	14.7	3
U	<9.9	<7.9	<7.1	<8.7
S	0.2716	-	-	-
V	0.092	-	-	-
In	<1.1	-	-	-
Te	<1.4	-	-	-
I	9.5	-	-	-
La	29	-	-	-
Bi	<1.0	-	-	-

Table 5.7 The specific surface areas of the coarse, medium, and fine fractions in Kaynaklar soil

Kaynaklar Soil Grain Fractions	**Sieve Analyses, %**	**Specific Surface Area, m^2/g**
Coarse (2000 µm-300 µm)	56.15	13.750
Medium(300 µm-45 µm)	38.19	14.378
Fine (<45)	4.85	15.844

5.2 The Properties of Compost Used in the Study

The general properties, namely; water content, organic matter content, pH, conductivity, salinity, and dissolved solids were analyzed in compost (Table 5.8). In addition, the chemical composition and elemental levels in compost are also detected by XRF analysis (Table 5.9).

Table 5.8 General properties of compost

Parameter	Value
pH	8.06
Original Water Content, %	25.70
Organic Matter Content, % dw	35.45
Conductivity, µs/cm	3530
Salinity, %	1.70
Dissolved solids in eluate, mg/kg	37400

The pH value of compost is slightly alkaline, water content and organic matter content are higher than the expected level in waste based fertilizers, which are required to be maximum 20% and minimum 25%, respectively (Official Gazette, 2010). The conductivity of compost is lower than the maximum allowable limit of 4 mmhos/cm defined in the same regulation.

Table 5.9 The chemical composition and elemental levels in compost

Element	**ppm**	**Element**	**ppm**	**Element**	**ppm**	**Element**	**ppm**
Na_2O	2,93	Cl	10240	**As**	**15,5**	La	13,3
MgO	8,57	Cr	130,3	Se	0,9	Ce	31,8
Al_2O_3	46,1	**Co**	**27,7**	Br	15,5	Hf	< 11
SiO_2	142,3	**Ni**	**52,6**	Rb	34,1	Ta	< 13
P_2O_5	8,245	**Cu**	**260,8**	Sr	373,7	W	< 8.0
K_2O	18,37	**Zn**	**595,3**	Y	11,9	Au	< 6.7
CaO	114,9	Ga	5,7	Zr	91,1	Th	1,3
TiO_2	5,03	Ge	1,5	Nb	6,2	U	6,9
MnO	0,77	**Cd**	**0,5**	Mo	< 2.8	Tl	1,5
Fe_2O_3	32,6	Mn	0,59	Ag	0,6	**Pb**	**158,6**
V_2O_5	101	Fe	22,54	Sn	10,1	Cs	< 4.0
SO_3	35910	**Hg**	**48,3**	Sb	4,7	Ba	686

As can be seen from Table 5.9, heavy metal concentrations in compost were lower than the limit values indicated in Turkish Soil Pollution Control Regulation (Official Gazette, 2001). In addition, these values are much lower than universal soil background heavy metal concentrations (Pais, et al., 1997).

CHAPTER SIX
RESULTS OF EXPERIMENTS AND DISCUSSION

In this chapter, the results of the experiments has conducted in the content of the thesis are given. The chapter consists of three major parts, namely; the investigation of diesel inhibition on studied soil and compost, the investigation of factors effecting the NAPLs remediation in slurry systems, and the investigation of fixed bed remediation systems for the factors effecting the NAPLs remediation. These parts include subtitles related with the investigated factors.

The slurry systems are investigated according to the solid/liquid ratio, initial contaminant concentration, contamination age, soil type, soil particle size, and presence of soil amendments. The fixed bed systems were studied to find the effects of water content, temperature, initial contaminant concentration, contamination age, soil type, and presence of soil amendments. The control sets are also operated for each of the parameters investigated.

6.1 Inhibition Effect of Diesel Oil on Soil and Compost Bacteria

Here, the effect of diesel oil contamination on soil and compost bacteria was investigated. First, the initial bacteria counts of clean Kaynaklar soil, compost used in the experiments and the compost-soil mixture (1/10) were detected, as well as the Kaynaklar soil and compost-soil mixture (1/10) contaminated with different diesel concentrations. Soil diesel concentrations of 2500 ppm, 5000 ppm, 10000 ppm, 25000 ppm, and 100000 ppm were studied. The bacteria amounts of clean and contaminated soil, compost, compost soil mixtures were counted after 48 (initial-according to the method referred in Chapter 4), 96, 192, and 384 hours of incubation at 28°C.

The bacterial counts of studied soils, compost, and compost-soil mixtures are given in Table 6.1.

Table 6.1 The bacterial counts of incubated materials, 10^{14}/g soil

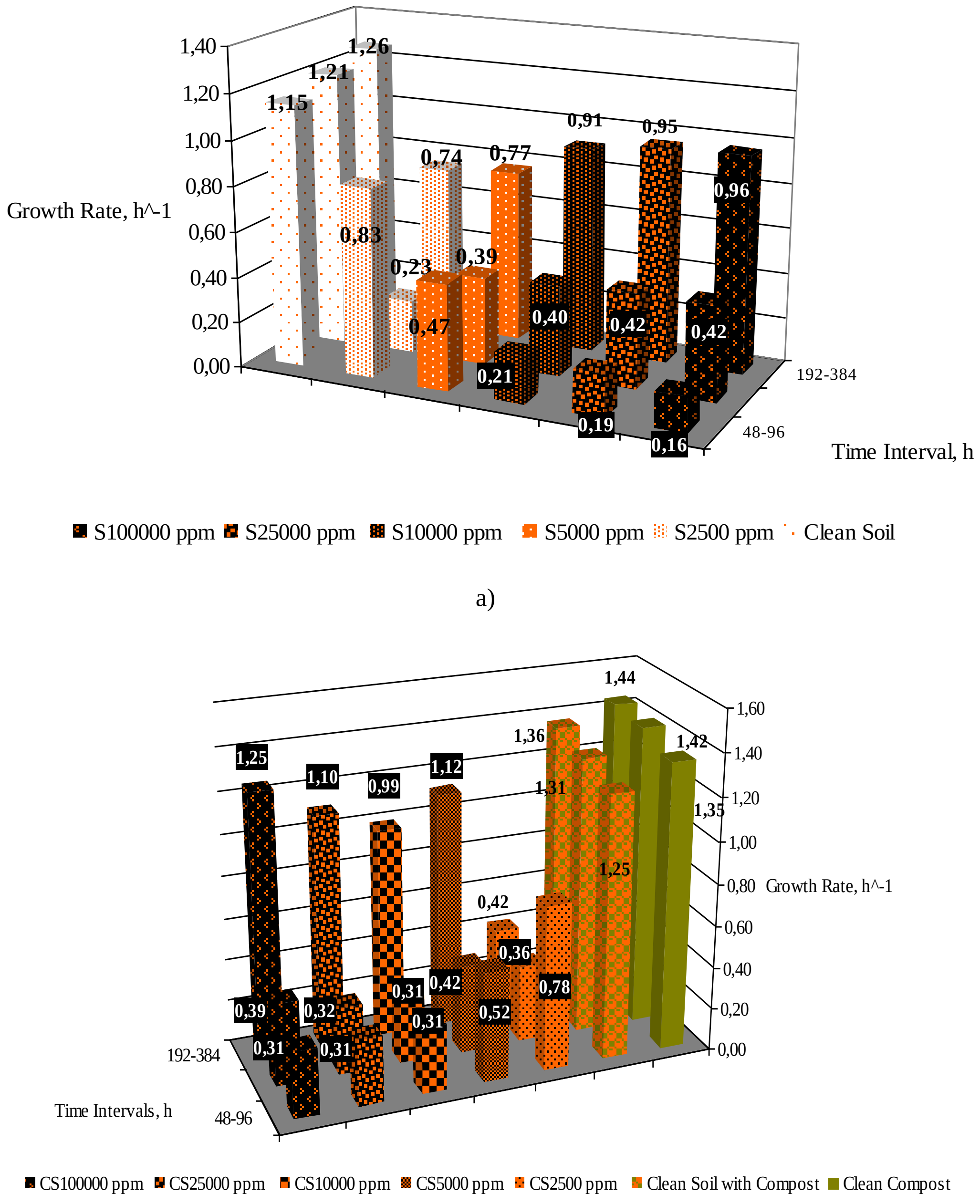
Used Material and Initial Diesel Concentration (ppm dw soil)	**Incubation Period, h**			
	48 (initial)	**96**	**192**	**384**
Clean Soil	273	328	444	686
Clean Compost	275	340	476	753
Clean- Compost added Soil	285	345	471	733
Soil- 2500 ppm	143	183	205	348
Soil-5000 ppm	38	60	98	245
Soil-10000 ppm	20	30	68	243
Soil-25000 ppm	85	94	134	317
Soil-100000 ppm	88	95	135	320
Compost +Soil-2500 ppm	223	260	295	375
Compost+Soil-5000 ppm	58	83	123	338
Compost+Soil-10000 ppm	88	103	133	323
Compost+Soil-25000 ppm	138	153	183	394
Compost+Soil-100000 ppm	168	183	220	460

As can be seen from the table, initial bacteria counts in clean soil, compost, and soil-compost mixture were close to each other, and these clean materials have higher initial bacteria counts than the contaminated materials. In contaminated materials, either compost added or not, the bacterial counts first decrease with incubation time, and then an increase have seen. The bacterial growth rates (h^{-1}) are calculated for the time intervals of 48-96 h, 96-192 h, and 192-384 h in studied materials and presented in Figure 6.1a and 6.1.b.

In Figure 6.1a, the bacterial growth rates of clean soil and contaminated soils are given, where the bacterial growths of compost, compost-soil mixture, and contaminated compost-soil mixtures are given in Figure 6.1b.

As can be seen in Figure 6.1a, the bacterial growth in clean soil is high in the first 48 h period, which than it shows a slow increase in the next incubation periods. The soil contaminated with 2500 ppm diesel, has lower bacterial count in the first 48 h period which is followed by a sharp decrease in the next 96 hours of incubation time. The bacterial growth in this soil increases to 0.74 h^{-1} in the last incubation period of

192 h. It is seen that, the bacterial growths of the soils in the first 48 h period of incubation decreases with increasing initial concentration. But the adaptation of the bacteria to the contaminated medium is getting faster as the initial contaminant concentration increases.



a)

b)

Figure 6.1 The bacterial growth rates (h^{-1}) of the bacteria in studied materials according to the initial diesel concentration a) Results with soils, b) Results with compost added (1/10) soils

In Figure 6.1b, It is seen that compost bacteria growth rate increase with extended incubation time as well as the bacteria present in compost-soil mixture. The bacterial growth rates in contaminated compost-soil mixtures are generally better than the growth rates observed in contaminated soils in the first 48 h incubation period. But in the second period (96 h), bacterial growth rates in compost-soil mixtures are decreasing with increasing diesel concentration. In the last period, lasting192 h, the bacterial growth rates in compost-soil mixtures increases significantly, and exceeds the rates found in incubated soils. This can be the result of the some type of bacterial strains in the compost, different from the soil, which are resistant to NAPLs and dominated in time. Nevertheless, the neither the final bacterial counts nor the bacterial growth rates of contaminated materials could reach the bacterial counts of clean materials at the end of the incubation period.

It is also seen that compost added soils final bacterial counts are 8% to 44% higher than the soil bacterial counts and this increase is parallel with increasing initial concentration.

Briefly, the presence of diesel oil in soil or compost-soil mixtures adversely effects the bacterial growth. This adverse effect can be named as inhibition, which has seen especially in the first 192 h (8 days) after the contaminants introduction to the soil. But, it can be said that soil and compost bacteria can adapt to the presence of contamination by domination of resistant strains with extending incubation times. It should be noted that the incubation studies were conducted at 28°C, which is available for upper-mesophilic group of bacteria.

6.2 Slurry System Remediation

The slurry system soil remediation studies were conducted under two major conditions, namely; without soil amendment and with soil amendment. In the remediation studies without any soil amendment, the effects of solid/liquid ratio, presence of light during the remediation, initial contaminant concentration, the presence of local microorganisms, the water content, the soil particle size, and the age of contamination were investigated and discussed.

The studies conducted with the presence of soil amendment were completed by addition of compost to the soil slurry and includes the investigation of following effects on soil remediation; the soil/compost ratio, initial contaminant concentration, and age of contamination.

6.2.1 Slurry System without Soil Amendment

In this part of the study, diesel contaminated soil was used and the systems were operated in a shaking incubator with 100 rpm under 25°C. The initial PAHs concentrations in slurry solid content are given in Table 6.2 with some important PAHs properties.

6.2.1.1 The Effect of Solid/Liquid Ratio on Soil Remediation in Slurry Systems

The contaminated Kaynaklar soil that has 100000 mg/kg diesel was used with 1/5, 1/10, and 1/20 solid/liquid ratios in slurry systems. The experiments were conducted by using sterilized soil to eliminate the possible effect of bacterial degradation on the remediation of NAPLs. The soil microbial mass was inhibited by using $HgCl_2$ and autoclaving prior to the diesel spiking, and the contaminated soils were immediately placed in to the remediation systems after spiking. The number of bacteria in the soil was detected throughout the remediation period and any activity could not be seen. The systems were operated for 8 hours. The pH, TPHs, and PAHs were followed during the experimental period and the results are presented below:

In the slurry system with different solid/liquid ratios, initial pH levels (Figure 6.2) were higher as the solid/liquid ratio increased. The pH level decreased slightly in the first two hours of the experiment and then leveled up gradually in next period.

Table 6.2 The initial PAHs concentrations in slurry solid content according to the initial diesel concentrations, with some important PAHs properties.

Studied PAHs				Initial Concentration in Soil, mg/kg		
Number of Benzene Rings	**Name**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**10000 ppm diesel**	**25000 ppm diesel**	**100000 ppm diesel**
3 Ring	Acenaphthylene	16.1	$9.12*10^{-4}$	0,0817	0,2042	0,8167
	Acenaphthene	3.9	$2.50*10^{-3}$	0,0369	0,0923	0,3690
	Fluorene	1.89	$8.42*10^{-3}$	0,3630	0,9075	3,6299
	Phenanthrene	1.15	$1.12*10^{-4}$	1,6030	4,0076	16,0305
	Anthracene	$4.34*10^{-2}$	$2.67*10^{-6}$	0,4336	1,0840	4,3360
	Carbozole	0.721	$2.66*10^{-4}$	0,4659	1,1647	4,6587
4 Ring	Fluoranthene	$2.60*10^{-1}$	$1.23*10^{-8}$	1,1266	2,8165	11,2660
	Pyrene	$1.35*10^{-1}$	$1.35*10^{-7}$	0,0711	0,1776	0,7105
	Benz(a)anthracene	$9.40*10^{-3}$	$3.05*10^{-8}$	1,9355	4,8387	19,3549
	Chrysene	$2.00*10^{-3}$	$6.23*10^{-9}$	1,3274	3,3184	13,2738
5&6 Ring	Benzo(b)fluoranthene	$1.50*10^{-3}$	$5.00*10^{-7}$	0,0493	0,1231	0,4925
	Benzo(k)fluoranthene	$8.00*10^{-4}$	$9.65*10^{-10}$	0,0048	0,0120	0,0479
	Benzo(a)pyrene	$1.62*10^{-3}$	$5.49*10^{-9}$	0,0302	0,0755	0,3022
	Dibenz(a,h)anthracene	$2.49*10^{-6}$	$1.00*10^{-10}$	0,0146	0,0364	0,1455
	Benzo(g,h,i)perylene	$2.6*10^{-4}$	$1.01*10^{-10}$	0,0291	0,0728	0,2912
	Indeno(1,2,3-c,d)pyrene	$2.20*10^{-5}$	$1.00*10^{-10}$	0,0037	0,0094	0,0375

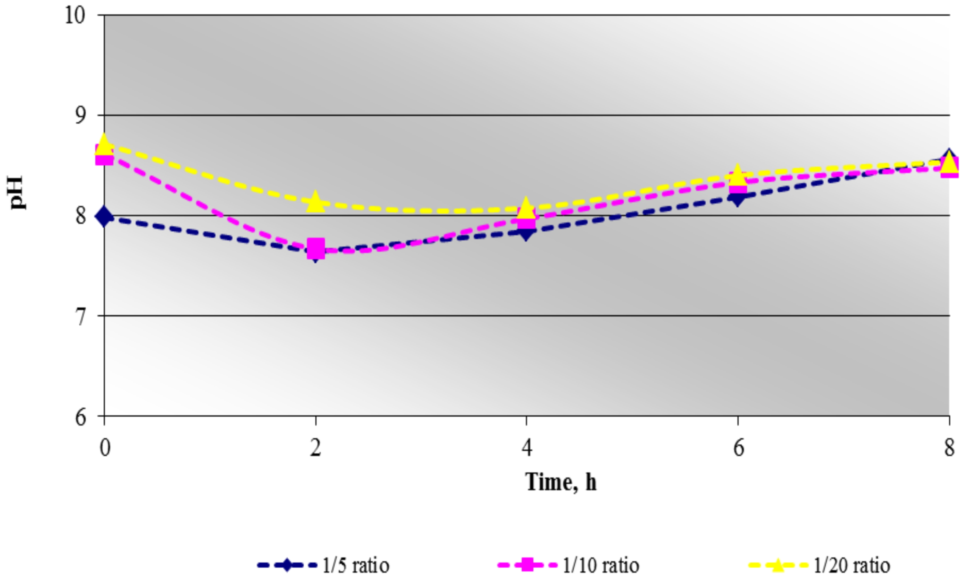


Figure 6.2 Slurry system pH variation with 1/5, 1/10, and 1/20 solid/liquid ratios

The systems TPHs removal efficiencies were calculated according to the total mass of the TPHs found in soil matrix, in liquid, and the floating portion. It is seen that the TPHs removal efficiencies in slurry systems are correlated with the solid/liquid ratio (S/L) in the reactors; as the S/L increases, the removal efficiencies decreases (Figure 6.3). But the rate of TPHs removal was faster with higher S/L ratio, especially in the first 4 hours of the experiment. In addition, the distribution of TPHs in the system showed that (Figure 6.4) the ratio of remaining TPHs concentration in soil is the highest in the system have the S/L of 1/5, where the floating TPHs has the higher ratios in the systems having 1/10 and 1/20 solids content. The lowest TPHs amount in the liquid fraction was found in the reactor with 1/5 S/L content. The final TPHs concentrations in soils in the reactors with 1/5, 1/10 and 1/20 solid/liquid ratios are 2570, 1310, and 540 ppm dw, respectively. But, the final soil concentrations with 1/5 and 1/10 S/L are not drastically different and 1/5 solid-liquid ratio is much economical in initial investment and operational costs of the treatment applications.

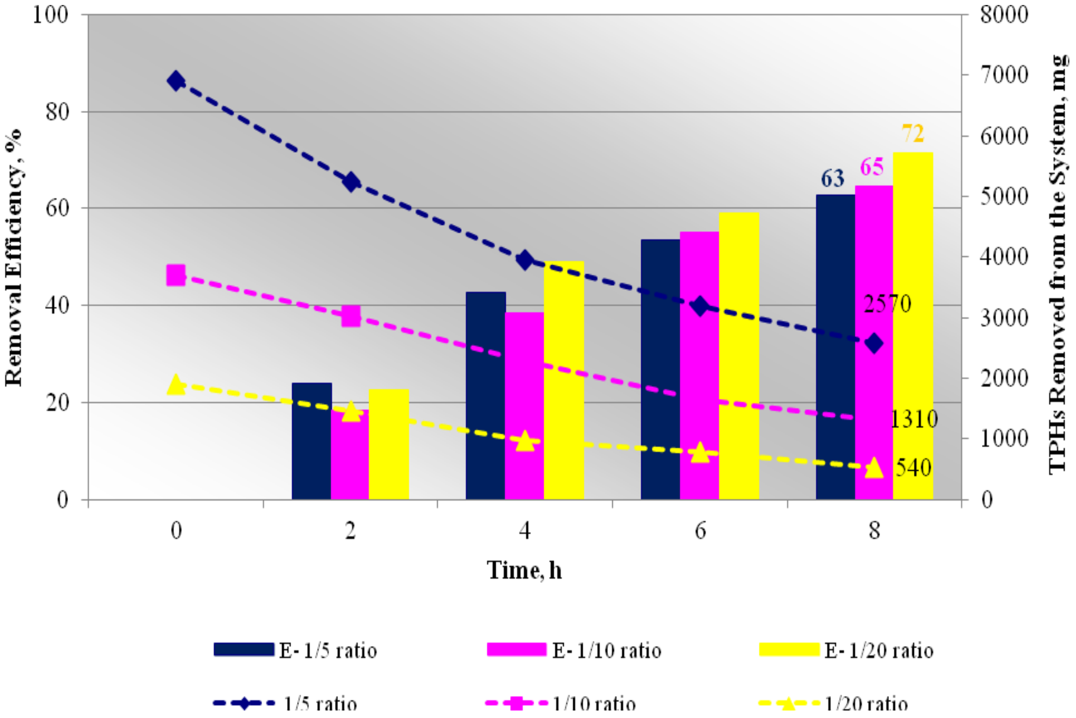


Figure 6.3 Residual concentration and removal rates of TPHs in slurry systems with 1/5, 1/10, and 1/20 solid/liquid ratios (100000 mg/kg diesel)

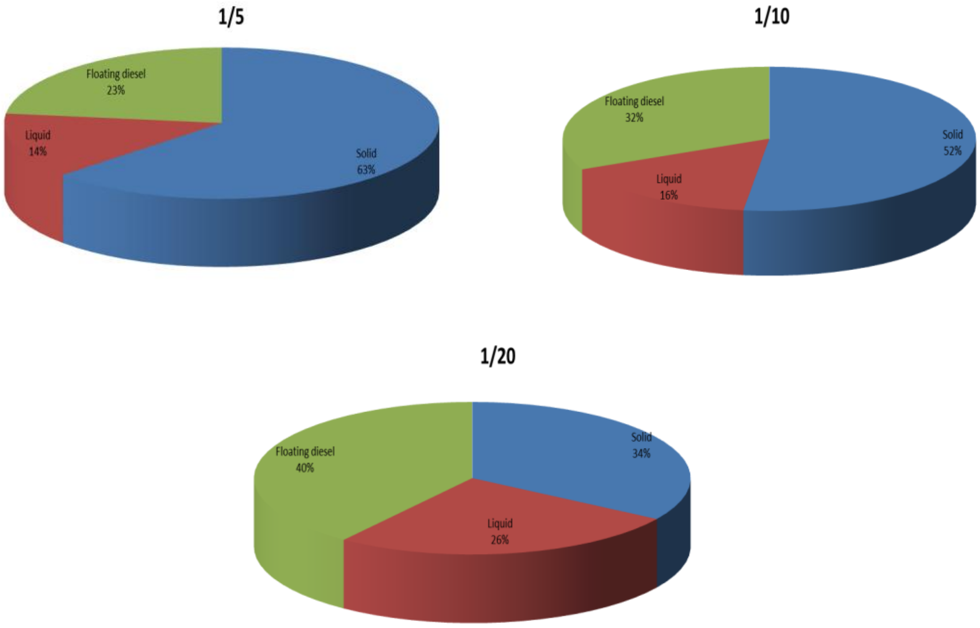


Figure 6.4 The distribution of residual TPHs (mg) in slurry systems as in solid, in liquid and asfloating with 1/5, 1/10, and 1/20 solid/liquid ratios (100000 mg/kg diesel)

Therefore, 1/5 and 1/1 solid/liquid ratios were applied in the following slurry systems operated in the content of the thesis.

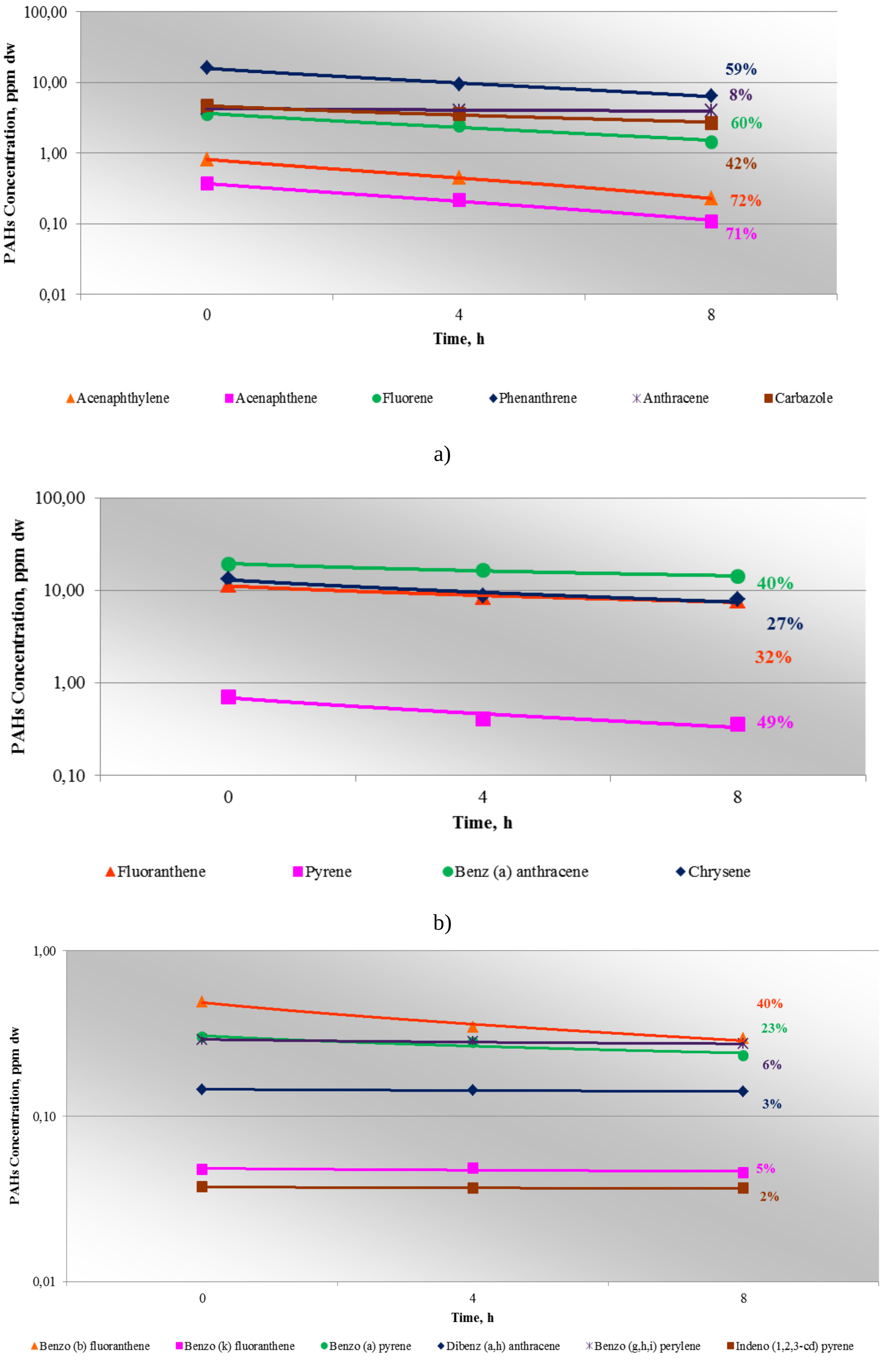
The PAHs in soil originated from diesel spiking was grouped and investigated according to their number of benzene rings; 3 ring PAHs, 4 Ring PAHs and 5&6 Ring PAHs.

The PAHs removal from the sterilized soil with 1/5 Solid/Liquid ratio is given in Figure 6.4. It is seen that, PAHs removal rates are decreasing with increasing number of benzene rings they are carrying. The PAHs with 3 Rings were removed 8-72% (ave. 52%), 4 Ring PAHs were removed between 27-49% (ave. 37%), and 5&6 Ring PAHs were removed 2-40% (ave. 13.2%) with S/L of 1/5.

The PAHs removals with 1/10 solid/liquid ratio are given in Figure 6.6. PAHs removal rates with 1/10 solid liquid ratio showed that the treatment efficiency decreases with increasing number of benzene rings. The PAHs with 3 Rings were removed 7-76% (ave. 52,7%), 4 Ring PAHs were removed between 28-56% (ave. 39.3%), and 5&6 Ring PAHs were removed 0.5-42% (ave. 12.1%).

PAHs removal with S/Lratio of 1/20 is given in Figure 6.7. PAHs removal rates with 1/20 solid liquid ratio showed that the treatment efficiency decreases with increasing number of benzene rings. The PAHs with 3 Rings were removed 8-82% (ave. 56.2%), 4 Ring PAHs were removed between 17-52% (ave. 34%), and 5&6 Ring PAHs were removed 0.7-42% (ave. 12.8%).

In all sets with different solid/liquid ratios, the PAHs removal efficiencies dropped with increasing number of benzene rings in the investigated groups. It is also seen that removals of PAHs in the same group may vary in a large interval. Any general relation between solid/liquid ratio and PAHs groups removals could not be recognized in these sets of experiments. A detailed discussion on the removal of PAHs in slurry systems will be given at the end of this chapter.

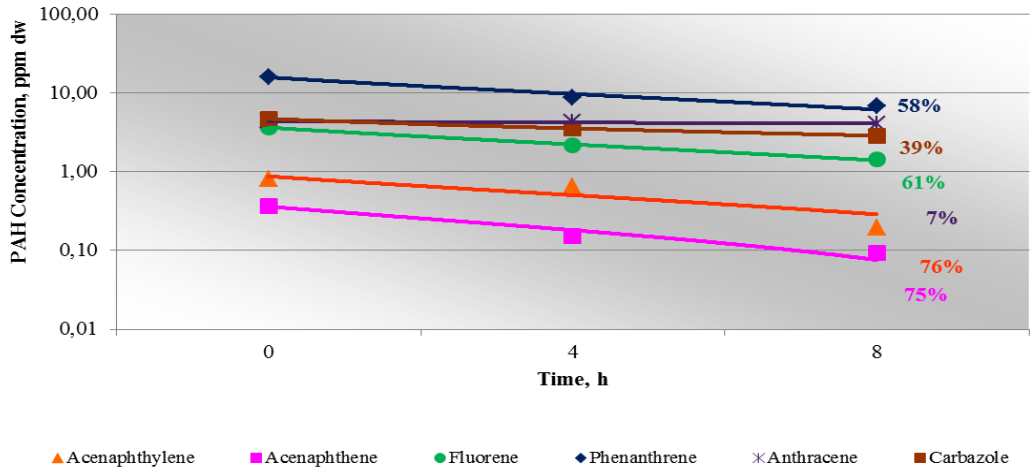


a)

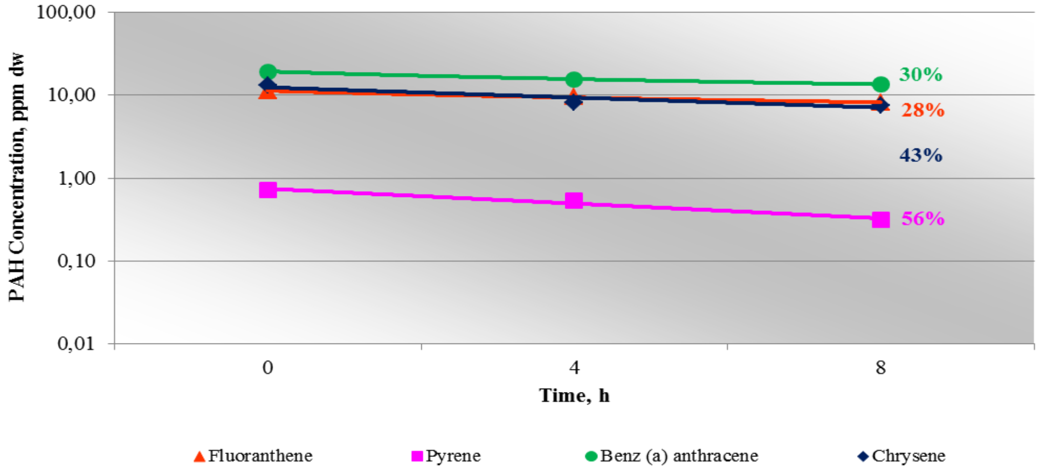
b)

c)

Figure 6.5 The removal of PAHs from the soil in the slurry system with 1/5 solid/liquid ratio(100000 mg/kg diesel); a) 3Ring PAHs, b) 4 Ring PAHs, and c) 5&6 Ring PAHs



a)



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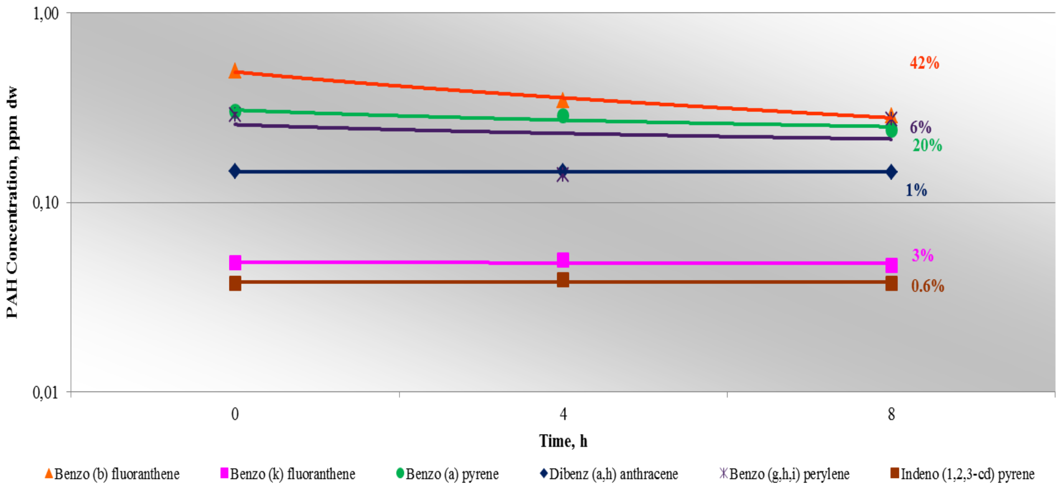
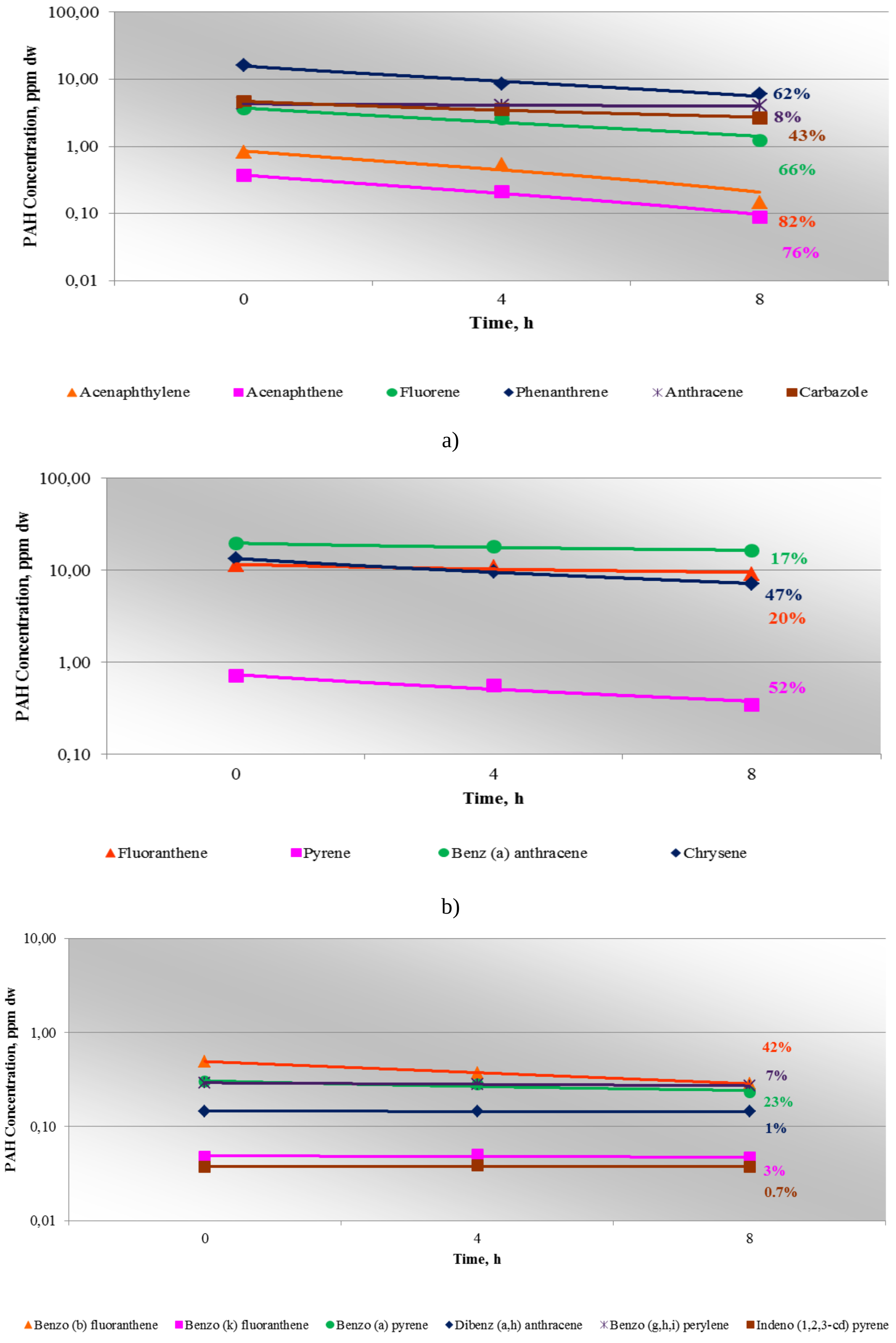


c)

Figure 6.6 The removal of PAHs from the soil in the slurry system with 1/10 solid/liquid ratio(100000 mg/kg diesel); a) 3Ring PAHs, b) 4 Ring PAHs, and c) 5&6 Ring PAHs



a)

b)

c)

Figure 6.7 The removal of PAHs from the soil in the slurry system with 1/20 solid/liquid ratio(100000 mg/kg diesel); a) 3Ring PAHs, b) 4 Ring PAHs, and c) 5&6 Ring PAHs

6.2.1.2 The Effect of the Presence of Light, the Soil Properties, and the Presence of Local Bacteria on Soil Remediation in Slurry Systems

Here, it is aimed to investigate and discuss the effects of soil type, presence of light, and presence of local bacteria on the efficiency of slurry soil remediation systems. The contaminated Kaynaklar soil and Beach sand having 25000 mg/kg diesel was used with a 1/5 solid/liquid ratio in the slurry systems studied in this part. The experiments were conducted by using soil with local bacteria with a control of sterilized soil under the light and dark medium. The number of bacteria in the soils was detected throughout the remediation period and reported, as well as produced CO_2 from the reactors. The systems were operated for 168 hours (7 days). The pH, TPHs, and PAHs were followed during the experimental period and the results are presented below:

The pH variations in the systems are presented in Figure 6.8.

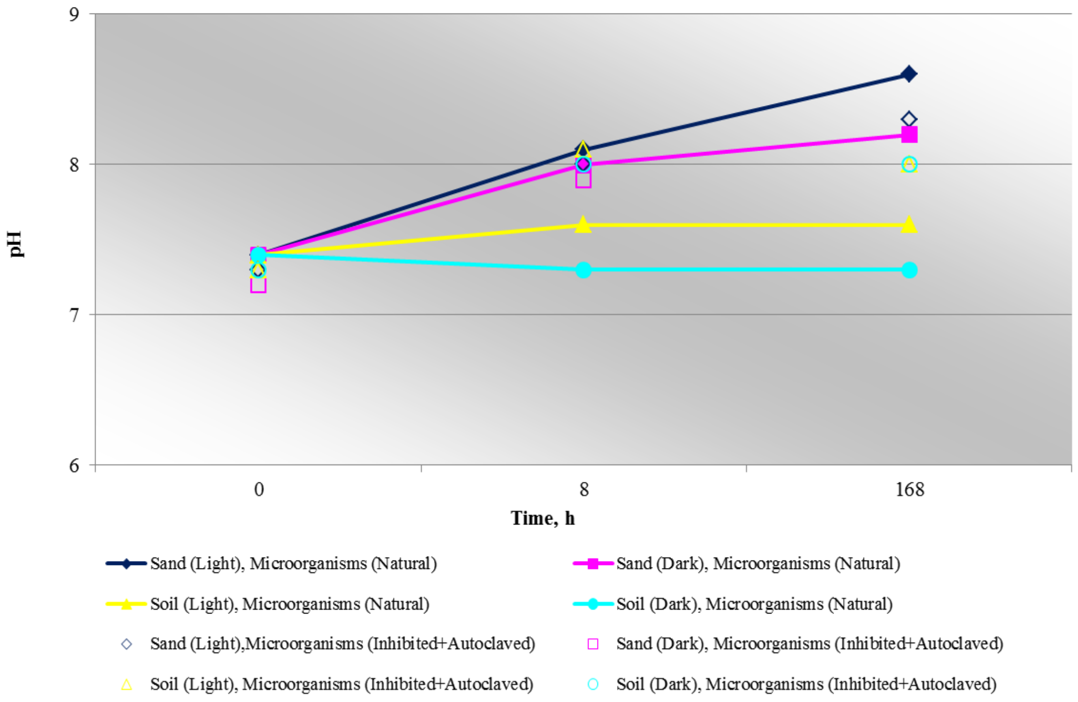
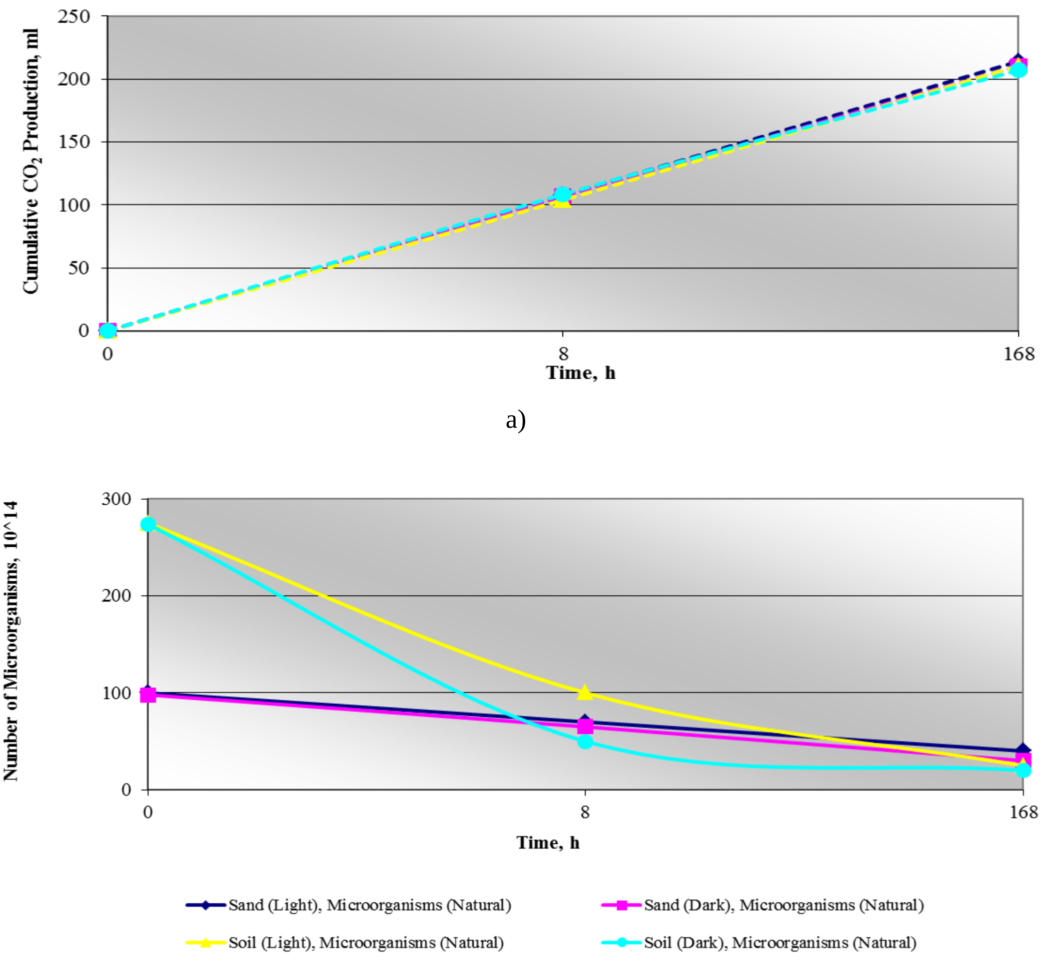


Figure 6.8 Slurry system pH variation with 1/5 solid/liquid ratio for Beach sand and Kaynaklar soil under light and dark environments (25000 ppm diesel)

The initial pHs of the Kaynaklar soils with local bacteria were between 7 and 8 and did not change significantly during the experiments, while the Beach sands pH level has increased up to 8.5 during the experiment. This increase can be explained by the calcite content of the Beach sand which may partially dissolve in humid environment and raise the pH level of the soil.

The cumulative CO_2 production from the systems and the variation in the number of bacteria in the soils were illustrated in Figure 6.9a and 6.9b.



a)

b)

Figure 6.9 a) CO_2 production from the systems and b) the number of bacteria in soils in the slurry system with 1/5 solid/liquid ratio for Beach sand and Kaynaklar soil under light and dark environments (25000 ppm diesel)

It is calculated that the unit CO_2 production from Kaynaklar soil and Beach sand is similar and around 2.9 ml/g soil. Any CO_2 production or bacterial growth in sterilized soils could not be seen during the experiments. It is seen that the number of bacteria decreases with extending experimental period. This may be related with the decreasing amount of substrate in the medium, or inhibitory effect of diesel compounds on the soil microbial population.

The TPHs removal from Beach sand and Kaynaklar soil, which were spiked with 25000 ppm diesel, under light and dark environments is illustrated in Figure 6.10. The TPHs removal rates in slurry systems in the first eight hours of the experiment are higher in both soils then the following remediation period. The removal efficiencies are between 84-91%. The experiments conducted with local bacteria resulted with 10-17% higher treatment efficiency than the experiments conducted with sterilized soils. But, this finding is also indicating that a considerable amount of TPHs is stripped from the system by volatilization (72-81%). The experiments completed in dark environment have slightly higher treatment efficiencies and the treatment efficiencies observed in Kaynaklar soil are 5 to 7% higher than the ones observed in Beach sand.

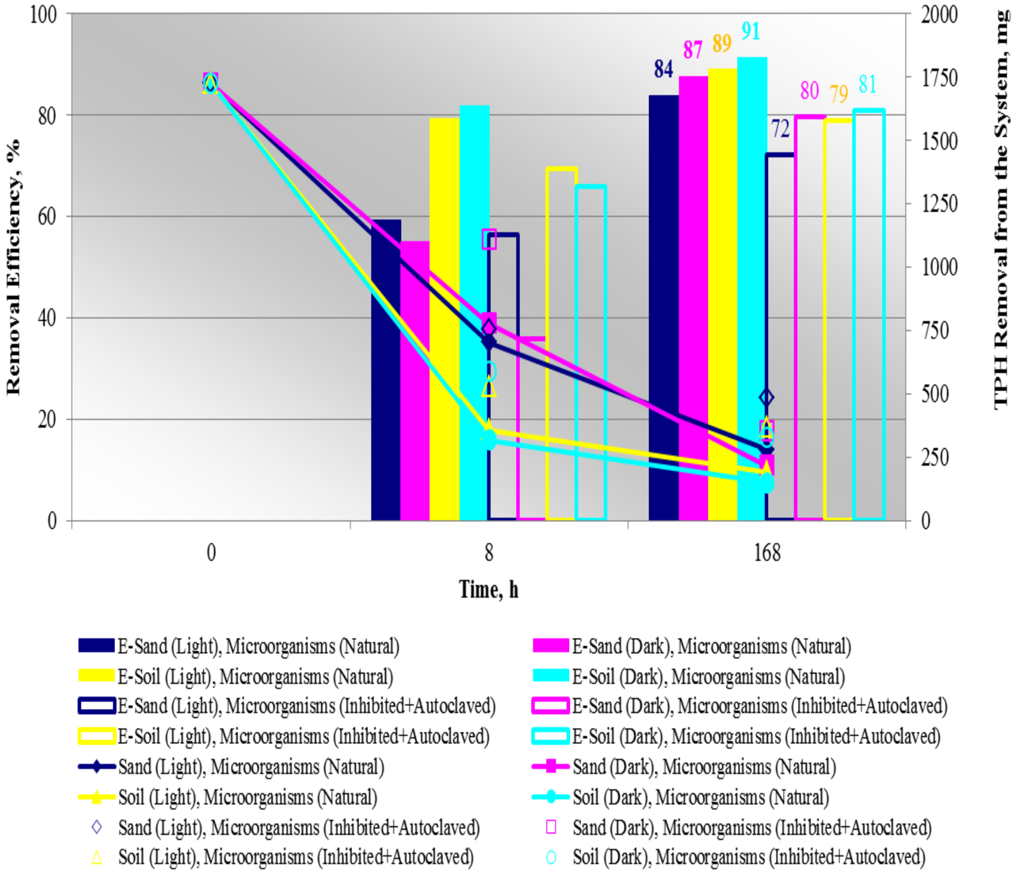


Figure 6.10 Residual concentration and removal rates of TPHs in slurry systems with 1/5, solid/liquid ratio for Beach sand and Kaynaklar soil under light and dark environments (25000 mg/kg diesel)

As it is mentioned above, the CO_2 production in the studied systems are very close to each other, but it should be emphasized that the initial bacterial count in Kaynaklar soil were much higher than Beach sand and that can be the reason for higher treatment efficiencies. It should be noted that, the treatment rate in Kaynaklar soil after the first eight hour of the experiment is lower, and the number of bacteria in studied soils are getting closer to each other in this period. That’s why, the final TPHs levels in the slurry systems were found in a narrow range (147-277 mg).

The TPHs remaining in the slurry systems at the end of the experimental period were also investigated according to the presence of local bacteria in the soil. In Figures 6.11 and 6.12, the distribution of final TPHs mass in the systems are given for the soils with local bacterial and for the sterilized soils (control), respectively.

