Experimental and Modeling Studies on Fate and Transport of Petroleum Contaminants in Soils with Plants

by

Raghupathy Karthikeyan

B.E., Tamil Nadu Agricultural University, India, 1993
M.S., The University of Georgia, 1997

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

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Department of Biological and Agricultural Engineering
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ABSTRACT

The US Air Force uses JP-8, a kerosene-based jet fuel, to run turbine engines. Billions of gallons are used each year and even small percent losses of JP-8 leaking from aboveground and underground storage tanks to soil and groundwater aquifers pose a potential threat to drinking water. The biotic fate processes of JP-8 in soils will help determine the bioremediation potential of JP-8 from accidental spills and leakages. Many US Army training reservations contain vehicle wash facilities where combat and other types of equipment are washed after field maneuvers. During this process, sediments containing petroleum hydrocarbons accumulate in sedimentation basins. A vegetative treatment system could be an inexpensive approach to treat these washwater sediments.

Experiments were conducted to differentiate between abiotic and biotic removal of JP-8 in soils with plants. Also, the effect of plant-induced water movement on the fate and transport of JP-8 in the subsurface was determined. Almost 86% of JP-8 disappeared in five months in the simulated surface spill experiments. The losses were not just due to volatilization but also due to biodegradation. The reduction in JP-8 concentration in planted soil systems where subsurface leakages were simulated was only 50% after twelve months. This shows that JP-8 leakages that occur near the groundwater table could persist for longer duration than those that occur near the soil surface. Downward movement of JP-8 was higher in unplanted soil columns compared to columns with plants. A one-dimensional mathematical model was developed to simulate advective transport, retardation, and first-order decay of soluble fractions of JP-8 in soil columns.

An inexpensive vegetation treatment system was established to treat sediments from Central Vehicle Wash Facility (CVWF) at Fort Riley, KS. The overall reduction in total petroleum hydrocarbon concentration was about 75%; however, significant differences among treatments were not found until 36 months. Sufficient reduction of petroleum hydrocarbons was obtained in fertilized soil with or without vegetation.

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DEDICATION

This dissertation is dedicated to *Amma*, *Appa*, *Nagarajan*, and *my beloved family*.

CHAPTER 1

OVERVIEW

1.1. INTRODUCTION

Earth is a water planet. Terrestrial water can be broadly grouped into fresh and salt waters. Fresh water can be surface water (e.g. rivers and lakes), groundwater (e.g. confined or unconfined aquifers), and glaciers. Groundwater has long been one of the world's most important natural, renewable resources. Approximately 96% of all fresh water in the United States is locked in groundwater, which serves as a drinking water source for more than 50% of the US population (Abriola, 1984; National Geographic, 1993). In the US, with the advance in pumping technology using cheap power, farmers started to utilize groundwater in largescale for irrigation (National Geographic, 1993). Commercial agriculture and industrialization resulted in contamination of groundwater sources in several areas of the US with potentially toxic chemicals, eventually degrading the quality of aquifers. During the past five decades, different classes of organic chemicals ranging from alkanes to aromatics, have been produced and utilized in day to day life (Watts, 1997). Currently, more than 60,000 organic compounds are produced, transported, utilized, and finally released in the environment (Watts, 1997). Particularly, production and consumption of petroleum-derived compounds has increased during this time period (Chambers, 1991; Watts, 1997).

Accidental spills or leakages during transport and handling, intentional disposal and dumping, and over-application of certain chemicals has resulted in contamination of terrestrial ecosystem including soils, sediments, and groundwater aquifers. Chemicals including petroleum hydrocarbons have been stored aboveground and in underground storage tanks. Any leakages from these storage tanks threatens groundwater with contamination. Usually massive marine oil spills attract immediate attention, and oil leakages that contaminate groundwater stay unnoticed for several years to decades (Atlas and Cerniglia, 1995; National Geographic, 1990). However, most of the chronic hydrocarbon exposure to general public results from smaller leakages that contaminate terrestrial environment. Hutchins et al. (1991) reported that approximately six million tons of petroleum-derived products spill and leak into soil each year in the US. Underground storage tanks buried below fuel stations, military installations, airports, and other fueling

facilities are prone to leaks. Such leaks are not detected easily because of lack of site monitoring.