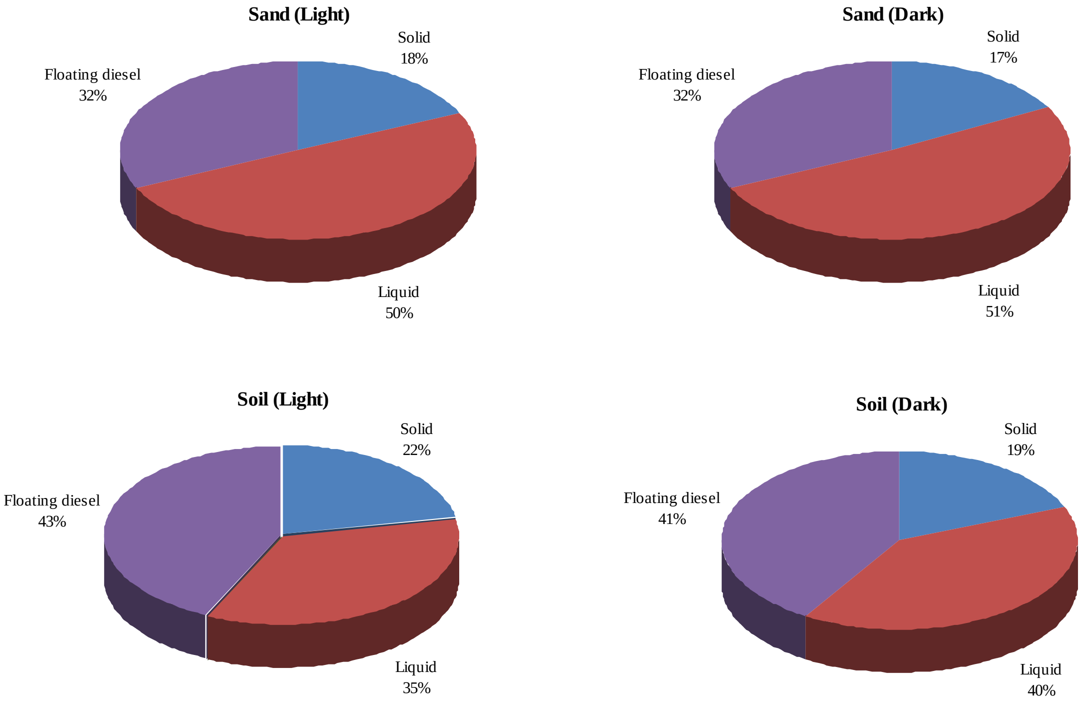


Figure 6.11 The distribution of residual TPHs (mg) in slurry systems as in solid, in liquid and as floating with 1/5solid/liquid ratio for Beach sand and Kaynaklar soil with local bacteria under light and dark environments (25000 mg/kg diesel)

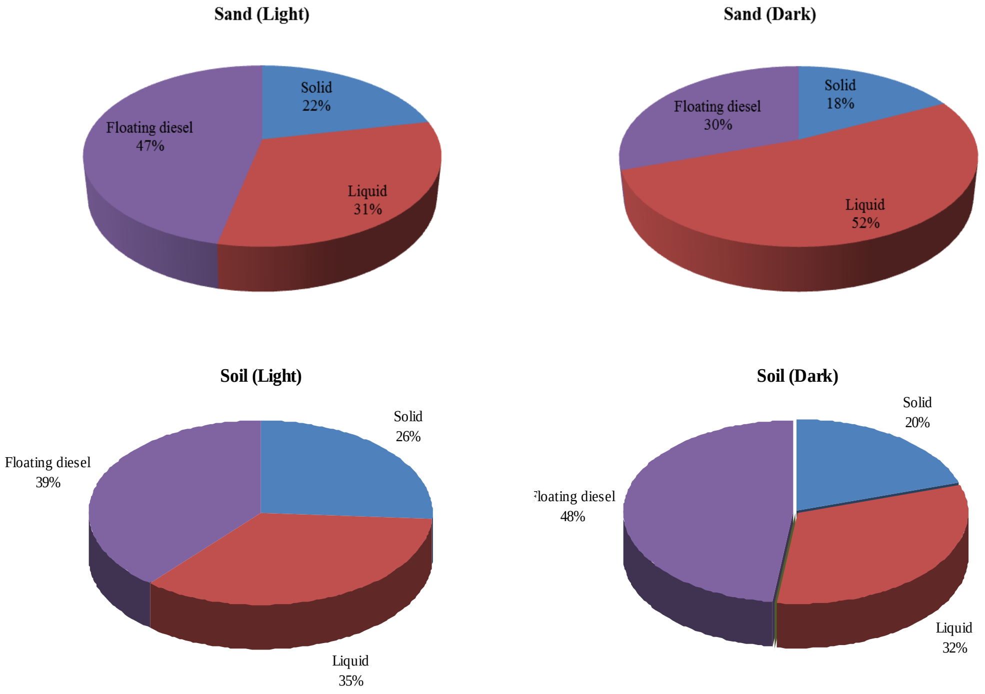
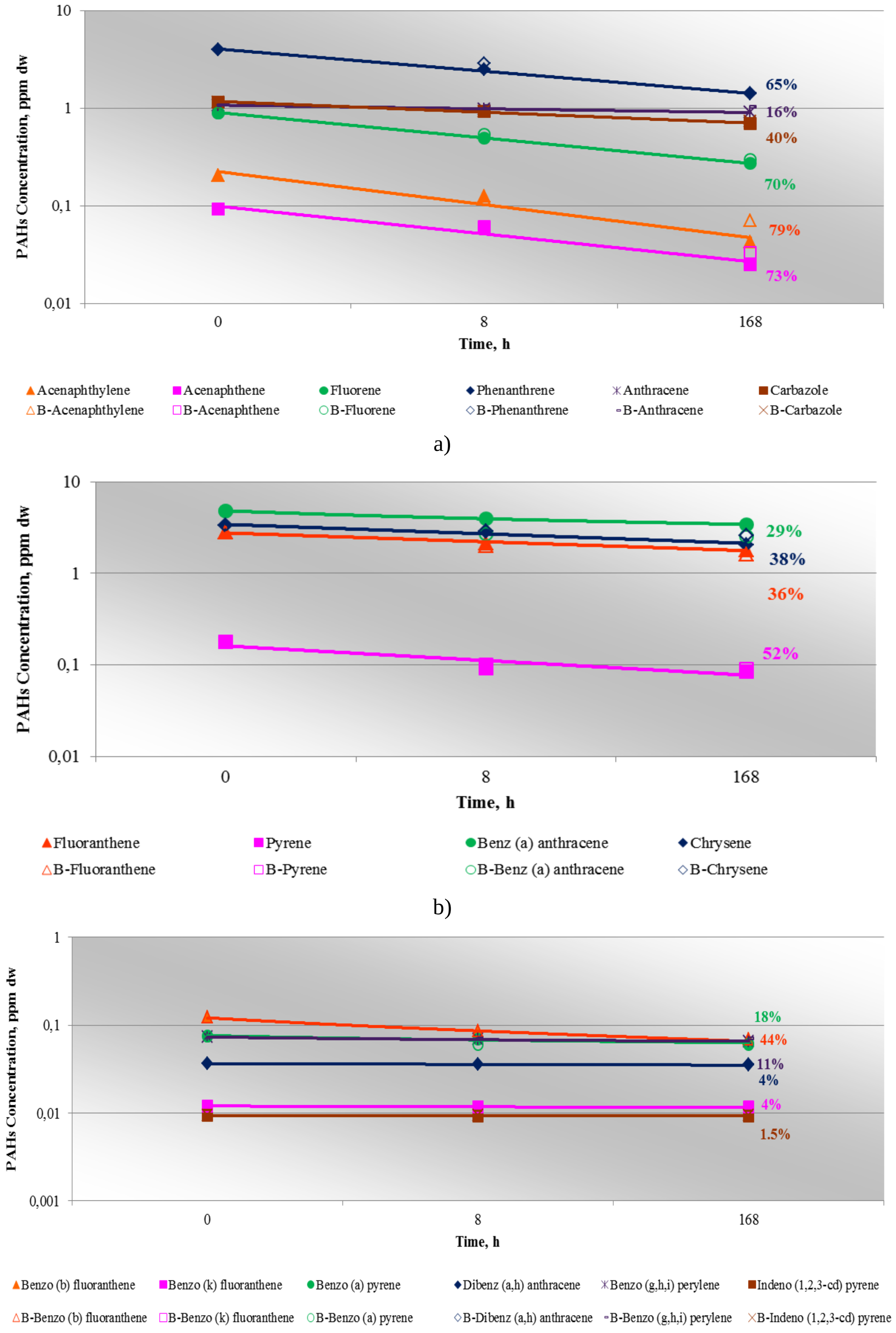


Figure 6.12 The distribution of residual TPHs (mg) in slurry systems as in solid, in liquid and as floating with 1/5solid/liquid ratio for sterilized Beach sand and Kaynaklar soil under light and dark environments (25000 mg/kg diesel)

It is recognized that the remaining TPHs in soils are lower in the systems operated with Beach sand, where TPHs mass in liquid are higher. This may be related with the low adsoption capacity of the Beach sand because of its narrow SSA and low organic matter content that allows the easier release of NAPLs from the spiked soils. In the systems operated with Kaynaklar soil, the soil TPHs has a portion of 19% in dark environment and 22% in light. In addition, the TPHs mass in liquid part is much lower than the systems operated with sand. The TPHs amounts in solid fraction are higher in the sterilized soils.

The PAHs removal from a 25000 ppm diesel spiked Kaynaklar soil and Beach sand (S/L =1/5) in a slurry system in light environment is presented in Figures 6.13 and 6.14, respectively. It is seen that, PAHs removal rates are decreasing with increasing number of benzene rings they are carrying for both soils. The PAHs with 3 Rings were removed 16-79% (ave. 57.2%), 4 Ring PAHs were removed between 29-52% (ave. 38.8%), and 5&6 Ring PAHs were removed 1.5-44% (ave. 13.8%) from Kaynaklar soil. With Beach sand, the PAHs with 3 Rings were removed 13-78% (ave. 60.7%), 4 Ring PAHs were removed between 20-55% (ave. 36%), and 5&6 Ring PAHs were removed 0.5-49% (ave. 13.9%) in the system.

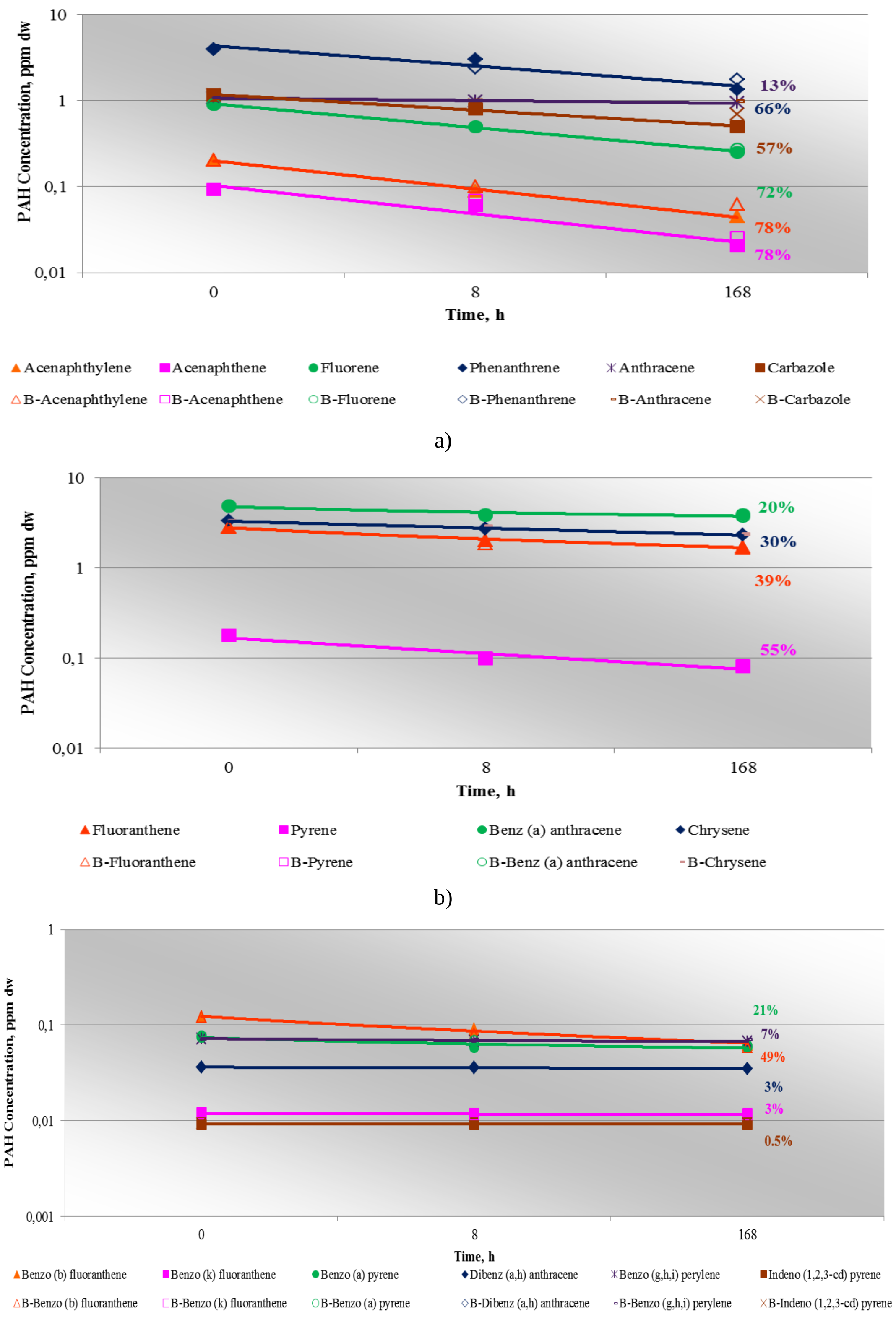


a)

b)

c)

Figure 6.13 The removal of PAHs from the soil in the slurry system with 1/5 solid/liquid ratio for Kaynaklar soil under light environments (25000 mg/kg diesel); a) 3Ring PAHs, b) 4 Ring PAHs, and c) 5&6 Ring PAHs



a)

b)

c)

Figure 6.14 The removal of PAHs from the soil in the slurry system with 1/5 solid/liquid ratio for Beach sand under light environments (25000 mg/kg diesel); a) 3Ring PAHs, b) 4 Ring PAHs, and c) 5&6 Ring PAHs

The PAHs removal efficiencies of sand and soil are not significantly different as well as the removals found in sterilized soils and PAHs removal from soils will be discussed at the end of this chapter.

The determination of the effect of local bacteria on the TPHs treatment from Beach sand and Kaynaklar soil is also studied with 10000 ppm initial diesel concentration in a slurry system with 1/5 solid/liquid ratio in light environment. The number of bacteria in the soils was detected throughout the remediation period and reported, as well as produced CO_2 from the reactors. The systems were operated for 168 hours (7 days). The pHs and TPHs were followed during the experimental period and the results are presented below:

The pH variations in the systems are presented in Figure 6.15.

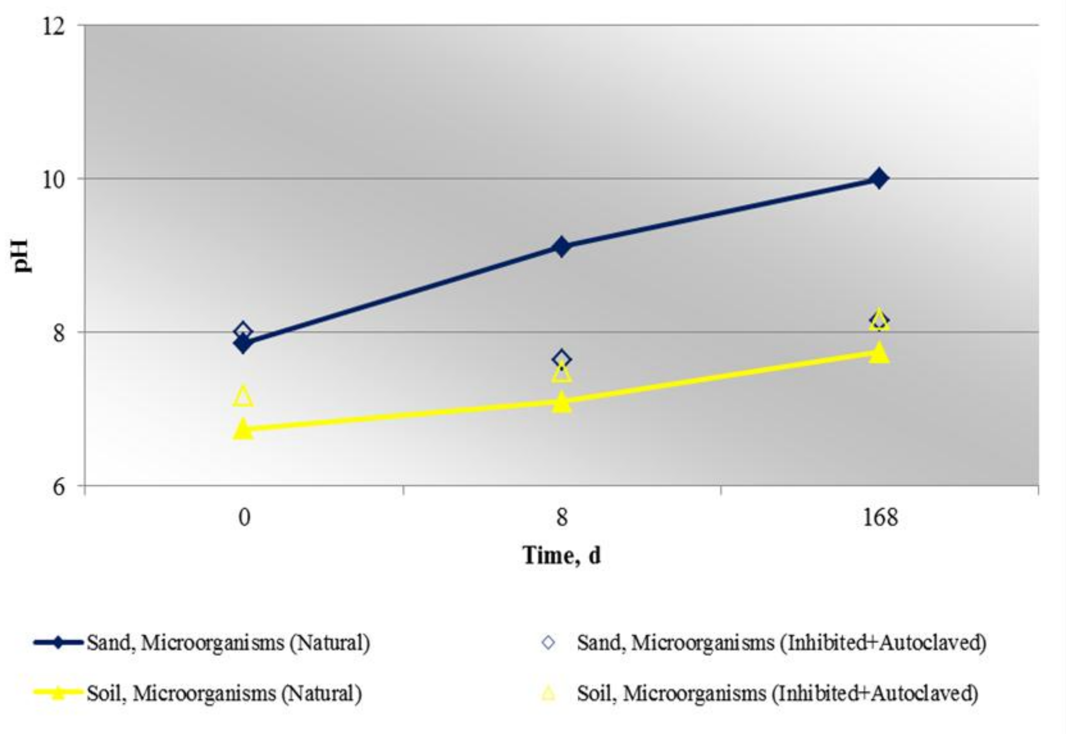
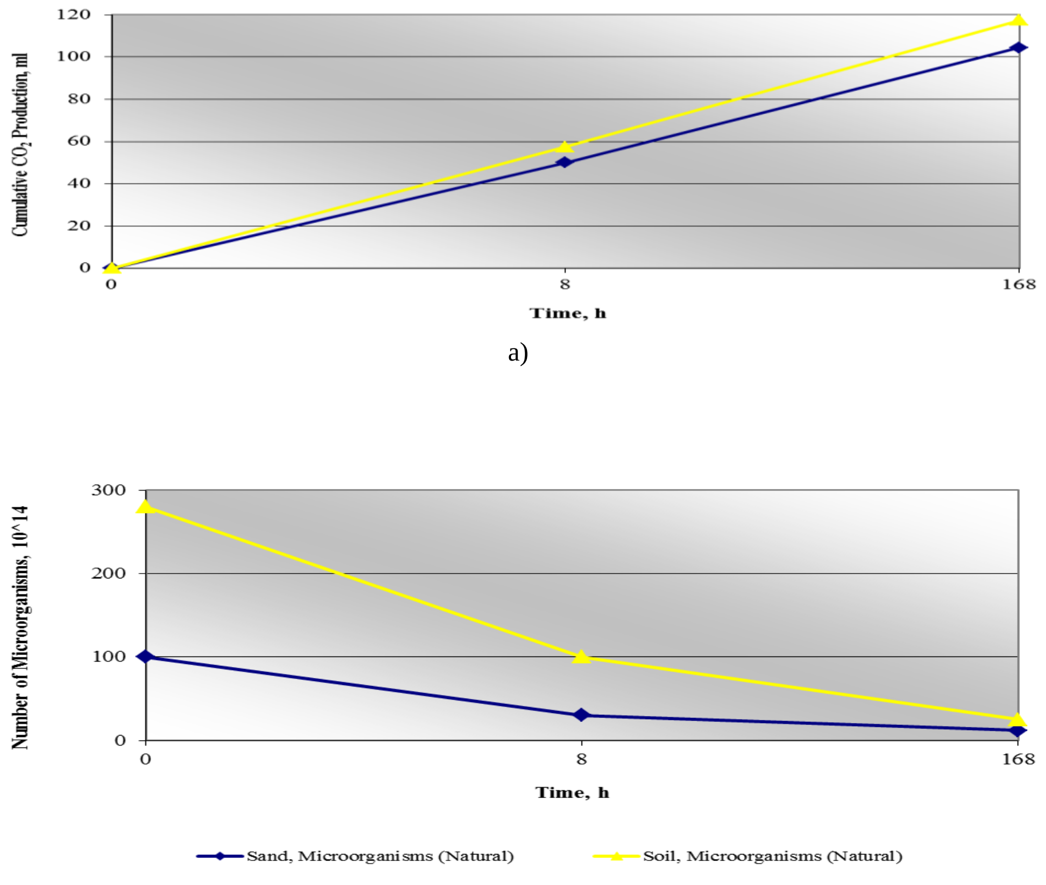


Figure 6.15 Slurry system pH variation with 1/5 solid/liquid ratio for Beach sand and Kaynaklar soil under light environment (10000 ppm diesel)

The initial pHs of the systems were in neutral interval at the beginning of the experiment and slightly raised during the experiments, especially in the system with Beach sand, which has calcite mineral component.

The cumulative CO_2 production from the systems and the variation in the number of bacteria in the soils were illustrated in Figure 6.16a and 6.16b. The unit CO_2 productions from Kaynaklar soil and Beach sand during the experimental period are close to each other in the sets with local bacteria and found as 1.4 ml/g soil and 1.6 ml/g soil, respectively. It is seen that number of bacteria in soils decreased in time- more significantly in Kaynaklar soil.



a)

b)

Figure 6.16 a) CO_2 production from the systems and b) the number of bacteria in soils in the slurry system with 1/5 solid/liquid ratio for Beach sand and Kaynaklar soil under light environment (10000 ppm diesel)

The TPHs removed from the system with Kaynaklar soil is 76% of the initial soil concentration, and TPHs removal from Beach sand was determined as 66% (Figure 6.17).

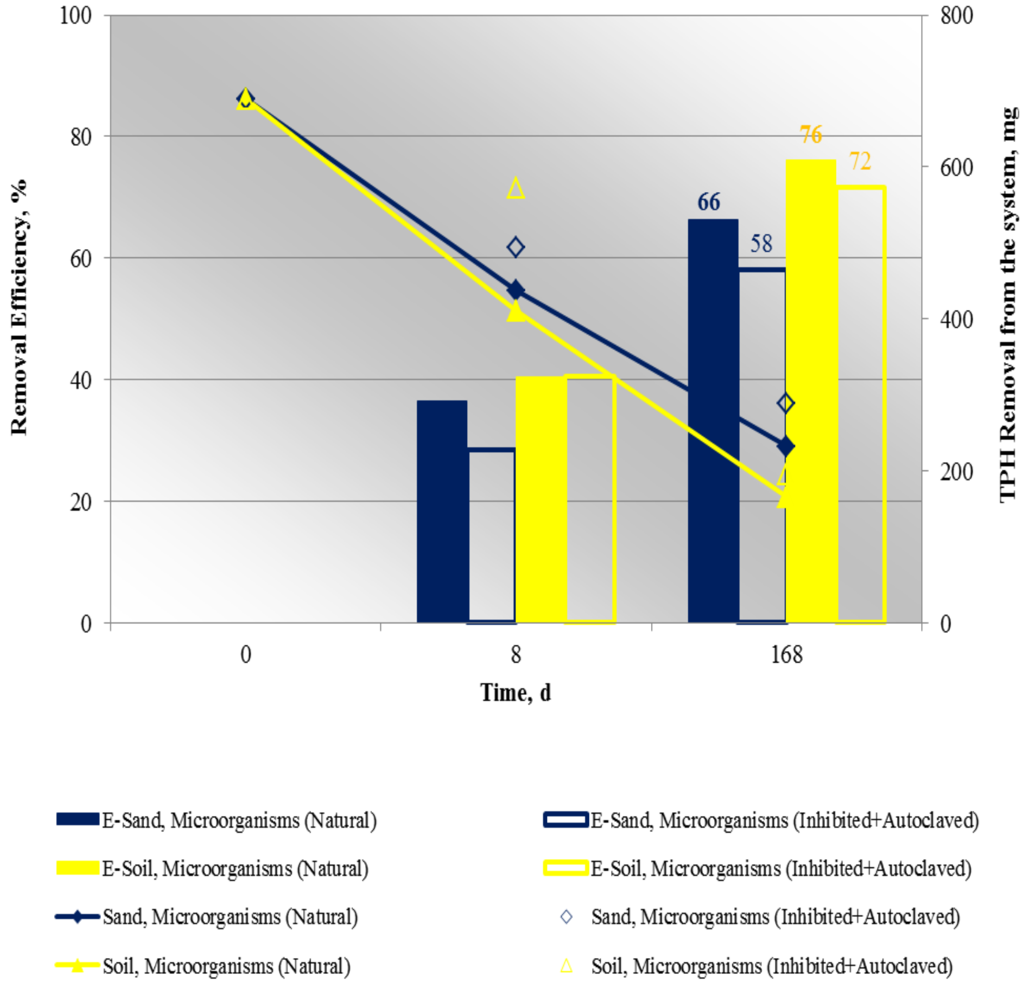


Figure 6.17 Residual concentration and removal rates of TPHs in slurry systems with 1/5, solid/liquid ratio for Beach sand and Kaynaklar soil under light environment (10000 mg/kg diesel)

It is also observed that, the final TPHs mass remained in the system with 10000 ppm of initial diesel concentration (232 mg for sand and 165 for soil) is lower than the remaining TPHs in the systems with 25000 ppm initial diesel (277 mg for sand and 190 mg for soil), both for the systems operated with sand and soil having local bacteria. Since the removals in sterilized soils are high, it can be said that 58-72% of TPHs are removed from the system by volatilization.

The TPHs remained in the system phases are also investigated here. Below, in Figures 6.18 and 6.19, the distribution of residual TPHs mass in solid, liquid and floating phases are given for the soils with local bacteria and sterilized soils, respectively.

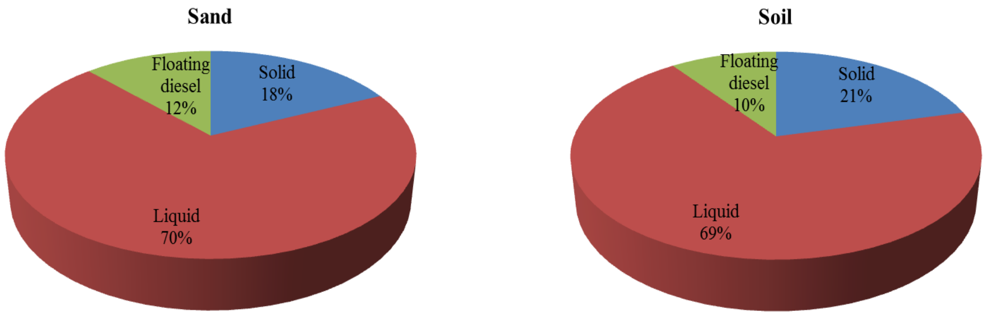


Figure 6.18 The distribution of residual TPHs (mg) in slurry systems as in solid, in liquid and as floating with 1/5 solid/liquid ratio for Beach sand and Kaynaklar soil with local bacteria under light environments (10000 mg/kg diesel)

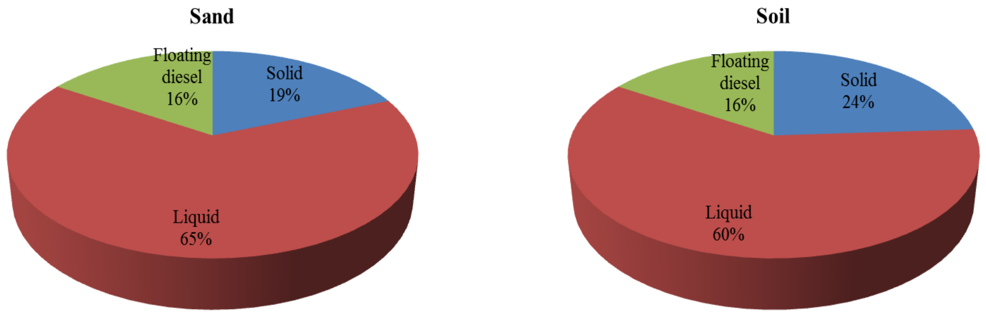


Figure 6.19 The distribution of residual TPHs (mg) in slurry systems as in solid, in liquid and as floating with 1/5solid/liquid ratio for sterilized Beach sand and Kaynaklar soil under light environments (10000 mg/kg diesel)

With 10000 ppm initial diesel concentration, the portion of the TPHs remain in the system were found higher in the liquid phase than the system operated with 25000 ppm initial diesel concentration, generally. Controversially, the amount of floating TPHs is lower. Here, it should be noted that the amount of diesel presented to the system initially is lower (10000 ppm), so the partitioning of TPHs in system phases is different than the system operated with 25000 ppm of initial diesel concentration.

6.2.1.3 The Effect of Soil Particle Size on Soil Remediation in Slurry Systems

In this part, the soil particle size effect on soil remediation in slurry systems was examined. The systems were operated by using coarse particles (2000-300 μm), medium particles (300-45 μm), and fine particles (<45μm) as well as bulk soil. The contaminated Kaynaklar soil having 100000 mg/kg diesel was used with a 1/1solid/liquid ratio in the slurry systems studied here. The bulk soil consists of 56.15% coarse, 38.99% medium, and 4.86% fine particles. The experiments were conducted by using soil with local bacteria with a control of sterilized soil in dark environment. The number of bacteria in the soils was detected throughout the remediation period and reported, as well as produced CO_2 from the reactors. The systems were operated for 60 days. The pH, TPHs, and PAHs were followed during the experimental period and the results are presented below:

The pH variation in the slurry systems with different particle sizes are given in Figure 20. It is recognized that pH of the systems remained in neutral interval with a small increase.

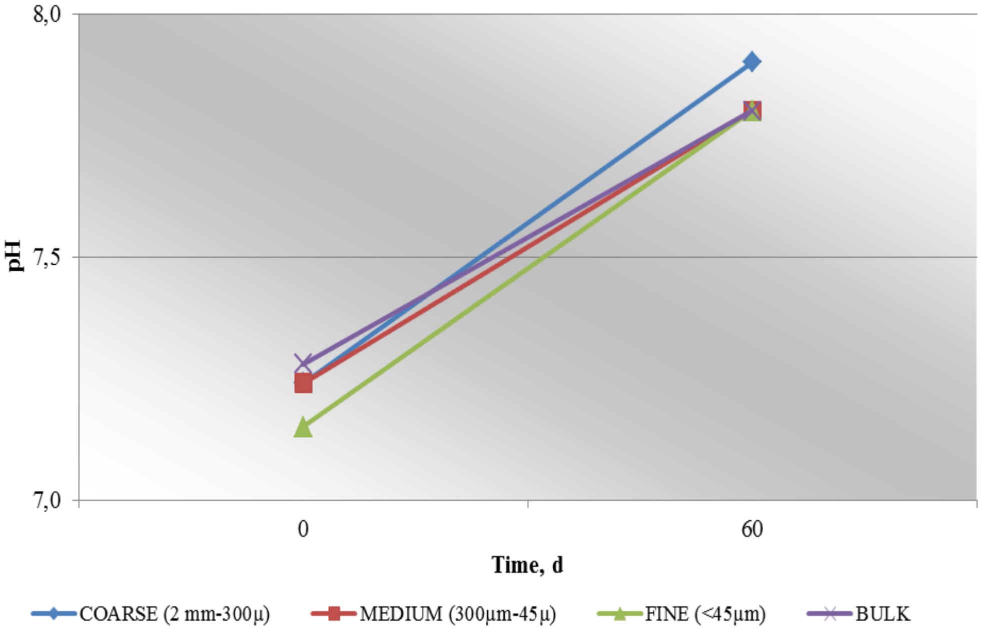
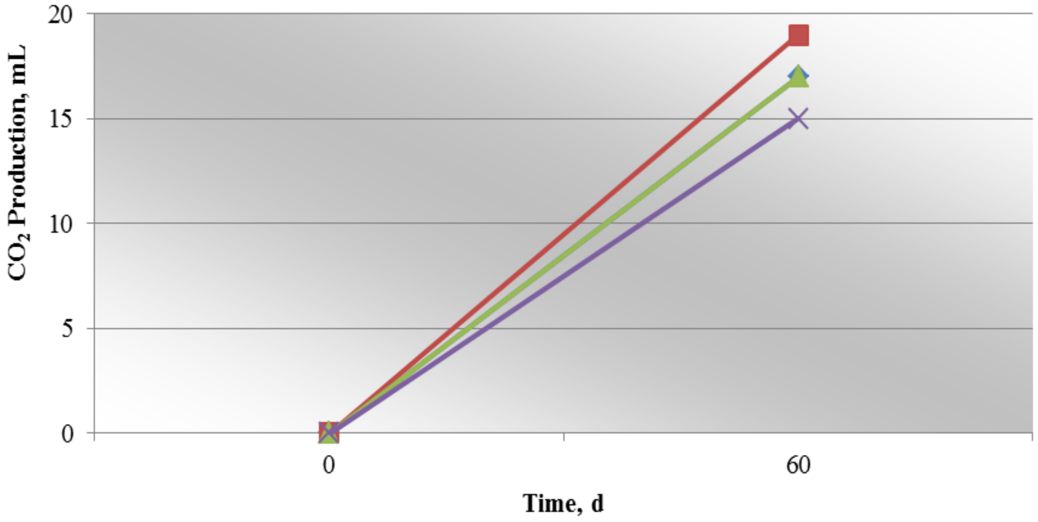
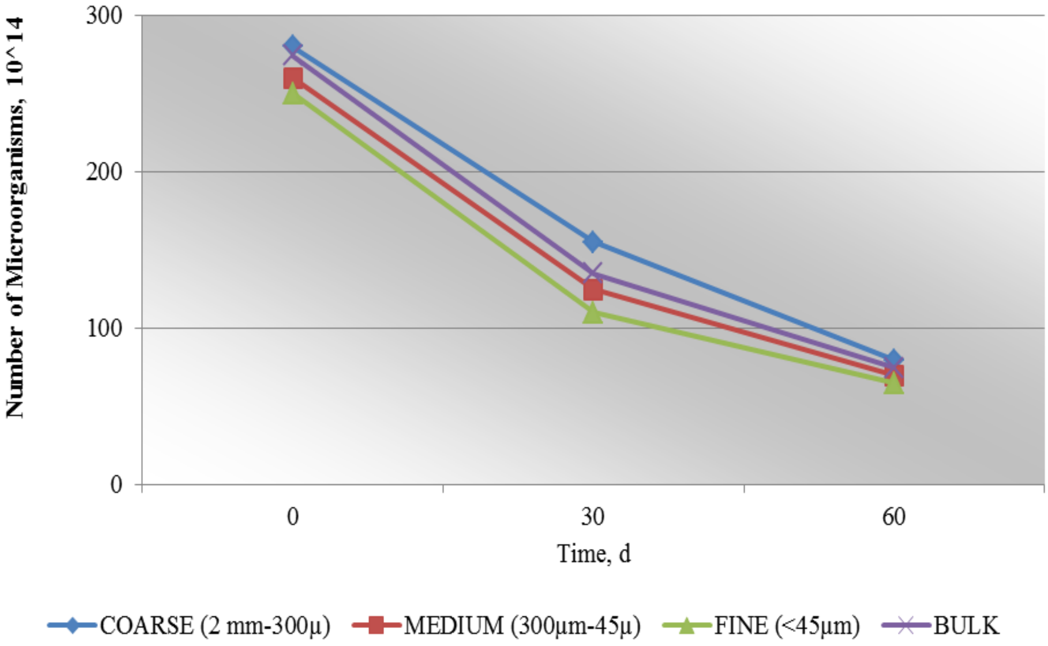


Figure 6.20 Slurry system pH variation with 1/1 solid/liquid ratio with Kaynaklar soil according to the soil particle size (100000 ppm diesel)

The cumulative CO_2 productions and bacterial counts of systems are given in Figure 6.21. The unit CO_2 productions from all systems were found very low; between 0.15-0.19 ml/g soil. This could be arise because of the initial concentration is as high as 100000 ppm diesel, which might be inhibitory for the local bacteria.



a)



b)

Figure 6.21 a) CO_2 production from the systems and b) the number of bacteria in soils in the slurry system with 1/1 solid/liquid ratio for Kaynaklar soil according to the soil particle size (100000 ppm diesel)

The initial bacteria population found in the soils showed that the number of bacteria downwards with decreasing particle diameter, which is not expected. In addition, with extending experimental period, the number of bacteria in soils is decreasing and closing to zero at the end of 60 days. This is another strong indicator of inhibition of bacteria because of high initial diesel concentration.

The TPHs remained in the system and removal rates are given in Figure 6.22. It can be seen that, the treatment efficiencies are increasing with increasing particle diameter. This can be explained with different SSAs of the particles. The bulk SSA of Kaynaklar soil is measured as 14.176 m^2/g, where its coarse fraction has a SSA of 13.75 m^2/g, medium fraction has 14.37 m^2/g of SSA, and fine fraction has SSA of 15.84 m^2/g. Therefore, desorption of TPHs from medium and fine grained soil is expected to be lower than coarse fraction, and the findings are compatible with the measured SSAs.

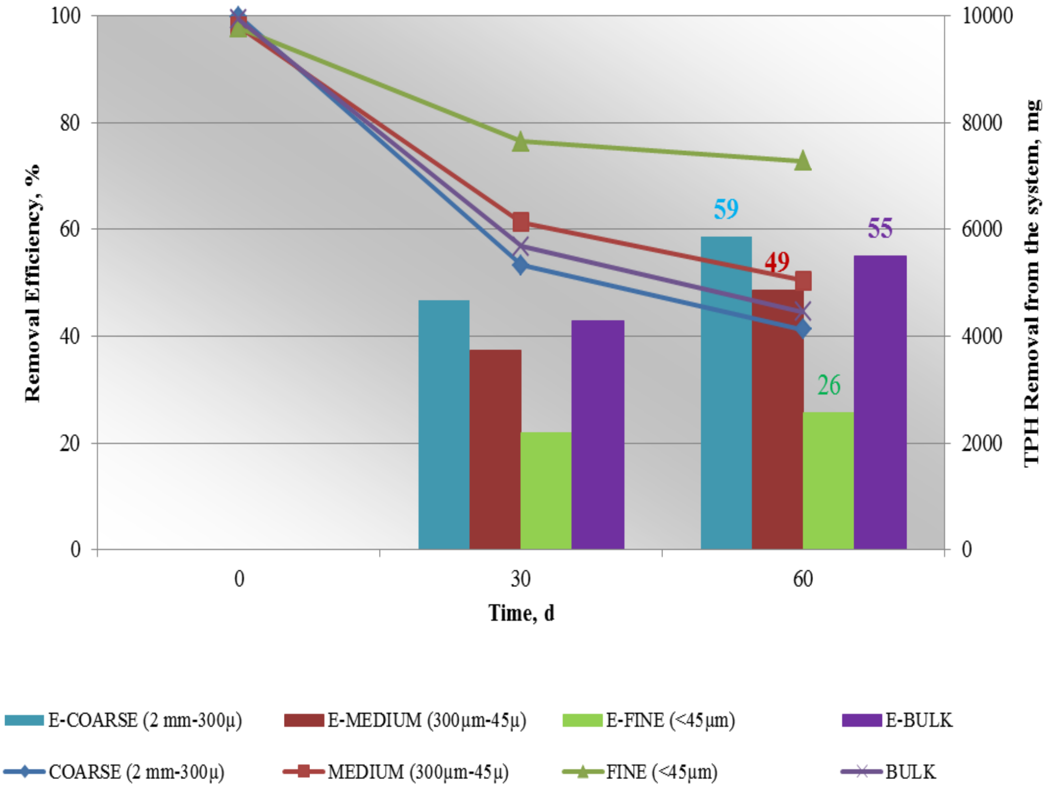


Figure 6.22 Residual concentration and removal rates of TPHs in slurry systems with 1/1, solid/liquid ratio for Kaynaklar soil (100000 mg/kg diesel)

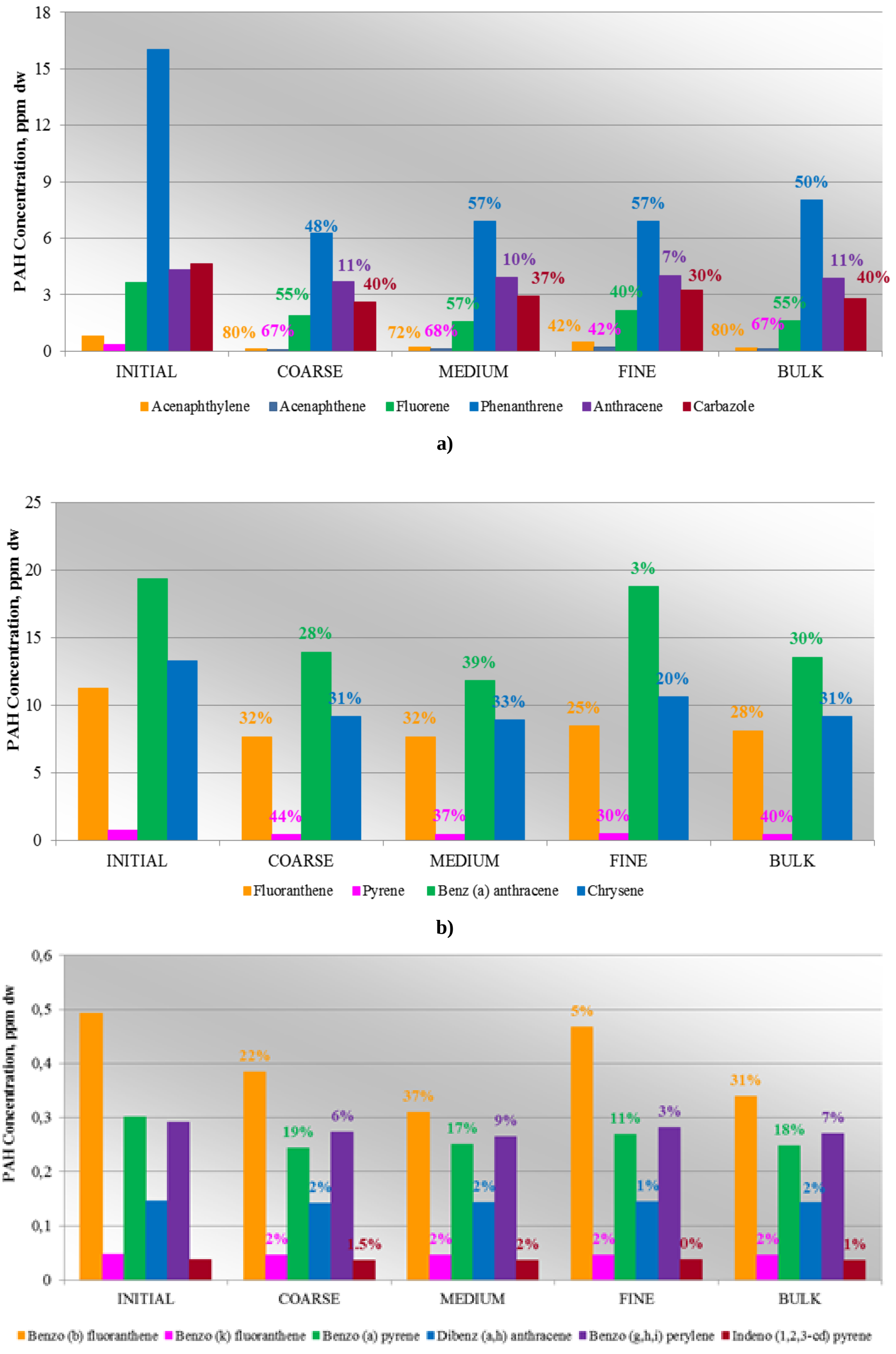
It is also recognized that the overall TPHs removal from the bulk Kaynaklar soil with 1/1 S/L ratio is significantly lower than the removals with lower S/L ratios (1/5, 1/10, and 1/20) discussed in Chapter 6.2.1.1. This finding is compatible with the previous results; the overall TPHs removal rates in the slurry systems are decreasing as the solid content in the reactor increases.

The distribution of residual TPHs in the systems showed that negligible amount of TPHs are a floated, 2-4% of TPHs are in liquid phase, and most of the remaining TPHs are found in solid phase of the system. These findings are also compatible with the findings with lower S/L ratios. As the solid content of the system increases, the floating diesel portion and the diesel portion in the liquid phase are decreasing.

PAHs removals from the soil contaminated with 100000 ppm diesel are also investigated with 1/1 solid/liquid ratio in slurry systems. The PAHs removal efficiencies are given in Figure 6.23 according to the number of benzene rings of the studied PAHs. In coarse soil fraction, the PAHs with 3 Rings were removed 15-84% (ave. 54.2%), 4 Ring PAHs were removed between 28-44% (ave. 33.8%), and 5&6 Ring PAHs were removed 1.5-22% (ave. 8.8%). For medium soil fraction, PAHs with 3 Rings were removed 10-72% (ave. 50.2%), 4 Ring PAHs were removed between 32-39% (ave. 35.3%), and 5&6 Ring PAHs were removed 2-37% (ave. 11.5%). The results showed that, 3 Rings PAHs were removed 7-57% (ave. 36.3%), 4 Ring PAHs were removed between 3-30% (ave. 19.5%), while 5&6 Ring PAHs were removed 0-11% (ave. 3.7%).

PAHs removals in bulk Kaynaklar soil are similar and compatible with the findings with its fraction; the PAHs with 3 Rings were removed 11-80% (ave. 50.5%), 4 Ring PAHs were removed between 28-40% (ave. 32.3%), and 5&6 Ring PAHs were removed 1-31% (ave. 10.2%).

PAHs treatment efficiencies show a similar trent with the finding s in previous parts of Chapter 6; as the number of benzene rings increase, the treatment efficiency decreases.



a)

b)

c)

Figure 6.23 The removal of PAHs from the soil in the slurry system with 1/1 solid/liquid ratio for soil particle fraction (100000 mg/kg diesel); a) 3Ring PAHs, b) 4 Ring PAHs, and c) 5&6 Ring PAHs

6.2.2 Slurry System Remediation with Soil Amendment

In this part of the thesis, the performance of a slurry system was investigated with diesel contaminated soil by addition of compost as soil amendment. The soil slurry systems operated are different from the ones in previous part of this chapter; the systems were aerated, and the solid/liquid ratio was applied as 1/1. These slurry systems were investigated according to the amount of compost added, the initial concentration of diesel in soil, and the contamination age. All of the slurry systems in this part of the study were operated for 60 days. Variations in pH, TPHs, CO_2 generation, bacteria counts and PAHs in the systems were followed and the findings are presented in below sub-chapters. The initial PAHs concentrations in the solid content of the slurry systems are given below in Table 6.3 with some important properties of PAHs.

6.2.2.1 The Effect of Initial Contaminant Concentration and Compost to Soil Ratio on Slurry Bioremediation of Diesel Contaminated Soils

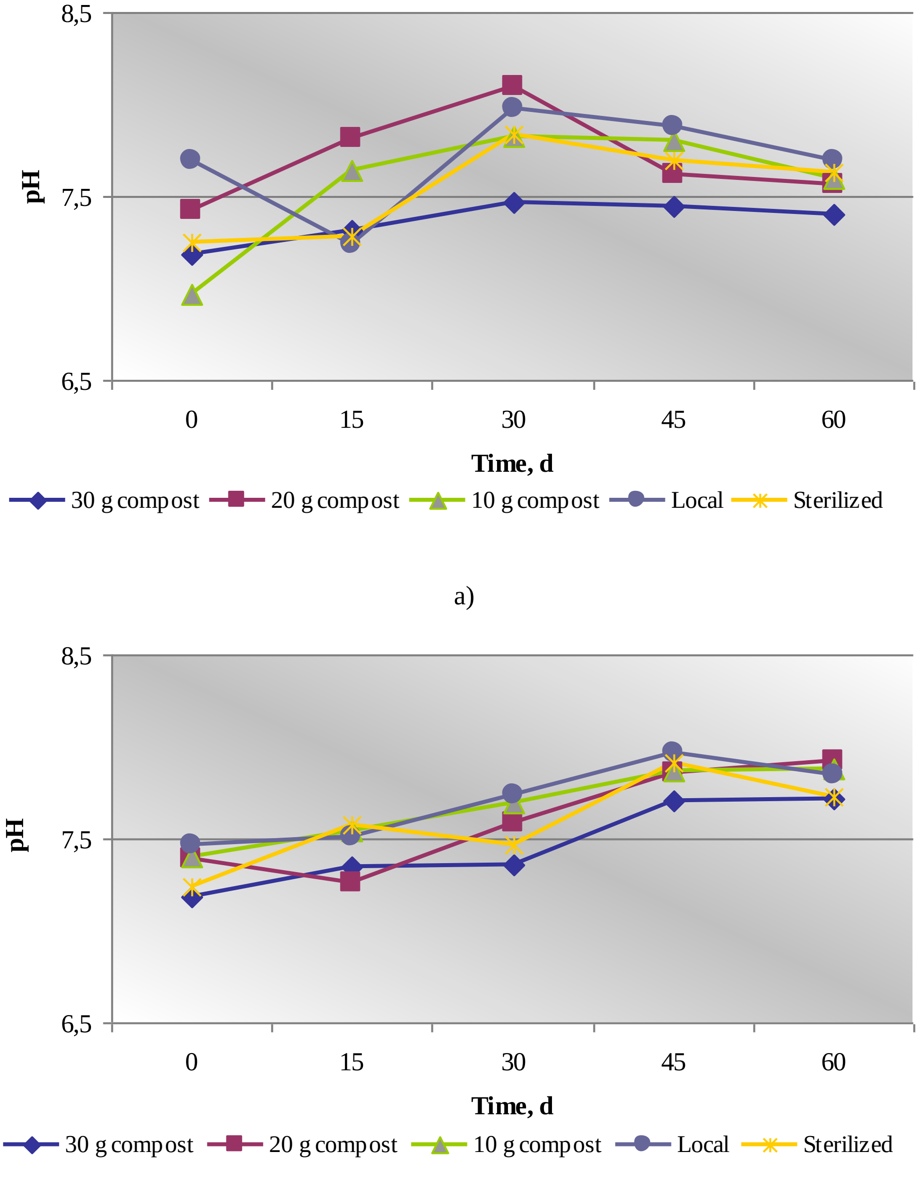
The Kaynaklar soil used in the slurry systems are contaminated with 25000 ppm and 100000 ppm diesel. The soil amount in the systems 100 g, and three different compost amounts were applied as compost-soil ratio; 30g compost/100g soil, 20g compost/100g soil, and 10g compost/100g soil. For keeping the mass of solids constant in the systems, 10 and 20 grams of glass beads were substituted to the systems with 20 g and 10 g of compost content, respectively. The control sets with soils having local bacteria and sterilized soils were operated only with 30g of glass beads substitution instead of compost.

The pH levels in the slurries with 25000 ppm and 100000 ppm initial soil diesel concentration are given in Figure 6.24. It is seen that, initial pH in slurries with 25000 ppm 100000 ppm initial soil diesel concentrations (IDCs) are similar and in neutral range. In the system with 25000 ppm IDC, pH rose to alkaline range in first 30 days and then closed to the neutral level at the end of the experimental period. In the system with 100000 ppm IDC, pH levels raised slightly during the whole

Table 6.3 The initial concentrations of PAHs in slurry solid content according to the initial diesel concentration and with their some important properties

Studied PAHs				**Initial Concentration in Soil, mg/kg**		
Number of Benzene Rings	**Name**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**10000 ppm diesel**	**25000 ppm diesel**	**100000 ppm diesel**
3 Ring	Acenaphthylene	16,1	$9{,}12 \times 10^{-4}$	0,0628	0,1571	0,6282
	Acenaphthene	3,9	$2{,}50 \times 10^{-3}$	0,0284	0,0710	0,2839
	Fluorene	1,89	$8{,}42 \times 10^{-3}$	0,2792	0,6981	2,7923
	Phenanthrene	1,15	$1{,}12 \times 10^{-4}$	1,2331	3,0828	12,3311
	Anthracene	$4{,}34 \times 10^{-2}$	$2{,}67 \times 10^{-6}$	0,3335	0,8338	3,3354
	Carbozole	0,721	$2{,}66 \times 10^{-4}$	0,3584	0,8959	3,5836
4 Ring	Fluoranthene	$2{,}60 \times 10^{-1}$	$1{,}23 \times 10^{-8}$	0,8666	2,1665	8,6661
	Pyrene	$1{,}35 \times 10^{-1}$	$1{,}35 \times 10^{-7}$	0,0547	0,1366	0,5466
	Benz(a)anthracene	$9{,}40 \times 10^{-3}$	$3{,}05 \times 10^{-8}$	1,4888	3,7221	14,8884
	Chrysene	$2{,}00 \times 10^{-3}$	$6{,}23 \times 10^{-9}$	1,0211	2,5527	10,2106
5&6 Ring	Benzo(b)fluoranthene	$1{,}50 \times 10^{-3}$	$5{,}00 \times 10^{-7}$	0,0379	0,0947	0,3789
	Benzo(k)fluoranthene	$8{,}00 \times 10^{-4}$	$9{,}65 \times 10^{-10}$	0,0037	0,0092	0,0369
	Benzo(a)pyrene	$1{,}62 \times 10^{-3}$	$5{,}49 \times 10^{-9}$	0,0232	0,0581	0,2324
	Dibenz(a,h)anthracene	$2{,}49 \times 10^{-6}$	$1{,}00 \times 10^{-10}$	0,0112	0,0280	0,1120
	Benzo(g,h,i)perylene	$2{,}6 \times 10^{-4}$	$1{,}01 \times 10^{-10}$	0,0224	0,0560	0,2240
	Indeno(1,2,3-c,d)pyrene	$2{,}20 \times 10^{-5}$	$1{,}00 \times 10^{-10}$	0,0029	0,0072	0,0288

experimental period and the stand between the interval of 7.8-8 at the end of the operational period.



b)

Figure 6.24 The variation of pH in the compost amended slurry systems a) 25000 ppm initial diesel, b) 100000 ppm initial diesel

The CO_2 productions and bacterial counts were also followed in the systems during the experimental period and the findings are given in Figure 6.25. Any CO_2

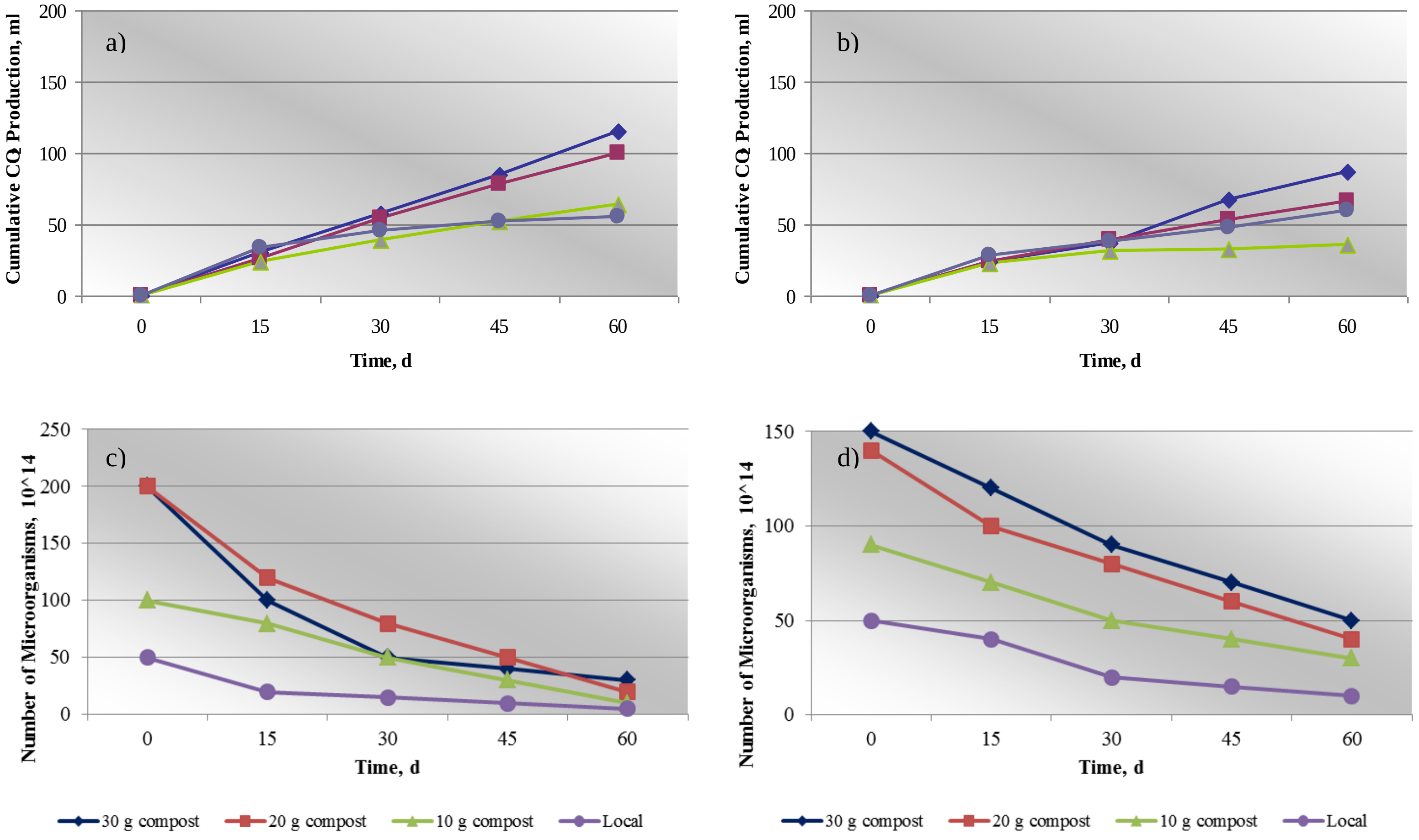
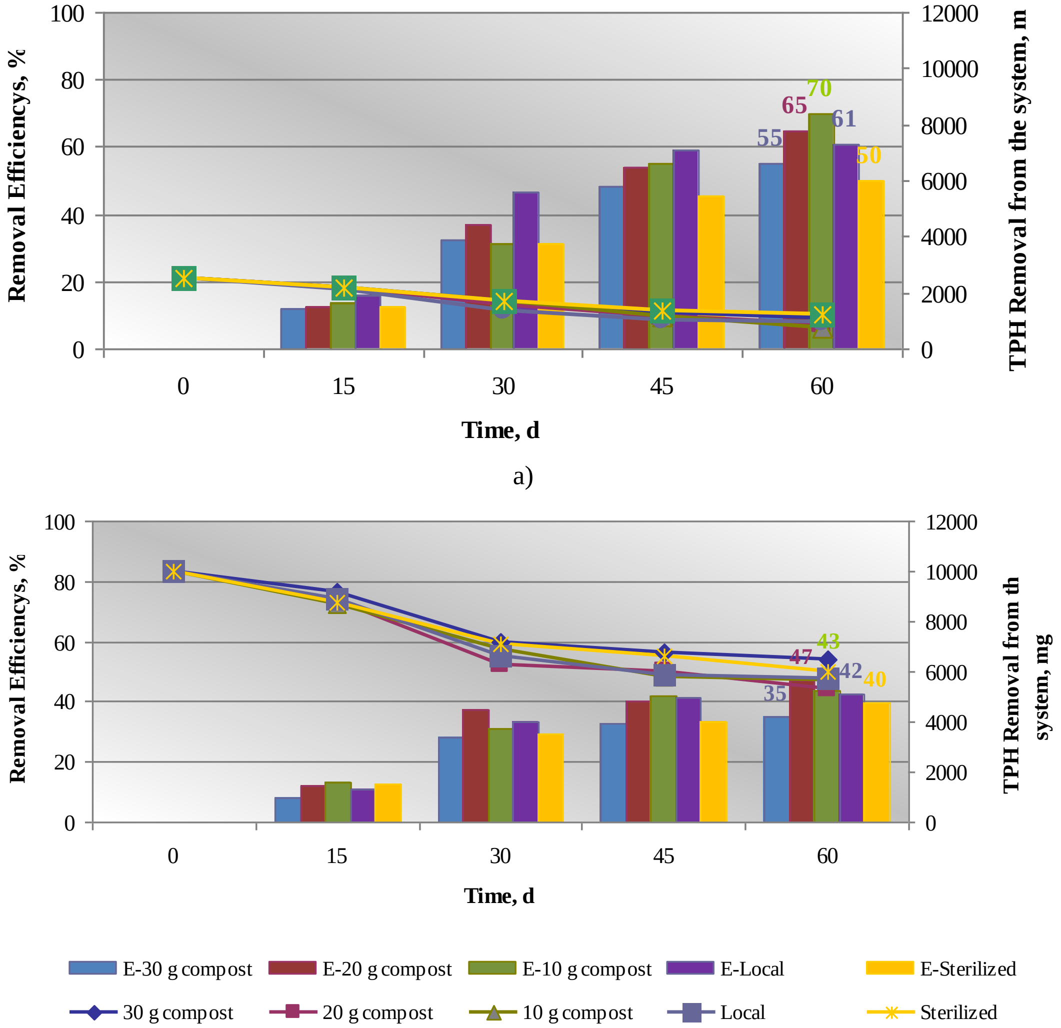


Figure 6.25 The cumulative CO$_2$ production and bacterial counts in slurry systems with the compost added soils and the soil with local bacteria a) CO$_2$ production with 25000 ppm IDC, b) CO$_2$ production with 100000 ppm IDC, c) Bacterial counts with 25000 ppm IDC, and d) Bacterial counts with 100000 ppm IDC

production or bacterial growth in sterilized soils could not be observed. It is seen that cumulative CO_2 productions in the system with initial soil diesel concentration of 25000 ppm dw is higher than the system with 100000 ppm dw soil diesel concentration.

Since the initial bacterial counts of the Kaynaklar soil and compost is close to each other, the initial bacterial counts in the systems are similar. It is seen that both in systems with IDC of 25000 ppm and 100000 ppm, the number of bacteria decreases with time. Additionally, the decrease in bacteria counts in the system with 100000 ppm IDC is significantly sharper in the first 15 days of the experiment. This situation indicates the inhibition effect of high initial concentration on both soil local bacteria and compost bacteria.

The TPHs removals from the systems and remaining TPHs in the systems are given in Figure 6.26. It is seen that the removal efficiencies are 10-22% higher in the system with 25000 ppm IDC. The removal efficiencies are decreasing with increasing compost amount in the system, which may be caused by the adsorption of NAPLs on the organic matter supplied by compost and/or hindered volatilization of TPHs from the system because of increasing solid content. The 1.4-6.3% of residual TPHs are found in the liquid fraction of the systems at the end of the treatment period. That means the transfer of NAPLs from solid content to liquid content is low when the medium is rich in organics.



a)

b)

Figure 6.26 The TPHs removal and the amount of TPHs remained in slurry systems with the compost added soils and the soil with local bacteria a) Results with 25000 ppm IDC, b) Results with 100000 ppm IDC

The PAHs removals from the slurry systems which compost added as amendment are also investigated and the results are presented in Figures 6.27 -6.35 according to the initial concentrations and number of benzene rings of the PAHs. In addition, the average PAHs removal rates from the soils in the system are summarized in Table 6.4 according to the compost added to the systems, PAH groups, and initial diesel concentration of soil.

Table 6.4 The summary of the average PAHs removal efficiencies from the soil slurry systems operated with compost amendment

PAHs groups according to number of benzene rings	**Compost Amount Added to the Slurry System, g**	**Average PAHs removal efficiencies, %**	
		25000 ppm IDC	**100000 ppm IDC**
3Ring PAHs	30	28.7	22.7
	20	43.2	39.3
	10	55.7	45.0
	0-Local bct.	46.8	41.2
	0-Sterile Soil	44.0	32.5
4Ring PAHs	30	6.6	5.8
	20	20.0	12.0
	10	31.8	22.5
	0-Local bct.	30.5	21.5
	0-Sterile Soil	27.3	11.5
5&6Ring PAHs	30	1.4	0.6
	20	2.4	3.0
	10	8.6	10.8
	0-Local bct.	10.8	5.5
	0-Sterile Soil	10.8	3.8

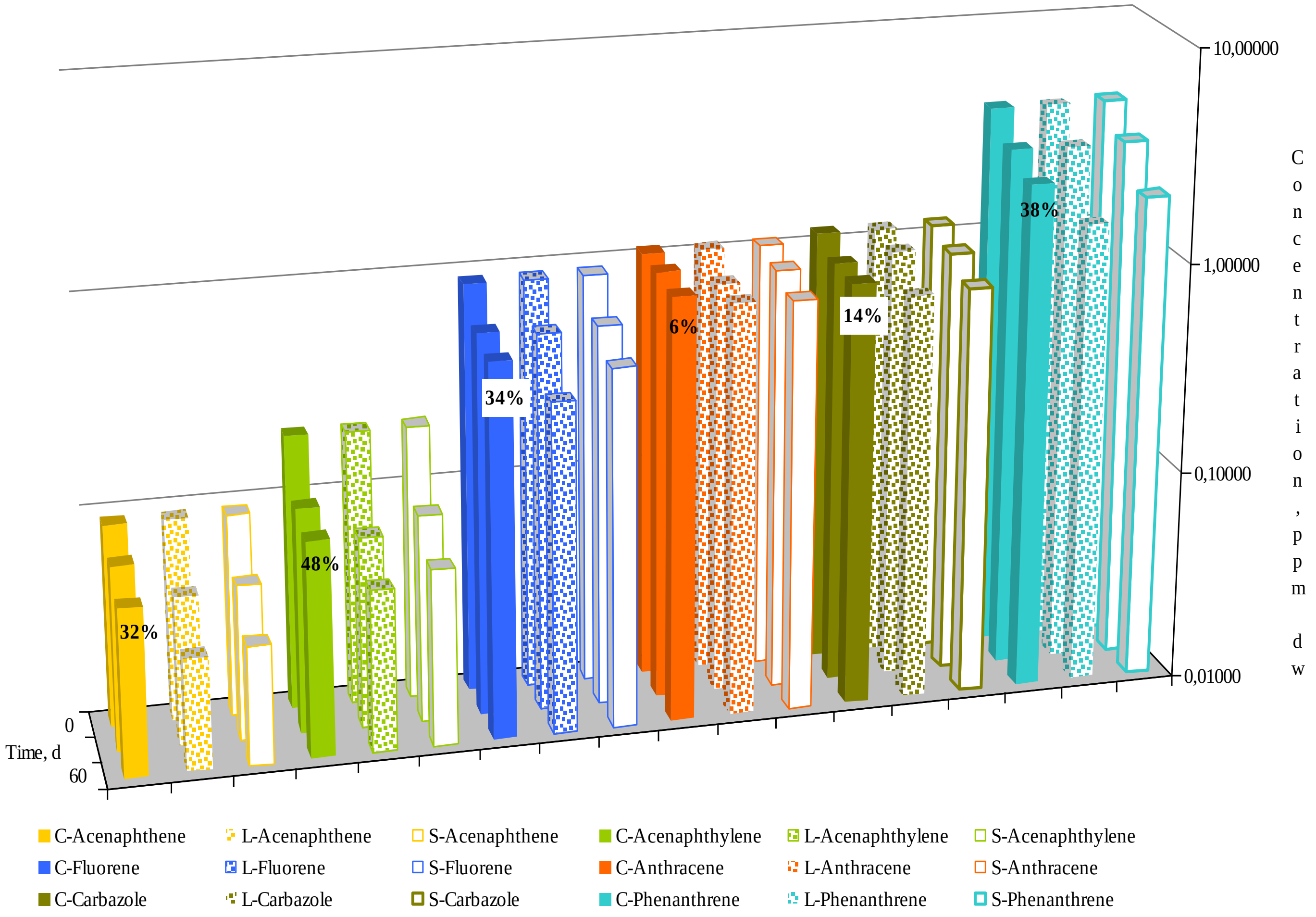


Figure 6.27a 3Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 30/100

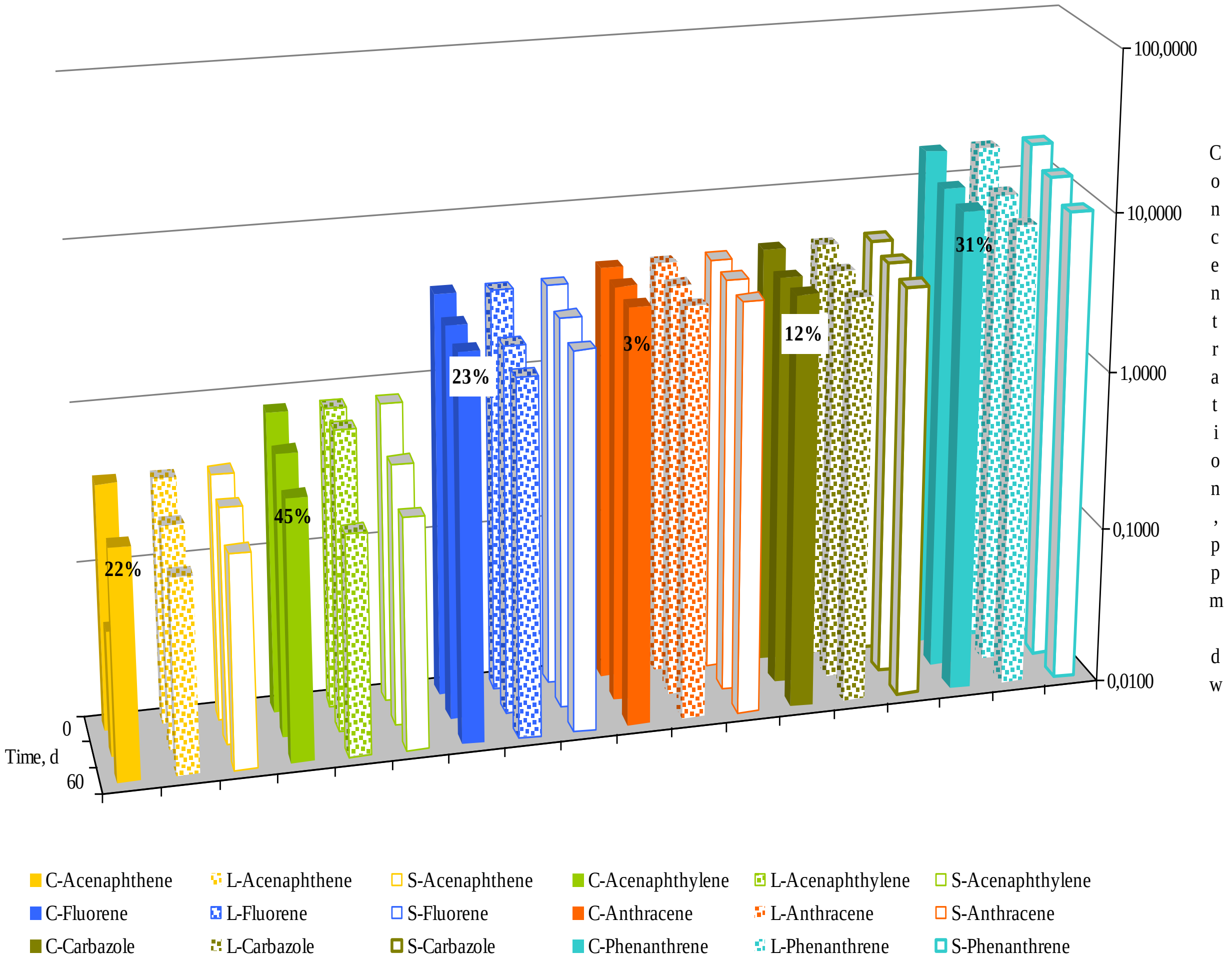


Figure 6.27b 3Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 30/100

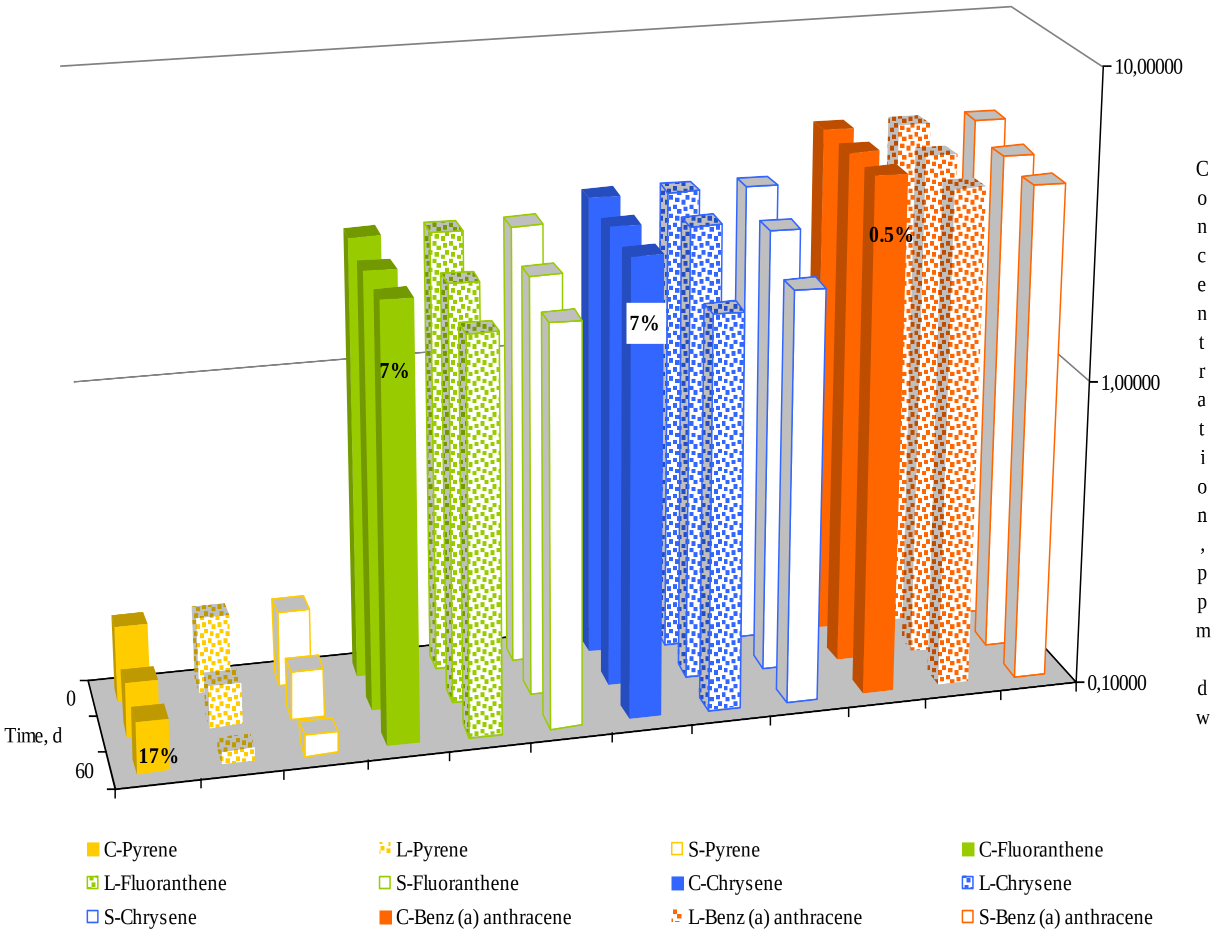


Figure 6.28a 4Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 30/100

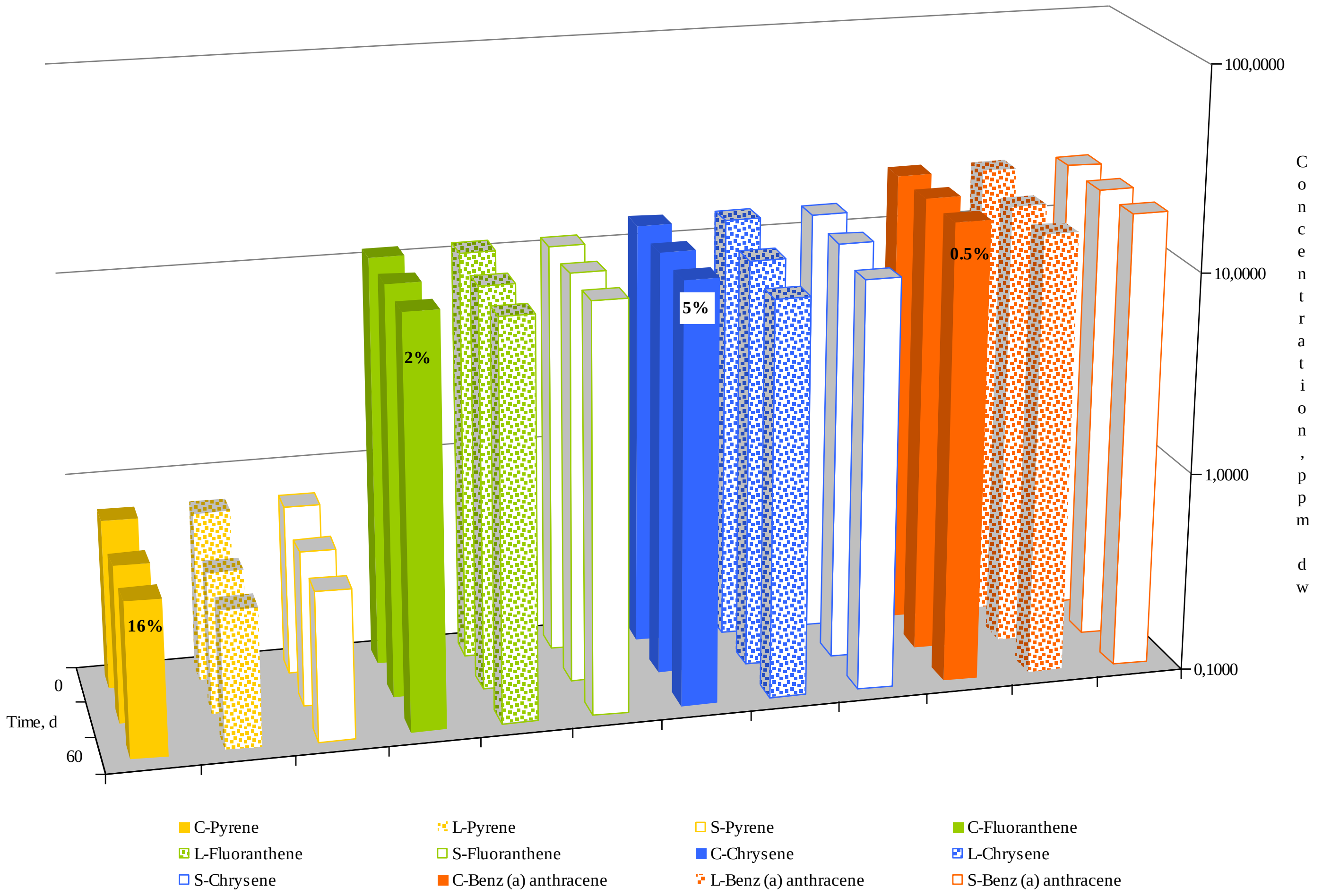


Figure 6.28b 4Ring PAHs removal from soil slurries contaminated with 100000 ppm diesel with compost –soil ratio of 30/100