Previous research had estimated that at least 300,000 of the three million underground gasoline and oil storage tanks in the US were leaking as of 1990 (Hutchins et al., 1991). This figure has been increasing because of deterioration of the tanks due to environmental factors over the years. Reinhard et al. (1997) estimated that 900,000 of the three million underground storage tanks in the US were leaking as of 1996. The leaks usually occur because of several factors including tanks rusting due to fluctuating groundwater table, microbial degradation of tank materials, and cracking of tanks caused by swell-shrink dynamics of subsurface materials, particularly clay soils. Incidents of petroleum contamination of groundwater have been documented by many researchers (Atlas and Cerniglia, 1995; Lovley, 1997; McKee et al., 1972; Newell et al., 1995; Osgood, 1974; Willams and Wilder, 1971; Yazicigil and Sendlein, 1981). All these studies have documented the widespread nature and long persistence of the petroleum-hydrocarbon contamination problem.

Petroleum is a mixture of organic compounds, with varying degrees of physical and chemical properties, with inert inorganic compounds (Heath et al., 1993). Constituents with low water solubility persist in the environment for longer periods of time and pose a chronic health hazard, whereas highly soluble constituents stay for shorter periods of time and pose acute toxic effects to living organisms (Heath et al., 1993; Overton et al., 1994; Racine, 1994; Song and Bartha, 1990). The overall toxicity of petroleum mixtures and refined petroleum products is difficult to assess, mainly because of varying toxic effects of individual compounds on biota within the same ecosystem (Overton et al., 1994). Several petroleum constituents and petroleum-derived products are found to be carcinogenic and mutagenic in animal and human cells *in vitro* (Overton et al., 1994). Petroleum when released in terrestrial environment may persist for several decades and eventually end up in the food chain via bioaccumulation (Overton et al., 1994).

Petroleum products are used extensively in the US Air Force and Army. The Air Force uses various kinds of jet fuels to run turbine engines (Martel, 1987; Totten, 1995). Since the 1950's, JP-4, a specific kind of jet fuel, was the largest volume jet fuel procured for the Air Force. The US Air Force changed their fuel usage from JP-4 to JP-8 in the 1990's (Totten, 1995). Due to this change, previous environmental impact assessments have to be updated because JP-8 has less aromatic hydrocarbons compared to JP-4. Only a few studies have been conducted on fate and environmental effects of JP-4 or JP-8 (Aelion and Bradley, 1991; Dean-Ross, 1993; Dean-Ross et al., 1992; Spain and Somerville, 1985). Previous studies conclude that majority of jet fuels disappear from the terrestrial environment through volatilization (Dean-Ross et al., 1992; Karthikeyan et al., 1999); however, remediation based on microbial processes can decrease the environmental effects of less-volatile hydrocarbons. Degradation of jet fuels by *in situ* microorganisms can be enhanced by altering the soil physical, chemical, and biological conditions (Karthikeyan et al., 1999). Vegetation could help manipulate the soil characteristics, alter local hydrology, and harbor diverse microorganisms (Anderson et al., 1993; Cunningham et al., 1996; Davis et al., 1993; 1998; Erickson et al., 1994; Shimp et al., 1993). This may improve the rate of jet fuel removal from the terrestrial environment.

Combat and military equipment are washed after field activities at wash facilities located in several US Army installations. Typically, high-pressure water hoses are used to remove sediment and dirt adhered to the combat equipment. This washing process results in sediments with hydrocarbons accumulating in sedimentation basins. US Army training reservations throughout the United States, including the two in the Great Plains/Rocky Mountain region, generate large quantities of such petroleum-contaminated sediments (Kulakow et al., 1998). These sediments are land applied or sent to landfill after dewatering; however, before landfill disposal or land application, these sediments should be treated to reduce petroleum hydrocarbon concentrations to meet the State and/or Federal regulatory

standards (Kansas Department of Health and Environment, 1999; Oliver et al., 1996). The treatment system should be easy to implement and maintain, and economical.

Removing petroleum spill/leakage from the subsurface or cleaning a contaminated aquifer is a critical but complex, if not virtually impossible, task. If the affected soil zone is of any reasonable size, excavation of the contaminated soil is infeasible and flushing of the chemical from the soil is impossible due to the capillary and sorptive forces that hold the contaminant in place. Many research articles emphasize the difficulties and costs involved in treating petroleum-contaminated soils, sediments, and groundwater supplies using various treatment methodologies (Abdul, 1992; Blake and Lewis, 1983; Borden and Kao, 1992; Boyd and Farley, 1992; Brown, 1994; DiGiulio, 1992; Hayes et al., 1989; Hunt et al., 1988a; 1988b; Marley et al., 1992; Travis and Macinnis, 1992). In 1996, approximately 25 million dollars were spent in the US for remediation of petroleum-contaminated soils (Cunningham and Ow, 1996). The primary methods of remediation are in two categories, *ex situ* and *in situ* methods. Recently, more emphasis has been placed on using *in situ* methods because of increased development of *in situ* biotechnologies, prohibitive costs of excavation and soil replacement, and unacceptable risk to the workers and environment during remediation with *ex situ* methods. *Ex situ* remediation usually consists of removal of the contaminated soil and transport to soil treatment beds, landfills, or incineration facilities. However, excavation of contaminated materials usually is feasible only for shallow, contained, and highly contaminated soils.