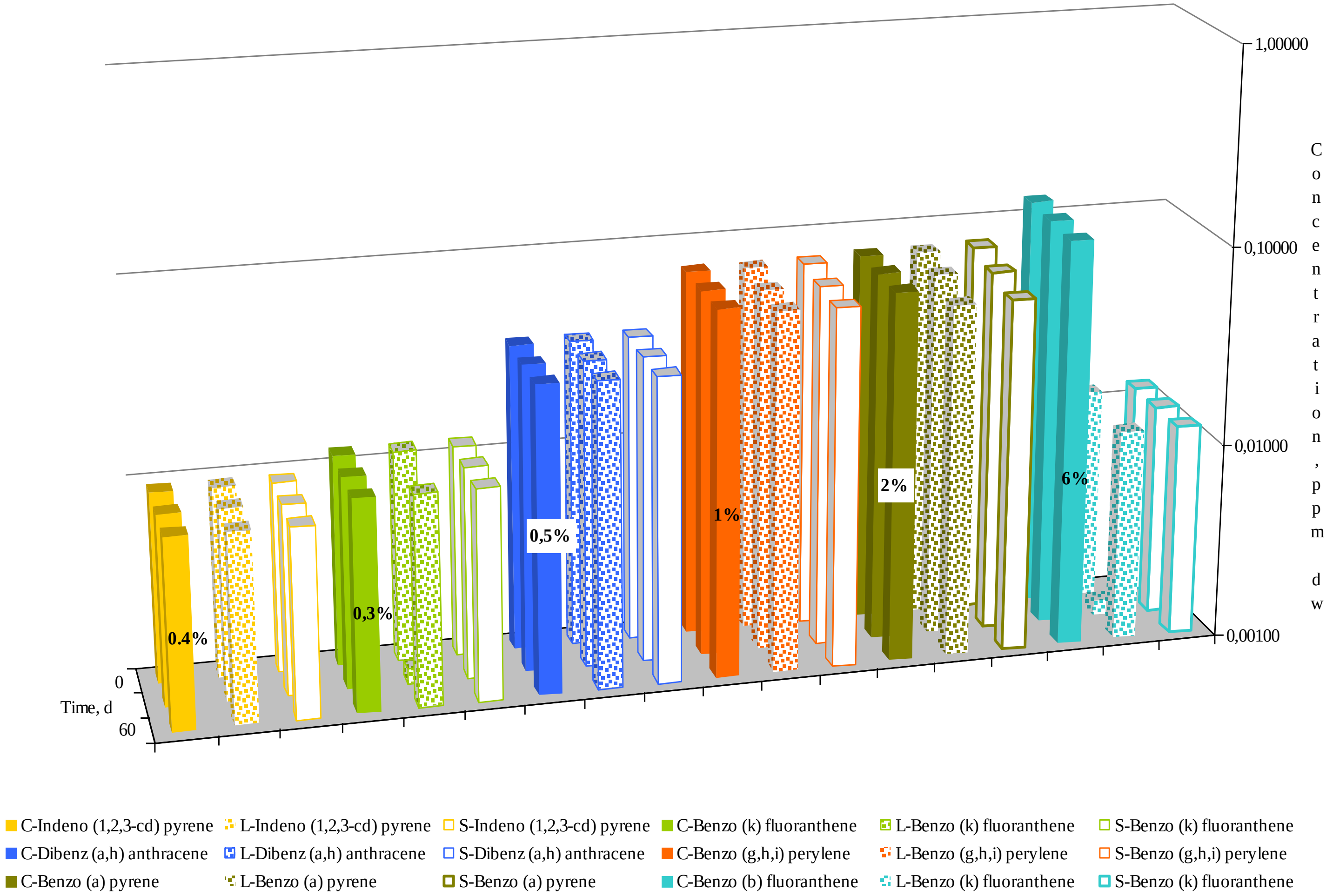


Figure 6.29a 5&6Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 30/100

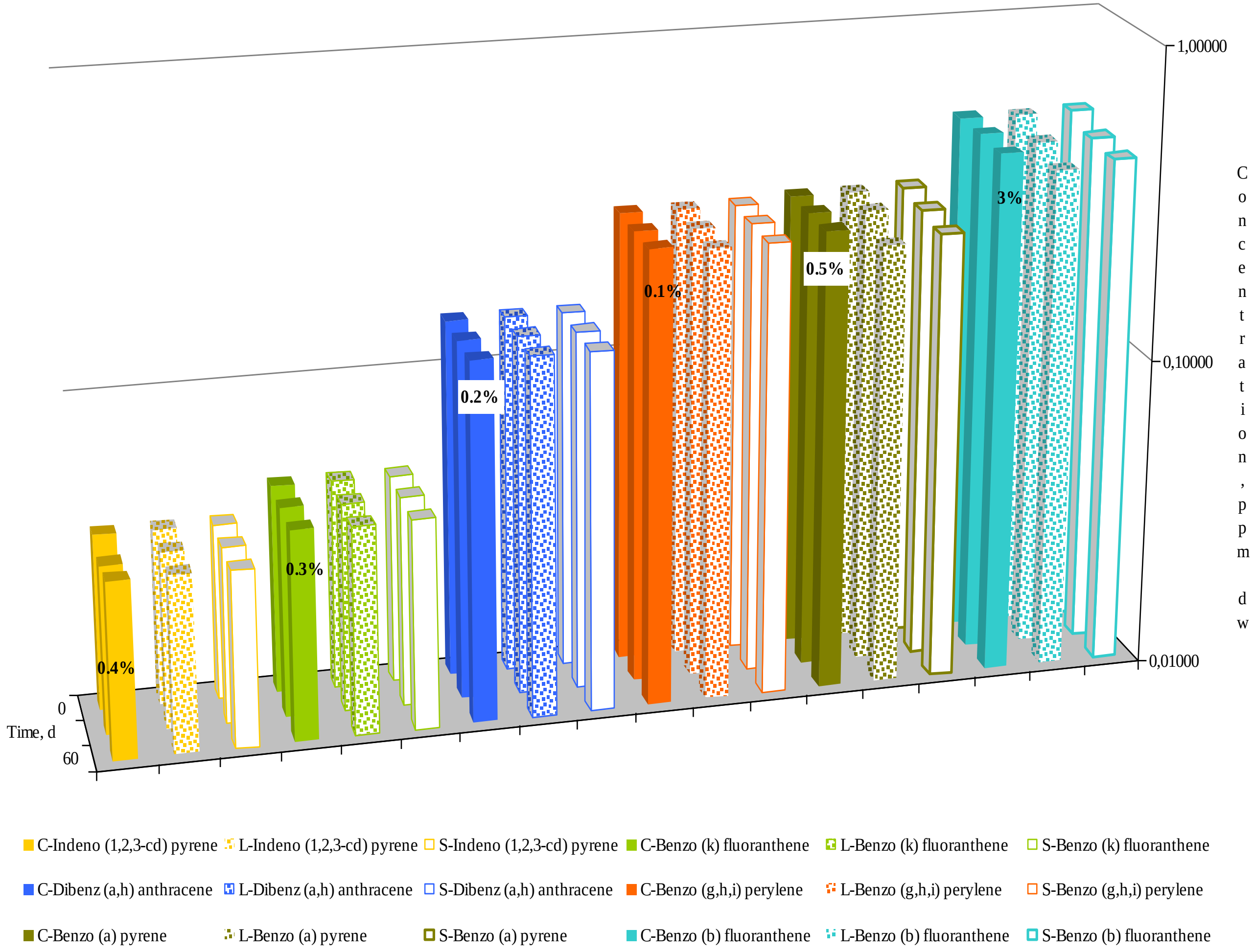


Figure 6.29b 5&6Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 30/100

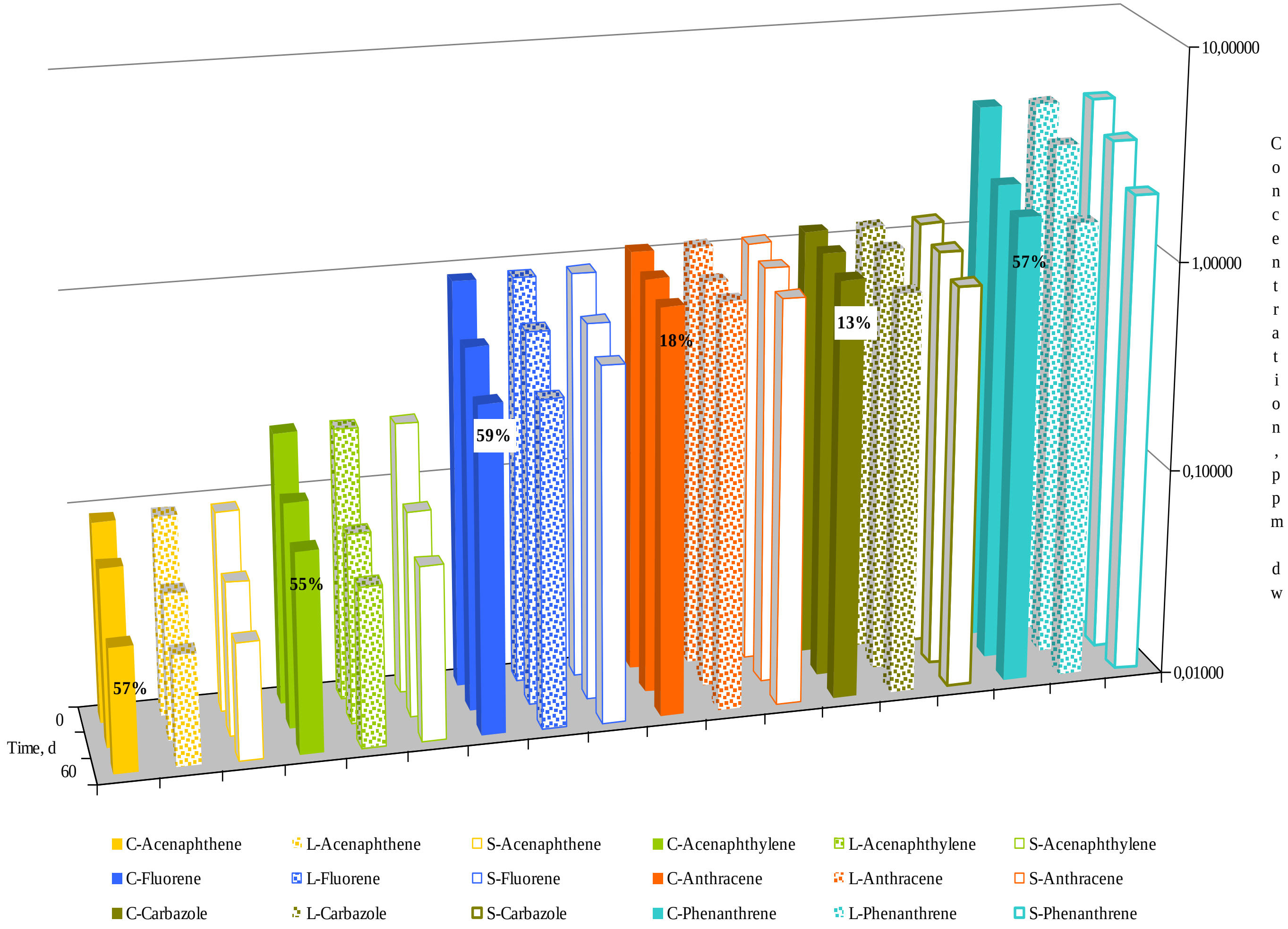


Figure 6.30a 3Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 20/100

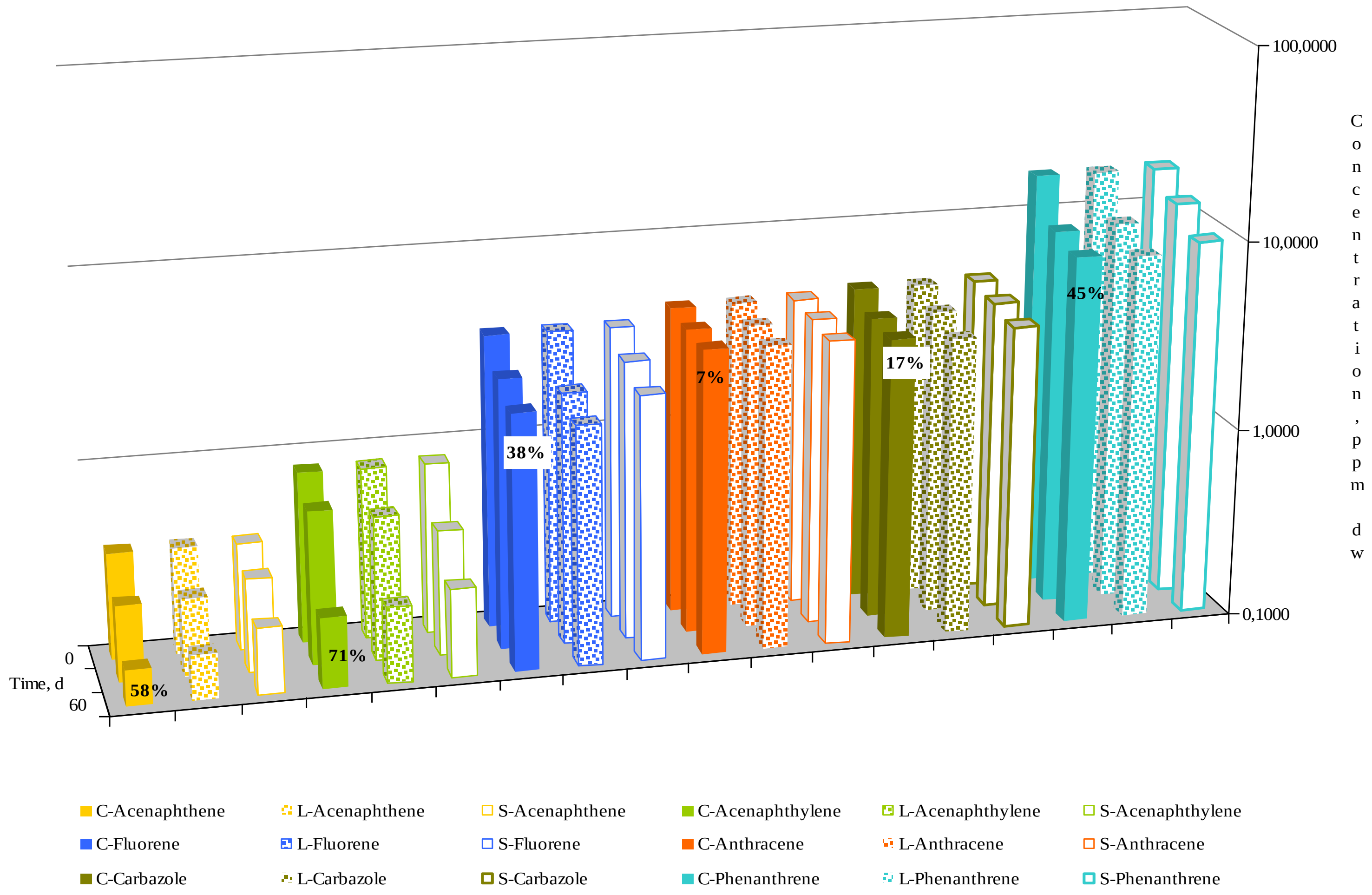


Figure 6.30b 3Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 20/100

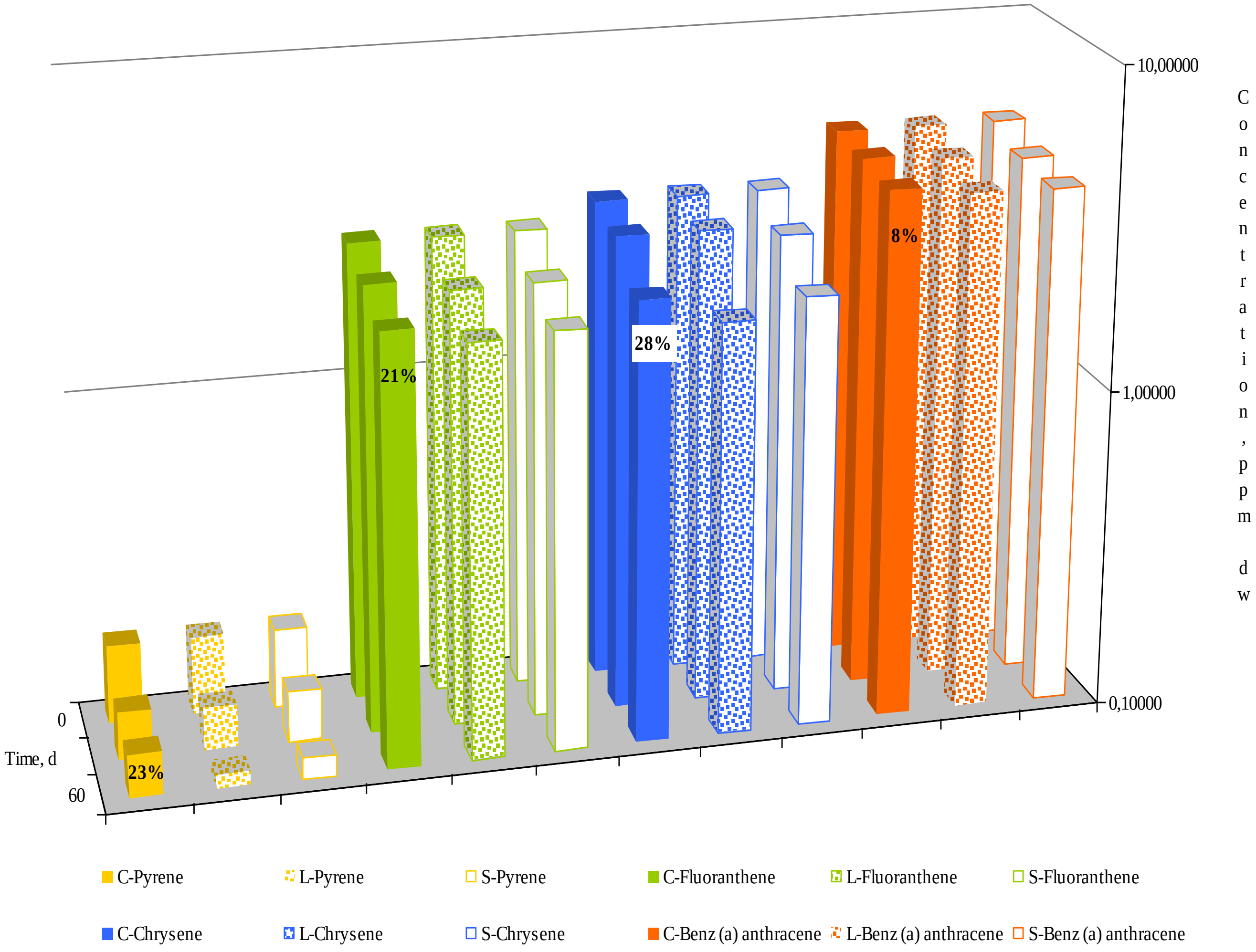


Figure 6.31a 4Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 20/100

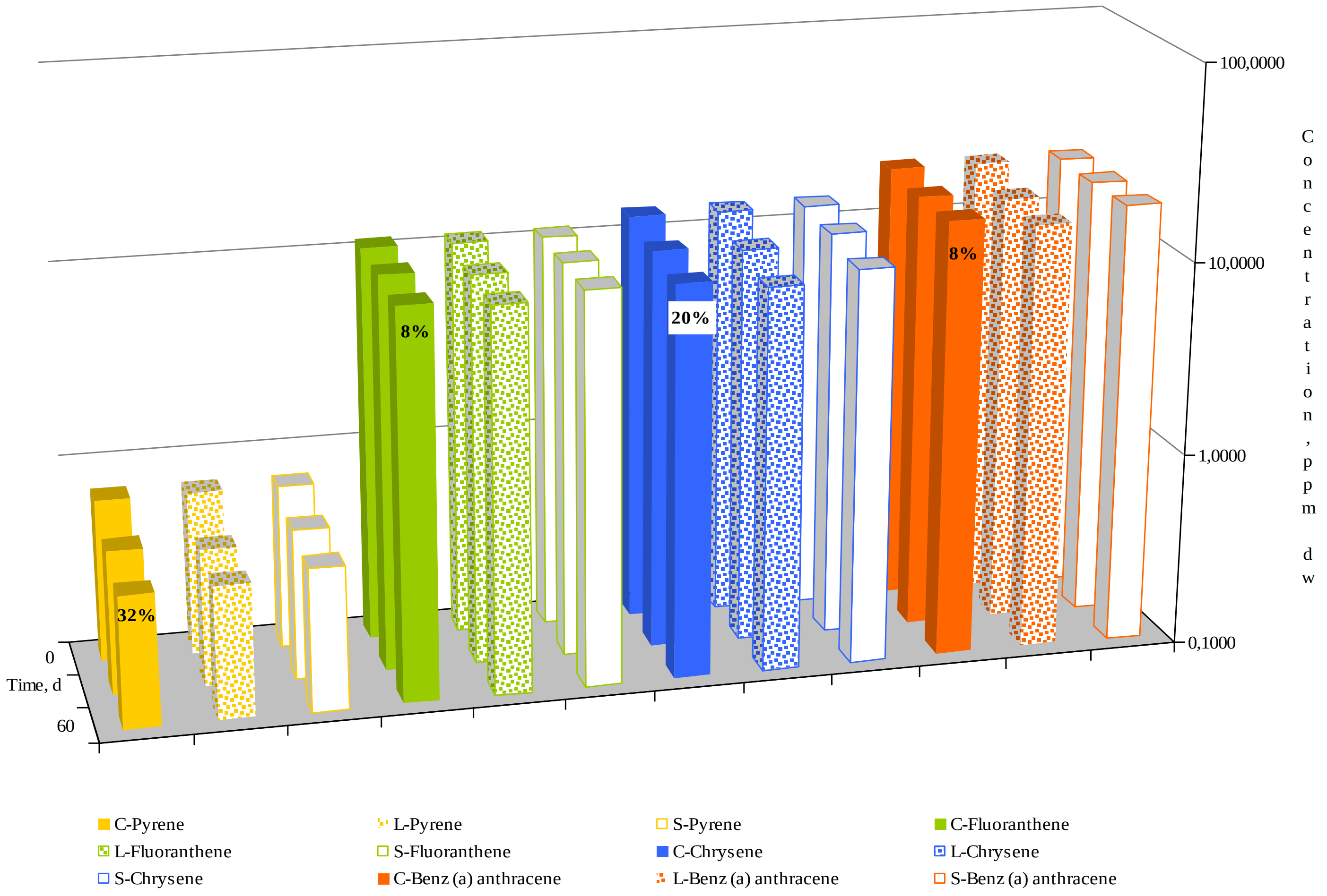


Figure 6.31b 4Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 20/100

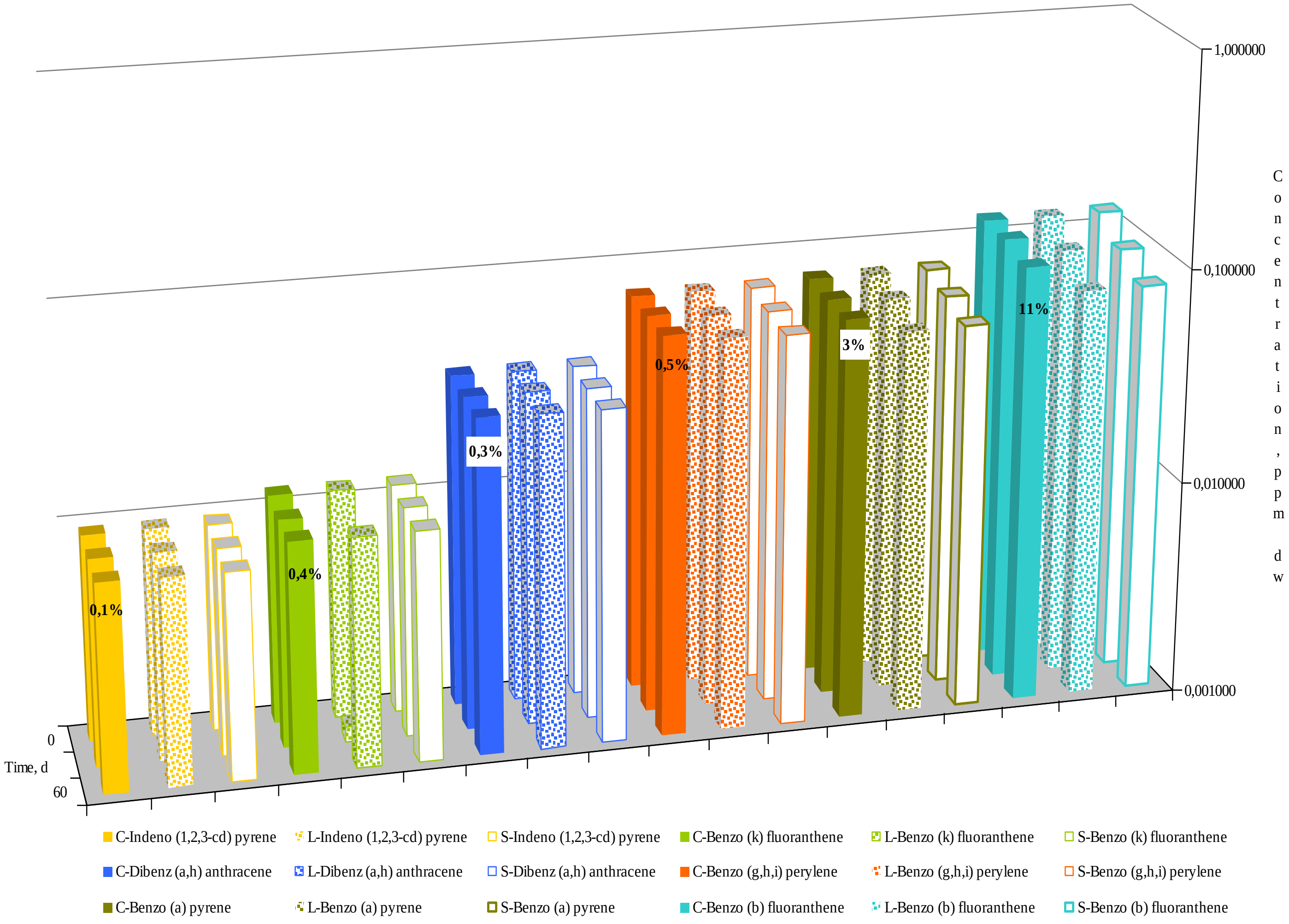


Figure 6.32a 5&6Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 20/100

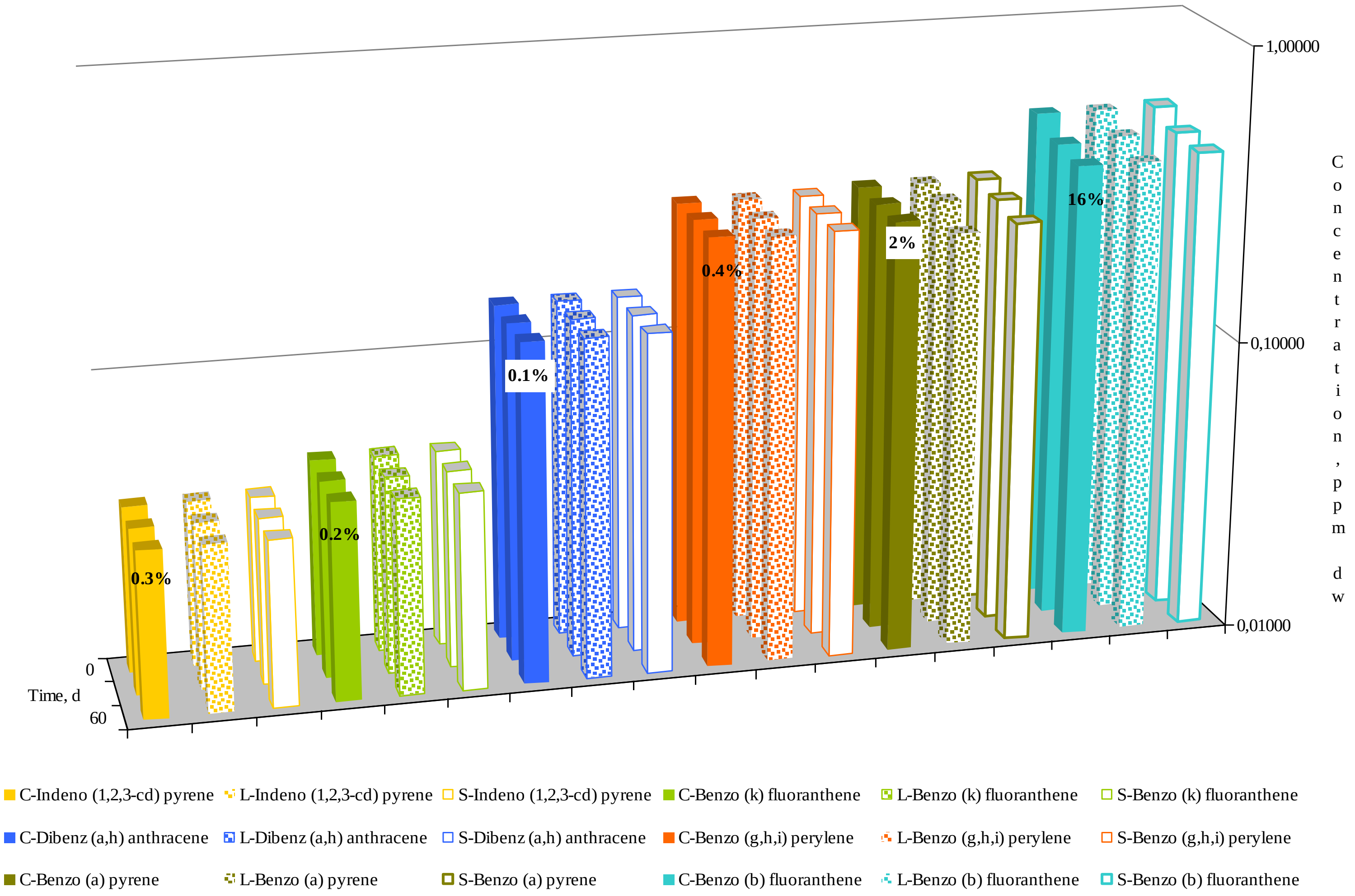


Figure 6.32b 5&6Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 20/100

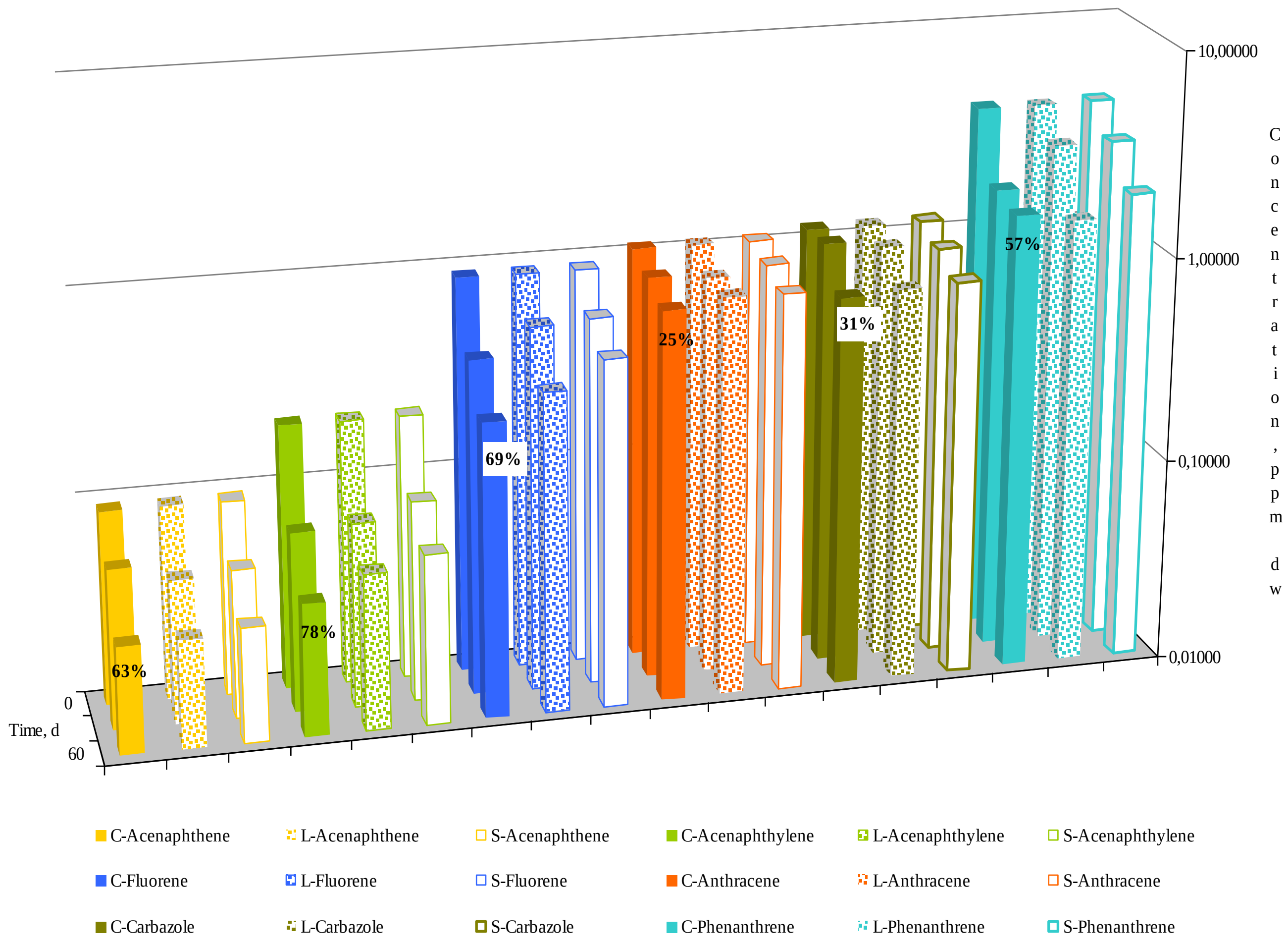


Figure 6.33a 3Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 10/100

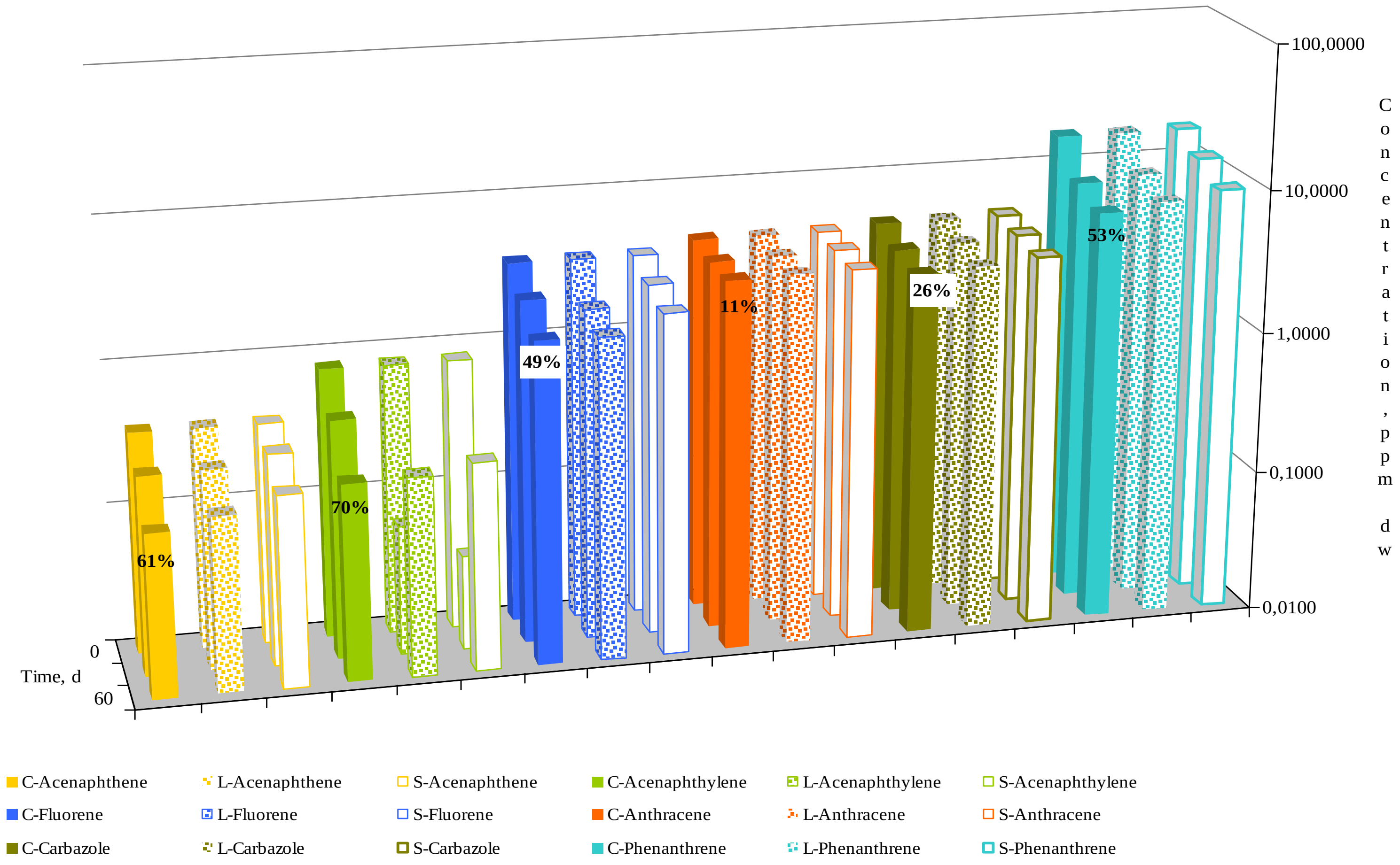


Figure 6.33b 3Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 10/100

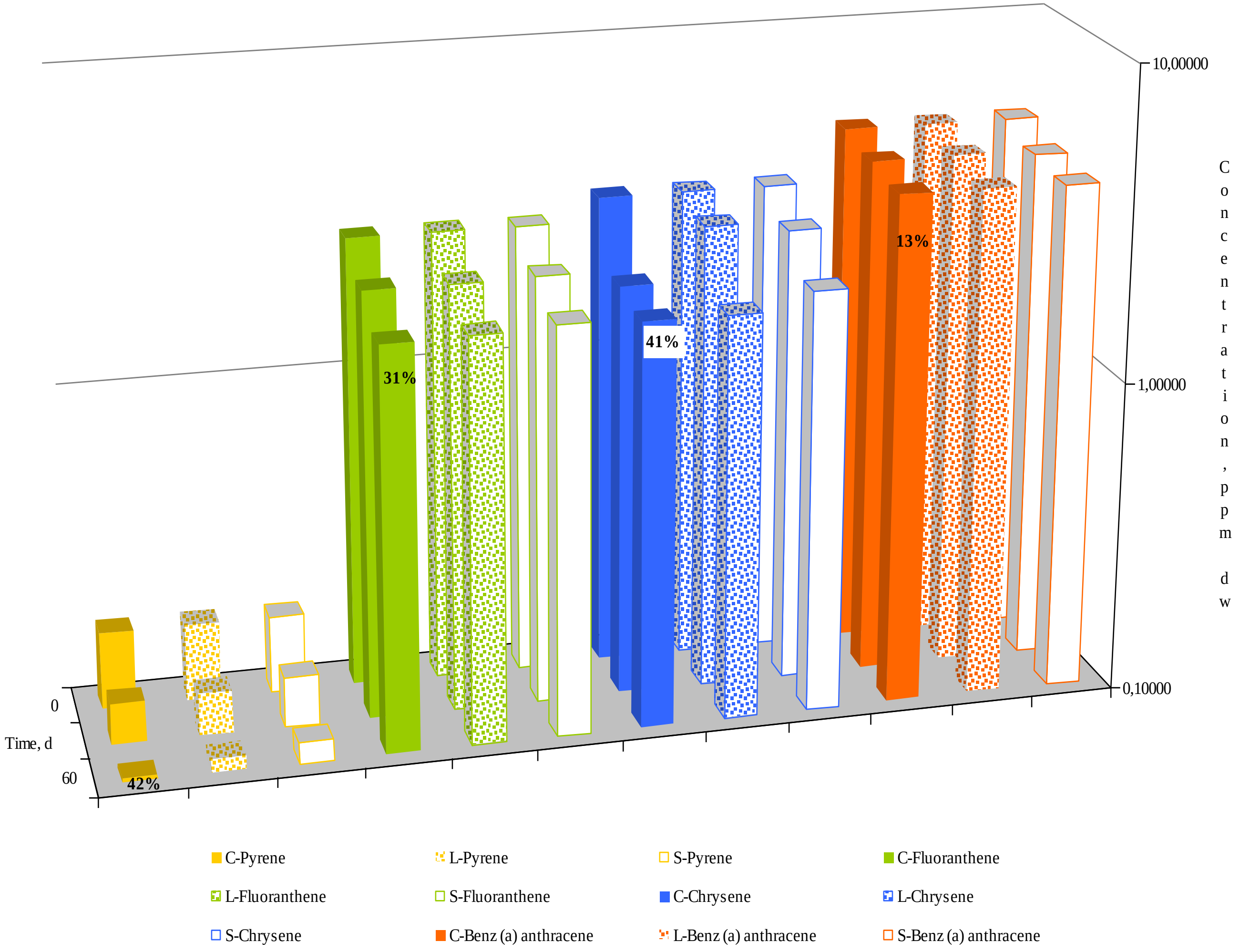


Figure 6.34a 4Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 10/100

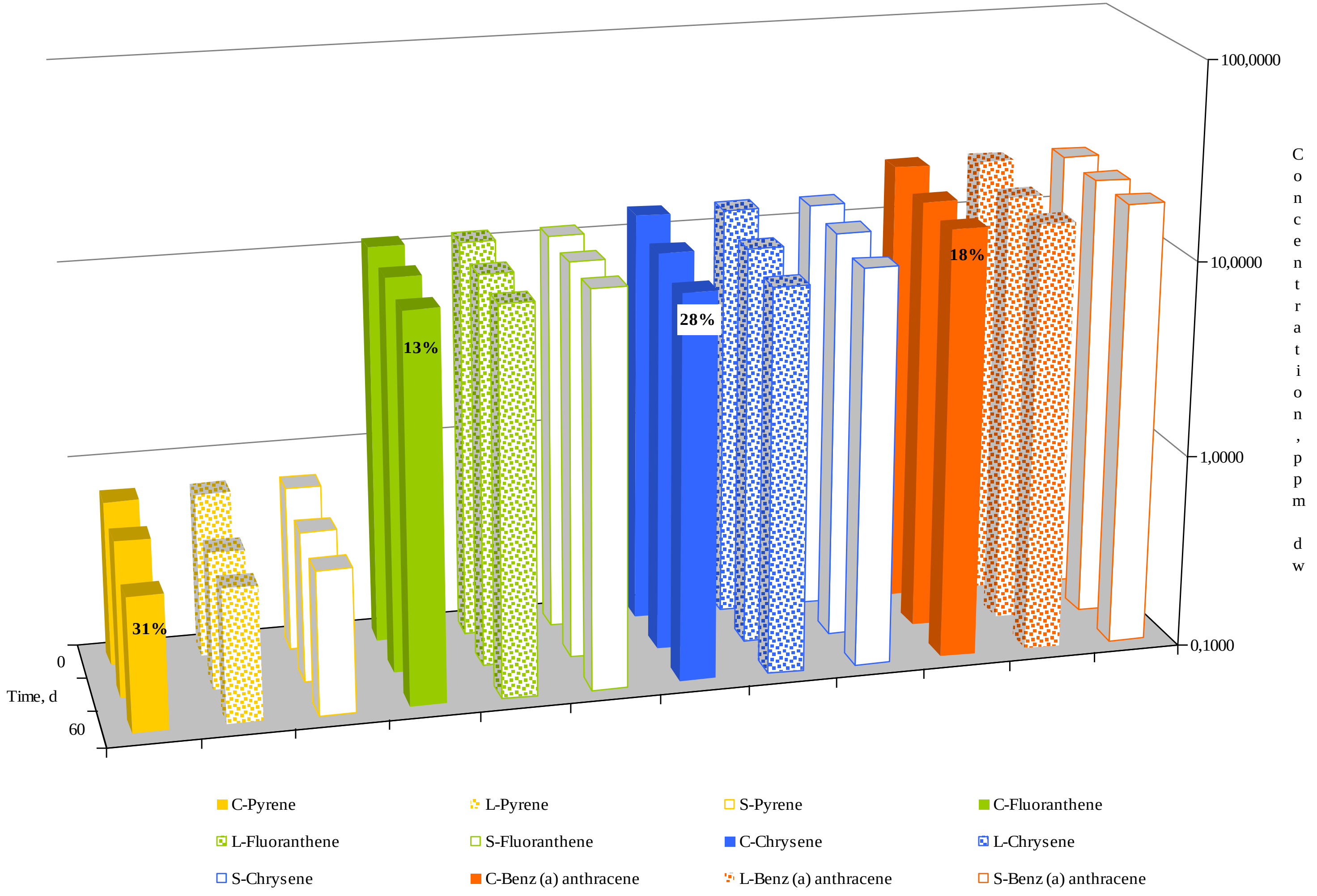


Figure 6.34b 4Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 10/100

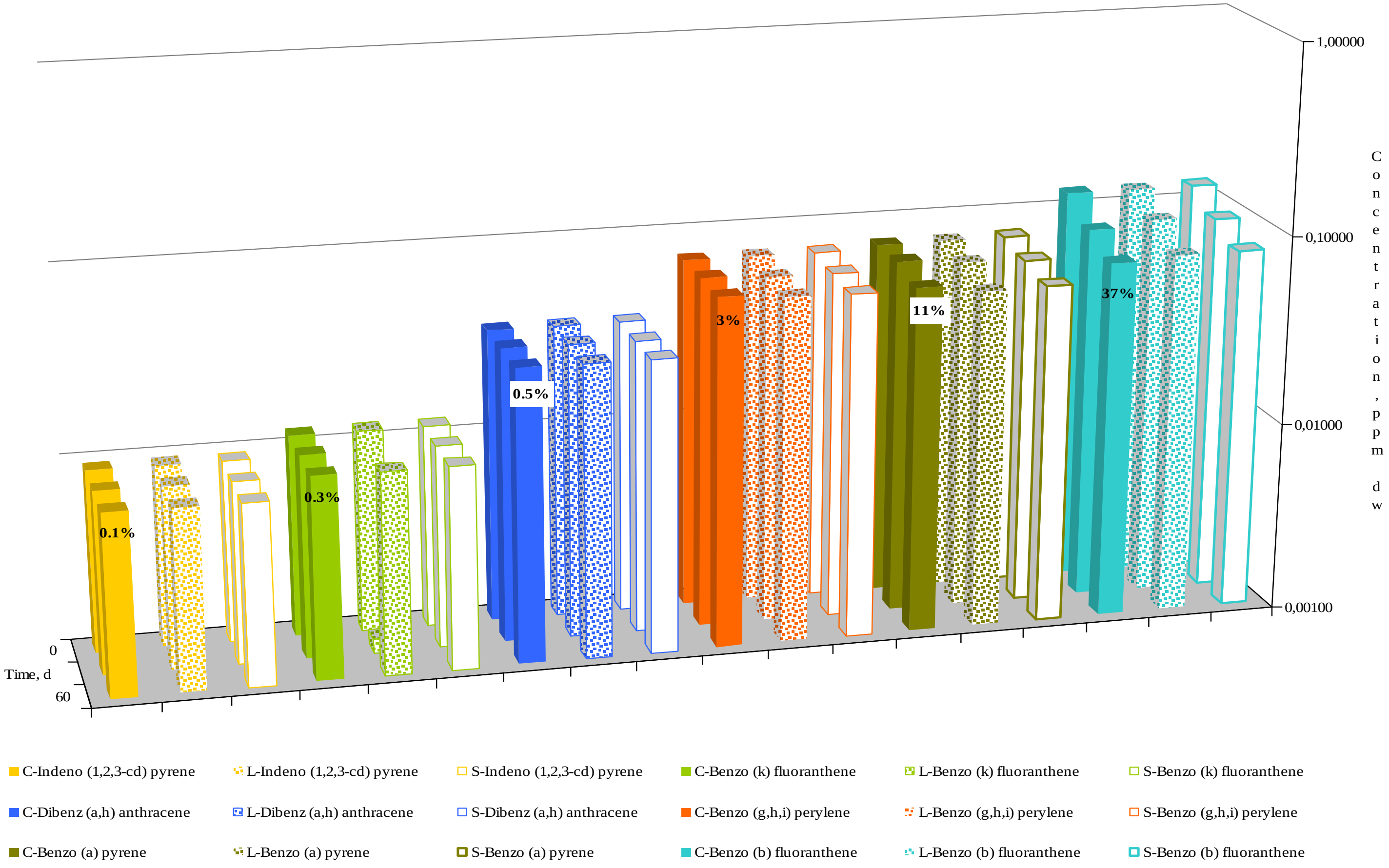


Figure 6.35a 5&6Ring PAHs removal from soil slurries contaminated with 25000ppm diesel with compost –soil ratio of 10/100

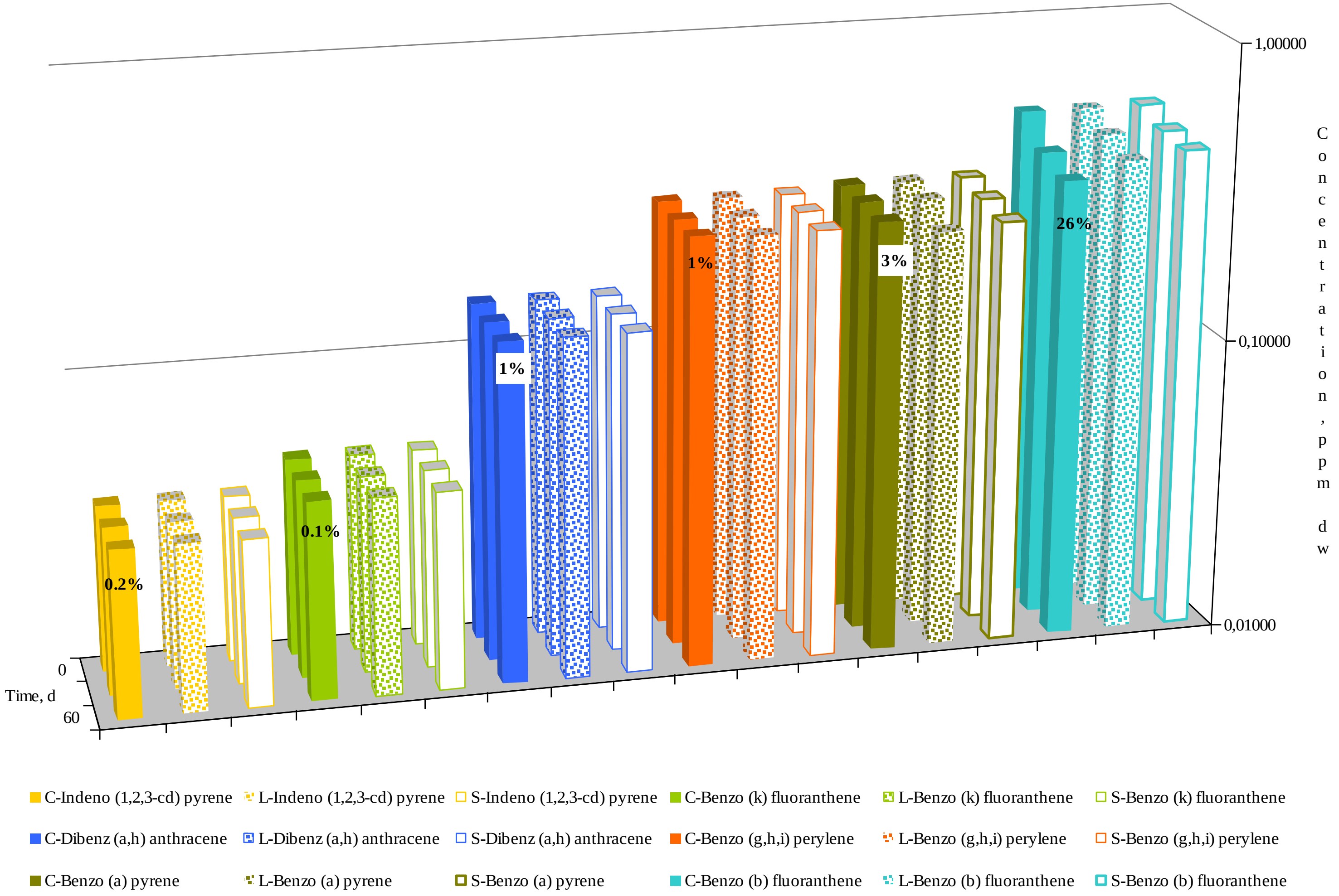


Figure 6.35b 5&6Ring PAHs removal from soil slurries contaminated with 100000ppm diesel with compost –soil ratio of 10/100

The overall efficiencies with 10g compost addition to 100 g of soil is higher than the efficiencies observed with soil local bacteria. But, it is also seen that increasing compost addition negatively affected the PAHs overall removal efficiency. The individual PAHs removal efficiencies are also summarized in Table 6.5 with important properties of PAHs.

Table 6.5 Individual PAHs removal rates in compost amended slurry systems according to the compost- soil ratio (C/S) and initial concentration

Studied PAHs				**Removal Efficiency, %**					
Number of Benzene Rings	**Name**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**25000 ppm Initial Diesel Concentration**			**100000 ppm Initial Diesel Concentration**		
				30/100 C/S	**20/100 C/S**	**10/100 C/S**	**30/100 C/S**	**20/100 C/S**	**10/100 C/S**
3 Ring	Acenaphthylene	16.1	$9.12*10^{-4}$	48	55	78	45	71	70
	Acenaphthene	3.9	$2.50*10^{-3}$	32	57	63	22	58	61
	Fluorene	1.89	$8.42*10^{-3}$	34	59	69	23	38	49
	Phenanthrene	1.15	$1.12*10^{-4}$	38	57	68	31	45	53
	Anthracene	$4.34*10^{-2}$	$2.67*10^{-6}$	6	18	25	3	7	11
	Carbozole	0.721	$2.66*10^{-4}$	14	13	31	12	17	26
4 Ring	Fluoranthene	$2.60*10^{-1}$	$1.23*10^{-8}$	2	21	31	2	8	13
	Pyrene	$1.35*10^{-1}$	$1.35*10^{-7}$	17	23	42	16	32	31
	Benz(a)anthracene	$9.40*10^{-3}$	$3.05*10^{-8}$	0.5	8	13	0	8	18
	Chrysene	$2.00*10^{-3}$	$6.23*10^{-9}$	7	28	41	5	20	28
5&6 Ring	Benzo(b)fluoranthene	$1.50*10^{-3}$	$5.00*10^{-7}$	6	11	37	3	16	26
	Benzo(k)fluoranthene	$8.00*10^{-4}$	$9.65*10^{-10}$	0	0	0.25	0	0	0
	Benzo(a)pyrene	$1.62*10^{-3}$	$5.49*10^{-9}$	1.5	3	11	0.5	2	3
	Dibenz(a,h)anthracene	$2.49*10^{-6}$	$1.00*10^{-10}$	0	0	0.5	0	0	1
	Benzo(g,h,i)perylene	$2.6*10^{-4}$	$1.01*10^{-10}$	1	0.5	3	0.3	0.3	1
	Indeno(1,2,3-c,d)pyrene	$2.20*10^{-5}$	$1.00*10^{-10}$	0	0	0.1	0	0	0

It is recognized that the higher removal rates are obtained in the PAHs having either higher water solubilities or vapor pressure, or both. This phenomenon will be discussed in detail at the end of this chapter.

6.2.2.2 The Effect of Contamination Age on Soil Remediation in Slurry Systems with Soil Amendment

In this part 10000 ppm and 25000 ppm diesel spiked and two years- aged Kaynaklar soils with soil- liquid ratio of 1/1 and compost-soil ratio (C/S) of 10g compost/100g soil were used in slurry systems. The systems were aerated and operated for 60 days. The controls with aged sterilized soil and the aged soil with local bacteria were also operated. pH, CO_2 production, bacterial counts, TPHs and PAHs are followed during the treatment period and the results are presented below.

In Figure 6.36 pH change in the systems are given. The initial pHs were in neutral level in all systems, while compost added systems followed much similar trends and their pH slightly raised at the end of the experimental period.

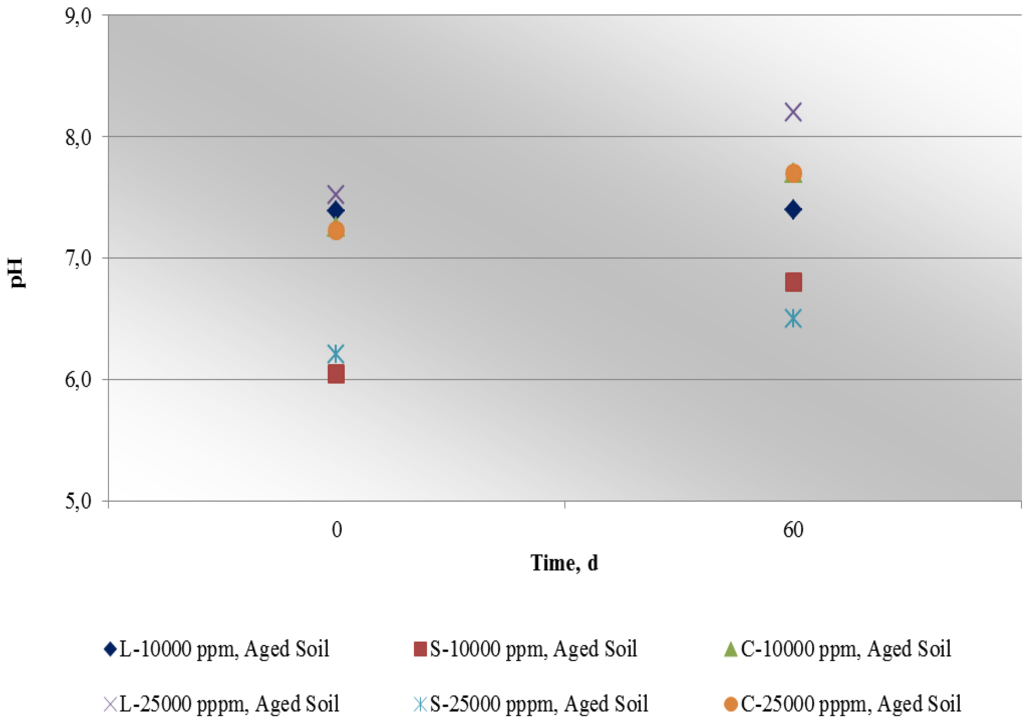
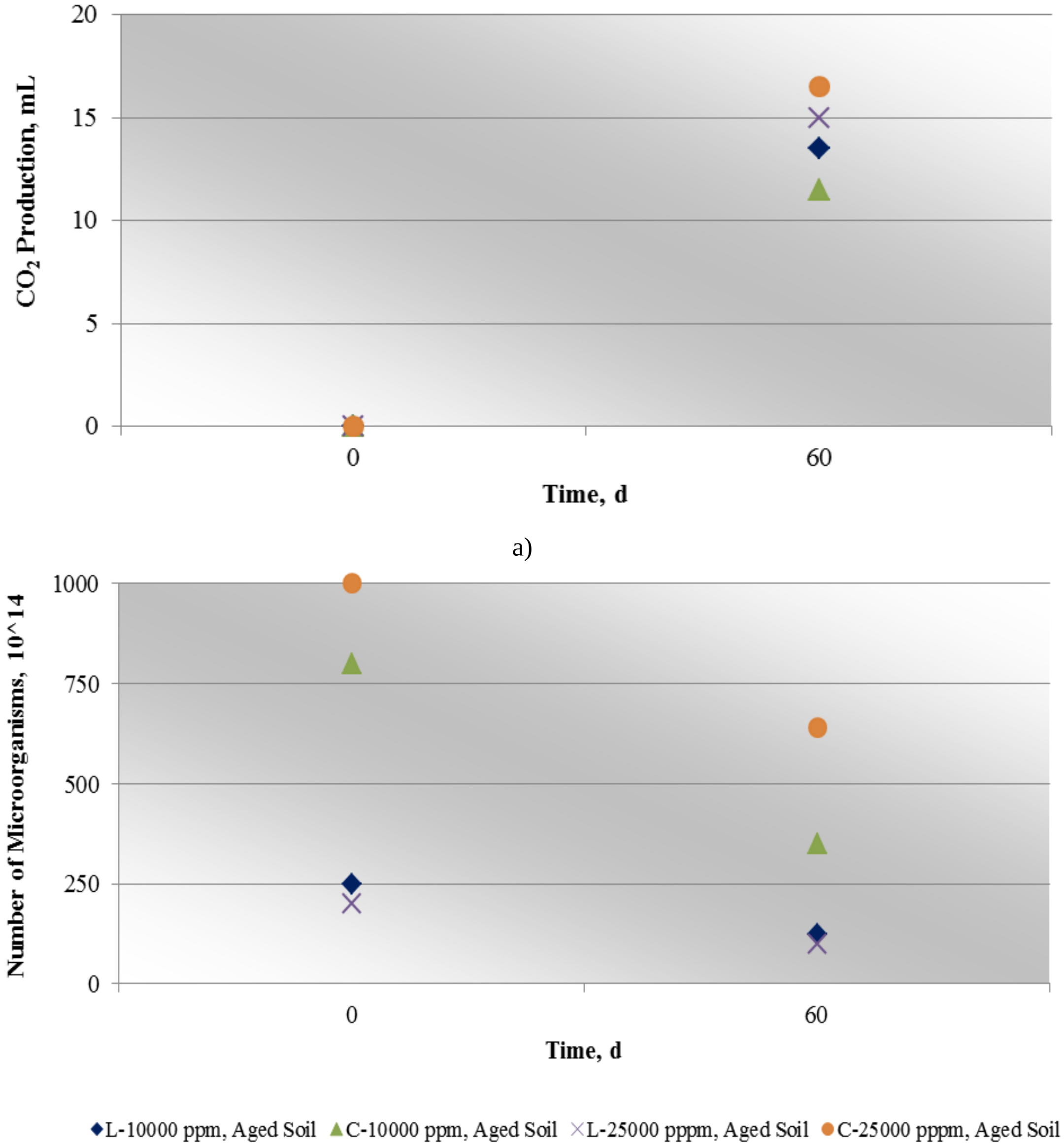


Figure 6.36 The pH changes in slurries operated with aged soil

CO_2 productions from the systems and change in number of bacteria in the slurries are given in Figure 6.37. Any CO_2 production or bacterial growth could not be observed in sterile soil slurries. The CO_2 productions in the slurries operated with 25000 ppm initial soil diesel concentration (IDC) were slightly higher than the soils having 10000 ppm IDC.



a)

b)

Figure 6.37 The CO2 production and the changes in number of bacteria present in the slurries operated with aged soil a) CO2 production, b) Number of bacteria

The TPHs removal efficiencies and the mass of remain TPHs in the slurry are given in Figure 6.38. It is seen that the TPHs removal efficiencies are higher with 25000 ppm IDC in soil. In addition, removals with the presence of compost in the slurries are higher then the ones found in sterilized soils and soils having local bacteria, both for 10000 ppm and 25000 ppm IDC It is also seen that the rate of TPHs removal is higher with initial concentration of 25000 ppm.

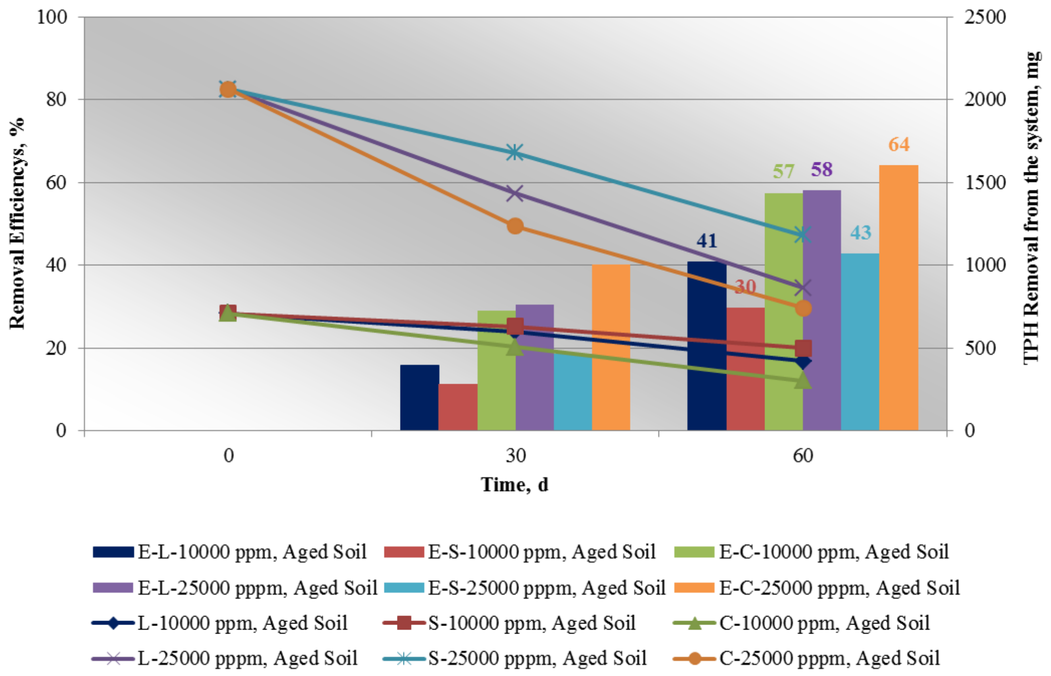
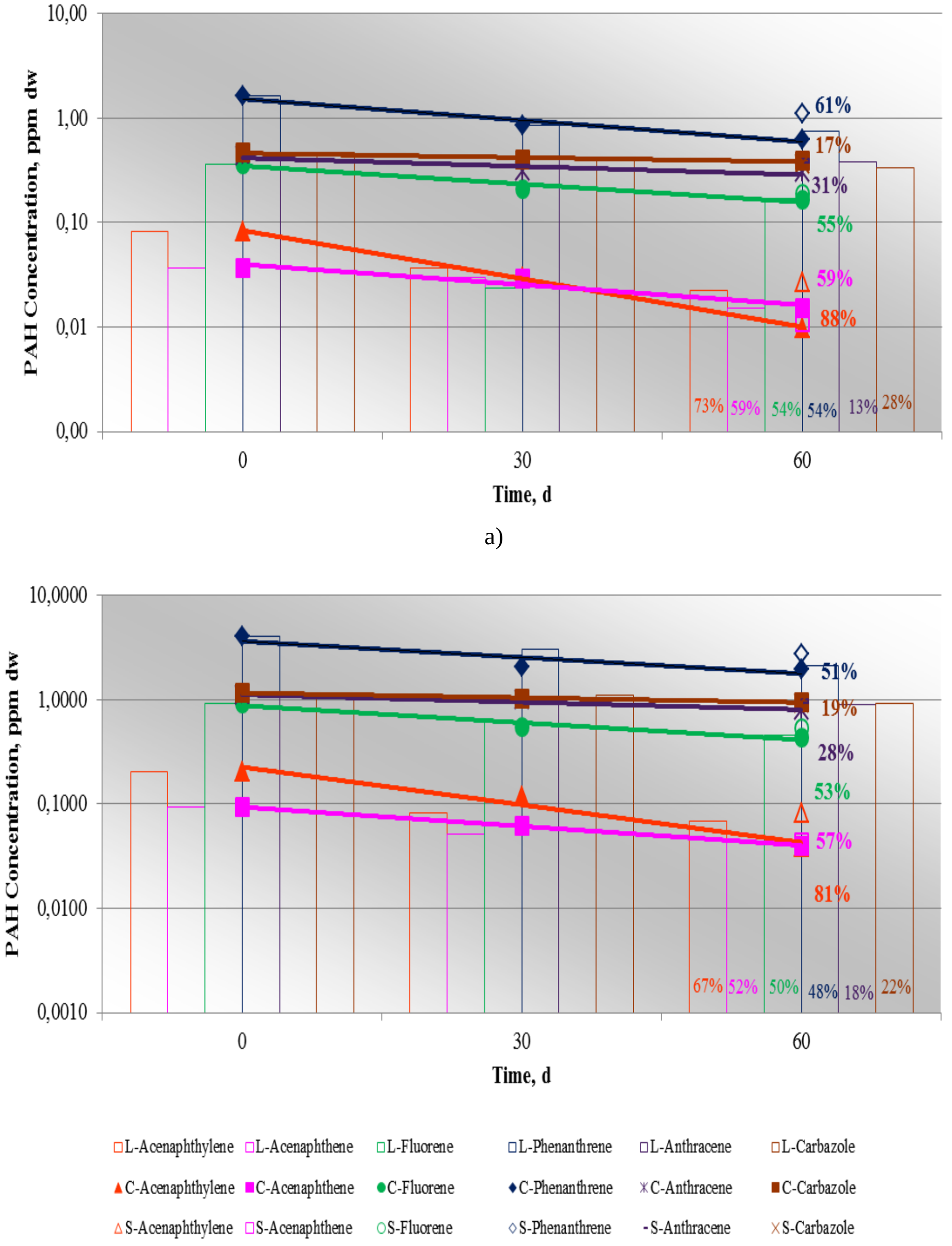


Figure 6.38 The TPHs removal efficiencies and the mass of remaining TPHs in the slurry systems with 10000 ppm and 25000 ppm IDC containing 10g compost/100 g soil

Here, according to the distribution of the residual TPHs in the slurries, 8 to 19% of the TPHs mass remained in the liquid phase of the system at the end of the remediation period.

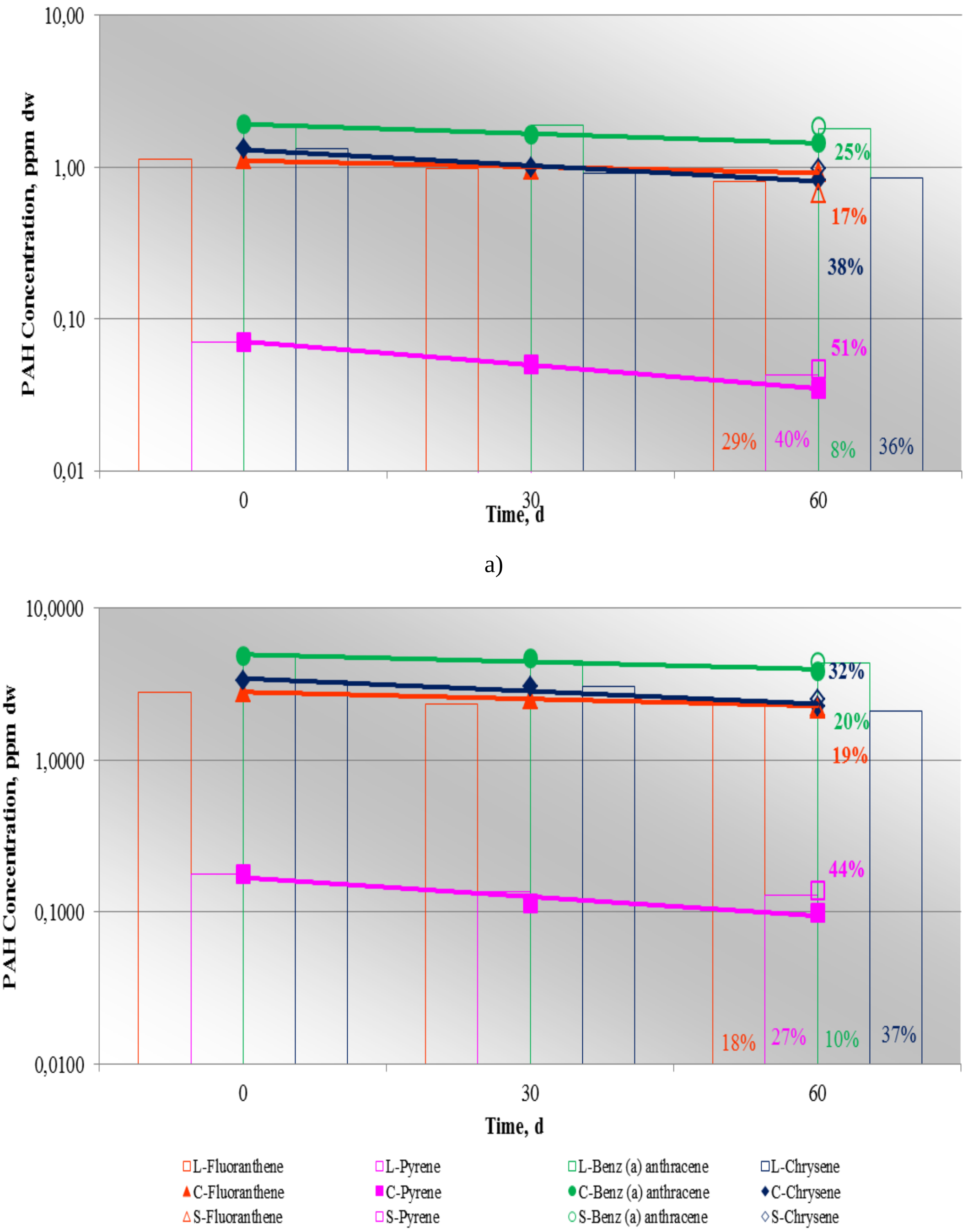
The PAHs removals in the systems were also investigated and the findings are given in Figures 6.39-6.41 according to the number of benzene rings of the PAHs.



a)

b)

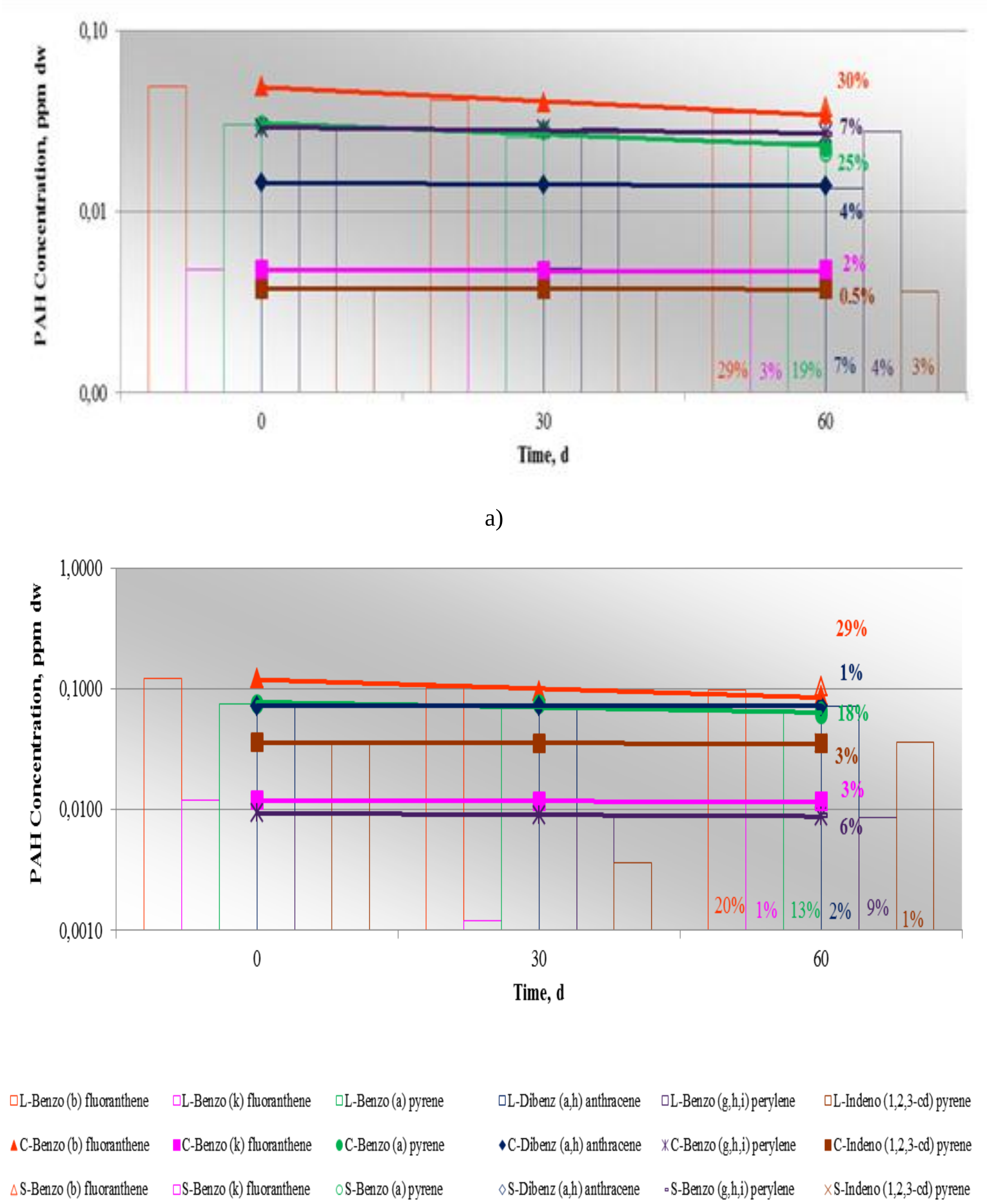
Figure 6.39 The removals of 3 Ring PAHs from slurries with aged soils and havin 10g/100g compost-soil ratio



a)

b)

Figure 6.40 The removals of 4 Ring PAHs from slurries with aged soils and havin 10g/100g compost-soil ratio



a)

b)

Figure 6.41 The removals of 5&6 Ring PAHs from slurries with aged soils and havin 10g/100g compost-soil ratio

The average treatment efficiencies of 3Ring PAHs were 51.8 and 48.2%, 4Ring PAHs were 32.8 and 28.8%, and 5&6Ring PAHs were 11.4 and 10.0% in the soils with 10000 ppm and 25000 ppm IDC, respectively. It is seen that the treatment efficiencies are decreasing both with increasing initial diesel concentration and number of benzene rings that PAHs have.

The removal efficiencies of individual PAHs are reported in Table 6.6 with some important properties of studied PAHs.

Table 6.6 The removal efficiencies of individual PAHs from aged soils in slurry systems

Studied PAHs		**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**Removal Efficiency, %**	
Number of Benzene Rings	**Name**			**10000 ppm diesel**	**25000 ppm diesel**
3 Ring	Acenaphthylene	16.1	$9.12*10^{-4}$	88	81
	Acenaphthene	3.9	$2.50*10^{-3}$	59	57
	Fluorene	1.89	$8.42*10^{-3}$	55	53
	Phenanthrene	1.15	$1.12*10^{-4}$	61	51
	Anthracene	$4.34*10^{-2}$	$2.67*10^{-6}$	31	28
	Carbozole	0.721	$2.66*10^{-4}$	17	19
4 Ring	Fluoranthene	$2.60*10^{-1}$	$1.23*10^{-8}$	17	19
	Pyrene	$1.35*10^{-1}$	$1.35*10^{-7}$	51	44
	Benz(a)anthracene	$9.40*10^{-3}$	$3.05*10^{-8}$	25	20
	Chrysene	$2.00*10^{-3}$	$6.23*10^{-9}$	38	32
5&6 Ring	Benzo(b)fluoranthene	$1.50*10^{-3}$	$5.00*10^{-7}$	30	29
	Benzo(k)fluoranthene	$8.00*10^{-4}$	$9.65*10^{-10}$	2	3
	Benzo(a)pyrene	$1.62*10^{-3}$	$5.49*10^{-9}$	25	18
	Dibenz(a,h)anthracene	$2.49*10^{-6}$	$1.00*10^{-10}$	4	1
	Benzo(g,h,i)perylene	$2.6*10^{-4}$	$1.01*10^{-10}$	7	6
	Indeno(1,2,3-c,d)pyrene	$2.20*10^{-5}$	$1.00*10^{-10}$	0.5	3

It is recognized that the treatment efficiencies of PAHs are related with their water solubility and/or vapor pressure, and this issue will be discussed at the end of this chapter. In addition, the removal efficiencies are lower with 4 Ring and 5&6 Ring PAHs relative to the freshly contaminated soils.

6.3 Fixed Bed Soil Remediation Systems

Fixed bed soil remediation studies were conducted with whether the existence of soil native bacteria are allowed or not, as well as the presence of additional substrate and bacteria obtained by compost addition. By this way, the effects of soil water content, initial contaminant concentration, temperature, contamination age, and soil type on thermal volatilization and bioremediation are investigated.

6.3.1 Fixed Bed Soil Remediation by Thermal Volatilization

In this part, the efficiency of thermal volatilization on NAPLs treatment from the soil was investigated. For this purpose the soil native bacteria was inhibited by autoclaving and $HgCl_2$ addition to detect the net volatilization of NAPLs. The systems were aerated according to Chapter 4 to supply volatilization. Parallel sets without aeration (blanks) were executed for comparing the results.

6.3.1.1 The Effect of Water Content, Initial Contaminant Concentration, and Temperature on Soil Remediation by Thermal Volatilization in Time

Here, the experiments were conducted in 1 L reactors under 25°C or 40°C which the temperature was kept constant in an incubator. The initial soil diesel concentrations of 10000 ppm, 25000 ppm, and 100000 ppm were examined as well as initial water contents of 20% and 40%. Water content, pH, change in TPHs and PAHs concentration in the systems were followed during the operational period of 60 days.

The changes in water content of the soils in the systems according to the initial contaminant concentration and incubation temperature are given in Figure 6. 42. The water content of the soils in the systems at 25°C has increased 5 to 15% in 60 days of operation time, where the water content of the soils at 40°C has decreased approximately 10%. The systems with no aeration (blanks) did not show any significant change in water content. This situation allows us to explain the different changes of water content; the air fed into the reactors were humidified by using before the inlet. The humidity of the inlet air is enough to raise the water content of the reactor at 25°C. Since the water loss from the reactor at 40°C is higher, the humidity of the inlet air is not enough to keep the water content at 40%, and the water in these reactors was stripped.

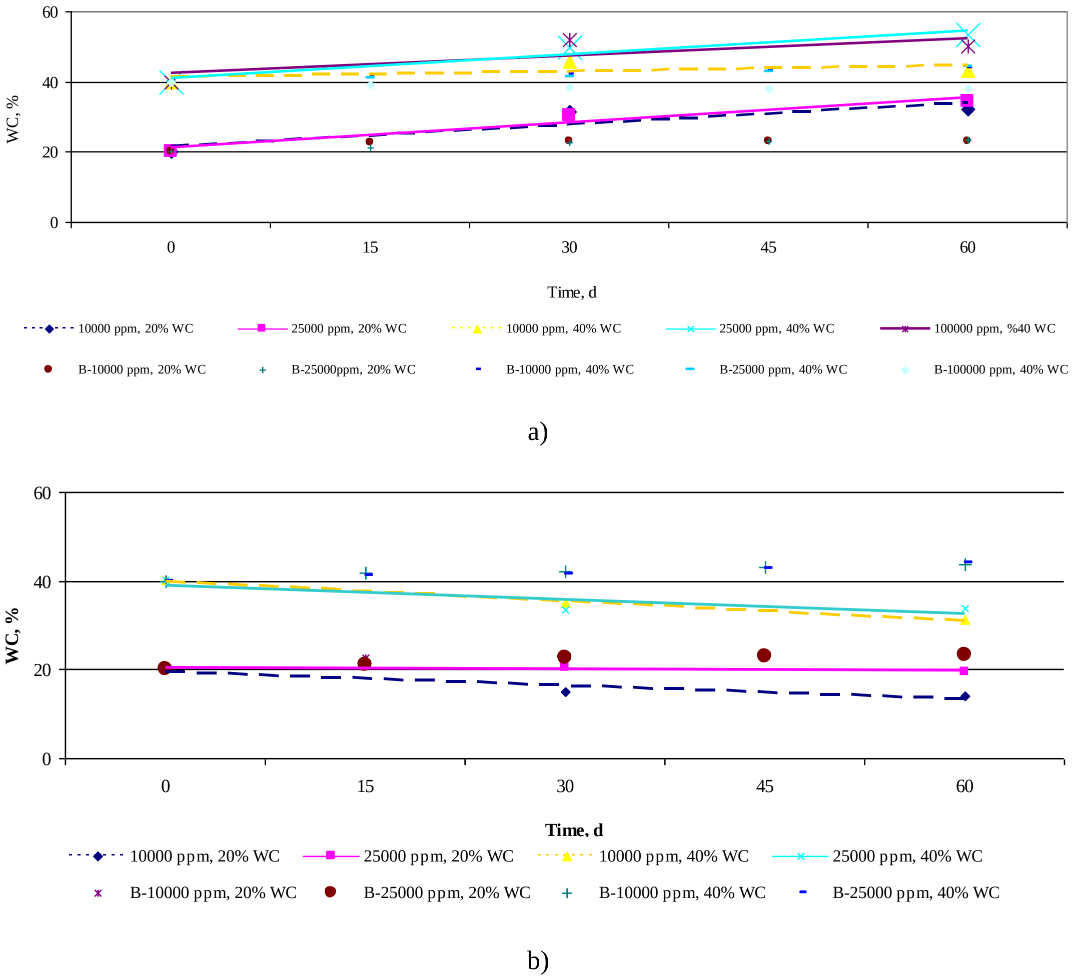
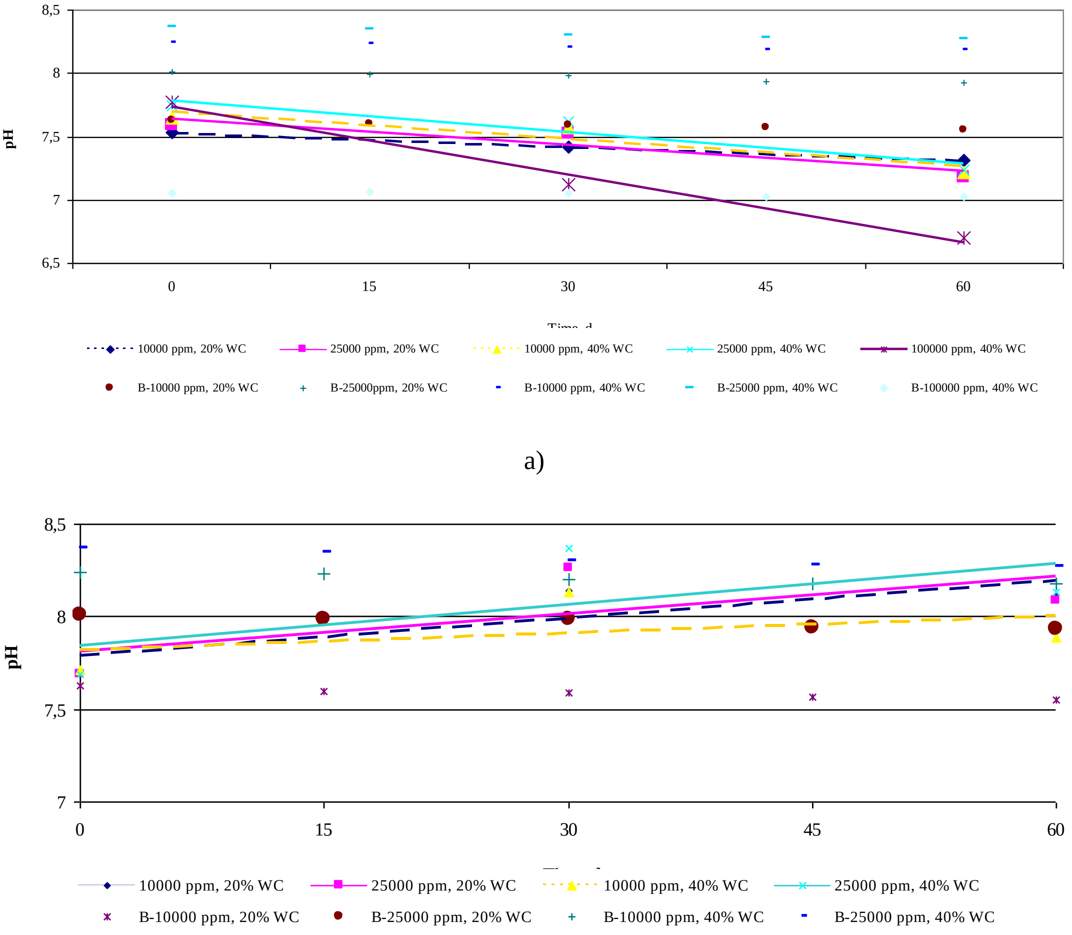


Figure 6.42 The changes in soil water content of fixed bed thermal volatilization reactors, a) at 25°C, b) at 40°C

The pH changes during thermal volatilization are presented in Figure 6.43. It is seen that initial soil pH levels in slightly alkaline range have decreased to neutral levels in the systems at 25°C, where pH of the soils in the systems have increased to alkaline range at 40°C. This may be related with the changing water content of the systems.



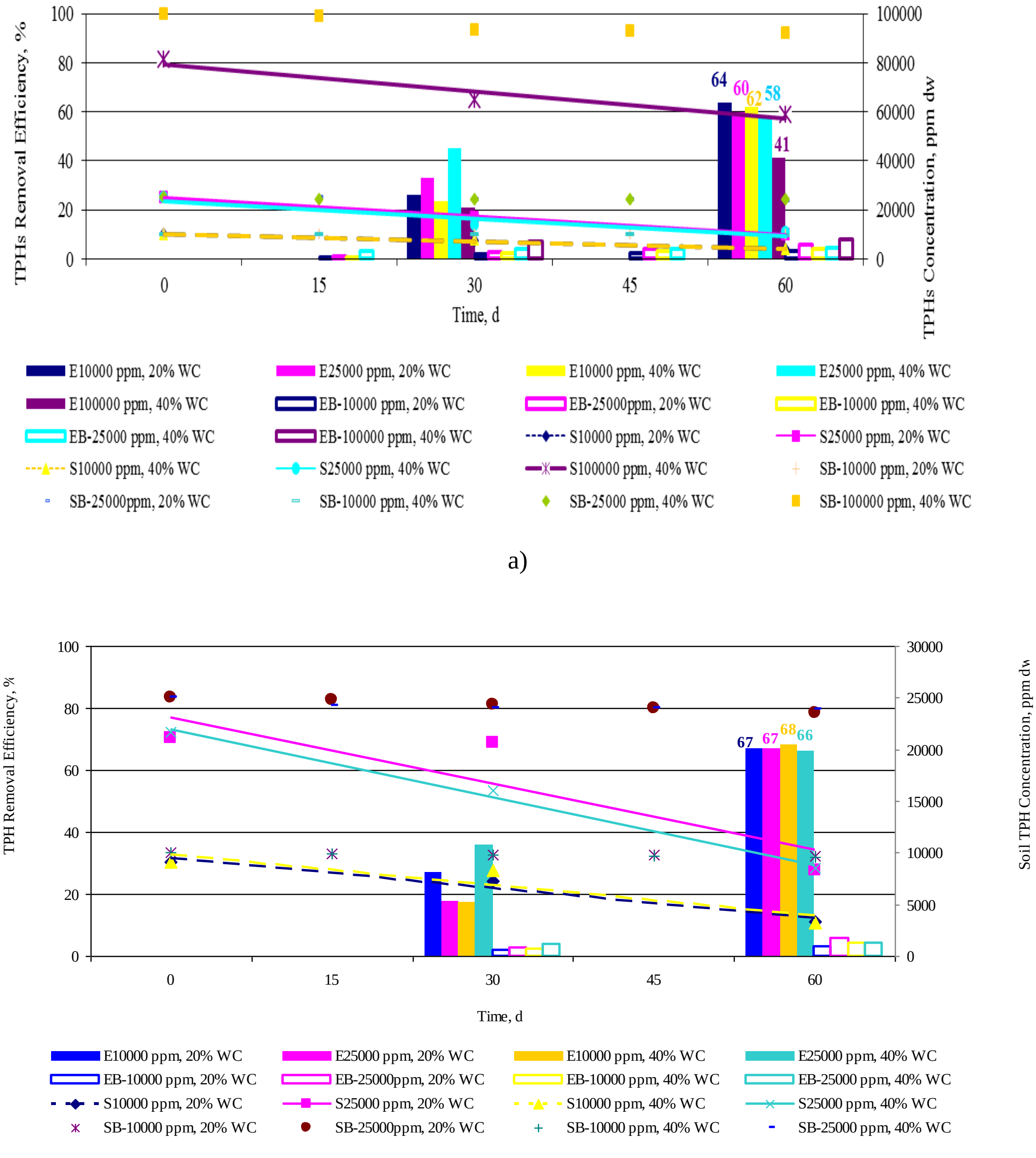
a)

b)

Figure 6.43 The changes in soil pH of fixed bed thermal volatilization reactors, a) at 25°, b) at 40°C

The TPHs concentrations in the fixed bed reactors operated as thermal volatilization systems are also followed during the operational period and the results are given in Figure 6.44 according to the applied temperatures. It was seen that as the initial diesel concentrations increase the volatilization efficiency decreases (Figure 6.44 a). Any significant effect of the initial water content on the removals of TPHs could not be seen, but it is recognized that the sets with final water content between 30-38% resulted with higher TPH removal efficiencies then the sets having 13-19% and 44-54% final water contents. This finding may be a useful data as the recommended water content for thermal volatilization systems of TPHs from soil.

It is also observed that, the systems operated at 40°C resulted with 3-9% higher TPH volatilization efficiencies then the systems operated at 25°C.

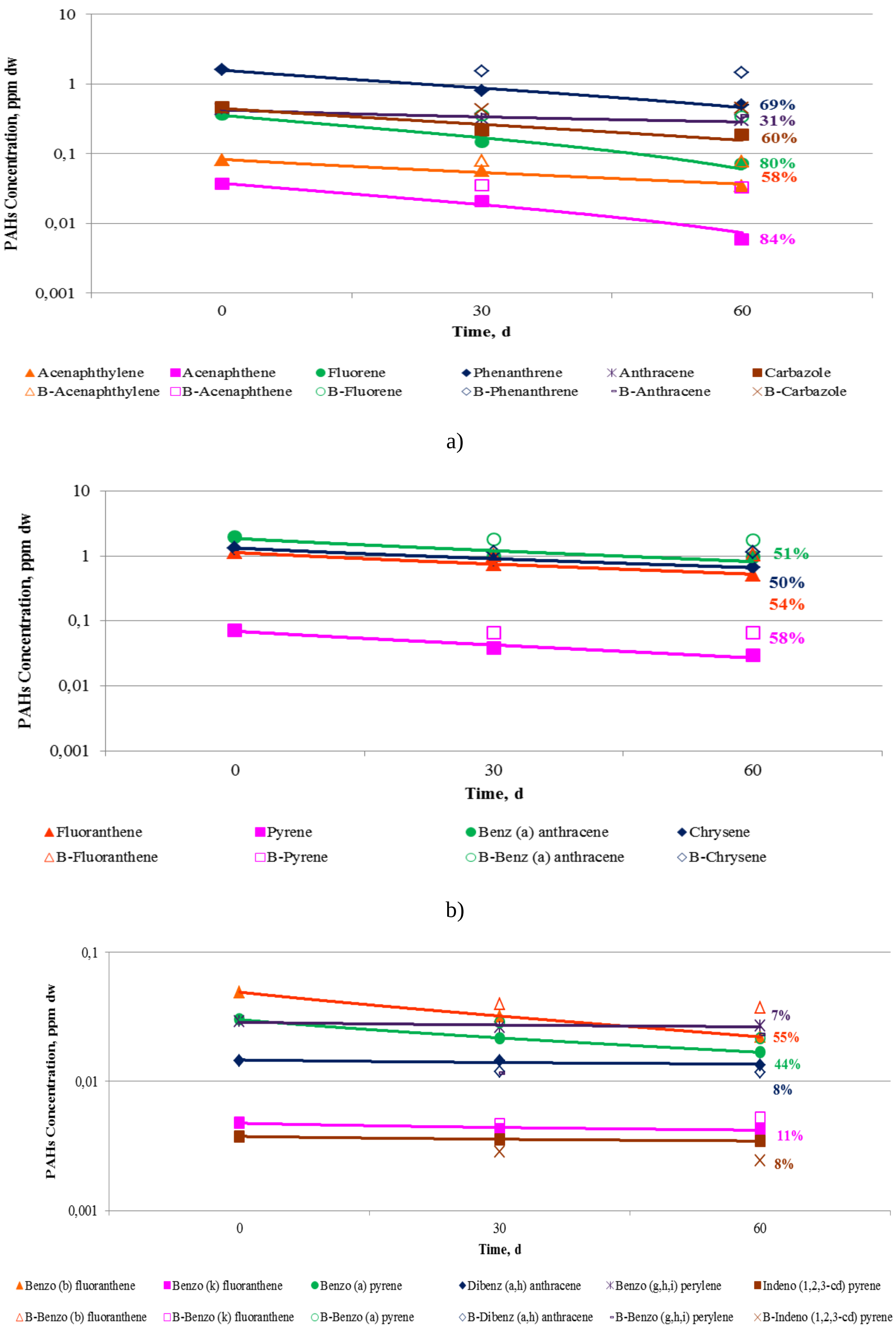


a)

b)

Figure 6.44 The changes in soil TPHs concentration of fixed bed thermal volatilization reactors, a) at 25°, b) at 40°C

The PAHs removal during the thermal volatilization of NAPLs from soils was also investigated and presented in Figures 6.45-6.52 according to the number of benzene rings of the PAH groups. The PAHs individual removal efficiencies are listed in Table 6.7 and average removal efficiencies calculated for PAH groups are given Table 6.8.



a)

b)

c)

Figure 6.45 PAHs removals in fixed bed thermal volatilization systems (IDC= 10000 ppm and 20% water content at 25°C, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

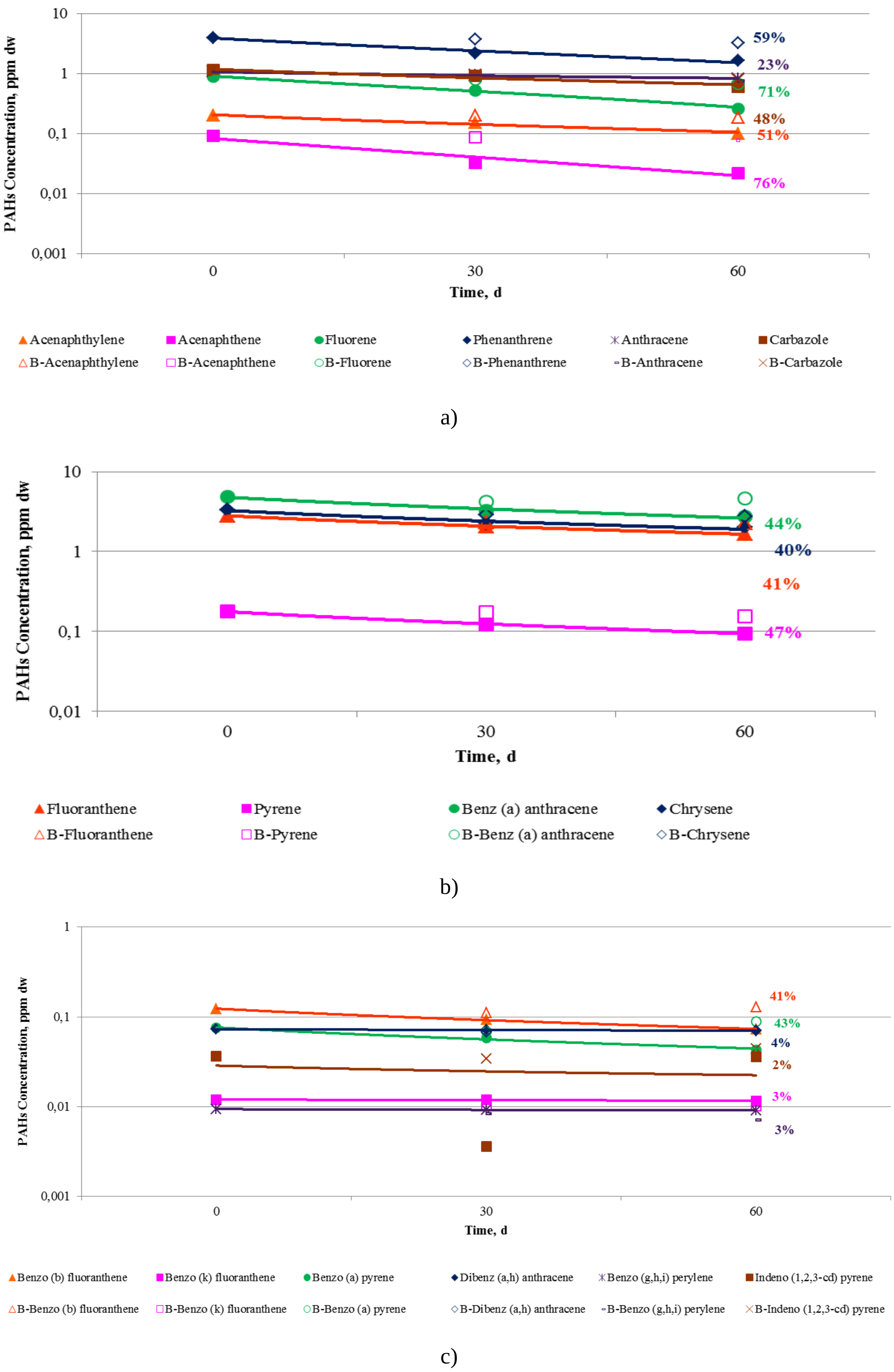


Figure 6.46 PAHs removals in fixed bed thermal volatilization systems (IDC= 25000 ppm and 20% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

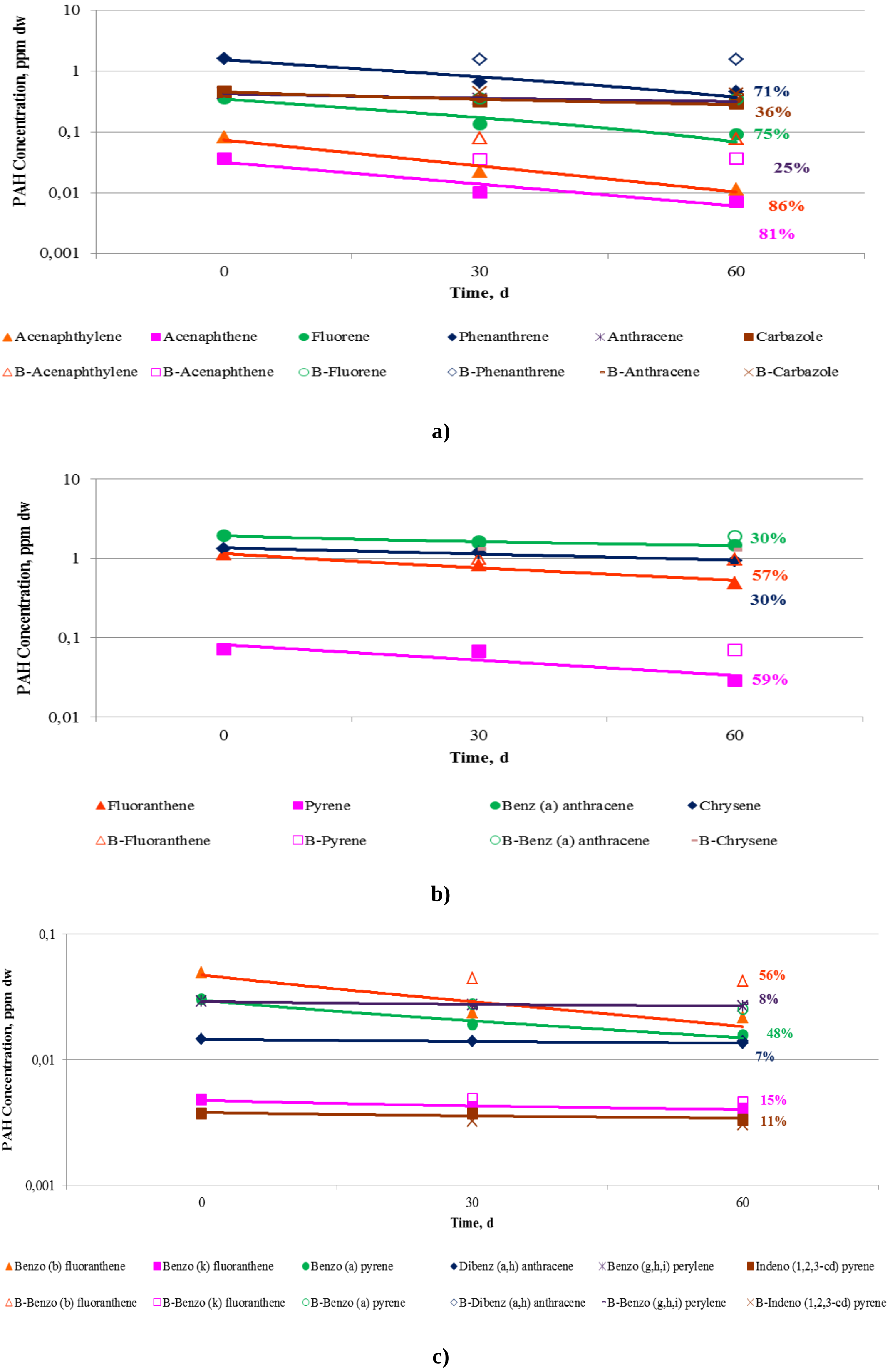
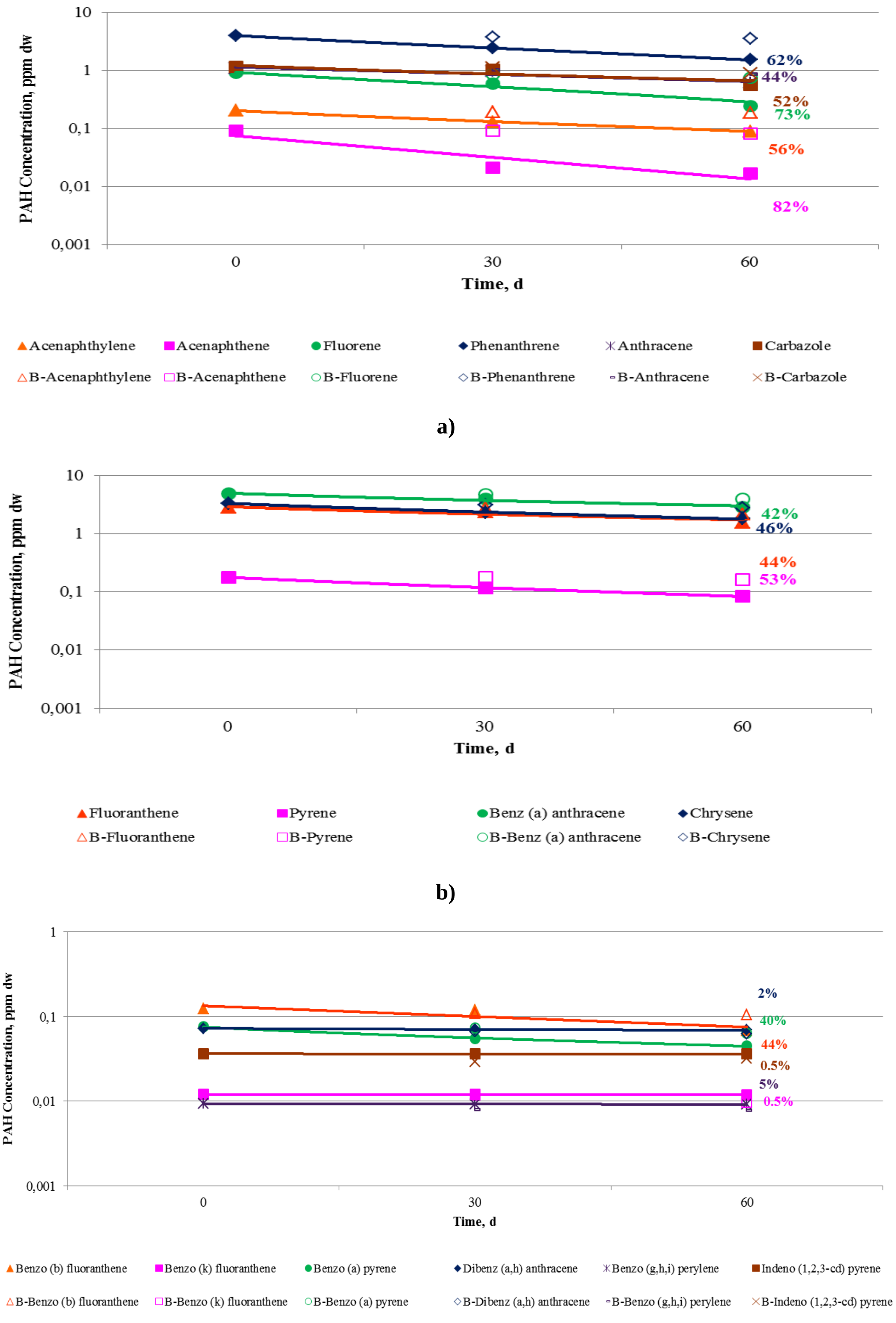


Figure 6.47 PAHs removals in fixed bed thermal volatilization systems (IDC= 10000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



a)

b)

c)

Figure 6.48 PAHs removals in fixed bed thermal volatilization systems (IDC= 25000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

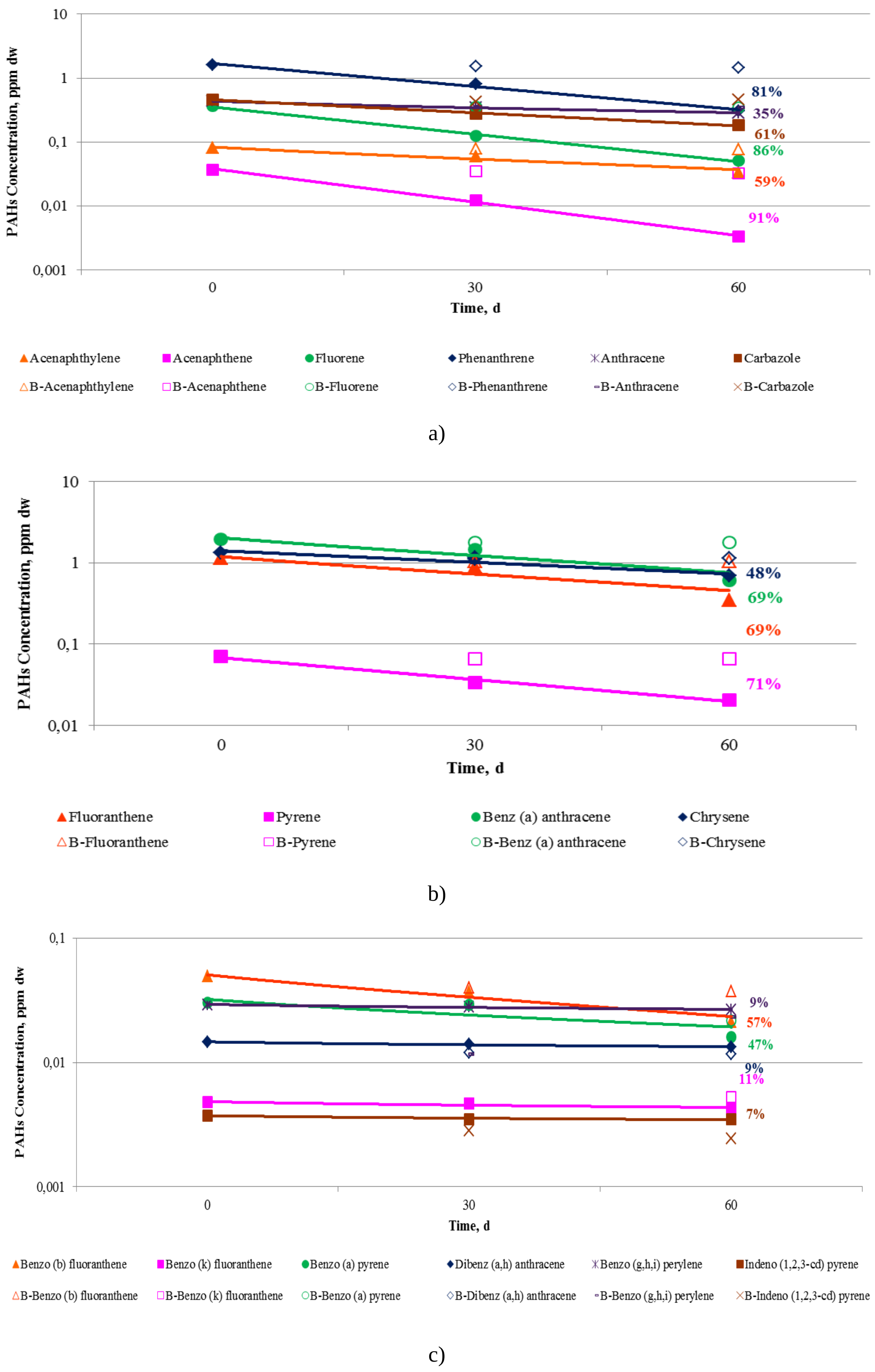
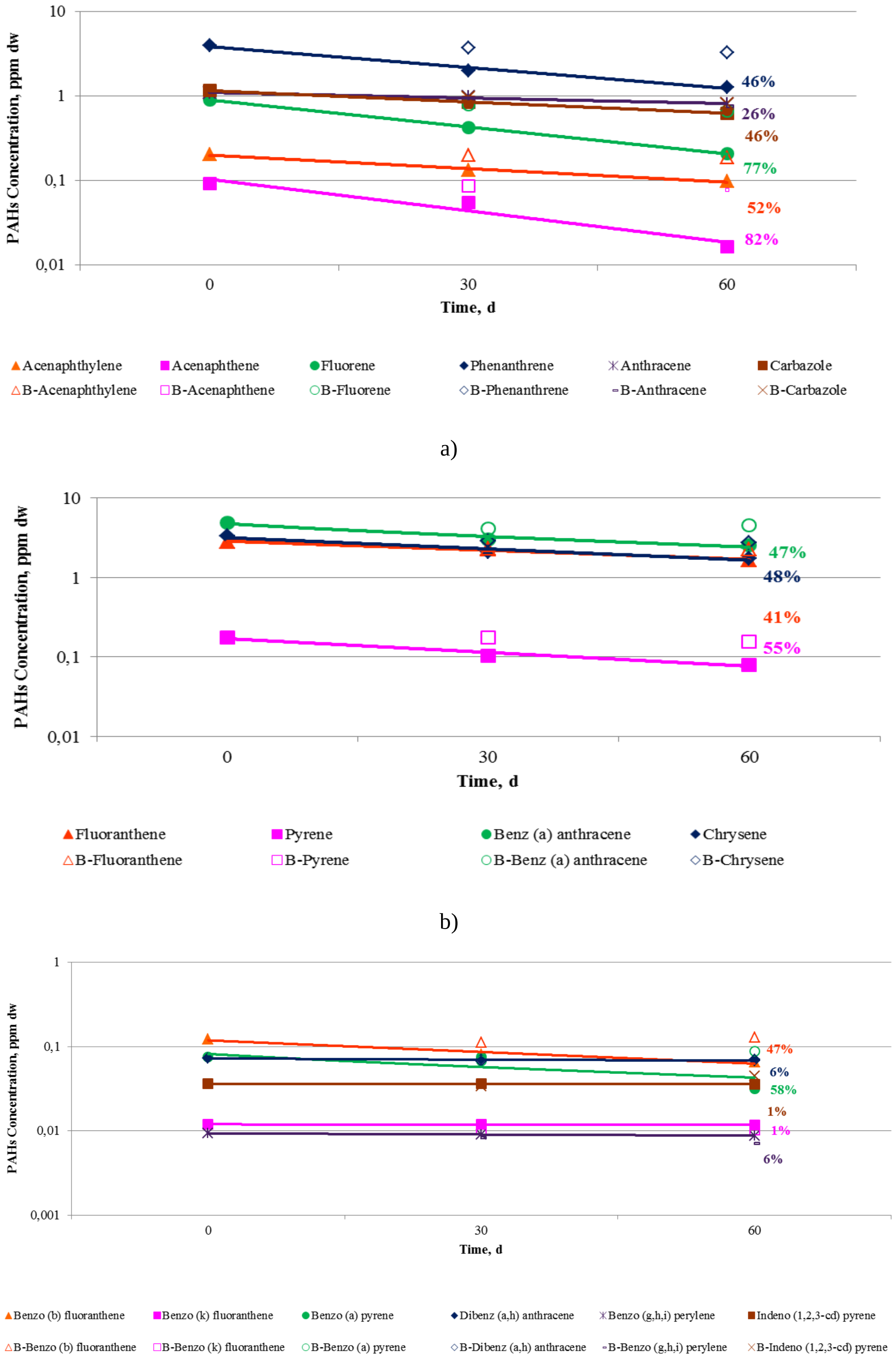


Figure 6.49 PAHs removals in fixed bed thermal volatilization systems (IDC= 10000 ppm and 20% water content at 40ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



a)

b)

c)

Figure 6.50 PAHs removals in fixed bed thermal volatilization systems (IDC= 25000 ppm and 20% water content at 40ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

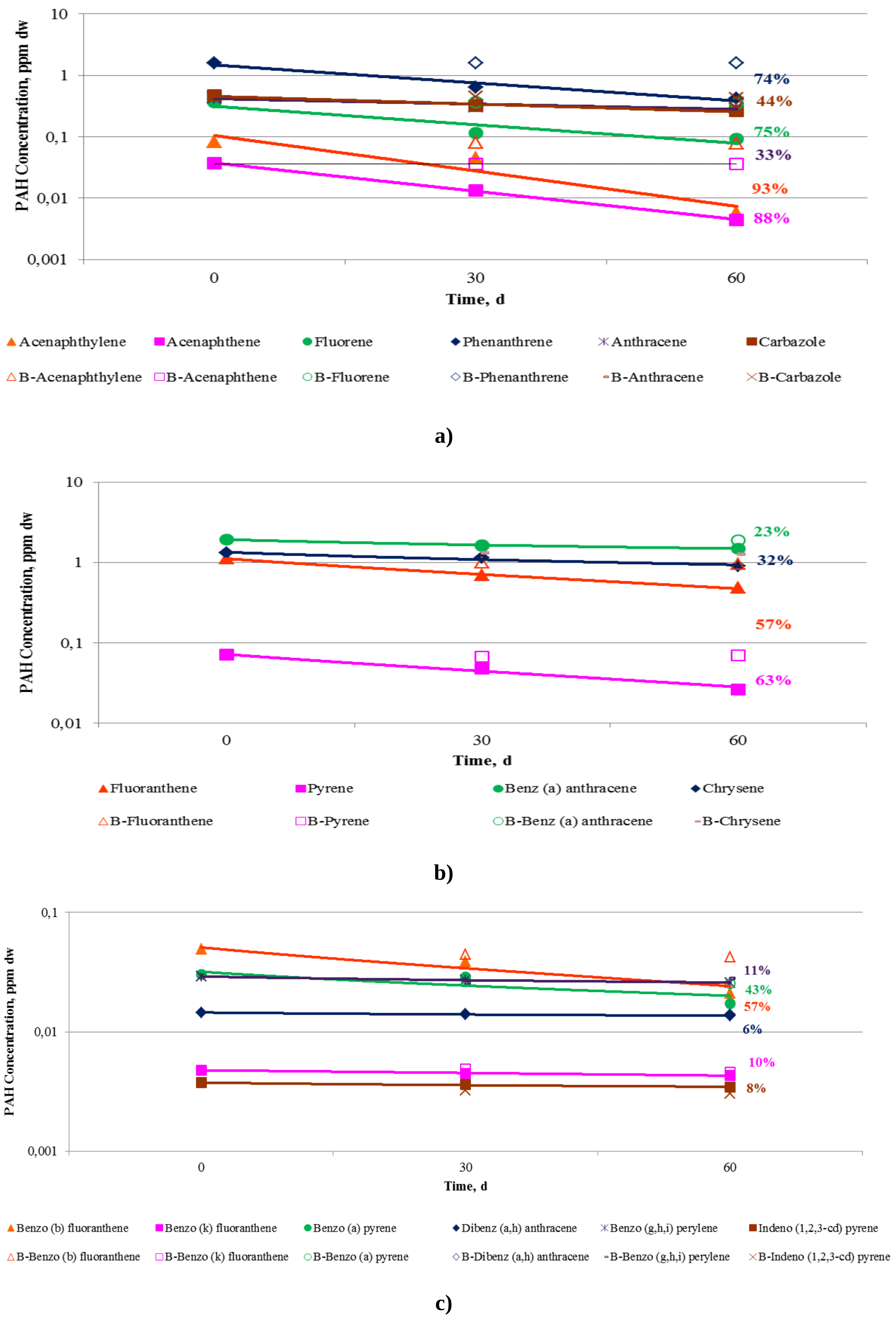
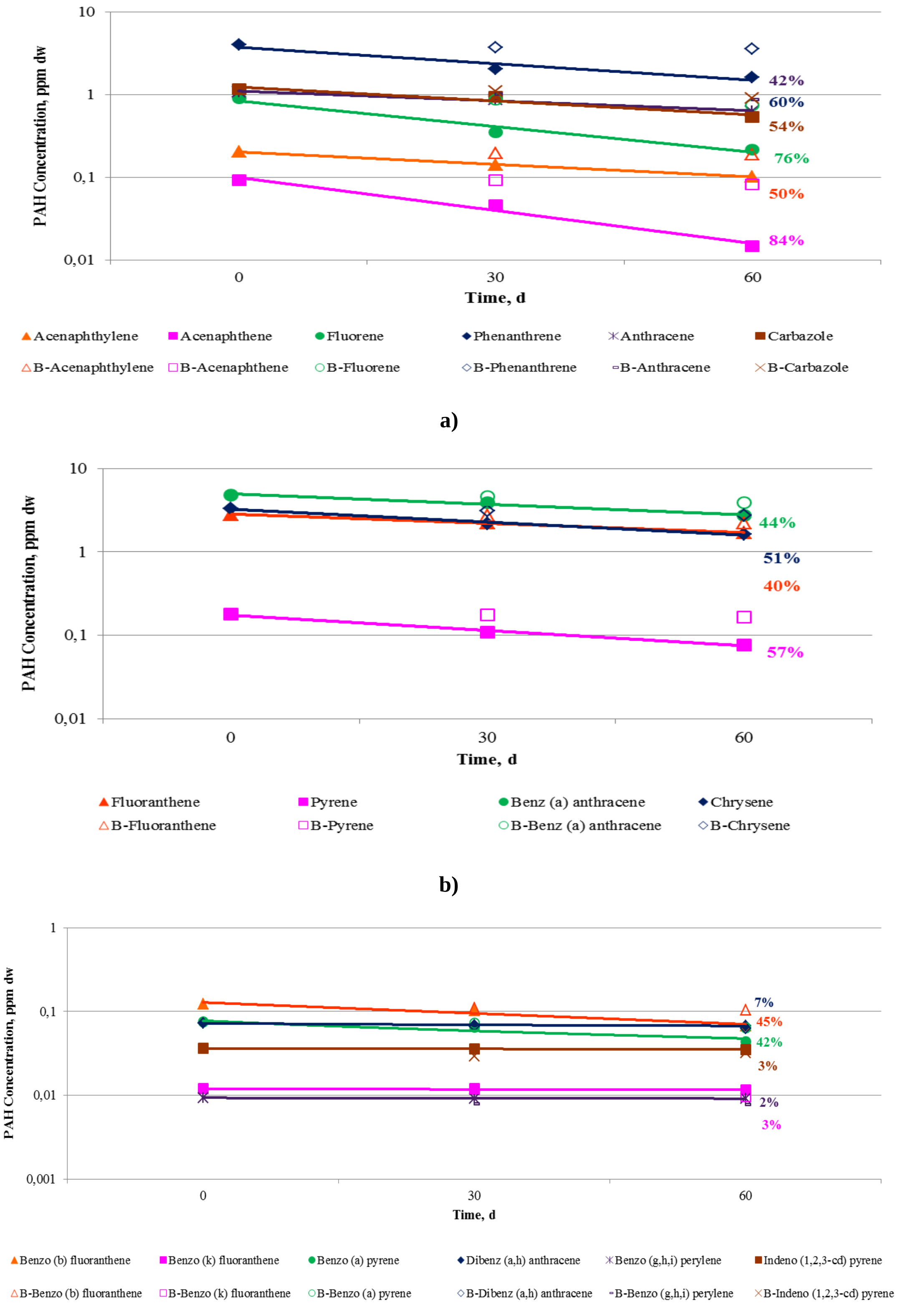


Figure 6.51 PAHs removals in fixed bed thermal volatilization systems (IDC= 10000 ppm and 40% water content at 40ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



c)

Figure 6.52 PAHs removals in fixed bed thermal volatilization systems (IDC= 25000 ppm and 40% water content at 40ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

Table 6.7 The removal rates of individual PAHs in fixed bed thermal volatilization systems

Studied PAHs				**PAHs Removal Efficiencies by Fixed Bed Thermal Volatilization, %**							
Number of Benzene Rings	**Name**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**10000 ppm IDC**				**25000 ppm IDC**			
				20% WC		**40%WC**		**20% WC**		**40% WC**	
				25°C	**40°C**	**25°C**	**40°C**	**25°C**	**40°C**	**25°C**	**40°C**
3 Ring	Acenaphthylene	16,1	$9,12*10^{-4}$	58	59	86	93	51	52	56	50
	Acenaphthene	3,9	$2,50*10^{-3}$	84	91	81	88	76	82	82	84
	Fluorene	1,89	$8,42*10^{-3}$	80	86	75	75	71	77	73	76
	Phenanthrene	1,15	$1,12*10^{-4}$	69	81	71	7	59	68	62	60
	Anthracene	$4,34*10^{-2}$	$2,67*10^{-6}$	31	35	25	33	23	26	44	42
	Carbozole	0,721	$2,66*10^{-4}$	60	61	36	44	48	46	52	54
4 Ring	Fluoranthene	$2,60*10^{-1}$	$1,23*10^{-8}$	54	69	57	57	41	41	44	40
	Pyrene	$1,35*10^{-1}$	$1,35*10^{-7}$	58	71	59	63	47	55	53	57
	Benz(a)anthracene	$9,40*10^{-3}$	$3,05*10^{-8}$	51	69	24	23	44	47	42	44
	Chrysene	$2,00*10^{-3}$	$6,23*10^{-9}$	50	48	30	32	40	48	46	51
5&6 Ring	Benzo(b)fluoranthene	$1,50*10^{-3}$	$5,00*10^{-7}$	55	57	56	57	41	47	44	45
	Benzo(k)fluoranthene	$8,00*10^{-4}$	$9,65*10^{-10}$	11	11	15	10	3	1	0.5	3
	Benzo(a)pyrene	$1,62*10^{-3}$	$5,49*10^{-9}$	44	47	48	43	43	58	40	42
	Dibenz(a,h)anthracene	$2,49*10^{-6}$	$1,00*10^{-10}$	8	9	7	6	4	6	5	7
	Benzo(g,h,i)perylene	$2,6*10^{-4}$	$1,01*10^{-10}$	7	9	8	11	3	6	2	2
	Indeno(1,2,3-c,d)pyrene	$2,20*10^{-5}$	$1,00*10^{-10}$	8	7	11	8	2	1	0.5	3

Table 6.8 PAHs groups average removal efficiencies obtained from fixed bed thermal volatilization systems according to the initial water content and experimental temperature

PAHs groups according to number of benzene rings	**Initial Water Content of the Soil, %**	**Average PAHs removal efficiencies, %**			
		10000 ppm IDC		**25000 ppm IDC**	
		25°C	**40°C**	**25°C**	**40°C**
3Ring PAHs	20	64	69	55	59
	40	62	68	62	61
4Ring PAHs	20	53	64	43	48
	40	43	44	46	48
5&6Ring PAHs	20	21	23	16	20
	40	24	23	15	17

As can be seen from the figures and from the Tables 6.7 and 6.8, the PAHs removal rates are strongly related with their number of benzene rings as well as initial contaminant concentration. The removal rates are decreasing with increasing initial concentration. The evaluation of the results according to the soil water content and applied temperature is a challenge; therefore Figure 6.53 is presented for better understanding of the phenomenon.

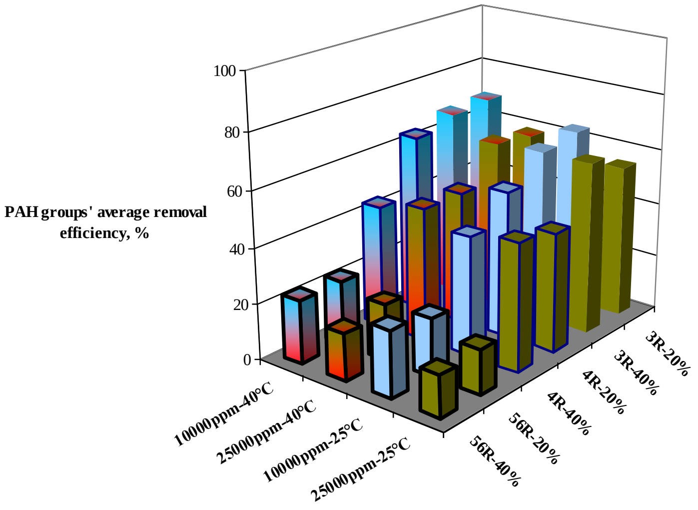


Figure 6.53 The effect of soil water content, initial diesel concentration and the temperature

Figure 6.53 describes that the soils having 40% initial water content resulted with slightly higher PAHs removal rates. In addition, the treatment efficiency is increasing with decreasing number of benzene rings when the temperature increases. The effects of PAHs’ water solubility and vapor pressure on volatilization efficiency will be discussed in detail at the end of this chapter.

6.3.1.2 The Effect of Soil Properties

In this part, the experiments were also conducted in 1 L reactors under 25°C and the temperature was kept constant in an incubator. As the previous fixed bed experiments were carried out with Kaynaklar soil, two other soils with different features were used here; Kutahya soil and River sand, in order to describe the effect of soil type on fixed bed thermal volatilization of NAPLs. The initial soil diesel concentration of 25000 ppm was examined with initial water contents of 20% and 40%. Water content, pH, and change in TPHs levels in the soils were followed during the operational period of 60 days. In addition, the findings from the thermal volatilization experiments for Kaynaklar soil with 25000 ppm IDC given in above parts in this chapter were used to evaluate the results.

The changes in water content of the soils in the systems according to the initial contaminant concentration and incubation temperature are given in Figure 6. 54.

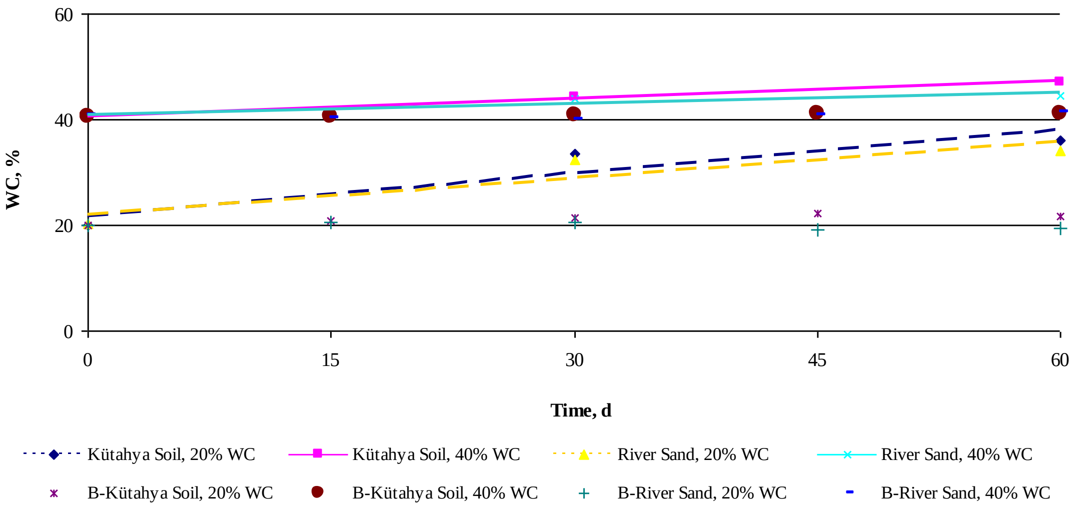


Figure 6.54 The change in water content in fixed bed thermal volatilization studies for Kutahya soil and River sand.

As can be seen from the figure, the water content of Kutahya soil has increased during the experimental period. The increase in water content was around 5% in soil with initial water content of 40%, where 15% increase has seen with Kutahya soil with 20% water content. River sand with 20% initial water content showed a large increase in water content, where River sand with 40% water content did not show any variation during the experimental period. These findings are similar with the ones found for Kaynaklar soil in chapter 6.3.1.1; the water content increases more significantly for the soils having 20 % water content.

The pH levels in Kutahya soil and River sand during fixed bed thermal volatilization experiments are given in Figure 6.55.

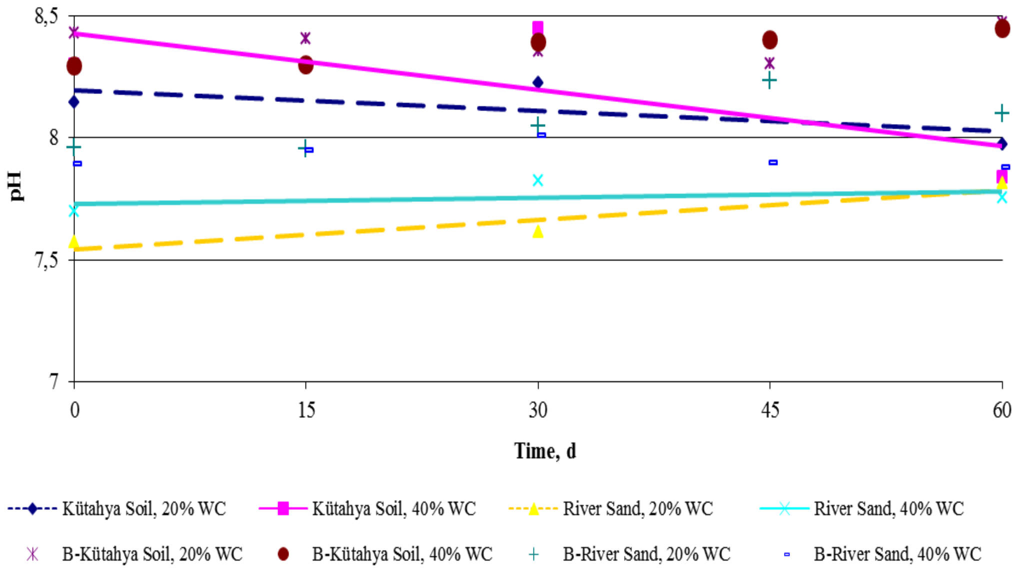


Figure 6.55 The change in soil pH in fixed bed thermal volatilization studies for Kutahya soil and River sand.

It is seen that, the pH level in Kutahya soil decreases from the interval of 8.2-8.4 to 8.0-8.1 interval as the experimental period extended, which is similar with the findings for Kaynaklar soil. Controversially, River sand pH level increased from 7.5 to 7.75 in the set with initial water content of 20%. The reason for this finding is the increased water content in this set (Figure 6.54) allowed the solubilization of

Carbonate group minerals which is found only in River soil (Table 5.4), and increased the soil pH.

The changes in TPHs concentration in soils studied in this part is given in Figure 6.56. The TPHs removal efficiencies for Kaynaklar soil is also added to the graphic for easy comparison of the results.

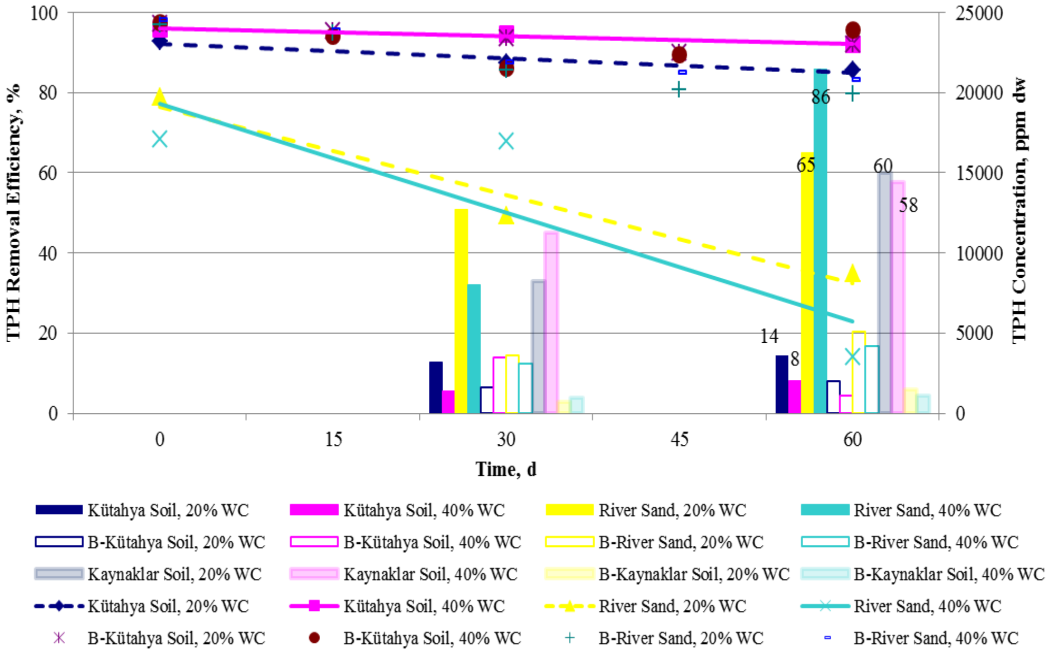


Figure 6.56 The change in soil TPHs levels andTPHs removal efficiencies in fixed bed thermal volatilization studies for Kutahya soil, River sand, and Kaynaklar soil for 25000 ppm IDC at 25°C

In Figure 6.56, significant differences between the TPHs removal rates from the sets with Kaynaklar soil, Kutahya soil, and River sand have seen. Kutahya soil resulted with 14 and 8% TPHs removals with the soils having 20 and 40% water content, respectively, where the remediations with Kaynaklar soil ended with 60 and 58& removal rates for 20 and 40% initial water contents (IWCs), respectively. River sand showed the highest TPHs removals as 65 and 86% for 20 and 40% IWCs. It is seen that TPHs removal rates are highly related with soils organic matter content, specific surface area (SSA), clay content, and porosity (Table 5.4). The higher the SSAs, clay content, and organic matter content the lower the TPHs removal efficiencies, and as the porosity decreases the TPHs removal rates have increased.