In situ methods emphasize free-product recovery and biorestoration. This technology was developed to treat contaminants adsorbed to soil particles and or dissolved in groundwater in contrast with conventional remediation of spill sites. Free-product recovery is normally obtained through pump-and-treat or *in situ* soil washing methods. It was found that many petroleum contamination problems can be treated by processes

based on native microorganisms (Alexander, 1985; Atlas and Cerniglia, 1995; McCarty, 1991; Thomas and Ward, 1989; Wilson and Brown, 1989; Wilson et al., 1986). Many petroleum hydrocarbons can serve as electron donors (food source) for *in situ* microorganisms under different environmental conditions (e.g. aerobic vs. anoxic vs. anaerobic) (Atlas and Cerniglia, 1995; McCarty, 1991).

Remediation of hydrocarbon-contaminated soil systems using vegetation and associated microorganisms has proven effective in several laboratory studies. There are several studies that showed aggressive roots of plants may expedite degradation of petroleum hydrocarbons in soil (Aprill and Sims, 1990; Gunther et al., 1996; Lee and Banks, 1993; Qui et al., 1994; Reilley et al., 1996; Schwab and Banks, 1994; Shimp et al., 1993; Sims and Overcash, 1983). Remediation using vegetation involves the processes of removal, containment, and destruction of contaminants by plant activity and/or growth. Plants can sequester contaminants, degrade contaminants through plant processes, and directly or indirectly stimulate contaminant-degrading microorganisms. Plants can supplement oxygen and nutrients for rhizosphere microorganisms through root exudates. Also, plant transpiration can create a soil-moisture (i.e., water potential) gradient that draws water and soluble contaminants from deeper soil or shallow groundwater layers toward the surface. The contaminants then can be degraded aerobically. Because of the removal of groundwater, the anaerobic (saturated) zones will be decreased and there will be chances for increased aerobic activity. There have been several field trials conducted to show the effectiveness of vegetation on degradation of petroleum-contaminated soils. Specifically, the establishment of native vegetation on petroleum-contaminated field sites has been proven to be an effective *in situ* remediation approach (Banks et al., 2000). A vegetative treatment system could be a low-maintenance and low-cost approach to treat the washwater sediments generated at US Army training reservations.

1.2. OBJECTIVES

The overall objective of this research was to determine how vegetation affects the fate of petroleum hydrocarbons in soils and sediments. Specific objectives were to

1. differentiate between abiotic and biotic removal of JP-8 in soils,
2. determine the effects of plant-induced water movement on fate and transport of JP-8 in soils,
3. develop and verify a 1-D mathematical model to simulate fate and transport of JP-8 in soil columns, and
4. determine the effects of vegetation in treating petroleum-contaminated sediments under field conditions.

CHAPTER 2

FATE AND TRANSPORT OF JET FUELS (JP-8) IN SOILS WITH PLANTS

2.1. INTRODUCTION

Soils near jet fuel storage tanks and aviation facilities are prone to contamination from accidental jet fuel spills and jet fuel leakages from underground storage tanks. Knowing the fate of jet fuel in soil could help in determining the persistence of jet fuel in the terrestrial environment. The transport of jet fuel in soils and particularly in aquifers is important because it determines the contamination of nearby groundwater sources. Jet fuels are petroleum derivatives and are often present as light nonaqueous phase liquids (LNAPL) in soil systems. This section briefly discusses the nature of petroleum hydrocarbons, nonaqueous phase liquids, history of jet fuel development, fate and transport of jet fuels in soils, microbial degradation of petroleum hydrocarbons, factors affecting microbial degradation, and previous studies on fate and transport of jet fuels in soils.