The effect of IWC on TPHs treatment efficiencies has differ according to the soil type. In Kutahya soil, the TPH removal efficiency with 20% water content was almost two times higher than the result with 40% water content. The difference gets smaller in Kaynaklar soil, the TPHs removals with 20 and 40% are almost the same. In River sand, the TPHs removal with 40% IWC increases and result in this set is 1.3 times greater than the result with 20% IWC. Hence, the abilities of soils to adsorb water and the aeration humidity have important effects on the remediation of TPHs in soils.

6.3.1.3 The Effect of Contamination Age

For the investigation of the effect of contamination age on the thermal volatilization of NAPLs from the soils, 1 L reactors were used in an incubator at 25°C. The initial Kaynaklar soil diesel concentrations of 10000 ppm, 25000 ppm, and 100000 ppm were examined with initial water content of 40%. Water content, pH, and change in TPHs levels in the soils were followed during the operational period of 60 days. The removal rates obtained from freshly contaminated Kaynaklar soil were used as control.

The change in water content of the systems is given in Figure 6.57.

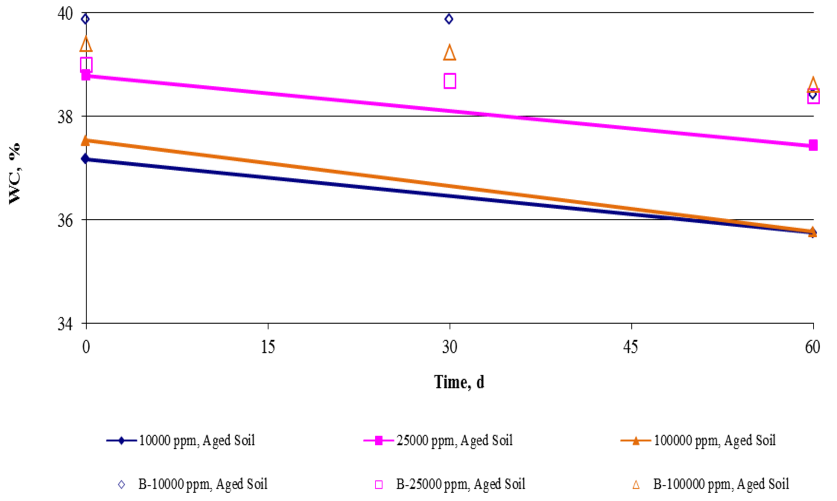


Figure 6.57 The changes in aged soil water contents of fixed bed thermal volatilization reactors, at 25ºC

It is seen that, the water contents of the aged Kaynaklar soils in studied sets decreased about 2% during the experiment, which is not very compatible with the results with freshly contaminated Kaynaklar soils, because of lower initial water contents of aged soils.

The pH levels (Figure 6.58) of the soils decreased from 7.30-7.55 interval to 7.2 in all sets, which is compatible with the previous finding with freshly contaminated Kaynaklar soil.

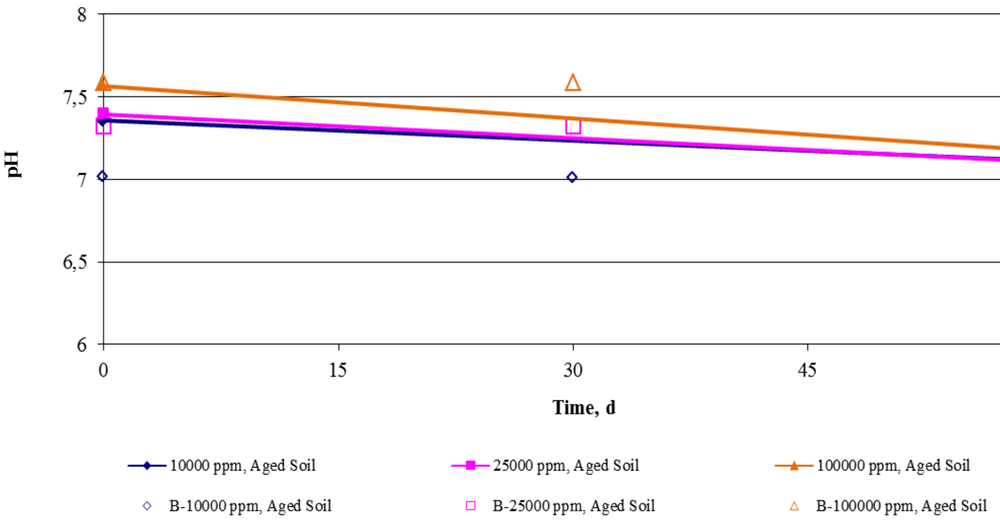


Figure 6.58 The changes in aged soil pH levels in fixed bed thermal volatilization reactors, at 25°C

The TPHs levels of soils during the experimental period were observed and both final TPHs concentrations and removal rates are illustrated in Figure 6.59.

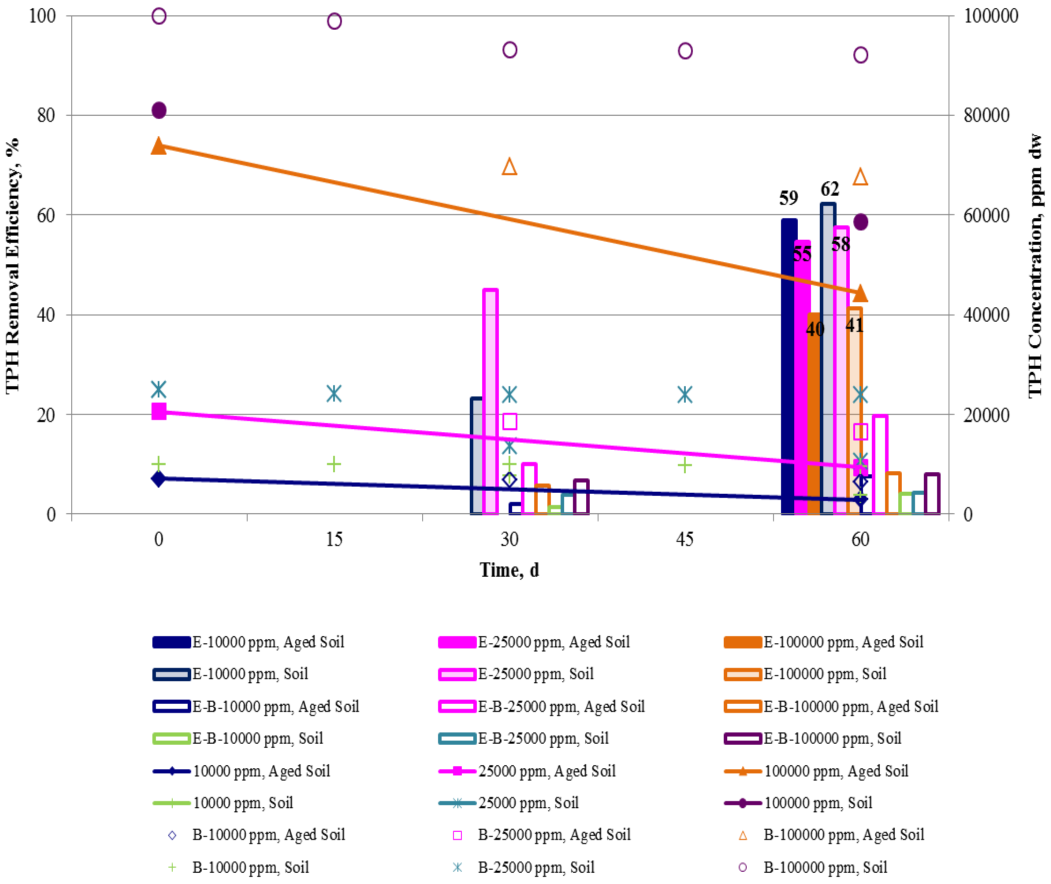


Figure 6.59 The changes in aged soil and soil TPHs concentration of fixed bed thermal volatilization reactors, at 25°C

The TPHs removals in aged soils were found 1-3% lower than the freshly contaminated soils. The difference between the removal rates of TPHs from aged and freshly contaminated soils are getting lower as the initial concentration increases. In addition, the removal rate decreases with increasing initial concentration in aged soils as it was found as in freshly contaminated soils.

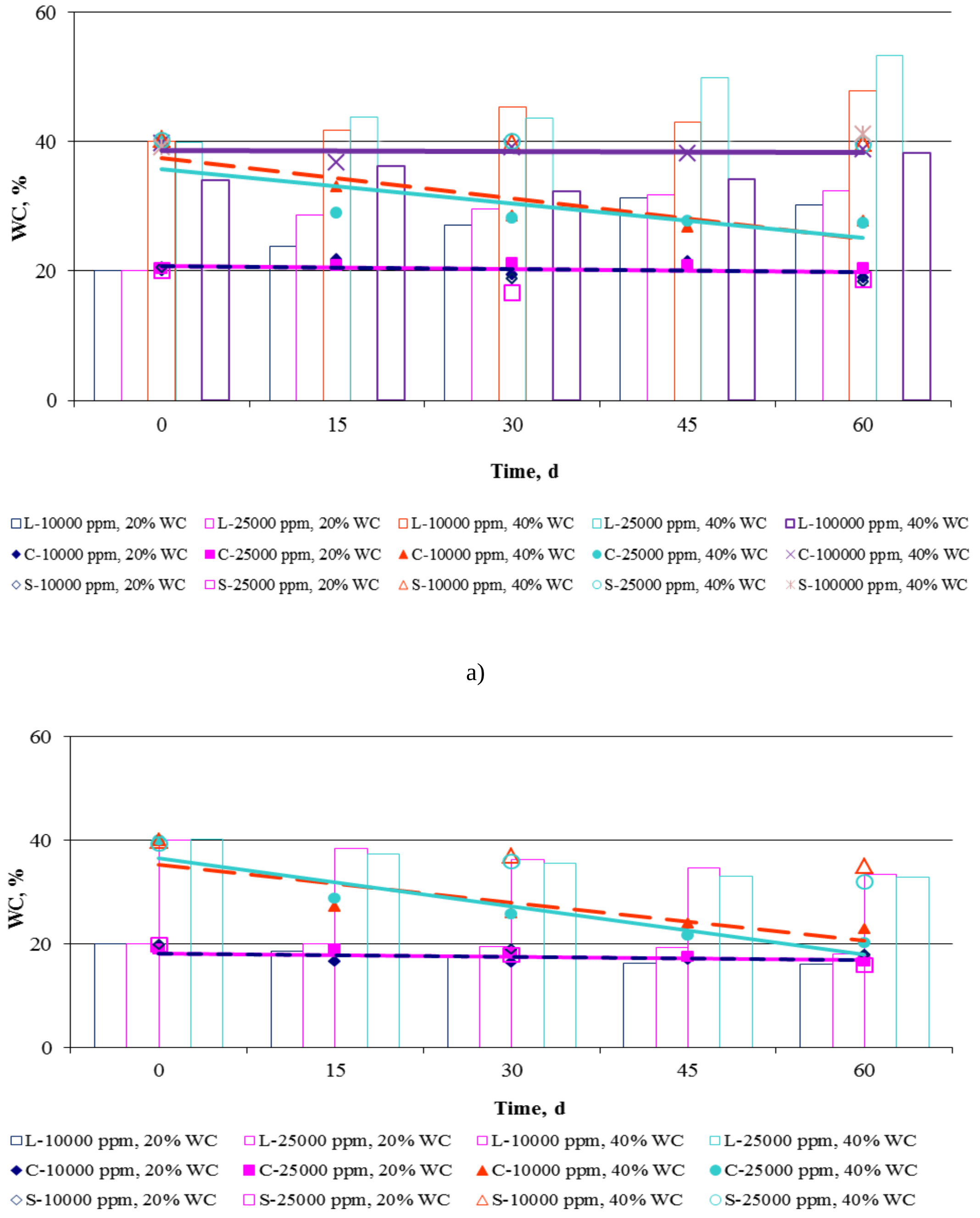
6.3.2 Fixed Bed Soil Bioremediation

In this section, the efficiency of bioremediation on NAPLs treatment from the soil was investigated. For this purpose the soil having native bacteria was used by addition of compost (1/10 of compost/soil ratio on dry basis) as soil amendment. The systems were aerated according to Chapter 4 to supply oxygen for the bacteria. Parallel sets with sterilized soils and the soils with local bacteria were also executed for comparing the results.

6.3.2.1 The Effects of Water Content, Initial Contaminant Concentration, Temperature, and Presence of Soil Amendment in Bioremediation of NAPLs Contaminated Soils

The experiments were conducted in 1 L reactors under 25°C or 40°C where the temperature was kept constant in an incubator. The initial soil diesel concentrations of 10000 ppm, 25000 ppm, and 100000 ppm were examined as well as initial water contents of 20% and 40%. The TPHs and PAHs removal from the soils were observed with local bacteria as well as compost amendment. Water content, pH, CO_2 generation, bacterial counts, changes in TPHs and PAHs concentration in the systems were followed during the operational period of 60 days. The system with 100000 ppm IDC was operated only with 40% water content and the PAHs were measured only in the system with 25000 ppm IDC. The compost amendment was supplied with a compost-soil ratio of 1/10.

In Figure 6.60, the changes in water content of the soils in the systems are presented according to the operation temperature. It is seen that the compost amended soils with initial water contents of 40% having 10000 and 25000 ppm of IDC showed a decrease in water content during the experimental period.

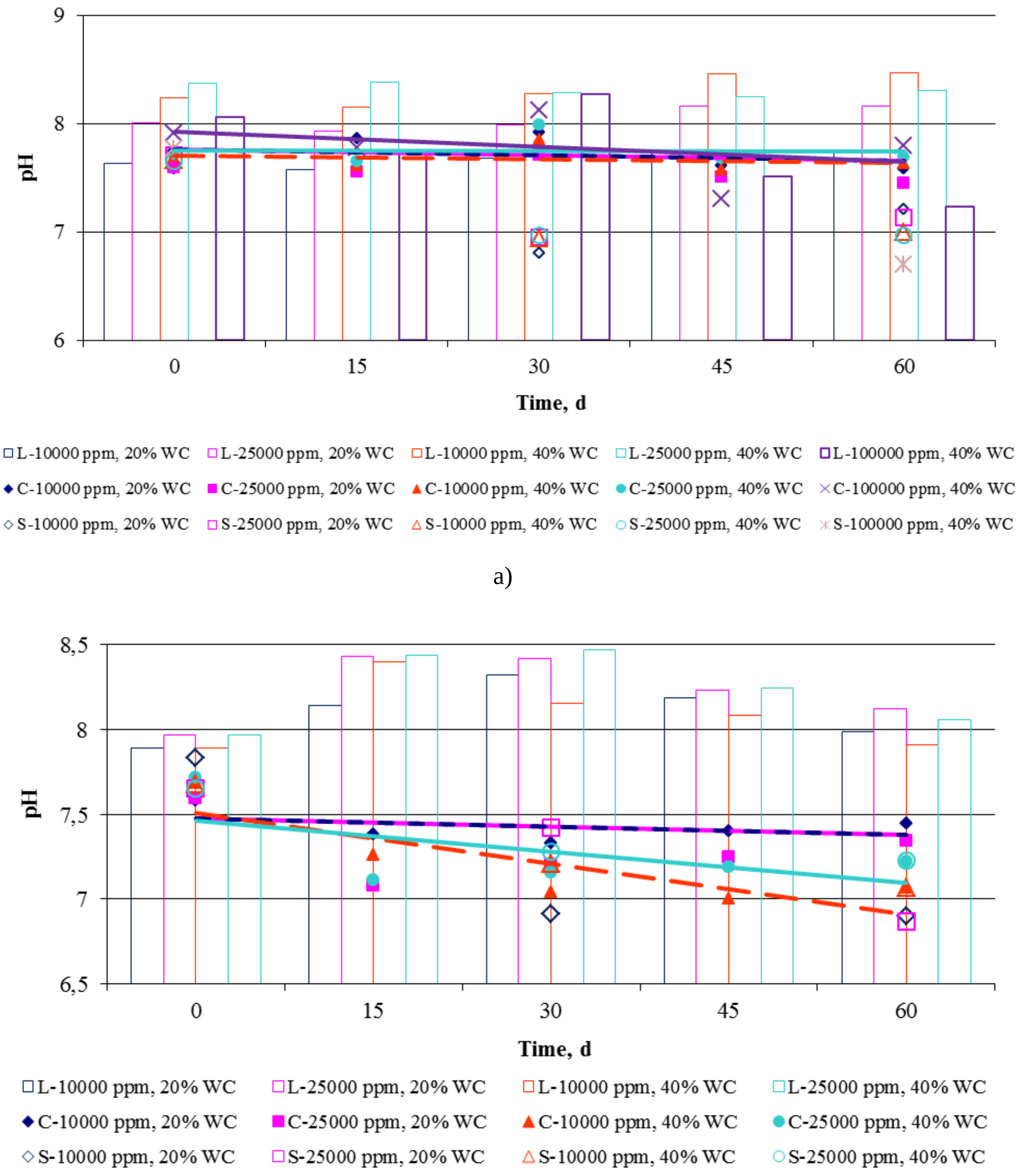


a)

b)

Figure 6.60 The changes in soil water content of fixed bed soil bioremediation reactors with compost amentment, a) at 25°, b) at 40°C

The initial pH levels of the soils were around 7.8 and these pH level were kept almost constant in the sets operated at 25°C, where the soils in sets with initial water content of 40% showed a decrease in pH to the level of 7.0 at 40°C (Figure 6.61).

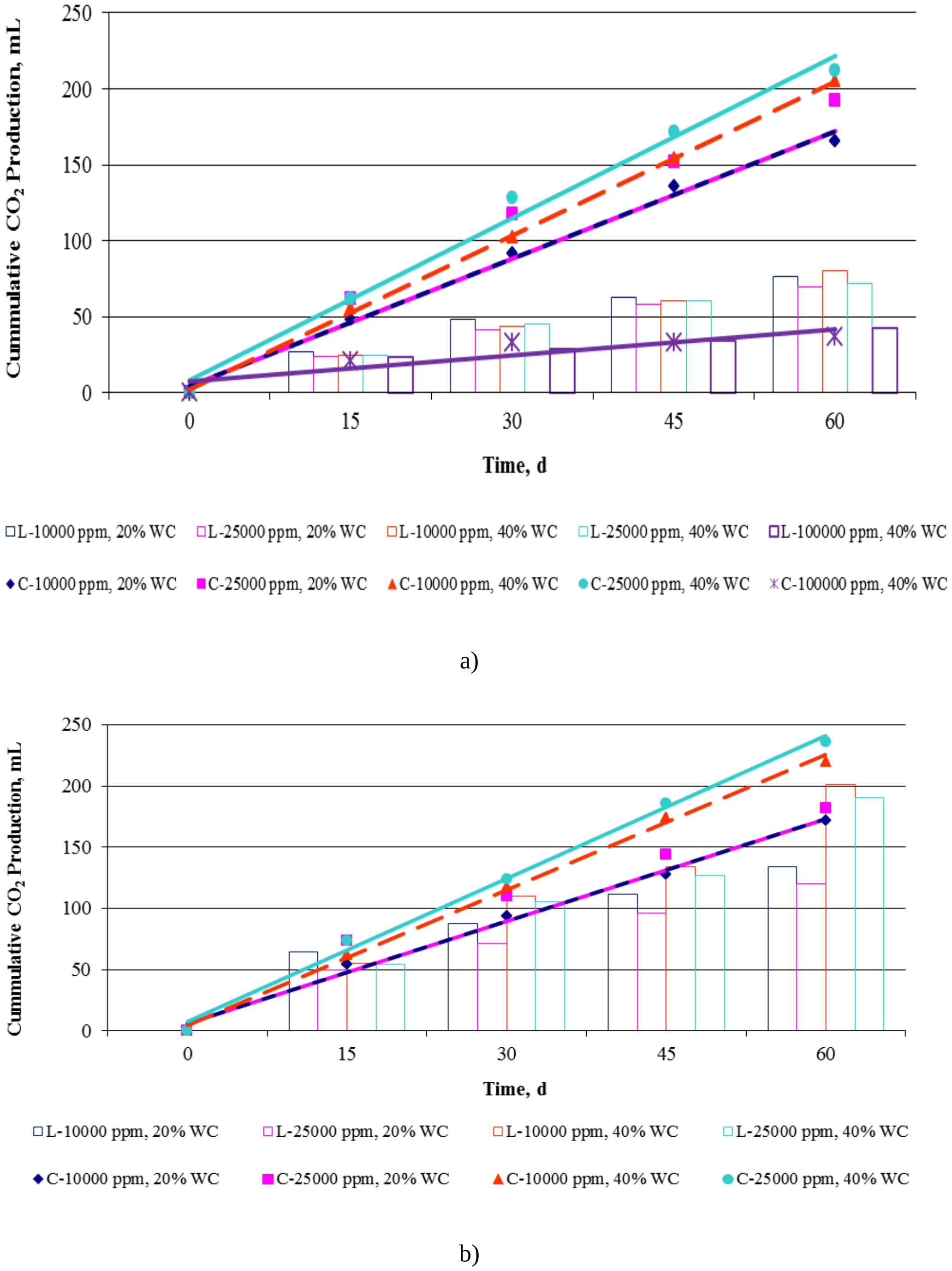


a)

b)

Figure 6.61 The changes in soil pH of fixed bed bioremediation reactors, a) at 25°, b) at 40°C

The cumulative CO_2 productions in the sets operated at 25°C and 40°C were given in Figure 6.62, and the changes in soil bacteria counts are presented in Figure 6.63. The cumulative CO_2 productions at 40°C is higher for the soils with 40% water content than the soils having water content of 20%. It was seen that CO_2 production in the soil with 100000 ppm IDC was the lowest at 25°C. For both temperatures, the soils having higher IWC resulted with higher CO_2 productions.



a)

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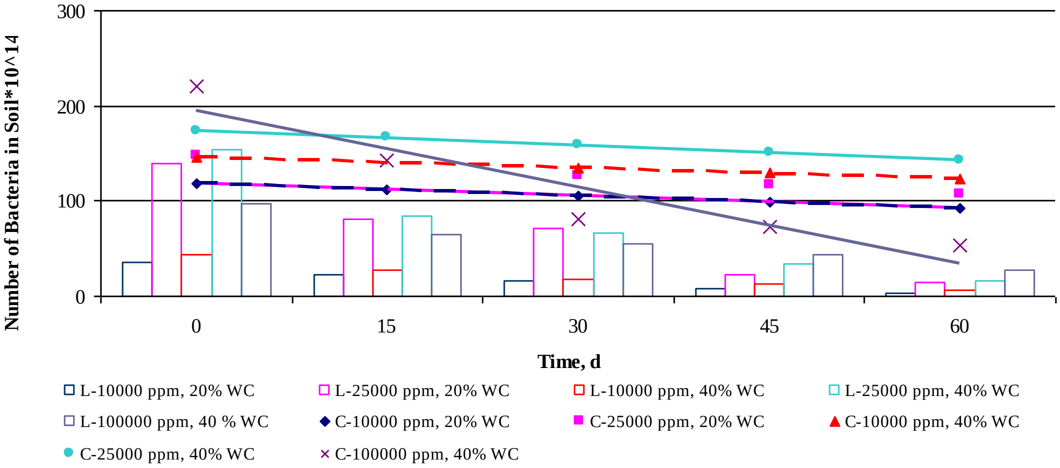
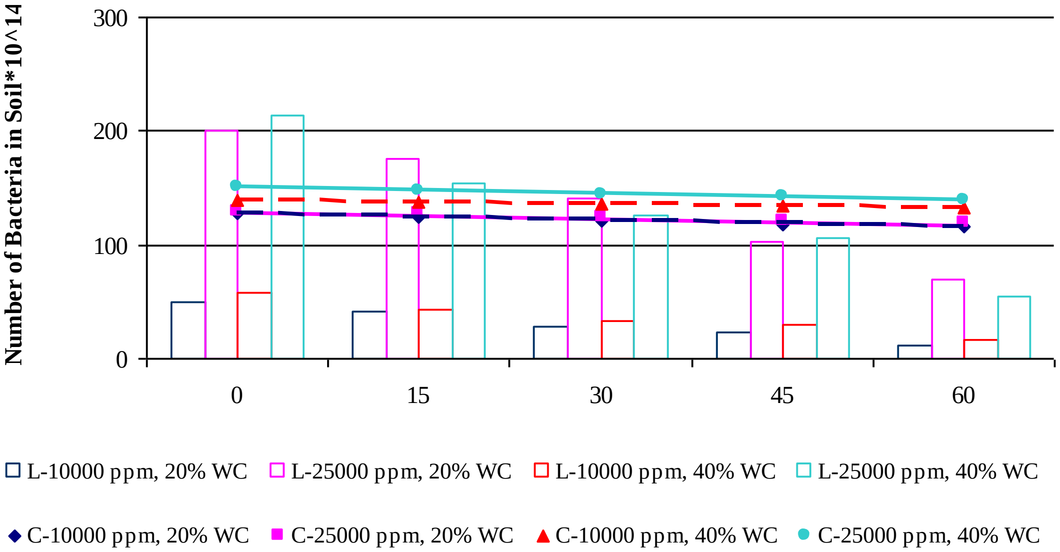
Figure 6.62 The cumulative CO_2 production in soils of fixed bed bioremediation reactors with compost amentment, a) at 25°, b) at 40°C



a)

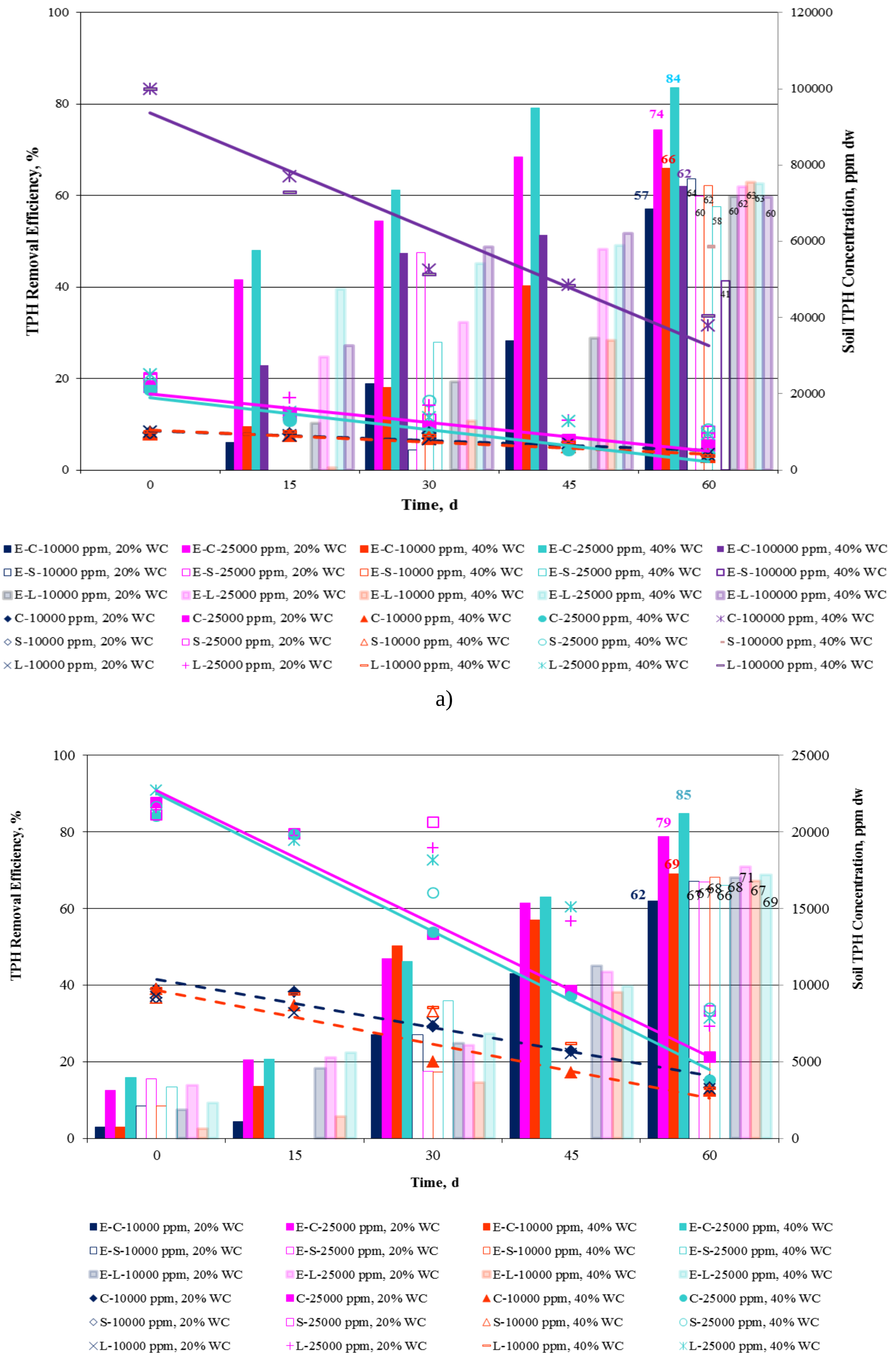


b)

Figure 6.63 The number of bacteria in soils of fixed bed bioremediation reactors with compost amendment, a) at 25°, b) at 40°C

The bacteria counts in the systems operated at 25°C slightly declined for the soil IDC of 10000 ppm and 25000 ppm, where decrease in the number of bacteria was very sharp with IDC of 100000 ppm which is compatible with the results obtained for cumulative CO_2 production.

The TPHs removal efficiencies and remaining TPH concentrations in the systems are given in Figure 6.64.



a)

b)

Figure 6.64 The changes in soil TPHs concentration and TPHs removal efficiencies in fixed bed bioremediation reactors, a) at 25°, b) at 40°C

It is recognized that the removal efficiency of TPHs in soil increases with increasing incubation temperature; the removal efficiencies obtained with 40°C are 1-5% higher than the removals obtained at 25°C. The effect of initial concentration is important; since the TPHs removal efficiencies are higher than the soils with 10000 ppm but lower than the soils with 100000 ppm IDC. This situation shows the inhibitory effect of increased initial concentration together with the results for CO_2 production and bacterial growth from the soil contaminated with 100000 ppm diesel initially.

The PAHs concentrations in soil during fixed bed bioremediation systems conducted with compost amendment were also observed during the sets operated at 25°C. With the 100000 ppm IDC, PAHs were studied with only 40% soil initial water content. The removal rates and residual concentrations of PAHs are given in Figures 6.65-6.69.

In addition, the individual removals of PAHs are summarized in Table 6.9 and the average removal rates calculated for to the PAH groups organized according to the number of benzene rings are given in Table 6.10.

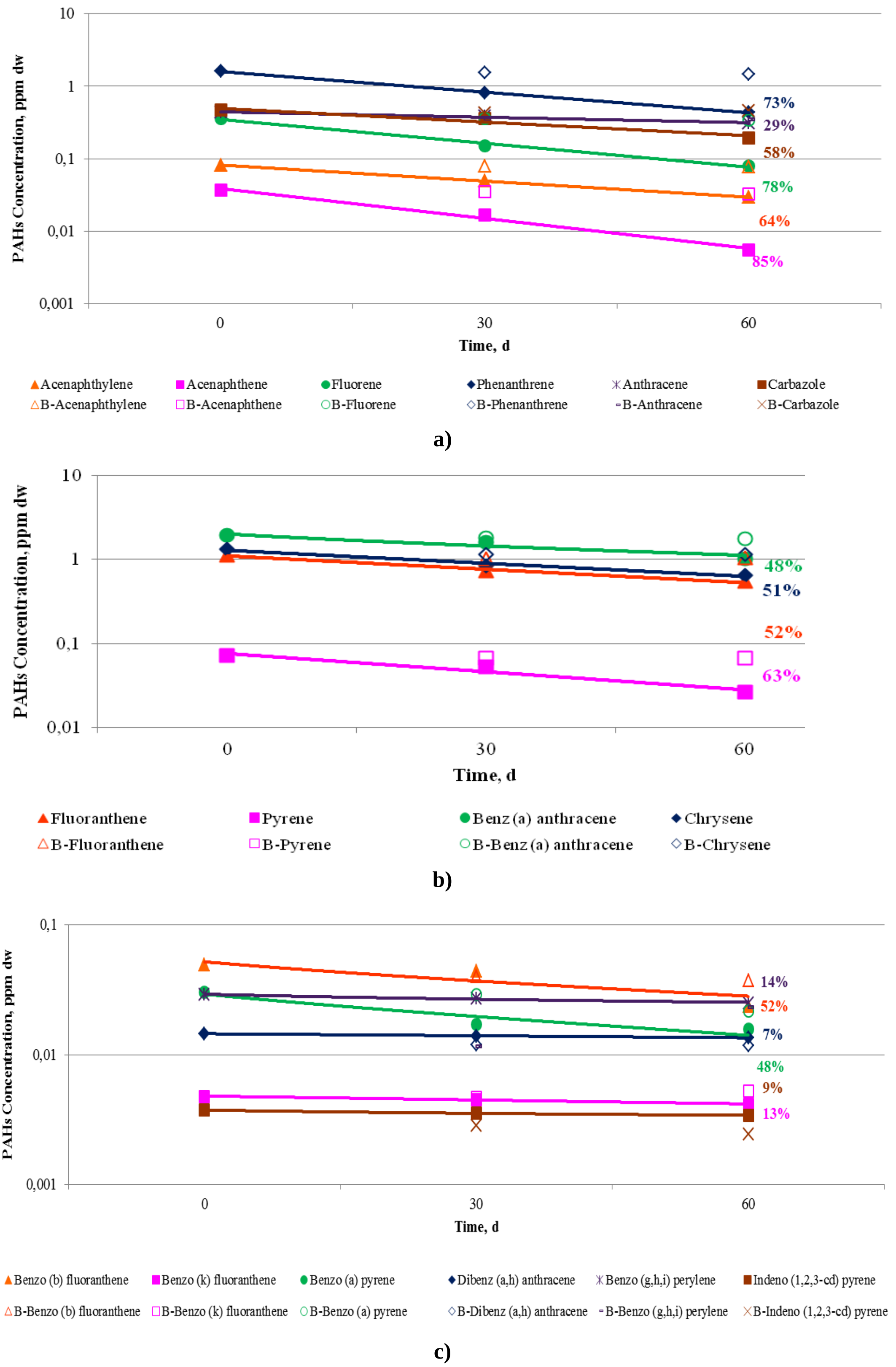


Figure 6.65 1 PAHs removals in fixed bed bioremediation systems (IDC= 10000 ppm and 20% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

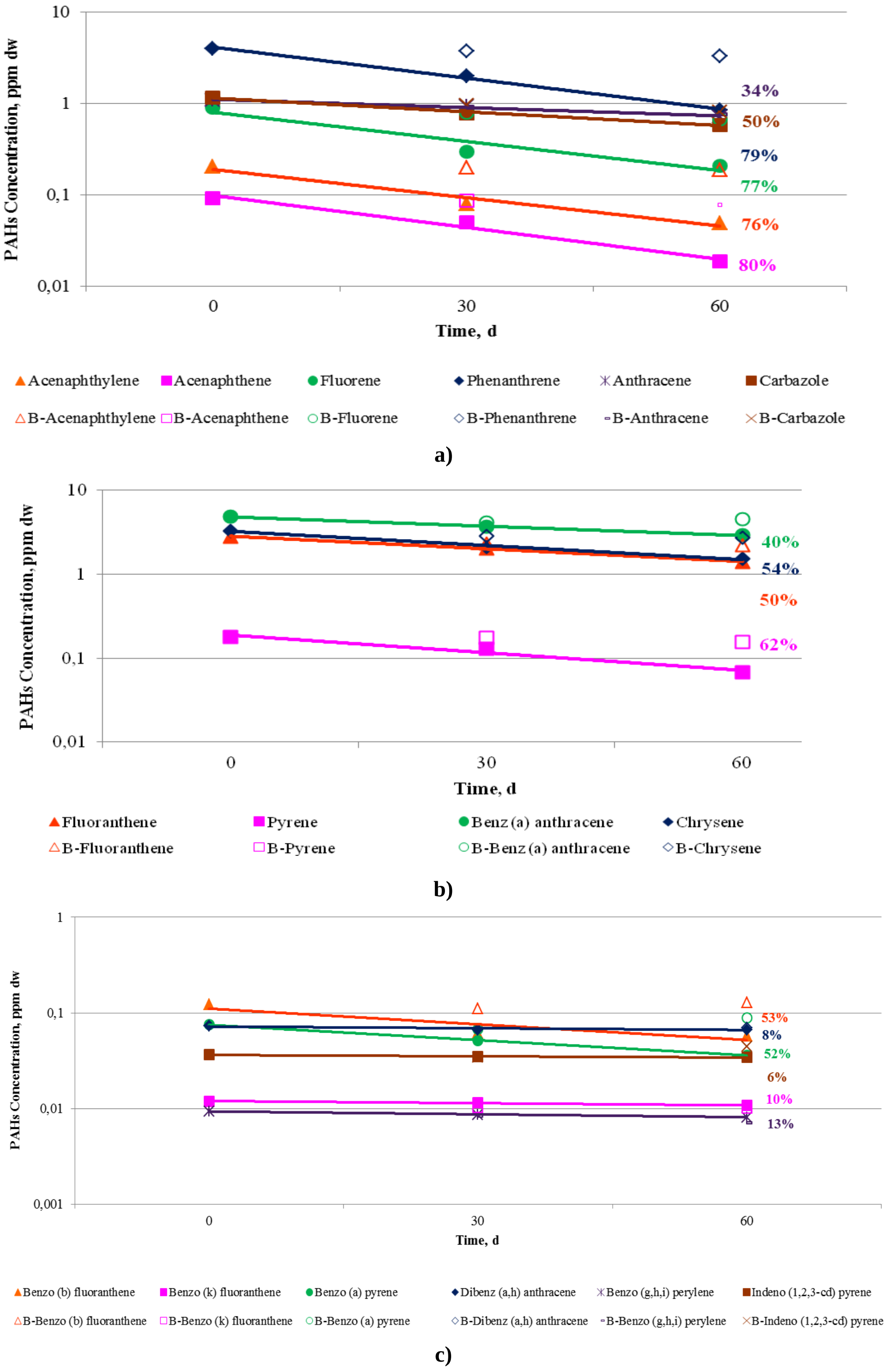


Figure 6.66 PAHs removals in fixed bed bioremediation systems (IDC= 25000 ppm and 20% water content at 25°C, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

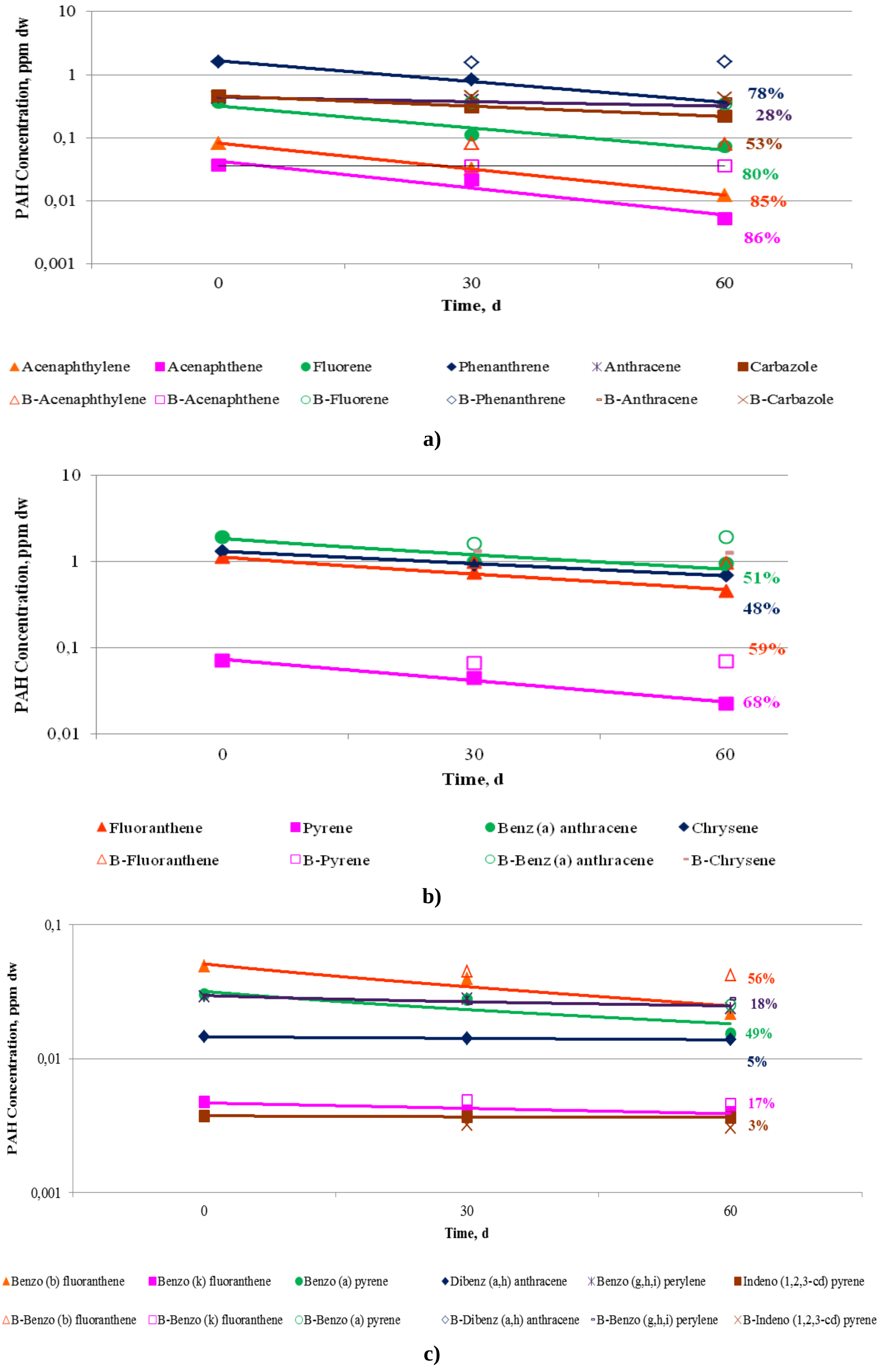
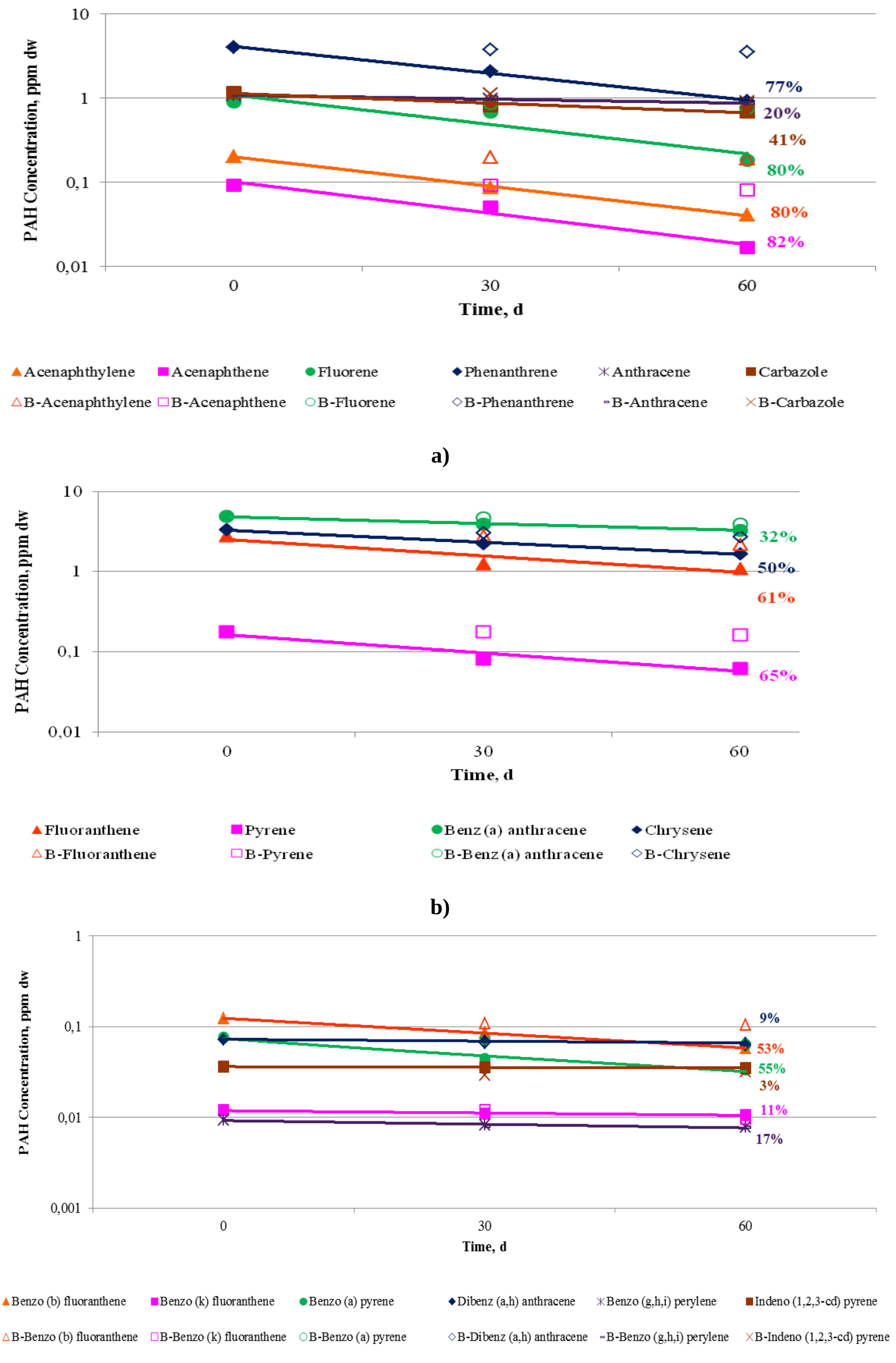
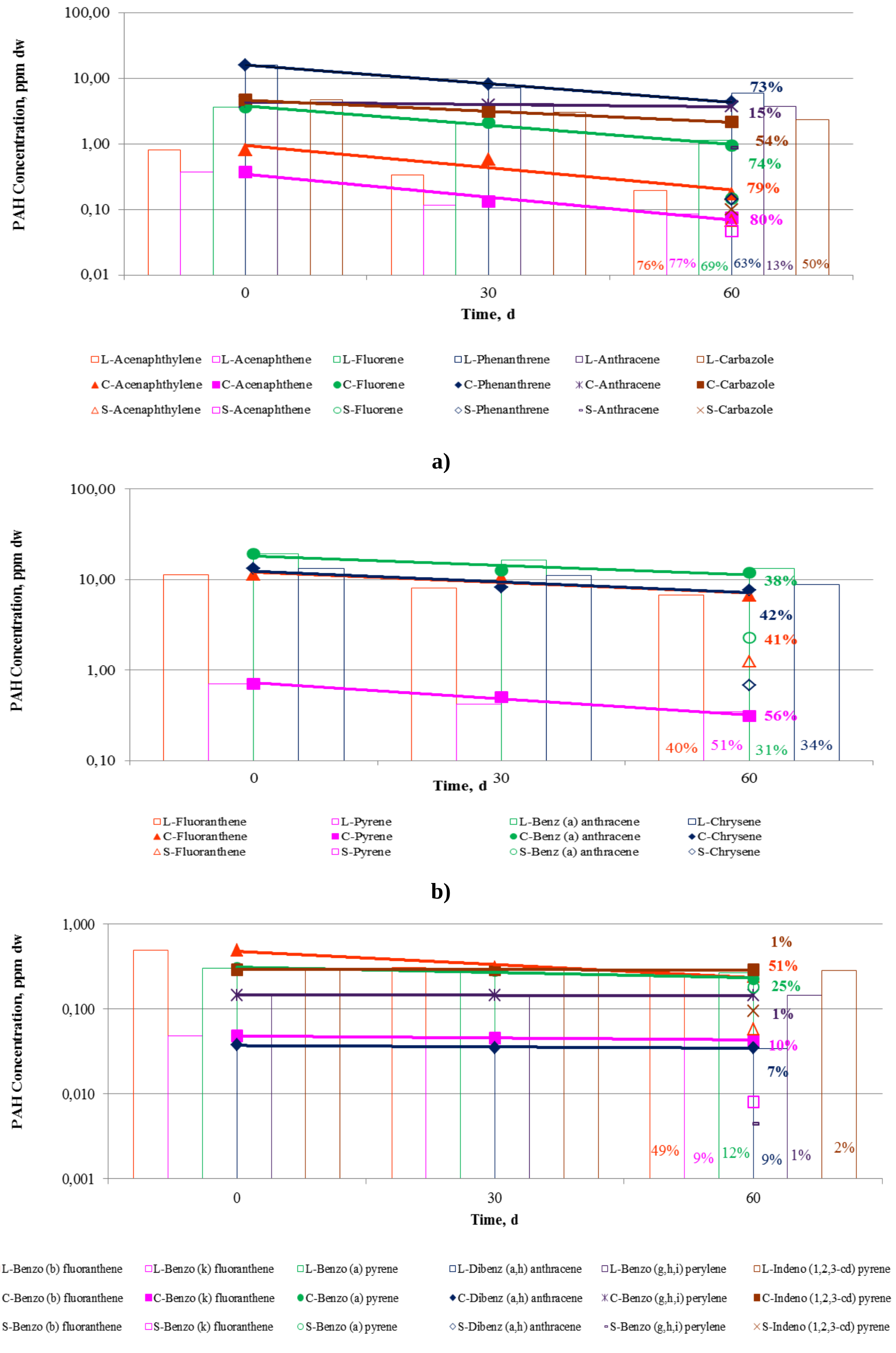


Figure 6.67 PAHs removals in fixed bed bioremediation systems (IDC= 10000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



c)

Figure 6.68 PAHs removals in fixed bed bioremediation systems (IDC= 25000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



a)

b)

c)

Figure 6.69 PAHs removals in fixed bed bioremediation systems (IDC= 100000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

Table 6.9 The removal rates of individual PAHs in fixed bed bioremediation systems

Studied PAHs				**PAHs Removal Efficiencies by Fixed Bed Bioremediation, %**					
Number of Benzene Rings	**Name**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**10000 ppm IDC, 25°C**		**25000 ppm IDC, 25°C**		**100000 ppm ID, C25°C**	
				20% WC	**40%WC**	**20% WC**	**40% WC**	**40%WC**	
				Compost	**Compost**	**Compost**	**Compost**	**Compost**	**Local**
3 Ring	Acenaphthylene	16,1	$9,12*10^{-4}$	64	85	76	80	79	76
	Acenaphthene	3,9	$2,50*10^{-3}$	85	86	80	82	80	77
	Fluorene	1,89	$8,42*10^{-3}$	78	80	77	80	74	69
	Phenanthrene	1,15	$1,12*10^{-4}$	73	78	79	77	73	63
	Anthracene	$4,34*10^{-2}$	$2,67*10^{-6}$	29	28	34	20	15	13
	Carbozole	0,721	$2,66*10^{-4}$	58	53	50	41	54	50
4 Ring	Fluoranthene	$2,60*10^{-1}$	$1,23*10^{-8}$	52	59	50	61	41	40
	Pyrene	$1,35*10^{-1}$	$1,35*10^{-7}$	63	68	62	65	56	51
	Benz(a)anthracene	$9,40*10^{-3}$	$3,05*10^{-8}$	48	51	40	32	38	31
	Chrysene	$2,00*10^{-3}$	$6,23*10^{-9}$	51	48	54	50	42	34
5&6 Ring	Benzo(b)fluoranthene	$1,50*10^{-3}$	$5,00*10^{-7}$	52	56	53	53	51	49
	Benzo(k)fluoranthene	$8,00*10^{-4}$	$9,65*10^{-10}$	13	17	10	11	10	9
	Benzo(a)pyrene	$1,62*10^{-3}$	$5,49*10^{-9}$	48	49	52	55	25	12
	Dibenz(a,h)anthracene	$2,49*10^{-6}$	$1,00*10^{-10}$	7	5	8	9	7	9
	Benzo(g,h,i)perylene	$2,6*10^{-4}$	$1,01*10^{-10}$	14	18	13	17	1	1
	Indeno(1,2,3-c,d)pyrene	$2,20*10^{-5}$	$1,00*10^{-10}$	9	3	6	3	1	2

Table 6.10 PAHs groups average removal efficiencies obtained from fixed bed bioremediation systems according to the initial water content and experimental temperature

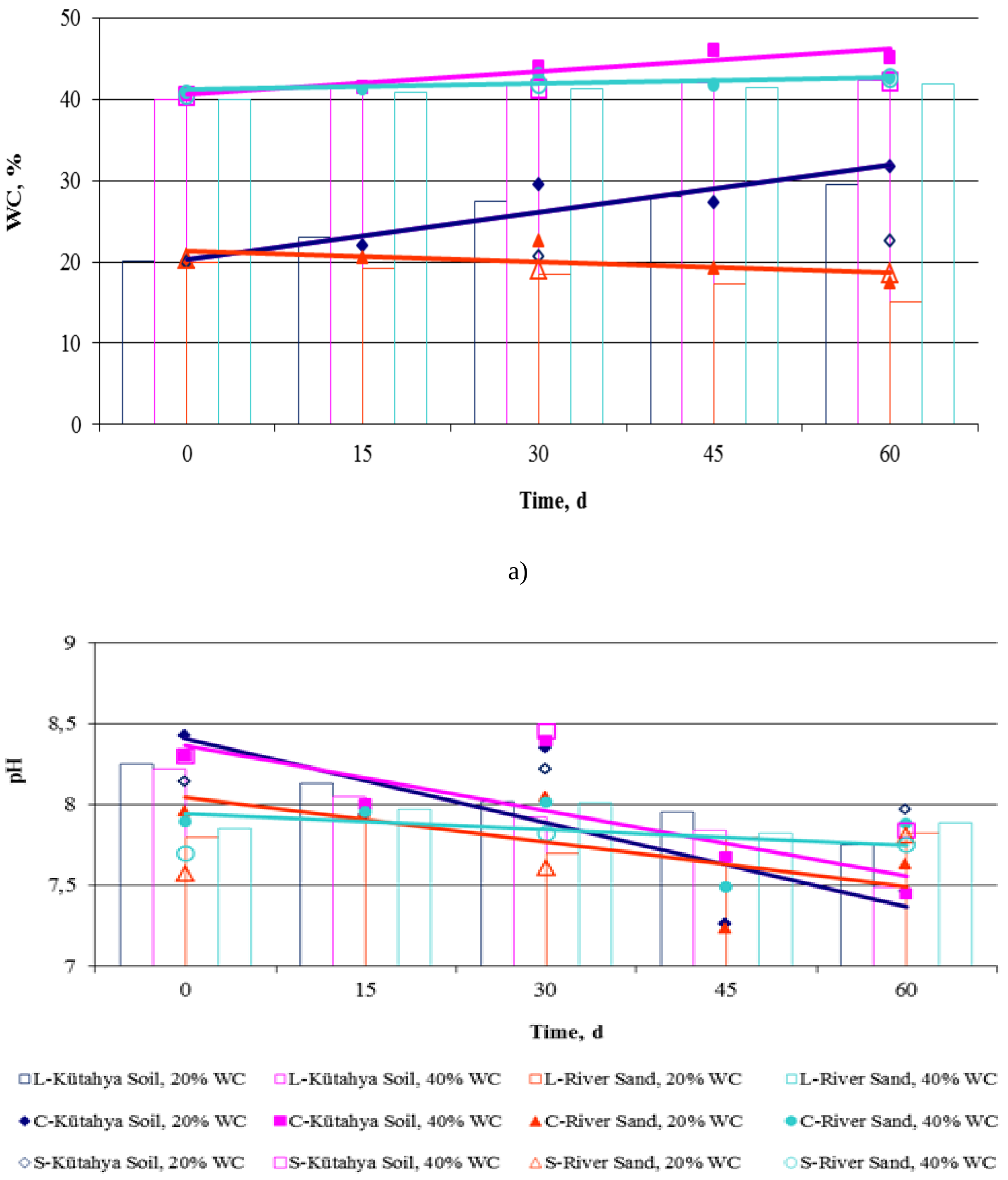
PAHs groups according to number of benzene rings	Initial Water Content of the Soil, %	Average PAHs removal efficiencies, % 10000 ppm IDC, 25°C Compost	25000 ppm IDC, 25°C Compost	100000 ppm IDC, 25ºC Compost	 Local
3Ring PAHs	20	65	66	-	-
	40	68	63	63	58
4Ring PAHs	20	54	52	-	-
	40	57	52	44	39
5&6Ring PAHs	20	24	24	-	-
	40	25	24	16	14

It was seen that the removal efficiencies of PAHs are slightly above with 10000 ppm IDC than the experiments with 25000 ppm IDC. But, the differences between the PAHs removals are more significant as the initial concentration has increase to 100000 ppm IDC. On the other hand, the effect of 1/10 (compost/soil) compost amendment could not achieve higher PAHs removals than the system operated with local bacteria at 100000 ppm IDC. This can be because of the inhibitory effect of high initial concentration on both soil and compost bacteria.

6.3.2.2 The Effect of Soil Properties on the Remediation of NAPLs in Fixed Bed Bioremediation Systems with Compost Amendment

In this part of the study, for investigating the soil type effect on bioremediation, two other types of soils namely; Kutahya soil and River sand were used with compost amendment. The initial soil diesel concentration of 25000 ppm was applied with 20% and 40% soil initial water content at 25°C. The systems were aerated as described in Chapter 4. Water content, pH, CO_2 production, bacterial counts, TPHs and PAHs levels were followed during the 60 days of operation time.

Below, in Figure 6.70, the changes in water content and pH of the soils studied are given. As it is illustrated, the both soils having initial water content of 40% did not show a significant increase in water content. Among the soils having 20% water content, the Kutahya soil water content showed an increase while the River sand did not show an important change.

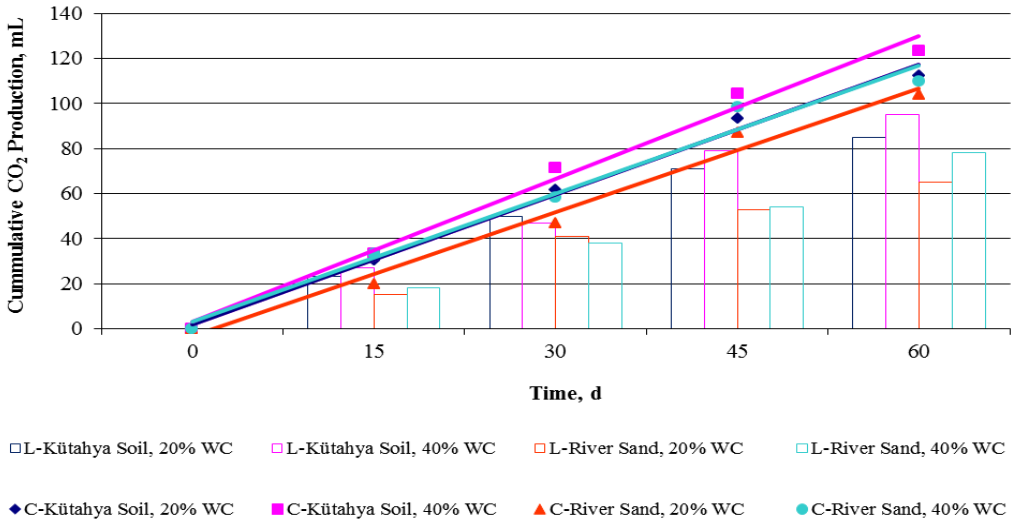


a)

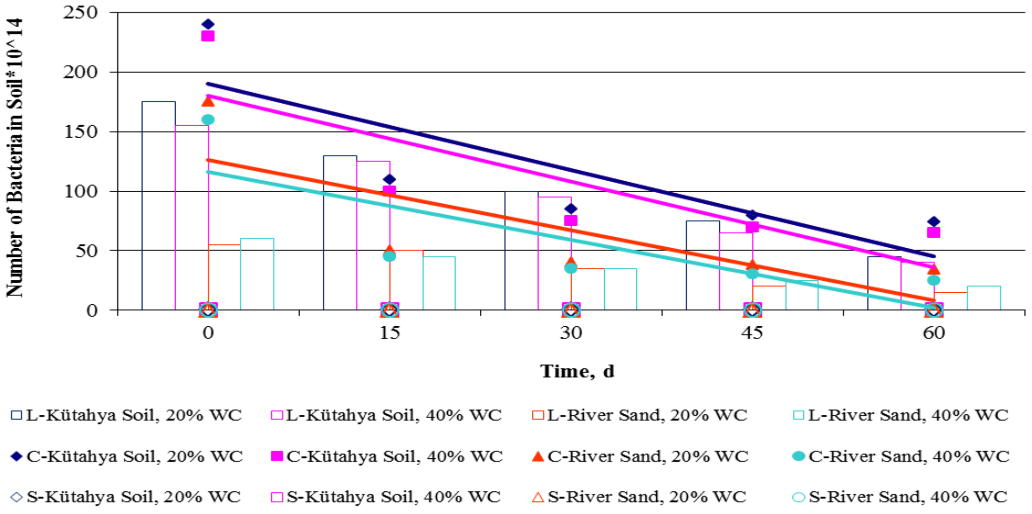
b)

Figure 6.70 The changes in Kutahya soil and River sand water content and pH in fixed bed bioremediation reactors at 25°C

The pH levels in all systems dropped significantly during the fixed bed bioremediation by compost amendment, which is an indicator of CO_2 production in the systems. The CO_2 production and bacterial counts of the systems are given in Figure 6.71.



a)



b)

Figure 6.71 CO_2 production and number of bacteria in Kutahya soil and River sand in fixed bed bioremediation system

The CO_2 generations from the systems are significant and higher in the soils having 40% water content. In addition CO_2 production in Kutahya soil is higher than River sand. This may be related with the different initial bacterial counts of the soils as given in Figure 6.71b. The number of bacteria in both soils declined during the operational period, probably due to the high IDC.

In Figure 6.72, the TPHs removal from the systems and residual TPHs concentrations are given.

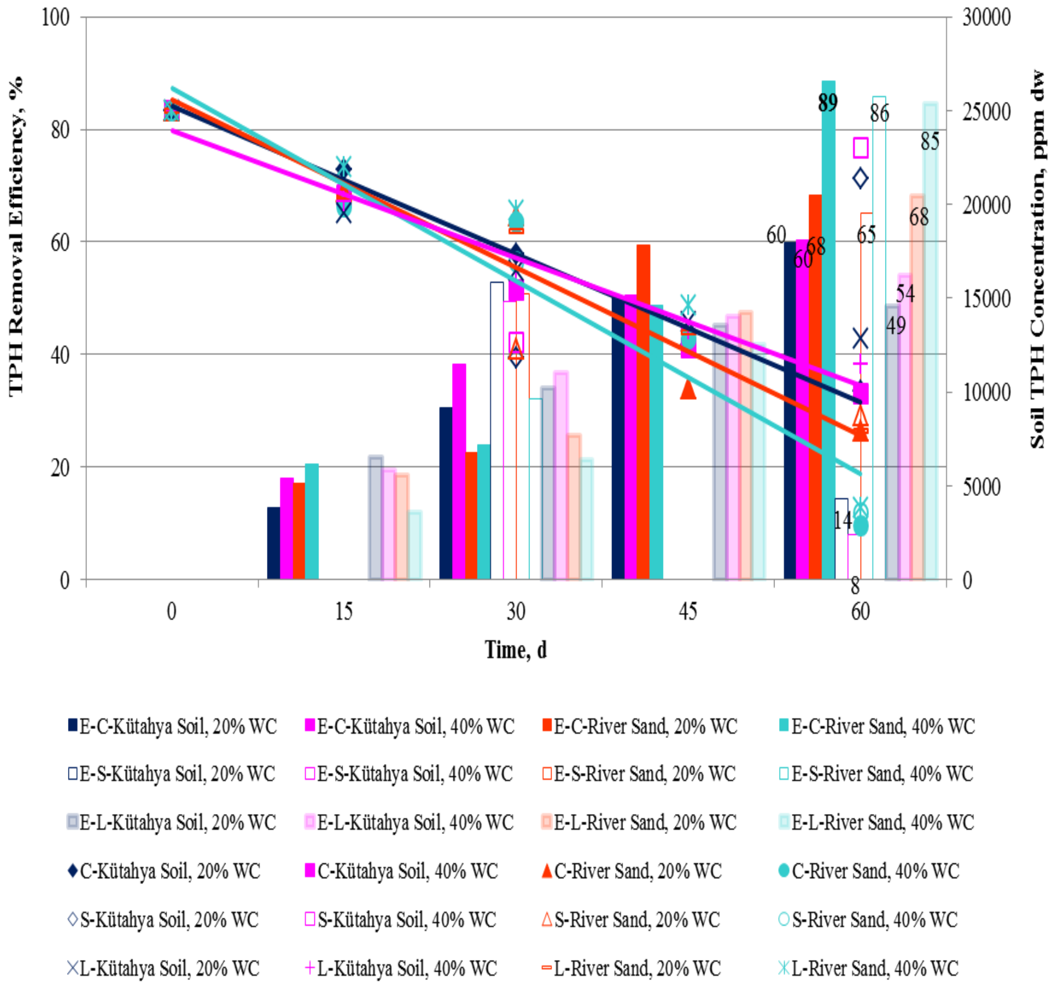
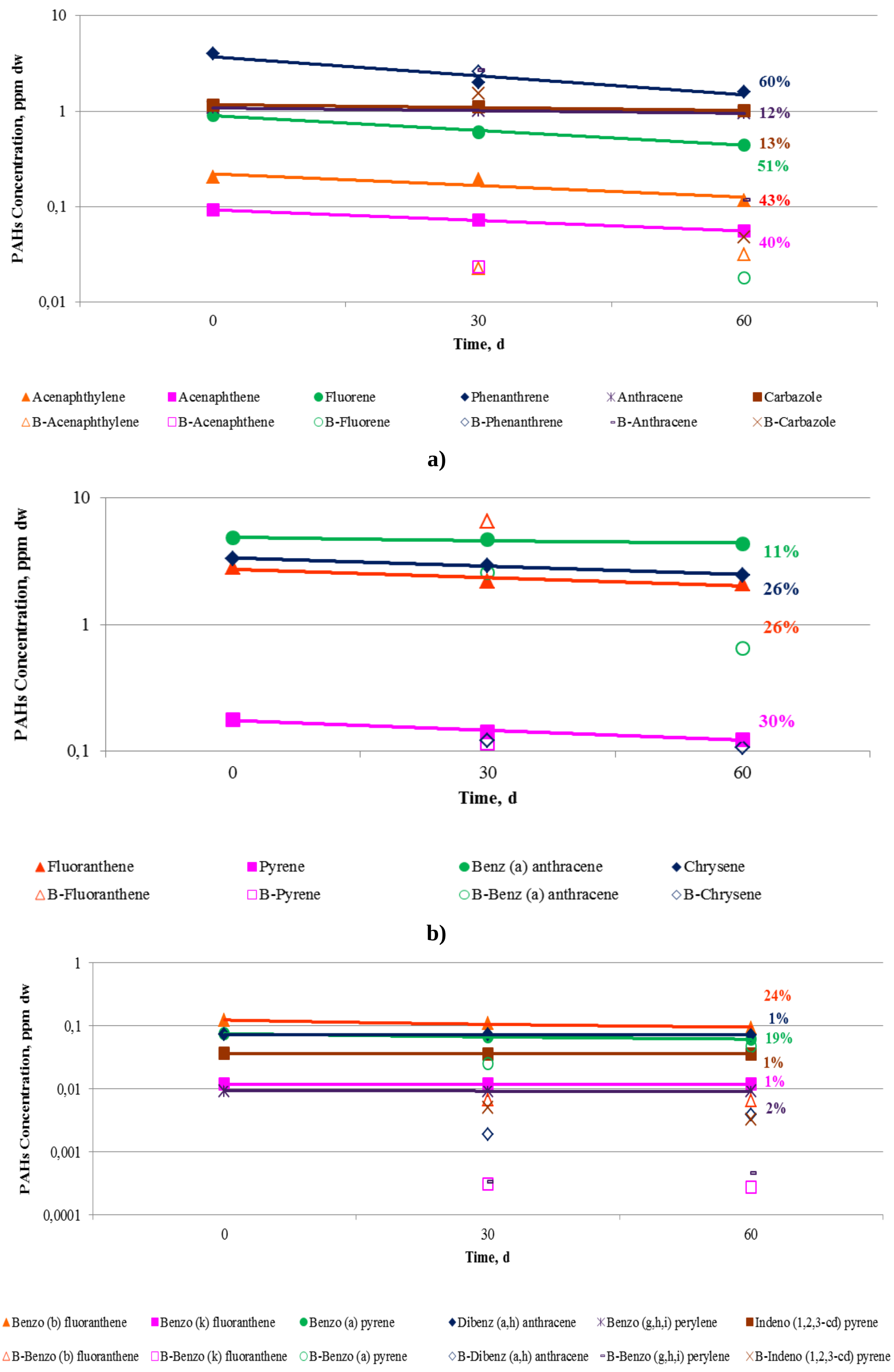


Figure 6.72 The change in soil TPHs levels andTPHs removal efficiencies in fixed bed bioremediation studies for Kutahya soil, River sand for 25000 ppm IDC at 25°C

The TPHs removals are lower in Kutahya soil (59.9% with 20% water content and 60.31% with 40% water content) than in River sand (68.3% with 20% water content and 88.6% with 40% water content). It is seen that higher TPHs removal efficiencies are obtained with higher initial water contents. On the other hand, the TPHs removal rates in Kaynaklar soil were 74.4 % with 20% water content and 83.6 % with 40% water content when compost amended. The results with local bacteria (without compost amendment) were 11% lower with 20% water content and and 6% lower with 40% water content for Kutahya soil. The TPHs removal efficiencies between compost amended River sand and River sand with local bacteria are not different from each other, but the removals with 40% water content are higher, too. The initial bacterial count of these soils are different; the highest in Kaynaklar and the lowest in River sand. Therefore, it is expected to yield a higher removal efficiency especially in Kutahya soil, but not only the initial bacterial counts, but also the other soil features such as organic matter content may influence the adsorption and removal of TPHs in soils.

The PAHs were also determined during the bioremediation tests conducted with different soil types. The results are given in Figures 6.73-6.76 according to the PAHs groups. In addition, the individual removal efficiencies of PAHs with some of their important features are given in Table 6.11 and the average removal rates calculated for PAHs groups are reported in Table 6.12.

The findings showed that higher PAHs removal efficiencies obtained with 40% initial water content, and the removal rates of PAHs are decreasing with increasing number of benzene rings they are having. It is also observed that, the PAHs removal rates are decreasing with increasing soil organic matter content which follows the order of Kutahya soil > Kaynaklar soil > River sand.

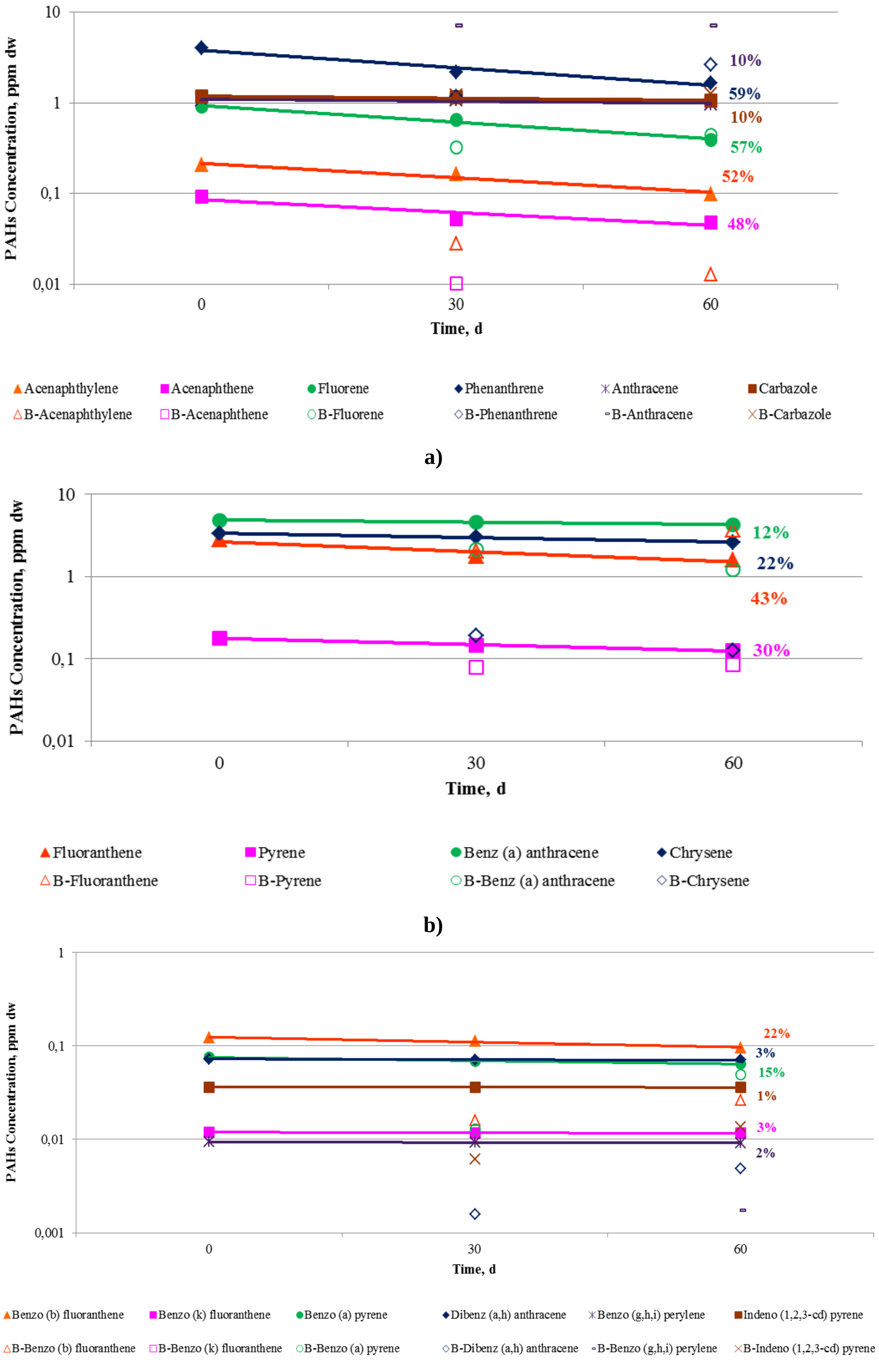


a)

b)

c)

Figure 6.73 1 PAHs removals of Kutahya soil in fixed bed bioremediation systems (IDC= 25000 ppm and 20% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



a)

b)

c)

Figure 6.74 PAHs removals of Kutahya soil in fixed bed bioremediation systems (IDC= 25000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

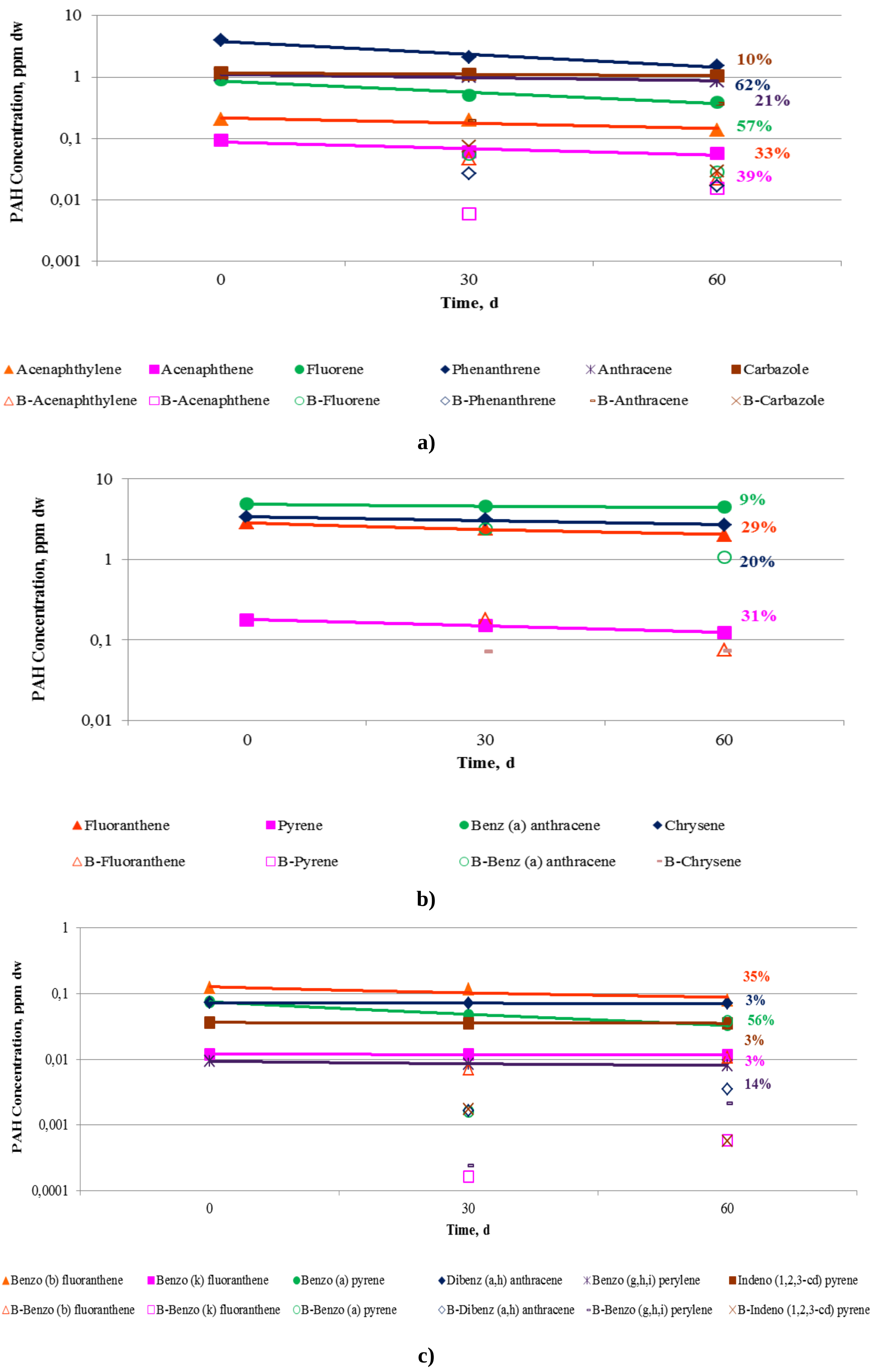


Figure 6.75 PAHs removals of River sand in fixed bed bioremediation systems (IDC= 25000 ppm and 20% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

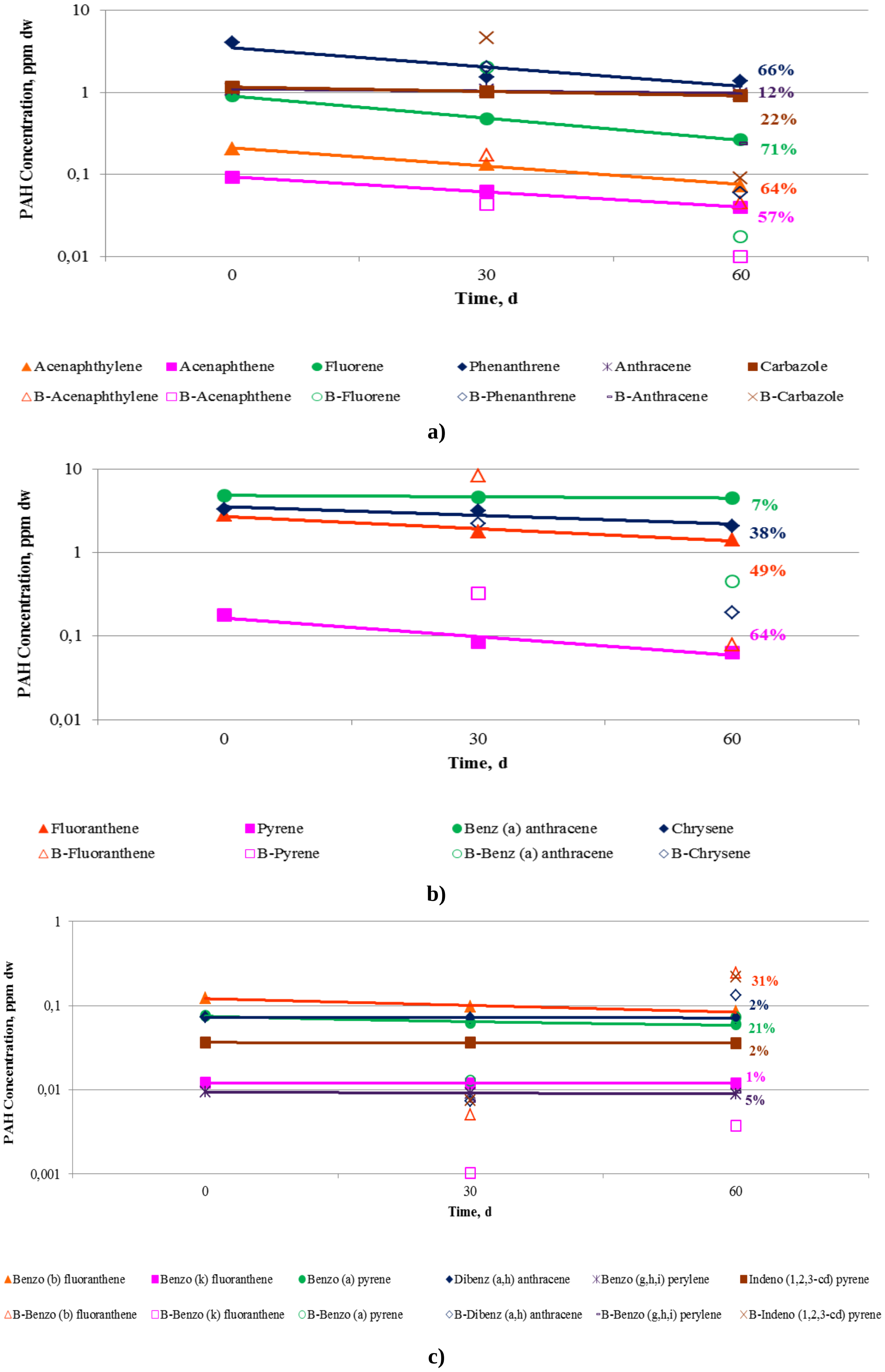


Figure 6.76 PAHs removals River sand in fixed bed bioremediation systems (IDC= 25000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

Table 6.11 The removal rates of individual PAHs in fixed bed bioremediation systems

Studied PAHs				**PAHs Removal Efficiencies by Fixed Bed Bioremediation, %**					
				25000 ppm IDC, 25°C					
Number of Benzene Rings	**Name**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**20% WC Kutahya soil**	**40%WC Kutahya soil**	**20% WC River sand**	**40% WC River sand**	**20% WC Kaynaklar soil**	**40% WC Kaynaklar soil**
3 Ring	Acenaphthylene	16,1	$9,12*10^{-4}$	43	52	33	64	76	80
	Acenaphthene	3,9	$2,50*10^{-3}$	40	48	39	57	80	82
	Fluorene	1,89	$8,42*10^{-3}$	51	57	57	71	77	80
	Phenanthrene	1,15	$1,12*10^{-4}$	60	59	62	66	79	77
	Anthracene	$4,34*10^{-2}$	$2,67*10^{-6}$	12	10	21	12	34	20
	Carbozole	0,721	$2,66*10^{-4}$	13	10	10	22	50	41
4 Ring	Fluoranthene	$2,60*10^{-1}$	$1,23*10^{-8}$	26	43	29	49	50	61
	Pyrene	$1,35*10^{-1}$	$1,35*10^{-7}$	30	30	31	64	62	65
	Benz(a)anthracene	$9,40*10^{-3}$	$3,05*10^{-8}$	11	12	9	7	40	32
	Chrysene	$2,00*10^{-3}$	$6,23*10^{-9}$	23	22	20	38	54	50
5&6 Ring	Benzo(b)fluoranthene	$1,50*10^{-3}$	$5,00*10^{-7}$	24	22	35	31	53	53
	Benzo(k)fluoranthene	$8,00*10^{-4}$	$9,65*10^{-10}$	1	3	3	1	10	11
	Benzo(a)pyrene	$1,62*10^{-3}$	$5,49*10^{-9}$	19	15	56	21	52	55
	Dibenz(a,h)anthracene	$2,49*10^{-6}$	$1,00*10^{-10}$	1	3	3	2	8	9
	Benzo(g,h,i)perylene	$2,6*10^{-4}$	$1,01*10^{-10}$	2	2	14	5	13	17
	Indeno(1,2,3-c,d)pyrene	$2,20*10^{-5}$	$1,00*10^{-10}$	1	1	3	2	3	3

Table 6.12 PAHs groups average removal efficiencies obtained from fixed bed bioremediation systems according to the initial water content and experimental temperature

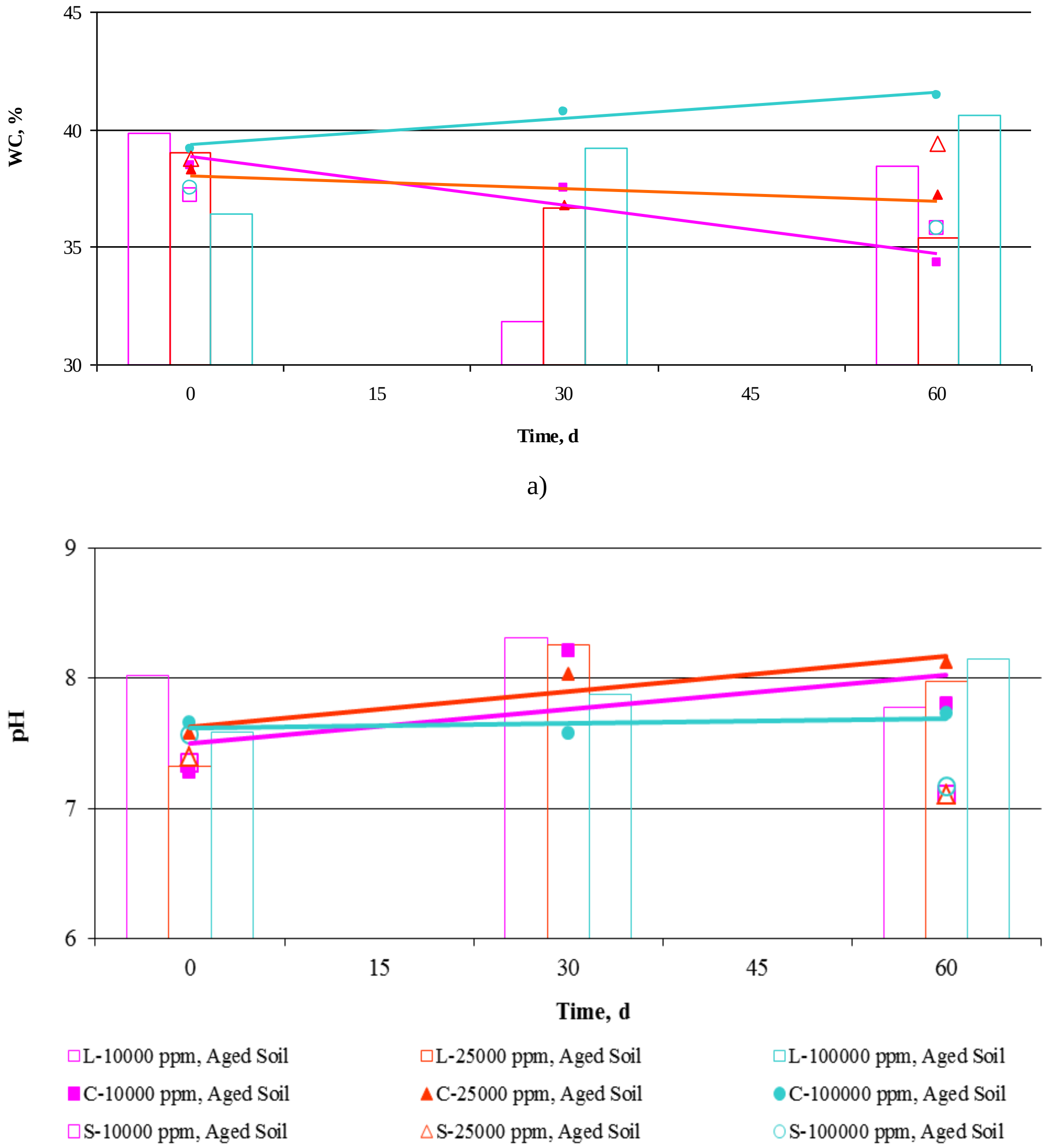
PAHs groups according to number of benzene rings	**Initial Water Content of the Soil, %**	**Average PAHs removal efficiencies, %**		
		25000 ppm IDC, 25°C		
		Kutahya soil	**River sand**	**Kaynaklar soil**
3Ring PAHs	20	37	37	66
	40	39	49	63
4Ring PAHs	20	23	22	51
	40	27	40	52
5&6Ring PAHs	20	8	19	19
	40	8	10	25

6.3.2.3 The Effect of Contamination Age on NAPLs Remediation in Fixed Bed Bioremediation Systems with Compost Amendment

In that part, 10000 ppm, 25000 ppm, and 100000 ppm of Kaynaklar soil IDCs were studied. The soils were aged for two years after contaminated with diesel. The soil initial water content of 40% was applied and the compos/soil ratio is adjusted as 1/10 on dry basis. The water content, pH, CO_2 evaluation, number of bacteria in soils, TPHs and PAHs levels were observed during the 60 days of operational time.

The water content and pH variations in the systems are given in Figure 6.77. The water contents of the soils changed unlikely. The soil with 100000 ppm IDC showed an increase in water content, the soil with 10000 ppm IDC showed an decrease, where the soil with 25000 ppm did not show any change. On the other hand, these changes are not as high as an indication of a strong biological degradation of NAPLs. In addition, pH changes in the systems during operational period are also minimal (< ±0.5) and show a small increases for all soil IDCs.

Figure 6.78 illustrates the CO_2 productions and changes in bacterial populations in the systems.

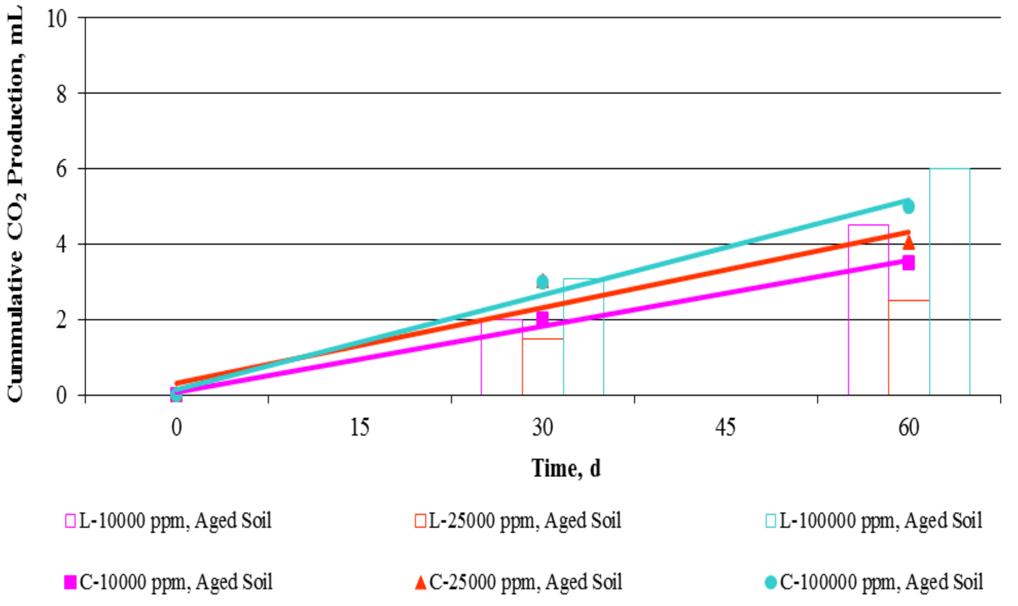


a)

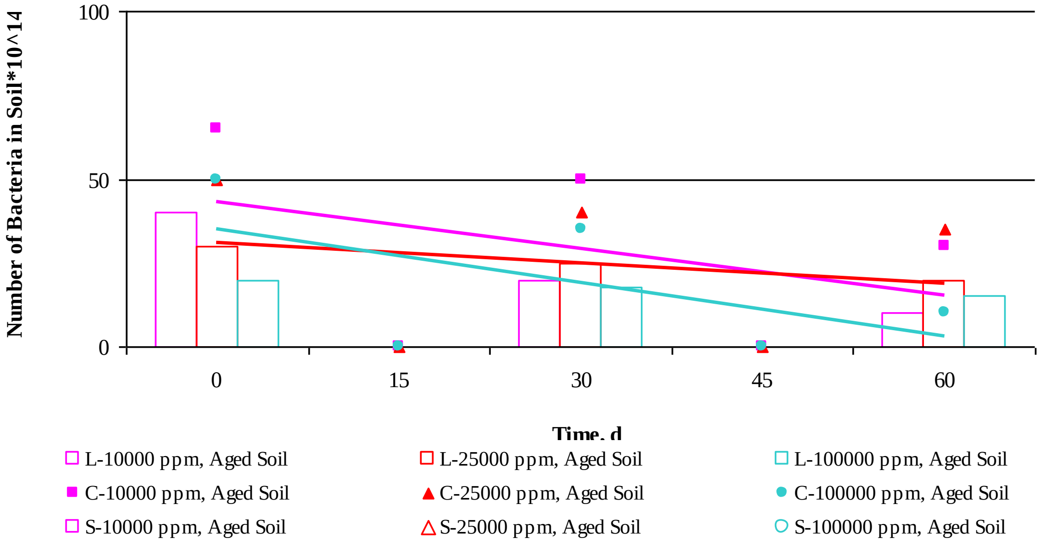
b)

Figure 6.77 The changes in water content and pH of the aged soils in fixed bed bioremediation systems with compost amendment a) Water content, b) pH

As it is seen in Figure 6.78, the CO_2 productions of the systems are very low and both the initial number of bacteria and its decline during the operational period explains the reason for low CO_2 production.



a)



b)

Figure 6.78 The changes in CO_2 production and number of bacteria in aged soil fixed bed bioremediation systems a) CO_2 Production b) Number of Bacteria in Soil

The reductions in TPHs concentrations and its removal rates are presented in Figure 6.79.

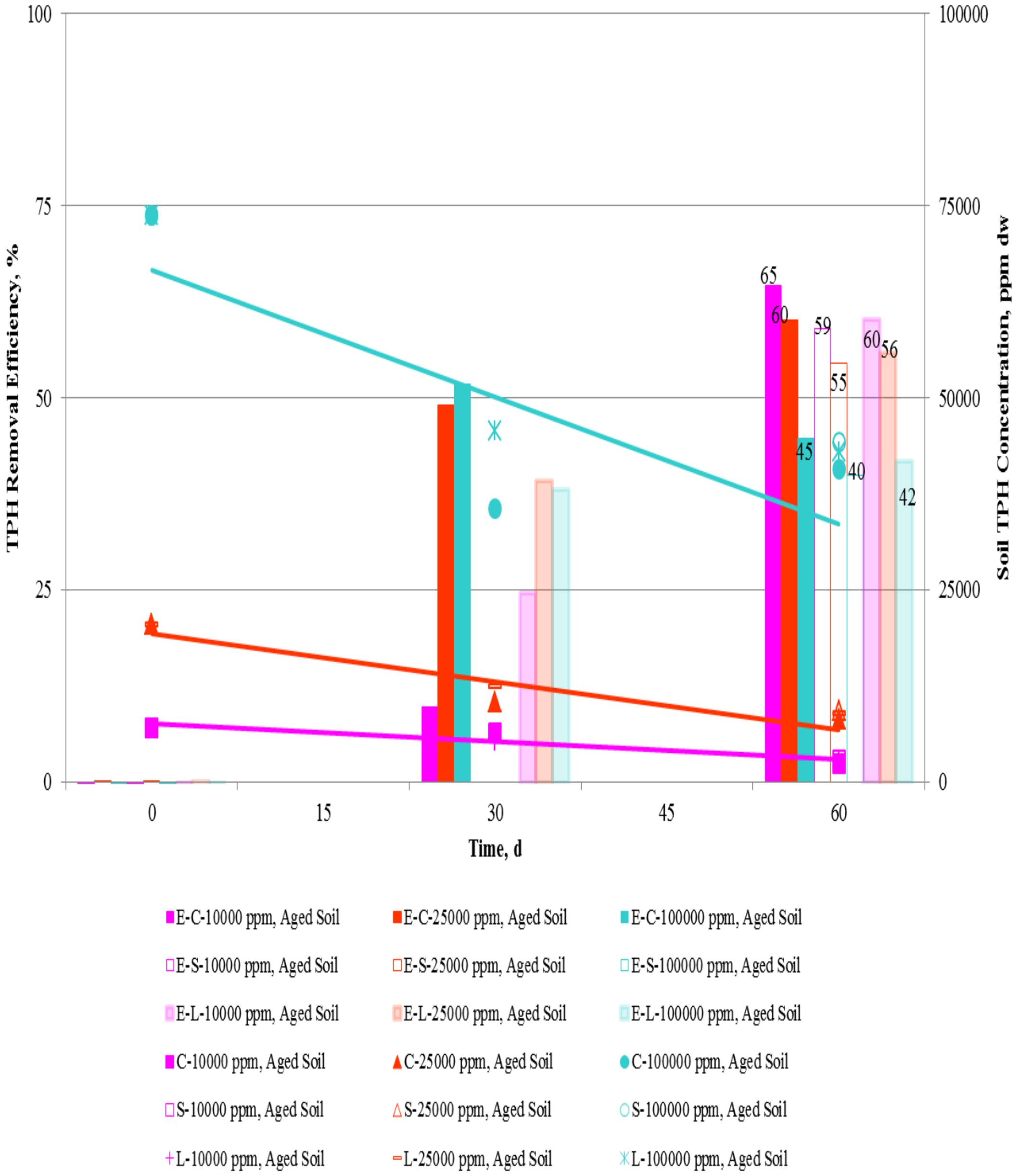


Figure 6.79 The changes in aged soil and soil TPHs concentration of fixed bed bioremediation reactors, at 25°C

The removal efficiencies of TPHs from soils are decreasing with increasing IDCs; 65% of TPHs were removed from the soil with 10000 ppm IDC, and 60% and 45% of the TPHs were removed from the soils having 25000 ppm, and 100000 ppm IDC. The results are not only in accordance with the results from the thermal volatilization studies, but also very similar, where the TPHs removals were 59%, 55%, and 40% for the soils having 10000 ppm, 25000 ppm, and 100000 ppm IDC with thermal volatilization. That’s why, we can evaluate the removal rates found in compost amended fixed bed bioremediation experiments are mostly due to the thermal volatilization because of poor CO_2 generation from these systems.

The PAHs removal and their final concentrations are given in Figures 6.80-6.82 according to the PAHs groups.

The individual removal rates of PAHs are given in Table 6.13 and the average removal rates of the PAHs groups are given in table 6.14, additionally.

It is observed that the PAHs removal rates are decreasing with increasing number of benzene rings and increasing initial soil diesel concentration. In addition, the removal rates are much lower than the freshly spiked soils having the same IDCs .

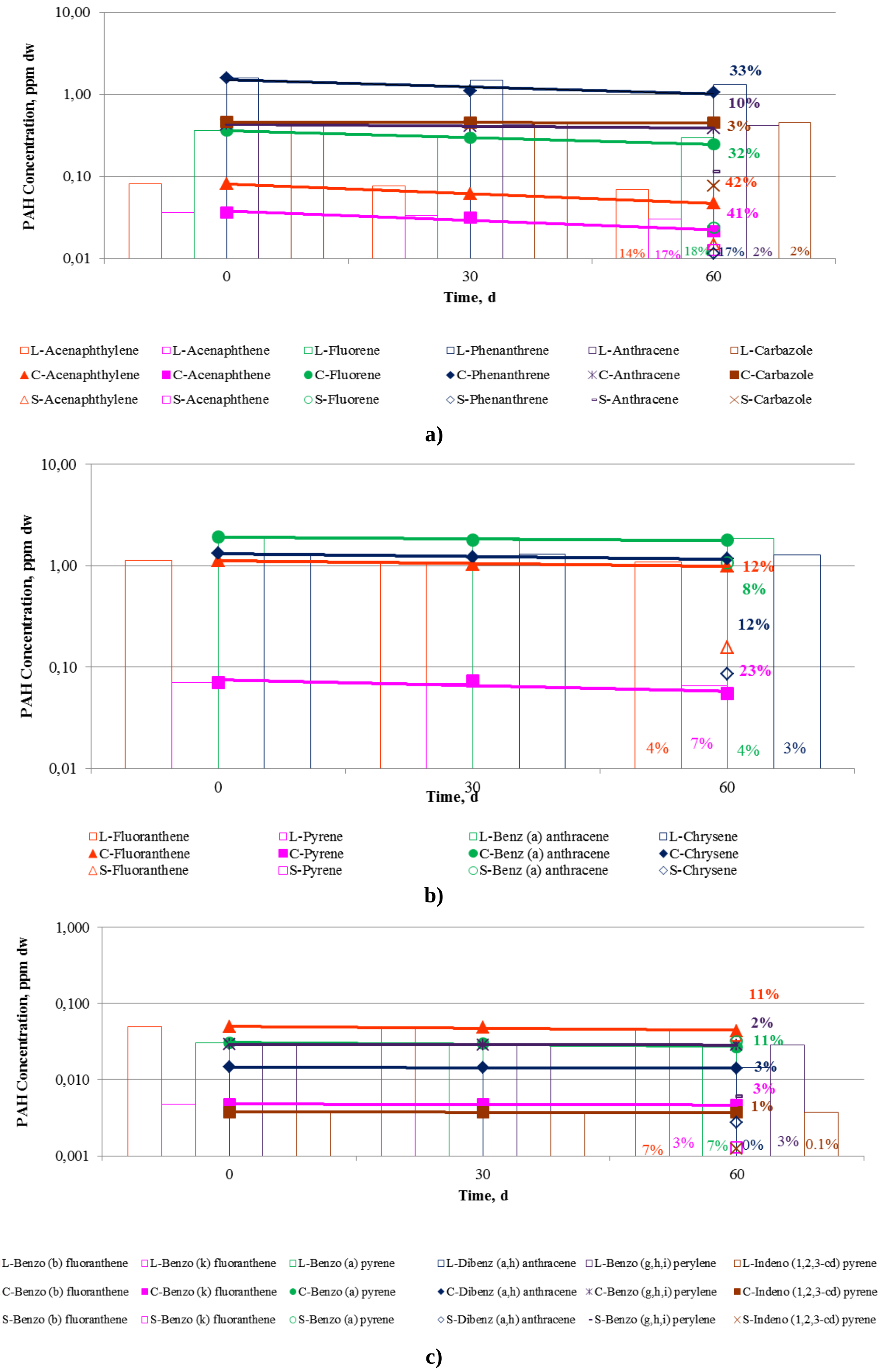
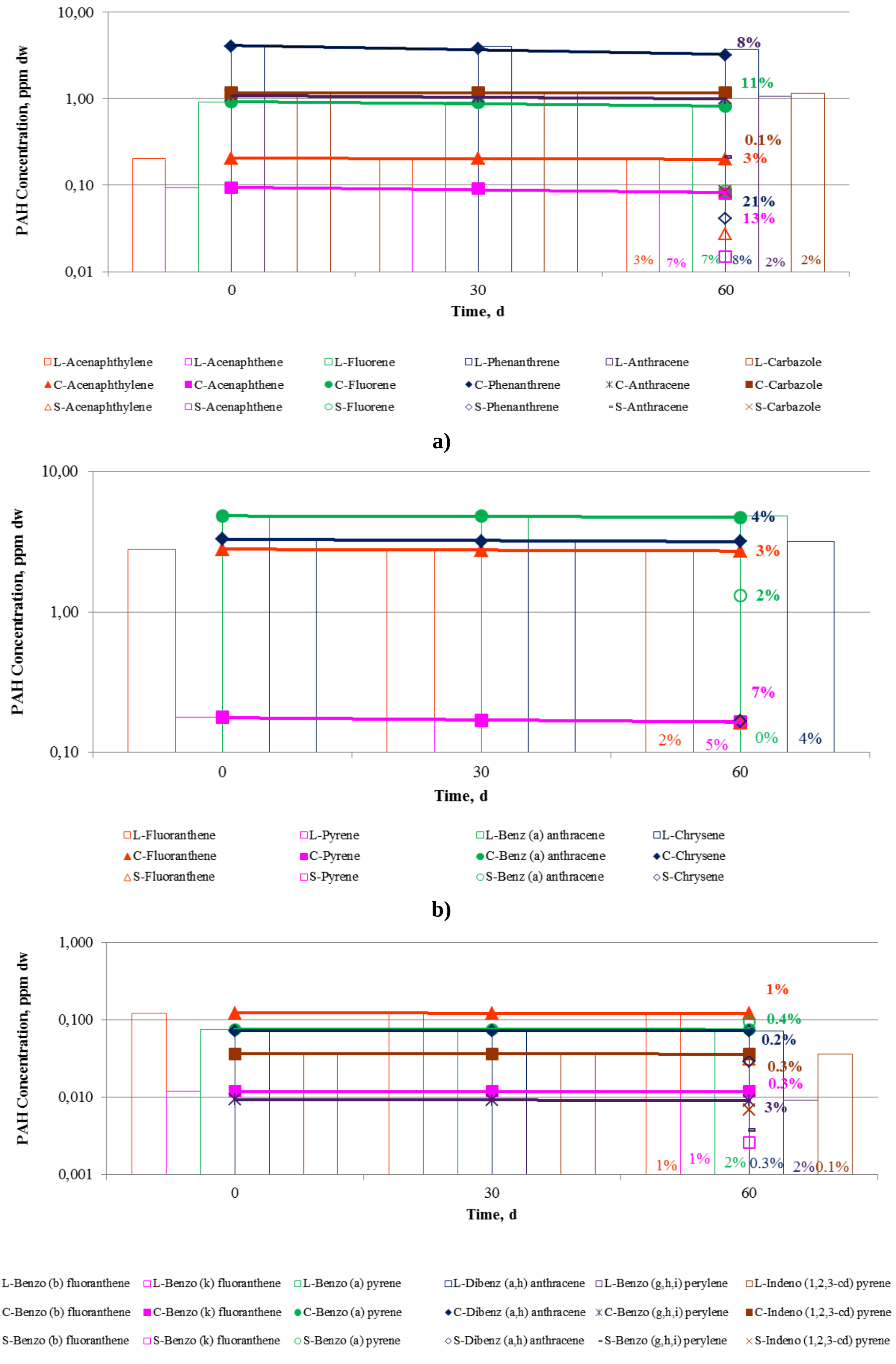


Figure 6.80 1 PAHs removals of aged soil in fixed bed bioremediation systems (IDC= 10000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs



a)

b)

c)

Figure 6.81 PAHs removals of aged soil in fixed bed bioremediation systems (IDC= 25000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

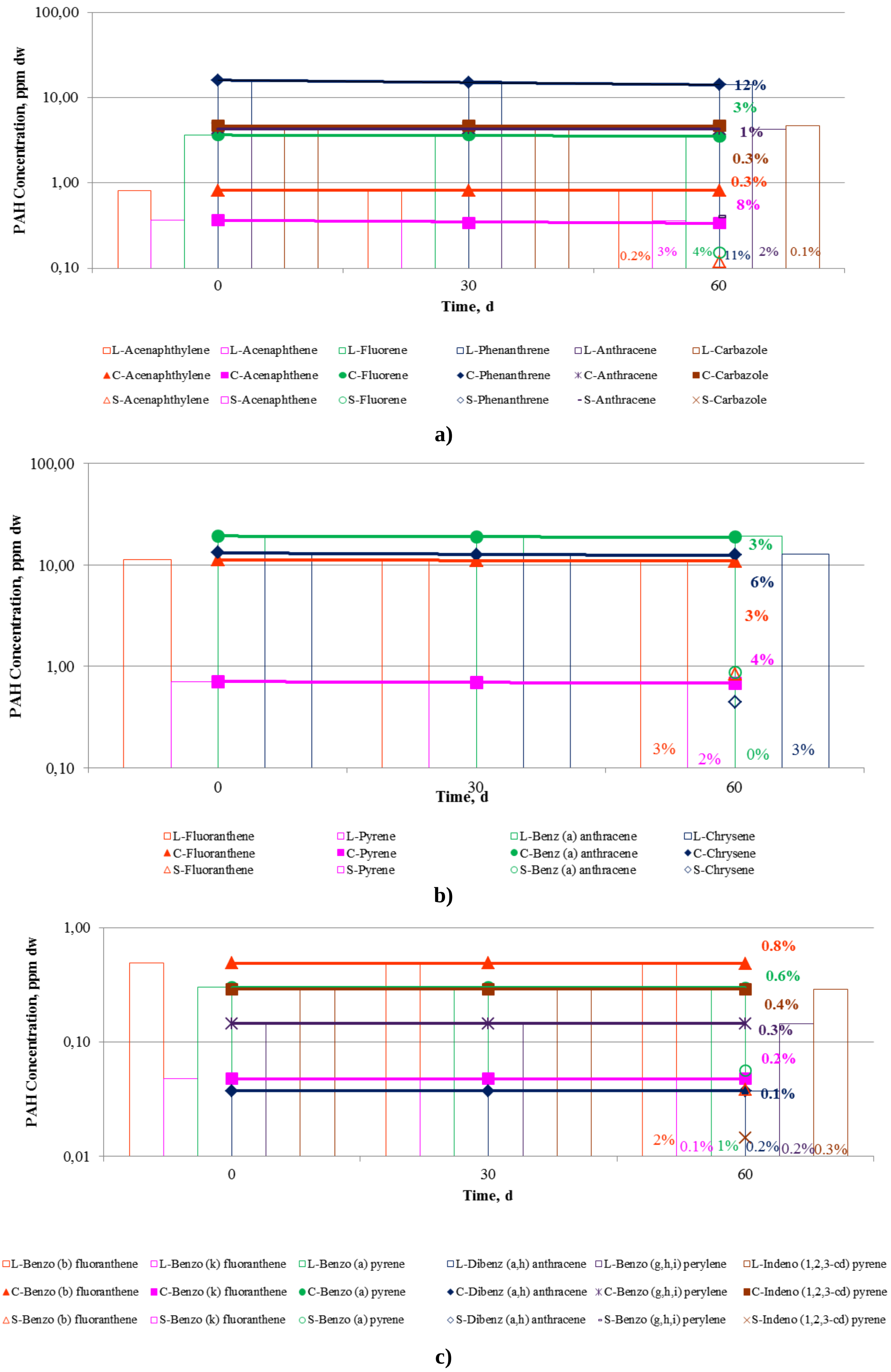


Figure 6.82 PAHs removals of aged soil in fixed bed bioremediation systems (IDC= 100000 ppm and 40% water content at 25ºC, a) 3Ring PAHs, b)4Ring PAHs, c)5&6Ring PAHs

Table 6.13 The removal rates of individual PAHs in fixed bed bioremediation systems-AGED

Studied PAHs				PAHs Removal Efficiencies by Fixed Bed Bioremediation, %					
Number of Benzene Rings	Name	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	10000 ppm IDC, 25°C 40%WC		25000 ppm IDC, 25°C 40% WC		100000 ppm ID, C25°C 40%WC	
				Compost	Local	Compost	Local	Compost	Local
3 Ring	Acenaphthylene	16,1	$9,12*10^{-4}$	42	14	3	3	0.3	0.2
	Acenaphthene	3,9	$2,50*10^{-3}$	41	17	13	7	8	3
	Fluorene	1,89	$8,42*10^{-3}$	32	18	11	7	3	4
	Phenanthrene	1,15	$1,12*10^{-4}$	33	17	21	8	12	11
	Anthracene	$4,34*10^{-2}$	$2,67*10^{-6}$	10	2	8	2	1	2
	Carbozole	0,721	$2,66*10^{-4}$	3	2	0.1	2	0.3	0.1
4 Ring	Fluoranthene	$2,60*10^{-1}$	$1,23*10^{-8}$	12	4	3	2	3	3
	Pyrene	$1,35*10^{-1}$	$1,35*10^{-7}$	23	7	7	5	4	2
	Benz(a)anthracene	$9,40*10^{-3}$	$3,05*10^{-8}$	8	4	2	0	3	0
	Chrysene	$2,00*10^{-3}$	$6,23*10^{-9}$	12	3	4	4	6	3
5&6 Ring	Benzo(b)fluoranthene	$1,50*10^{-3}$	$5,00*10^{-7}$	11	7	1	1	0.8	2
	Benzo(k)fluoranthene	$8,00*10^{-4}$	$9,65*10^{-10}$	3	3	0.3	1	0.2	0.3
	Benzo(a)pyrene	$1,62*10^{-3}$	$5,49*10^{-9}$	11	7	0.4	2	0.6	1
	Dibenz(a,h)anthracene	$2,49*10^{-6}$	$1,00*10^{-10}$	3	0.2	0.2	0.3	0.1	0.2
	Benzo(g,h,i)perylene	$2,6*10^{-4}$	$1,01*10^{-10}$	2	3	3	2	0.3	0.1
	Indeno(1,2,3-c,d)pyrene	$2,20*10^{-5}$	$1,00*10^{-10}$	1	0.1	0.1	0.1	0.4	0.3

Table 6.14 PAHs groups average removal efficiencies obtained from fixed bed bioremediation systems according to the initial water content and experimental temperature-AGED

PAHs groups according to number of benzene rings	**Initial Water Content of the Soil, %**	**Average PAHs removal efficiencies, %**					
		10000 ppm IDC, 25°C		**25000 ppm IDC, 25°C**		**100000 ppm IDC, 25°C**	
		Compost	**Local**	**Compost**	**Local**	**Compost**	**Local**
3Ring PAHs	40	27	12	9	5	4	3
4Ring PAHs	40	14	5	4	3	4	2
5&6Ring PAHs	40	5	3	0.8	1	0.4	0.6

6.4 Discussion of Results

The findings from the experimental studies are discussed in this section. The discussions are given according to the common parameters followed in studied systems, such as initial NAPLs concentration in soils, the soil type, and the contamination age with regard to the presence of bacteria and presence of soil amendment, as well as specific parameters of the studied systems, namely; solid/liquid ratio, soil particle size, and presence of light for slurry systems and temperature and initial water content in fixed bed systems. In addition, the fates of PAHs are extensively discussed in another subtitle.