2.1.1. Petroleum hydrocarbons in the environment

Petroleum and the products made from petroleum are easily recognized and understood by common people but are highly complex materials to chemists and scientists. Petroleum derivatives such as gasoline and diesel are made primarily of only two elements; carbon and hydrogen. These two elements can be arranged in infinite combinations resulting in diverse group of compounds. The demands we place on our fuels with regards to improved performance, reduction in emission, and demand for low cost force the manufacturers to constantly change their products. This ultimately results in slight changes in each batch of every petroleum product produced. As the products are distributed, they continue to change. Consequently every tank of petroleum product is unique in its detailed chemical makeup.

The actual number of individual compounds that are present in crude oil is not known. Estimates on the number of hydrocarbons present in crude oil range from 20,000 to 5,000,000. The compounds with similar physical and chemical properties can be grouped. Typically petroleum hydrocarbons are a mixture of aromatic and aliphatic hydrocarbons of diverse properties. These hydrocarbons can be distilled based on volatility into volatiles,

aromatics, and resins (Solomons, 1996). The volatile compounds include n-alkanes, branched alkanes, and cycloalkanes. Compounds with two or more benzene rings are known as polycyclic aromatic hydrocarbons (PAHs) (Leahy and Colwell, 1990; Rathbone et al., 1998).

Several anthropogenic activities result in petroleum hydrocarbon pollution in the environment. Industrial activities including crude oil exploration, petroleum production, processing, refining, distillation, storage, and disposal contribute to a significant petroleum hydrocarbon load in the ecosystem. Burning fossil fuels in processing industries, power plants, and automobiles release large amounts of petroleum products and byproducts. Accidental spills and leakages from above and belowground petroleum storage tanks, gas stations, and fueling facilities introduce petroleum hydrocarbons in the environment as well (Rathbone et al., 1998; Sims and Overcarsh, 1983; Wilson and jones, 1993).

2.1.2. Nonaqueous phase liquids

Due to the differences in physical (e.g. hydrophobicity, surface tension) and chemical (e.g. solubility) properties, two liquids can be phase-separated and exist as two immiscible liquids. When petroleum hydrocarbons come in contact with water, they may stay as a separate phase. These hydrocarbons are known as nonaqueous phase liquids (NAPLs) (Newell et al., 1995). Light NAPL (LNAPL) will float on top of water while denser NAPL (DNAPL) will sink to the bottom of water (Newell et al., 1995).

Surface and groundwater quality is affected by both DNAPL and LNAPL. Examples of LNAPL contamination include underground and aboveground storage tank leaks and accidental spills of gasoline-range hydrocarbons (e.g. gasoline, kerosene, jet fuel), fuel additives (e.g. methyl tertiary-butyl ether, MTBE, ethyl alcohol), and other volatile compounds (e.g. benzene, toluene, ethylbenzene, xylene). The solubility of these compounds in water range from highly soluble to sparingly soluble (Newell et al., 1995). Trichloroethylene (TCE) and polychloroethylene (PCE) are examples of DNAPL compounds that contaminate surface and groundwater. Both LNAPL and DNAPL

compounds once released in the environment can persist for longer periods of time resulting in long-term water contamination problems.

2.1.3. Jet fuels

Jet fuels are a particular group of refined petroleum products. They have been used to run aircraft turbine engines (Martel, 1987; Totten, 1995). A brief history of jet fuel development and usage in US Air Force is briefly presented here and details can be found in Martel (1987) and Totten (1995). Even though the jet engines were more tolerant to any fuels, the fuel system and other engine components were sensitive to the fuel's chemical and physical properties (Totten, 1995). Standards and specifications for the fuels to be used in jet engines were developed in order to ensure the safety of the aircraft. The first standardized jet fuel, Jet Propellant (JP)-1, was introduced in 1944 (Martel, 1987). This jet fuel differed from its British avian fuel counterpart but resembled the US aviation gasoline (Martel, 1987). JP-1 was a narrow-cut kerosene with a low freezing point and high flash point (Martel, 1987; Totten, 1995). Later it was realized that the JP-1 production process was inefficient. Hence a wide-cut distillation process was introduced. This distillation process resulted in a fuel with constituents ranging from aromatic fraction to kerosene fractions. However, the resultant fuel, JP-2, did not meet the safe aviation standards (Martel, 1987; Totten, 1995).

The next generation of jet fuels, JP-3, was also a wide-cut distillate with a high vapor pressure. This fuel was used for some time but due to technical issues encountered at high-altitude flights it was discontinued (Martel, 1987; Totten, 1995). Wide-cut distillation process was continued to produce an improved product, JP-4. JP-4 was mainly composed of gasoline and kerosene range compounds resulting in superior quality as compared to JP-3 (Martel, 1987; Totten, 1995). JP-4 has been widely used in the US Air Force for decades.