6.4.1. The Effect of Initial Soil NAPLs Concentration on the Treatment Efficiency of Soil Remediation Systems

In the content of the thesis, slurry and fixed bed soil remediation systems were operated with soils having 10000 ppm, 25000 ppm, and 100000 ppm. Below, in Table 6.15, the removal efficiencies of TPHs found in slurry and fixed bed systems for different initial concentrations are summarized. The results only for Kaynaklar soil are given in the table for clearer identification of the phenomenon.

According to the Table 6.15, it is seen that TPHs removal efficiencies are decreasing with increasing initial diesel concentration, more significant in slurry remediation technique. There are two exceptions in the fixed bed systems;

bioremediation systems with local bacteria and bioremediation systems with compost amendment.

In slurry systems, by increasing sterile soil diesel concentration from 25000 ppm to 100000 ppm the total decrease in the efficiency is 32%. With local bacteria, the difference between the TPHs treatment efficiencies in the soils having 25000 ppm and 100000 ppm diesel has increased to 19%. The decreases in the TPHs removal efficiencies in the soils with 25000 ppm diesel and 100000 ppm diesel were 10% and 19% for the sterilized soil and the soil with local bacteria, respectively. The decrease in TPHs removal efficiencies was between 18-27% with compost amended soils when the diesel concentration has risen from 25000 ppm to 100000 ppm.

The efficiencies of fixed bed systems, both with local bacteria and with addition of compost, are higher for 25000 ppm and 100000 ppm than the slurry systems with the same initial diesel concentrations.

Table 6.15 The summary of TPHs removal efficiencies in studied systems at the end of the operational period according to the initial concentration, %

Studied system and its properties				**Initial Diesel Concentration, ppm dw**		
				10000	**25000**	**100000**
Slurry System*	**Sterilized Soil**			ND	50	40
	Local Bacteria			ND	61	42
	Compost Amendment, compost/soil dw/dw		**1/10**	ND	70	43
			2/10	ND	65	47
			3/10	ND	55	35
Fixed Bed System	**Sterilized Soil (TV)**	**25°C**	**%20 WC**	64	60	40
			%40 WC	62	58	62
		40°C	**%20 WC**	66	67	ND
			%40 WC	68	66	ND
	Local Bacteria	**25°C**	**%20 WC**	60	62	ND
			%40 WC	63	63	60
		40°C	**%20 WC**	68	71	ND
			%40 WC	67	69	ND
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%20 WC**	57	74	ND
			%40 WC	66	84	62
		40°C	**%20 WC**	62	79	ND
			%40 WC	69	85	ND

* only with solid/liquid ratio of 1/1, ND: Not Detected, TV: Thermal Volatilization

The results in fixed bed systems showed that, in sterile soils, the decreases in TPHs removal efficiencies with increasing initial diesel concentration are more significant at 25°C than at 40°C. This may be because of the higher volatilization of diesel compounds with increasing temperature. With local bacteria, TPHs removal rates increases 2-3% when the diesel concentration raised from 10000 ppm to 25000 ppm independent from the soil moisture and temperature.

In compost amended fixed bed systems, the TPHs remediation efficiency is increasing as the initial diesel concentration increases from 10000 ppm to 25000 ppm. The increases are more significant in the systems having 40% water content. But, when the initial diesel concentration has increased to 100000 ppm, the removal efficiency of TPHs decreases as in other treatments, whether with bacteria or not.

It should be also noted that, an important portion of TPHs are removed by thermal volatilization as it is seen from the results of the sets conducted with sterilized soils. The extent of the thermal volatilization vary between 40-70% in slurry systems (at 25°C) and vary 58-64% and 66-68% in fixed bed systems at 25°C and 40°C, respectively.

6.4.2 The Effect of Soil Properties on NAPLs Treatment Efficiency in Soil Remediation Systems

In the content of the thesis, the effect of soil type on the remediation of NAPLs was investigated both in slurry and fixed bed reactors. Below, in Table 6.16, the removal efficiencies of TPHs in both reactor types are summarized according to the soil types used in the systems. Here, all sets were operated at 25°C

It is seen that, except the fixed bed remediation sets with compost amendment in soil having 20% water content, the TPHs removal efficiencies are the highest in sand samples. In slurry systems, TPHs were removed from the Beach sand with efficiencies of 72% and 84% in the sets conducted with the sterilized soil and the soil having local bacteria, respectively, where the TPHs removals in Kaynaklar soil were 50% (sterilized soil) -61% (soil with local bacteria).

Table 6.16 The summary of TPHs removal efficiencies in studied systems at the end of the operational period according to the soil type, %

Studied system and its properties				**Soil Type**			
				Kaynaklar soil	**Kutahya soil**	**River sand**	**Beach sand**
Slurry System* (25000 ppm)	**Sterilized Soil**			50	ND	ND	72
	Local Bacteria			61	ND	ND	84
Fixed Bed System (25000 ppm)	**Sterilized Soil (TV)**	**25°C**	**%20 WC**	60	14	65	ND
			%40 WC	58	8	86	ND
	Local Bacteria	**25°C**	**%20 WC**	62	49	68	ND
			%40 WC	63	54	85	ND
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%20 WC**	74	60	68	ND
			%40 WC	84	60	89	ND

* only with solid/liquid ratio of 1/5, ND: Not Detected, TV: Thermal Volatilization

With the sterilized soils in fixed bed systems, River sand TPHs were achieved to be treated up to 68 % (with 20% initial water content) and 85% (with 40% initial water content), where maximum TPHs removals in Kaynaklar soil was 63% (with 40% initial water content) and in Kutahya soil it was 54% (with 40% initial water content).

This data indicates that, i) volatilization is an effective way to remove TPHs from soils, ii) in the soils having relatively high water content (40%) fixed bed treatment with local bacteria results with higher removal efficiencies, and iii) the TPH removal efficiencies with local soil bacteria are 2% (Kaynaklar soil) - 46% (Kutahya soil) higher than the efficiencies obtained in the sets with sterilized soils depending on the soil type.

The fixed bed bioremediation studies with compost amendment resulted with higher TPHs removal efficiencies in Kaynaklar soil (74%) than River Sand (68%)

with 20% water content, but, this is the only exception in the sets conducted with different soil types.

Generally the remediation efficiencies follow the rank of Sand(s) > Kaynaklar soil > Kutahya soil. This rank is in opposite direction with the organic matter content, specific surface area of the related soils, which were given in Table 5.4. Therefore, it can be concluded that thermal volatilization, which is the dominant process to remove NAPLs from soils, is dependent on soil properties. If the properties of the soils (organic matter content, SSA, and porosity) are compared, it is seen that the levels of all these parameters, and peculiarly SSA of Kutahya soil is significantly higher (58.798 m^2/g) than the other soils (0.786-14.176 m^2/g) used in the experiments. The lowest TPHs removal efficiencies were obtained with Kutahya soil in all sets, especially in the set with sterilized soil (8-14%). Therefore, it may be concluded that the specific surface area of the soil is a major factor effecting its physical remediation when the contamination with NAPLs are considered.

6.4.3 The Effect of Contamination Age on NAPLs Treatment Efficiency in Soil Remediation Systems

Two years aged contaminated soils having different initial concentrations are studied in the content of the study. Both slurry and fixed bed remediation systems were operated with aged soils. The TPHs removal efficiencies obtained from these tests are given in Table 6.17.

When the results from the experiments conducted with freshly spiked soils are regarded (Table 6.15), the TPHs removal efficiencies obtained in aged soils are much lower, especially in slurry systems operated with sterile soil and local soil. In addition, it is recognized that fixed bed systems operated with the highest diesel concentration in soil (100000 ppm) resulted with much lower removal efficiencies (40-45%) compared to the lower IDC (55-65%). The difference between the TPHs removal efficiencies in freshly contaminated soils and aged soils are also more significant with 100000 ppm IDC. 17-22% lower efficiencies were obtained. That’s why, it can be concluded that the contamination age adversely effect the efficiency of NAPLs removal from the soils, not only in thermal volatilization but also in bioremediation.

Table 6.17 The summary of TPHs removal efficiencies in studied systems at the end of the operational period with aged soils, %

Studied system and its properties				**Initial Diesel Concentration, ppm dw**		
				10000	**25000**	**100000**
Slurry System*	**Sterilized Soil**			30	43	ND
	Local Bacteria			41	58	ND
	Compost Amendment, compost/soil dw/dw		**1/10**	57	64	ND
Fixed Bed System	**Sterilized Soil**	**25°C**	**%40 WC**	59	55	40
	Local Bacteria	**25°C**	**%40 WC**	60	56	42
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%40 WC**	65	60	45

* only with solid/liquid ratio of 1/1, ND: Not detected

6.4.4 The Effect of Specific Parameters of Slurry Remediation Systems on NAPLs Treatment Efficiency

In this part, the effects of particular parameters of slurry remediation systems are discussed regarding the NAPLs treatment from soils.

6.4.4.1 The Effect of Solid/Liquid Ratio

The TPHs removal efficiencies from slurry systems studied in the content of the thesis are summarized in Table 6.18 according to the solid/liquid ratios applied. As can be seen from the table, the increases of TPHs removals with decreasing S/L draws attention in the system operated with 100000 ppm IDC. Here, it is interesting that, even the lowest removal efficiencies are obtained in the set having 100000 ppm

IDC, the removal efficiencies with 10000 ppm IDC were lower than the removals obtained with 25000 ppm IDC.

In addition, in the system operated with sterile soils, the remediation interval for 1/1 S/L was 168 h, but TPHs removal efficiency was still much lower (50% with 25000 ppm IDC and 40% for 100000 ppm IDC) than the systems operated with 1/5 S/L ratios (79% for 25000 ppm IDC and 63% for 100000 ppm IDC) having the remediation interval of 8 hours. Therefore, another output of the study appears at that point; the NAPLs in soils are mainly desorbed from the soil in a short time interval in slurry systems.

Table 6.18 The summary of TPHs removal efficiencies in studied systems at the end of the operational period according to the solid/liquid ratio, %

Studied system and its properties		**S/L* Ratio**	**Time, h**	**Initial Diesel Concentration, ppm dw**		
				10000	**25000**	**100000**
Slurry System	**Sterilized Soil**	**1/1**	168	ND	50	40
		1/5	8	72	79	63
		1/10	8	ND	ND	65
		1/20	8	ND	ND	72
	Local Bacteria	**1/1**	168	ND	61	42
		1/5	168	76	89	ND

*Solid/Liquid (S/L) Ratio, ND: not detected

6.4.4.2 The Effect of Particle Size

The effect of soil particle size on the remediation of NAPLs in slurry systems is studied and the TPHs removals are presented in Table 6.19.

Table 6.19 The summary of TPHs removal efficiencies in studied systems at the end of the operational period according to the particle size, %

Studied system and its properties		**Particle Size**			
		Coarse	**Medium**	**Fine**	**Bulk**
Slurry System (100000 ppm)	**Local Bacteria**	59	49	26	55

As can be seen from the table, the TPHs removal efficiencies are decreasing with decreasing particle size. This is an expected result, since the adsorption of contaminants on soil particles increases with increasing SSA. Here, the SSAs of coarse, medium and fine particles are 13.75 m^2/g, 14.37 m^2/g, and 15.84 m^2/g, respectively. The removal of TPHs in bulk is compatible with the removals in particle size fractions due to their weight distribution in soil given in Chapter 5. The initial bacterial counts in size fractions are similar as it is illustrated in Figure 6.21b.

6.4.4.3 The Effect of Light

The presence of light is also investigated in slurry systems and the removal efficiencies of TPHs are given in Table 6.20. It is seen that the systems performed slightly better in dark environment. With the soils having local bacteria 1-2% higher removal efficiencies obtained. Besides the findings, it should be indicated that in field application, to supply enough light for the bacteria in large slurry systems is not possible.

Table 6.20 The summary of TPHs removal efficiencies in studied systems at the end of the operational period according to the presence of light, %

Studied system and its properties		**Initial Diesel Concentration , ppm dw 25000**	
		Dark	**Light**
Slurry System*	**Sterilized Soil**	80	79
	Local Bacteria.	91	89

* only with solid/liquid ratio of 1/5

6.4.5 The Effect of Specific Parameters of Fixed Bed Systems on NAPLs Treatment Efficiency

In this part, the effects of particular parameters of fixed bed remediation systems are discussed regarding the NAPLs treatment from soils.

6.4.5.1 The Effect of Temperature

The discussion on temperature effect on NAPLs removal from soils is given here for the results obtained in fixed bed systems (Table 6.21). As it was mentioned in section 6.4.1; an important portion of TPHs are removed by thermal volatilization. The extent of the thermal volatilization vary between 58-64% and 66-68% in fixed bed systems at 25°C and 40°C, respectively. In addition, the average TPHs removal efficiencies in the soils having local bacteria for 10000 ppm and 25000 ppm IDC was 62% at 25°C and was 69% at 40°C,while the compost amended soils having same concentrations resulted with 70% and 73% average TPHs removal efficiencies at 25°C and 40°C, respectively. The average removal rates in the sets at 40°C are always 7% higher than the sets with average removal rates at 25°C. Hence, it is seen that the results obtained at 40°C are always higher than the results obtained at 25°C, whether the system has bacteria or not.

Table 6.21 The summary of TPHs removal efficiencies in fixed bed systems at the end of the operational period according to the temperature , %

Studied system and its properties				**Initial Diesel Concentration, ppm dw**	
				10000	**25000**
Fixed Bed System	**Sterilized Soil**	**25°C**	**%20 WC**	64	60
			%40 WC	62	58
		40°C	**%20 WC**	66	67
			%40 WC	68	66
	Local Bacteria	**25°C**	**%20 WC**	60	62
			%40 WC	63	63
		40°C	**%20 WC**	68	71
			%40 WC	67	69
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%20 WC**	57	74
			%40 WC	66	84
		40°C	**%20 WC**	62	79
			%40 WC	69	85

6.4.5.2 The Effect of Water Content

The effect of initial water content and its change may be important on NAPLs remediation in soils. That’s why, the systems and TPHs removals are investigated due to their initial and final water contents as can be seen in Table 6.22.

Table 6.22 The summary of TPHs removal efficiencies in fixed bed systems at the end of the operational period according to the initial water content and its change, %

Studied system and its properties				**Initial Diesel Concentration, ppm dw**					
				10000			**25000**		
				Initial WC	**Final WC**	**RE, %**	**Initial WC**	**Final WC**	**RE, %**
Fixed Bed System	**Sterilized Soil**	**25°C**	**%20 WC**	21	18	**64**	20	19	**60**
			%40 WC	40	40	**62**	40	40	**58**
		40°C	**%20 WC**	20	18	**66**	20	18	**67**
			%40 WC	40	35	**68**	40	32	**66**
	Local Bacteria	**25°C**	**%20 WC**	20	30	**60**	20	32	**62**
			%40 WC	40	48	**63**	40	53	**63**
		40°C	**%20 WC**	20	16	**68**	20	18	**71**
			%40 WC	40	33	**67**	40	33	**69**
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%20 WC**	20	19	**57**	20	20	**74**
			%40 WC	40	28	**66**	40	27	**84**
		40°C	**%20 WC**	20	18	**62**	19	17	**79**
			%40 WC	40	23	**69**	40	20	**85**

ND: Not detected

The sets operated at 25°C showed small changes in their water contents in average. Among these sets, the ones having 20% initial water content showed small increases, and the ones having 40% initial water contents does not show any increase, but small decreases. The soils lost their humidity significantly in the fixed bed systems operated at 40°C. Among those, the decreases are more significant in the ones having 40% initial water content. The compost amended sets with 40% initial water content showed the highest water loss, which is followed by the sets with local bacteria. The least water losses were seen in the sets with sterile soils with 40% initial water content. In most of the systems, especially the ones with 10000 ppm IDC, the highest TPHs removal efficiencies were seen in the sets which lost highest amount of water. Therefore, water loss from the system may be used as a tool to identify the extent of remediation.

6.4.6 CO_2 Production and Bacterial Counts

Both the CO_2 production and change in bacterial counts are evaluated here to recognize their relation with NAPLs removal from soils. The CO_2 productions from soils are given with TPHs removal rates in Table 6.23 and the initial and final bacterial counts in the same seta are given in Table 6.24.

Table 6.23 The summary TPHs removal efficiencies (%) in studied systems at the end of the operational period according to the CO_2 production (mL/g soil)

Studied system and its properties				**Initial Diesel Concentration, ppm dw**					
				10000		**25000**		**100000**	
				CO_2 mL/g	**RE, %**	**CO_2 mL/g**	**RE, %**	**CO_2 mL/g**	**RE, %**
Slurry System*	**Local Bacteria**			ND	**ND**	1.98	**61**	1.85	**42**
	Compost Amendment, compost/soil dw/dw		**1/10**	ND	**ND**	0.54	**70**	1.55	**43**
			2/10	ND	**ND**	1.09	**65**	0.89	**47**
			3/10	ND	**ND**	1.15	**55**	0.87	**35**
Fixed Bed System	**Local Bacteria**	**25°C**	**%20 WC**	0.51	**60**	0.53	**62**	ND	ND
			%40 WC	0.47	**63**	0.48	**63**	0.29	**60**
		40°C	**%20 WC**	0.89	**68**	0.80	**71**	ND	ND
			%40 WC	1.34	**67**	1.27	**69**	ND	ND
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%20 WC**	1.11	**57**	1.28	**74**	ND	ND
			%40 WC	1.37	**66**	1.41	**84**	0.25	**62**
		40°C	**%20 WC**	1.15	**62**	1.21	**79**	ND	ND
			%40 WC	1.47	**69**	1.57	**85**	ND	ND

* only with solid/liquid ratio of 1/1, ND: Not detected

In the sets with fixed bed reactors, the TPHs removal efficiency increases with increasing CO_2 production, especially in the sets with compost amendment. But, in the slurry systems, the CO_2 data alone data did not give any meaningful results.

When the bacterial counts given in Table 6.24 are compared with the CO_2 productions given in Table 6.23, it is seen that the data are compatible in general.

Table 6.24 The summary of bacterial counts in studied systems at the end of the operational period, cfu10^{14}/g soil

Studied system and its properties				**Initial Diesel Concentration, ppm dw**					
				10000		**25000**		**100000**	
				İnitial	**Final**	**İnitial**	**Final**	**İnitial**	**Final**
Slurry System*	**Local Bacteria**			ND	ND	50	5	50	10
	Compost Amendment, compost/soil dw/dw		**1/10**	ND	ND	100	10	90	30
			2/10	ND	ND	200	20	140	40
			3/10	ND	ND	200	30	150	50
Fixed Bed System	**Local Bacteria**	**25°C**	**%20 WC**	35	3	140	14	ND	ND
			%40 WC	44	7	154	17	98	27
		40°C	**%20 WC**	50	12	200	70	ND	ND
			%40 WC	58	17	214	54	ND	ND
	1/10 Compost Amendment, compost/soil dw/dw	**25°C**	**%20 WC**	118	92	148	107	ND	ND
			%40 WC	146	123	174	143	220	53
		40°C	**%20 WC**	128	115	130	119	ND	ND
			%40 WC	140	132	150	139	ND	ND

* only with solid/liquid ratio of 1/1, ND: Not detected

But, the CO_2 productions in slurry systems and in fixed bed systems are not very similar. In slurry systems, the relation between the average bacterial counts during the operational time and CO_2 production is found as it is given in Equation 6.1;

$$P_{CO2}= 0.0294*B \qquad (R^2 =0.7195) \qquad \text{Eq. 6.1}$$

where P_{CO2} is the mL CO_2 production in the system and B is the bacterial count in the medium (10^{14} cfu/g).

The same relation is given with Equation 6.2 for fixed bed bioremediation systems;

$$P_{CO2}= 0.0094*B \qquad (R^2 =0.7427) \qquad \text{Eq. 6.2}$$

therefore, both the CO_2 productions and the bacterial counts in fixed bed systems are well correlated with the TPHs removal efficiencies. The CO_2 productions and bacterial counts in slurry reactors are also correlated, but these data are not correlated with TPHs removal efficiencies. The fluctuations in bacterial counts during the operational period in slurry systems may be the reason of this incompatibility.

6.4.7 The Fate of PAHs in Soil Remediation Systems

The treatability of PAHs in slurry systems and fixed bed systems are also studied in the content of the thesis. PAHs are investigated both individually and as groups according to the benzene rings they are having. In Table 6.25 the average PAHs removal rates obtained in the content of the study are presented according to the applied remediation system, system properties, and initial contaminant concentration.

As can be seen from the table, the removal rates of PAHs are decreasing with increasing number of benzene rings they have. For better understanding the removal efficiency differences between the applied remediation techniques Figure 6.83 and Figure 6.84 are presented for the slurry and fixed bed remediation systems, respectively.

As can be seen in Figure 6.83; in the slurry system, a sharp decline has seen in PAHs removal efficiencies with increasing number of benzene rings. Minimum and maximum removal efficiencies for three ring PAHs are 22.7 and 55.7%, for four ring PAHs are 5.8 and 31.8%, and for five and six ring PAHs are 0.6 and 10.8% were found in slurry systems according to Table 6.25.

The PAHs removal efficiencies are higher in fixed bed systems than slurry systems. The removal efficiencies are decreasing with increasing number of benzene rings, similar with slurry systems. Minimum and maximum removal efficiencies for three ring PAHs are 23.0 and 69.0%, for four ring PAHs are 39.0 and 64.0%, and for five and six ring PAHs are 14.0 and 25.0% were found in fixed bed systems according to Table 6.25.

Table 6.25 The summary of PAHs average removal efficiencies in studied systems at the end of the operational period according to their benzene ring groups, %

Studied system and its properties				**Initial Diesel Concentration, ppm dw**								
				10000			**25000**			**100000**		
				3Ring	**4Ring**	**5&6Ring**	**3Ring**	**4Ring**	**5&6Ring**	**3Ring**	**4Ring**	**5&6Ring**
Slurry System*	**Sterilized Soil**			ND	ND	ND	44.0	27.0	10.8	32.5	11.5	3.8
	Local Bacteria			ND	ND	ND	46.8	30.5	10.8	41.2	21.5	5.5
	Compost Amendment, compost/soil dw/dw		**1/10**	ND	ND	ND	55.7	31.8	8.6	45.0	22.5	10.8
			2/10	ND	ND	ND	43.2	20.0	2.4	39.3	12.0	3.0
			3/10	ND	ND	ND	28.7	6.6	1.4	22.7	5.8	0.6
Fixed Bed System	**Local Bacteria**	**25°C**	**%20 WC**	64	53	21	55	43	16	ND	ND	ND
			%40 WC	62	43	24	62	46	15	58	39	14
		40°C	**%20 WC**	69	64	23	59	48	20	ND	ND	ND
			%40 WC	68	44	23	61	48	17	ND	ND	ND
	1/10 Compost Amendment, dw/dw	**25°C**	**%20 WC**	65	54	24	66	52	24	ND	ND	ND
			%40 WC	68	57	25	23	52	24	63	44	16

* only with solid/liquid ratio of 1/1, ND: Not detected

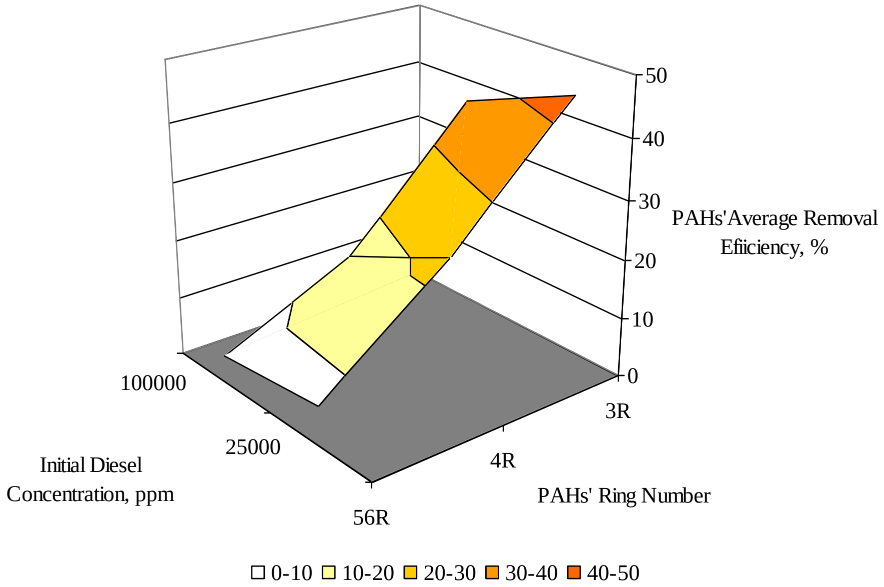


Figure 6.83 The PAHs average removal efficiencies according to the ring numbers in slurry systems

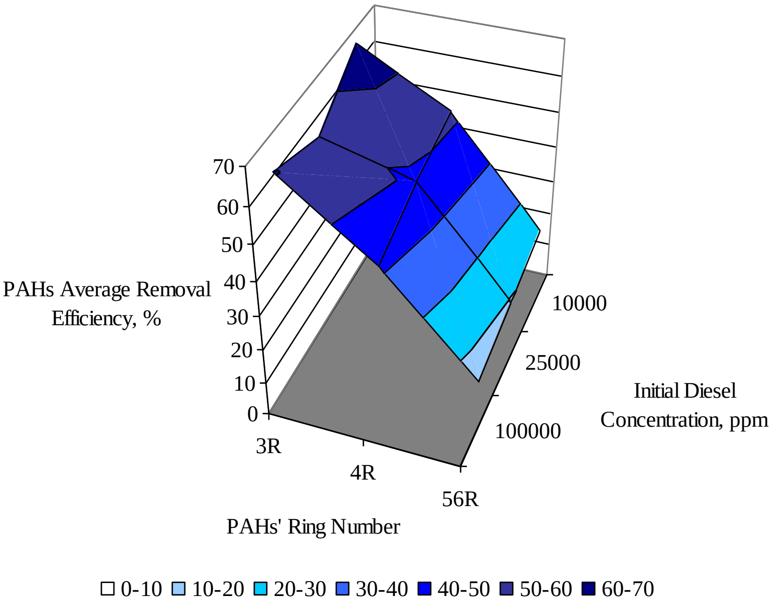


Figure 6.84The PAHs average removal efficiencies according to the ring numbers in fixed bed systems

The individual removal efficiencies of the PAHs are also investigated in this part. As it is given in Chapter 3, PAHs has different water solubilities and vapor pressures, decreasing with the number of benzene rings they have. In Figure 6.85, the relation between individual PAHs removal rates and their water solubilities are given, and in Figure 6.86 the relation between PAHs removal rates and their vapor pressures are given for the soils having local bacteria in the slurry and fixed bed systems having 25000 ppm IDC.

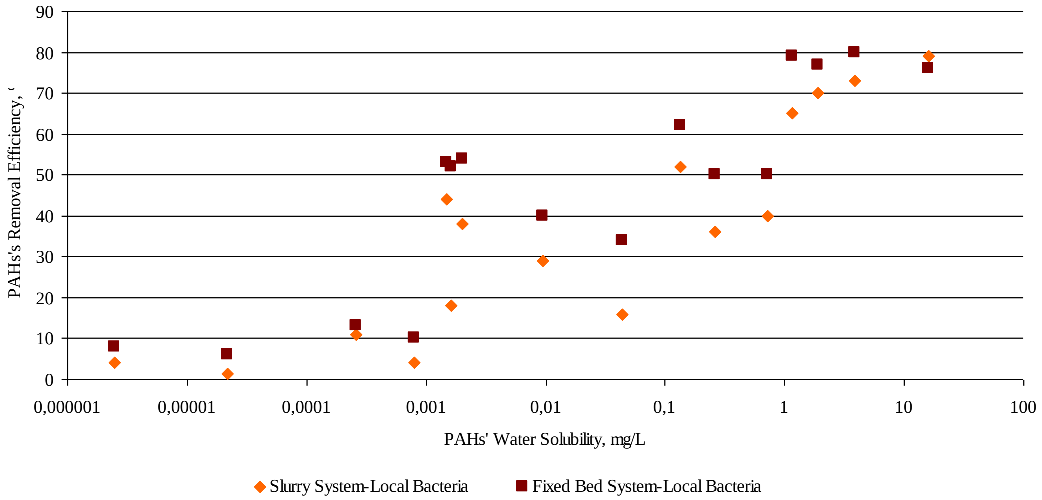


Figure 6.85 Removal rates of individual PAHs vs their water solubilities with local bacteria

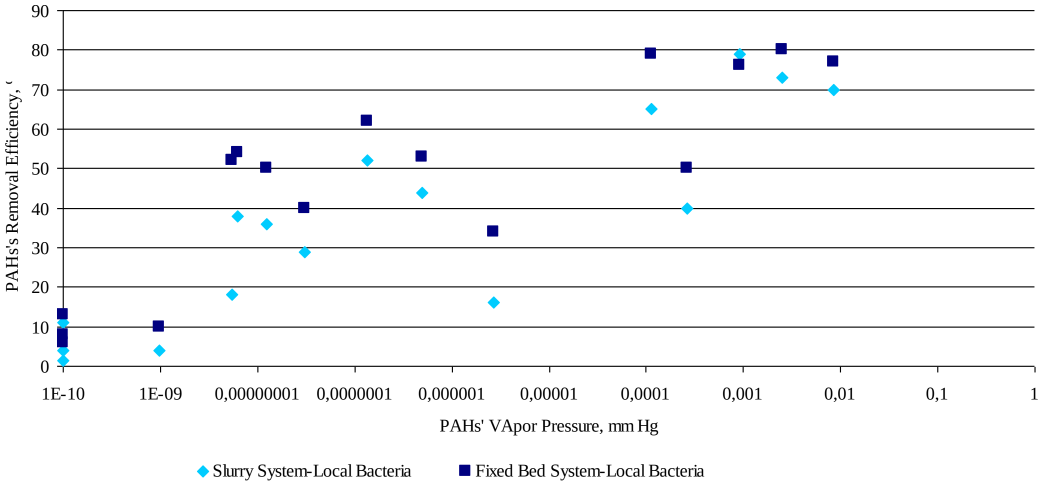


Figure 6.86 Removal rates of individual PAHs vs their vapor pressures with local bacteria

As can be seen from the figures, PAHs removal rates are strongly correlated both with their water solubility and vapor pressure, which are determining the extent of their bioavailability and volatilities. The same situation has seen in the sets with compost amendment (Figures 8.87 and 6.88).

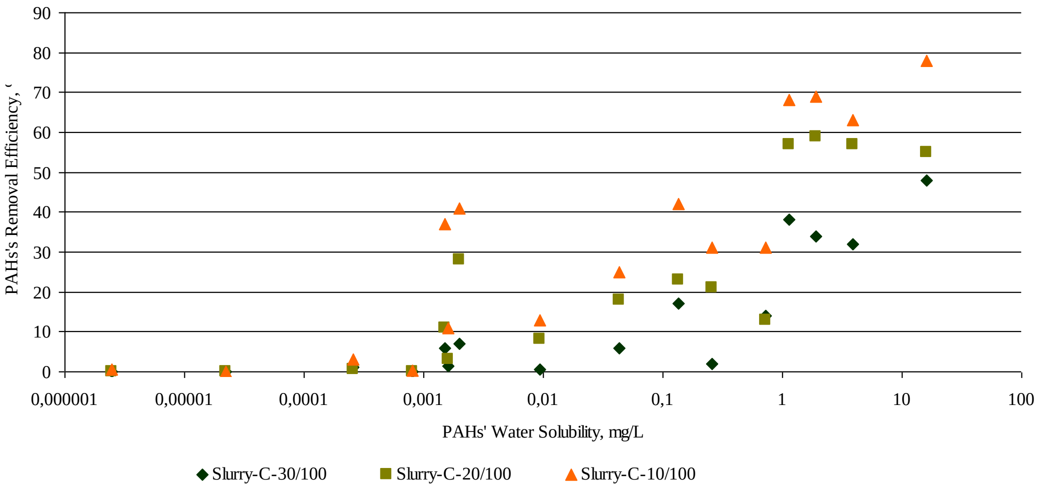


Figure 6.87 Removal rates of individual PAHs vs their water solubilities with compost amendment in slurry system

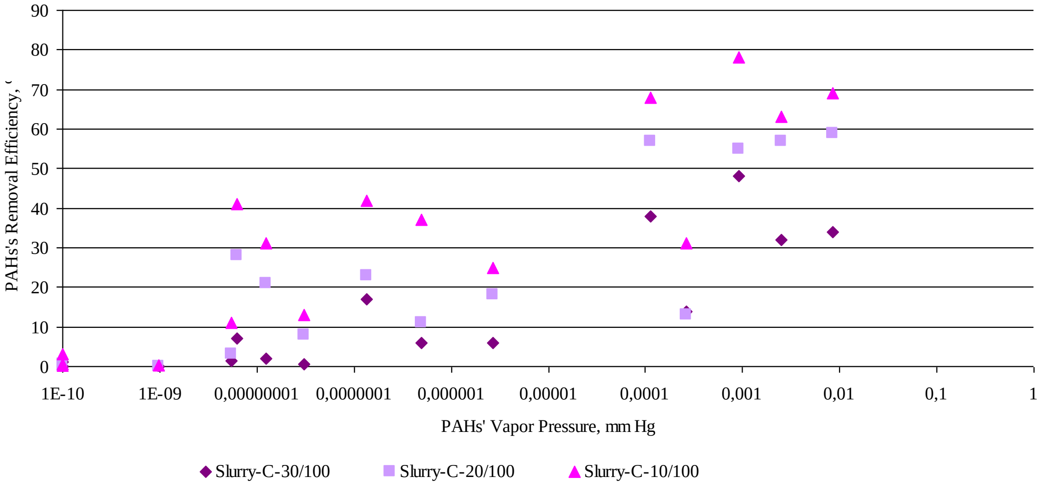


Figure 6.88 Removal rates of individual PAHs vs their vapor pressures with compost amendment in slurry systems

The relation between PAHs removals and their water solubilities or vapor pressures are also strong with the compost amended sets. The same correlations were also be obtained in the sets with sterile soils, but in such case vapor pressure is a more important property of the PAHs, which dominates the treatment process.

CHAPTER SEVEN
CONCLUSIONS

The aim of this thesis is to identify the factors effecting the remediation of NAPLs in the soils. For this purpose, two major types of treatment systems used for the remediation of soils - namely; slurry and fixed bed- were studied.

Slurry systems are the reactors where soil and water are contacted and agitated for the aeration purposes to remove contaminants from the soils. The major parameters may effect the NAPLs treatment in slurry systems are solid/liquid ratio, initial contaminant concentration, presence of local bacteria, and presence and amount of soil amendments which are examined in the content of the study.

Fixed bed systems allow contaminated soil to be treated without agitation, but by air supply which accelerates the removal of NAPLs from the soil by physical forces and supports their microbial degradation. The temperature, water content, initial contaminant concentration, presence of local bacteria, and presence and amount of soil amendments are the major factors which may effect the remediation of NAPLs from the soil and they were examined in the content of the thesis.

The presence and the dosage of surfactants or bio-surfactants in the medium, and enhancement of bacterial growth by specific bacteria are the other factors that effect the remediation of NAPLs from the soils. Since these materials are only commercially available and they increase the cost of remediation, the investigations on these factors are out of the scope of the thesis. Solid waste compost was used as soil amendment, which is not costly and easy to obtain.

Soil remediation is not only dependent to the type of remediation and the system conditions supplied, but also to the properties of soil. Therefore, four different types of soil contaminated with NAPLs were used to examine their treatability.

Diesel oil was used as a typical contaminant, since it mainly consists of petroleum hydrocarbons and PAHs, which are the major parameters indicating a pollution of NAPLs in soil.

The treatment performances of the studied systems were followed by observing the TPHs and PAHs levels in the soils. Besides the abovementioned factors which may affect the NAPLs treatment performance in soil remediation systems, the changes in pH and the cumulative CO_2 production from the bioremediation systems were followed during the remediation interval.

The systems were also operated with sterile soils to define the extent of volatilization losses of NAPLs during the remediation. The results from the systems operated with soil having local bacteria and compost amended soils were compared with the results from sterile soils to identify the normalized treatment efficiencies with the presence of bacteria.

In addition, the inhibitory effect of NAPLs on soil local bacteria was investigated with the soils having different levels of initial contaminant concentration in the presence and absence of compost as soil amendment.

The properties of the soils used in the study are given in Chapter 5, and the results from the experimental studies are presented in Chapter 6, as well as the discussion of the results. According to the findings, the following points are concluded:

- According to the inhibition tests; the presence of NAPLs in soil or incompost-soil mixtures adversely effects the bacterial growth. This adverse effect can be named as inhibition, which has seen especially in the first 192 h (8 days) after the contaminants introduction to the soil. But, it can be said that soil local bacteria and compost bacteria can adapt to the presence of contamination by domination of resistant strains with extending incubation times. It should be noted that the incubation studies were conducted at 28°C according to the test method, which is available for upper-mesophilic group of bacteria.

- In the content of the thesis, slurry and fixed bed soil remediation systems were operated with soils having 10000 ppm, 25000 ppm, and 100000 ppm initial diesel concentration (IDC). In general, TPHs removal efficiencies are decreasing with increasing initial diesel concentration both in slurry and fixed bed systems without compost amendment, the decline in TPHs removal efficiencies is more significant in slurry remediation technique.

- In slurry systems, by increasing sterile soil diesel concentration from 25000 ppm to 100000 ppm the total decrease in the efficiency is 10%. With local bacteria, the difference between the TPHs treatment efficiencies in the soils having 25000 ppm and 100000 ppm diesel has increased to 19%. The decrease in TPHs removal efficiencies was between 18-27% with compost amended soils when the diesel concentration has risen from 25000 ppm to 100000 ppm. That’s why, it may be concluded that the dominant remediation process of soil NAPLs is volatilization in slurry systems and this process is adversely effected by the presence of bacteria and organic matter in the system.

- The efficiencies of fixed bed systems, both with local bacteria and with addition of compost, are higher for 25000 ppm and 100000 ppm than the slurry systems with the same initial diesel concentrations.

- The results in fixed bed systems showed that, in sterile soils, the decreases in TPHs removal efficiencies with increasing initial diesel concentration are more significant at 25°C than at 40°C. This may be because of the higher volatilization of diesel compounds with increasing temperature.

- With local bacteria, TPHs removal rates increases 2-3% compared to the sterile soil when the diesel concentration raised from 10000 ppm to 25000 ppm independent from the soil moisture and temperature.

- In compost amended fixed bed systems, the TPHs remediation efficiency is increasing as the initial diesel concentration increases from 10000 ppm to 25000 ppm. The increases are more significant in the systems having 40% water content. But, when the initial diesel concentration has increased to 100000 ppm, the removal efficiency of TPHs decreases as in other treatments, whether with bacteria or not. This may be related with the intersectional area between the soil and air & water, which probably mostly covered by adsorbed NAPLs and blocked because of high concentration of diesel contamination in the soil.

- From the results of the sets conducted with sterilized soils, it was seen that an important portion of TPHs are removed by thermal volatilization. The extent of the thermal volatilization vary between 40-70% in slurry systems (at 25°C) and vary 58-64% and 66-68% in fixed bed systems at 25°C and 40°C, respectively. This is a very important finding of the study, which explains the treatment of NAPLs are greatly dependent to physical separation which is mostly related with their own properties.

- In slurry systems, TPHs were removed from the Beach sand with efficiencies of 72% and 84% in the sets conducted with the sterilized soil and the soil having local bacteria, respectively, where the TPHs removals in Kaynaklar soil were 50% (sterilized soil) - 61% (soil with local bacteria). With the sterilized soils in fixed bed systems, River sand TPHs were achieved to be treated up to 68 % (with 20% initial water content) and 85% (with 40% initial water content), where maximum TPHs removals in Kaynaklar soil was 63% (with 40% initial water content) and in Kutahya soil it was 54% (with 40% initial water content). Therefore it can be concluded that; i) volatilization is an effective way to remove TPHs from soils, ii) in the soils having relatively high water content (40%) fixed bed treatment with local bacteria results with higher removal efficiencies, and iii) the TPH removal efficiencies with local soil bacteria are 2% (Kaynaklar soil) - 46% (Kutahya soil) higher than the efficiencies obtained in the sets with sterilized soils depending on the soil type.

- Generally the remediation efficiencies follow the rank of Sand(s) > Kaynaklar soil > Kutahya soil. This rank is in opposite direction with the organic matter content, specific surface area, and porosity values of the related soils, which were given in Table 5.4. Therefore, it can be concluded that thermal volatilization, which is the dominant process to remove NAPLs from soils, is also dependent on soil properties.

- If the properties of the soils (organic matter content, SSA, and porosity) are compared, it is seen that the levels of all these parameters, and peculiarly SSA of Kutahya soil is significantly higher (58.798 m^2/g) than the other soils (0.786-14.176 m^2/g) used in the experiments. The lowest TPHs removal efficiencies were obtained with Kutahya soil in all sets, especially in the set with sterilized soil (8-14%). Therefore, it may be concluded that the specific surface area of the soil is a major factor effecting its physical remediation when the contamination with NAPLs are considered.

- The TPHs removal efficiencies obtained in aged soils are much lower than the freshly spiked soils, especially in slurry systems operated with sterile soil and local soil. In addition, it is recognized that fixed bed systems operated with the highest diesel concentration in soil (100000 ppm) resulted with much lower removal efficiencies (40-45%) compared to the lower IDC (55-65%). The difference between the TPHs removal efficiencies in freshly contaminated soils and aged soils are also more significant with 100000 ppm IDC; 17-22% lower efficiencies were obtained. That’s why, it can be concluded that the contamination age adversely effect the efficiency of NAPLs removal from the soils, not only in thermal volatilization but also in bioremediation.

- TPHs removal efficiencies increasing with decreasing S/L in the system operated with 100000 ppm IDC. Therefore, low S/L used in slurry systems may result with higher NAPLs removals from the system.

- In the slurry system operated with sterile soils, the remediation interval for 1/1 S/L was 168 h, but TPHs removal efficiency was still much lower (50% with 25000 ppm IDC and 40% for 100000 ppm IDC) than the systems operated with 1/5 S/L ratios (79% for 25000 ppm IDC and 63% for 100000 ppm IDC) having the remediation interval of 8 hours. Therefore, another output of the study appears at that point; a considerable portion of NAPLs in soils may be desorbed from the soil in a short time interval such as 8 h in slurry systems.

- It is found that, the TPHs removal efficiencies are decreasing with decreasing particle size in slurry systems. This is an expected result, since the adsorption of contaminants on soil particles increases with increasing SSA. The SSAs of the studied coarse, medium and fine particles are 13.75 m^2/g, 14.37 m^2/g, and 15.84 m^2/g, respectively. The removal of TPHs in bulk is compatible with the removals in particle size fractions due to their weight distribution in soil. The initial bacterial counts in size fractions were similar.

- It is seen that the slurry systems performed slightly better in dark environment. With the soils having local bacteria 1-2% higher removal efficiencies obtained. This difference is quite low and can be neglected. Besides the findings, it should be indicated that in field application, to supply enough light for the bacteria in large slurry systems is not possible or feasible.

- As it was concluded above, an important portion of NAPLs are removed from the soils by volatilization. The extent of the thermal volatilization vary between 58-64% and 66-68% in fixed bed systems at 25°C and 40°C, respectively. In addition, the average TPHs removal efficiencies in the soils having local bacteria for 10000 ppm and 25000 ppm IDC was 62% at 25°C and was 69% at 40°C, while the compost amended soils having same IDCs resulted with 70% and 73% average TPHs removal efficiencies at 25°C and 40°C, respectively. The average removal rates in the sets at 40°C are always 7% higher than the sets with average removal rates at 25°C. Hence, it is seen that the results obtained at 40°C are always higher than the results obtained at 25°C, whether the system has bacteria or not.

- The effect of water content and its change may be important on NAPLs remediation in soils. The sets operated at 25°C showed small changes in their water contents in average. The soils lost their humidity significantly in the fixed bed systems operated at 40°C. The compost amended sets with 40% initial water content showed the highest water loss, which is followed by the sets with local bacteria. The least water losses were seen in the sets with sterile soils with 40% initial water content. In most of the systems, especially the ones with 10000 ppm IDC, the highest TPHs removal efficiencies were seen in the sets which lost highest amount of water. Therefore, the extent of water loss may be used as a tool to follow the remediation process, which helps the stripping of NAPLs from the system.

- In the sets with fixed bed reactors, the TPHs removal efficiency increases with increasing CO_2 production, especially in the sets with compost amendment. The bacterial counts are compared with the CO_2 productions from the systems and it is seen that the data are compatible in general. But, the CO_2 productions from a unit of bacteria in slurry systems and in fixed bed systems are different. Both the CO_2 productions and the bacterial counts in fixed bed systems are well correlated with the TPHs removal efficiencies. The CO_2 productions and bacterial counts in slurry reactors are also correlated, but these data are not correlated with TPHs removal efficiencies. The fluctuations in bacterial counts during the operational period in slurry systems may be the reason of this incompatibility.

- The removal rates of PAHs are decreasing with increasing number of benzene rings they have. In the slurry system, a sharp decline has seen in PAHs removal efficiencies with increasing number of benzene rings. Minimum and maximum removal efficiencies for three ring PAHs are 22.7 and 55.7%, for four ring PAHs are 5.8 and 31.8%, and for five and six ring PAHs are 0.6 and 10.8% were found in slurry systems. The PAHs removal efficiencies are higher in fixed bed systems than slurry systems. Minimum and maximum removal efficiencies for three ring PAHs are 23.0 and 69.0%, for four ring PAHs are 39.0 and 64.0%, and for five and six ring PAHs are 14.0 and 25.0% were found in fixed bed systems.

- PAHs have different water solubilities and vapor pressures, decreasing with the number of benzene rings they have. PAHs removal rates are strongly correlated both with their water solubility and vapor pressure, which are determining the extent of their bioavailability and volatilities. The same situation has seen in the sets with compost amendment.

- The effect of their water solubility and vapor pressure on PAHs remediation were also be observed in the sets with sterile soils, but in such case vapor pressure is a much important property of the PAHs, where their volatilization dominates the treatment.

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