Aviation gasoline was originally used in the US Navy aircraft carriers (Martel, 1987). But later, the US Navy created a fuel similar to jet fuel by mixing aviation gasoline and kerosene. This mixture was called JP-5. JP-5 met not only the safe flight standards but also safe onboard storage requirements (Martel, 1987; Totten, 1995). JP-6 was a kerosene-based fuel, similar to JP-5, but with a lower freezing point (Martel, 1987). This was used in the US Air

Force only for a short time period. An improved fuel, JP-7, was developed by a totally different manufacturing process – blending different fractions and removing aromatic compounds of petroleum (Martel, 1987). JP-7 had less corrosive compounds because of this special blending process but did not possess desired aviation fuel properties. JP-7 was discontinued after a brief period and replaced by JP-8 (Martel, 1987; Totten, 1995).

About 99% of JP-8 is composed of kerosene-range compounds (Martel, 1987; Totten, 1995). Currently six billion gallons of JP-8 are produced worldwide and 4.6 billion gallons are used in the US each year (Mayfield, 1996). JP-8 has the following additives as well: a corrosion inhibitor, an icing inhibitor, and a lubricity enhancer (Martel, 1987; Totten, 1995). These additives provide the desired physical and chemical properties to JP-8 used in high altitude flights under adverse environmental conditions. JP-8 has the desired minimum flash point (less than 40°C) and an acceptable freeze point of -47°C (Martel, 1987; Totten, 1995; Mayfield, 1996).

2.1.4. Fate and transport of jet fuel in soils

The fate and transport of JP-8 in the terrestrial environment determine the persistence of JP-8 in soil systems. The fate processes of JP-8 can be abiotic or biotic. The biotic fate processes of JP-8 in soils will help determine the bioremediation potential of JP-8 from accidental spills and leakages. Jet fuels similar to JP-8 have been shown to be readily degraded in soils and sediments under both laboratory and field conditions (JP-4: Bradley et al., 1992; Cho et al., 1997; Yocum et al., 1995; Jet-fuel mixture: Landmeyer et al., 1996). In general, heavier petroleum hydrocarbons such as diesel and crude oil persist in the environment longer than jet fuels, while gasoline disappears sooner than jet fuels (Autry and Ellis, 1992).

Based on the water-filled pores pace, subsurface porous media can be arbitrarily divided into unsaturated or vadose zone and saturated zone. JP-8, when introduced into the environment, can exist in both zones depending on the fate and transport properties. Typically, JP-8 will partition into NAPL, aqueous, sorbed, and gaseous phases. In the vadose zone, all four phases may exist while the gaseous phase will be absent in the saturated zone. JP-8 constituents will migrate from one phase to another phase depending on the phase

equilibrium conditions. Environmental factors (e.g. soil type, water velocity), physical and chemical properties of JP-8 (e.g. solubility, Henry's coefficient), and other anthropogenic activities (e.g. irrigation, land use changes) will alter the equilibrium conditions and drive the phase exchange. JP-8, once introduced into terrestrial ecosystems, will dissolve in subsurface and surface water, move by advection and dispersion with water, sorb to soil organic matter, degrade (both biotic and abiotic), and volatilize. The subsurface fate of any chemical, here JP-8, will primarily be determined by groundwater flow (advection and dispersion), dissolution and migration (diffusion), sorption to porous media, volatilization, and degradation (Newell et al., 1995). General discussion on LNAPL fate and transport processes in the subsurface is provided in detail by Newell et al. (1995) while processes specific to JP-8 are presented here.

Transport

Migration (transport) of JP-8 in the subsurface can be conceptualized as depicted in Figure 2.1. When a small amount of JP-8 is released at the soil surface, a fraction of JP-8 moves downward through soil pores due to gravity and a fraction volatilizes to atmosphere (Newell et al., 1995). Soil capillary forces, porosity, and hydrostatic forces control further movement. In the vadose zone, JP-8 is held by the capillary fringe; a fraction adheres to soil particles, a fraction stays as NAPL phase, and a fraction dissolves in pore water. Dissolved fraction moves with pore water velocity. The direction of the flow is governed by soil matric potential. If JP-8 is continuously released, JP-8 migration could eventually reach beyond the capillary fringe to groundwater table. Once JP-8 meets groundwater table, due to hydrophobicity, JP-8 will stay in immiscible phase. There will be a lateral slide of JP-8 on top of the groundwater table (i.e. floating, because JP-8 is LNAPL), a dissolution of fraction of JP-8 in groundwater, and sorption of JP-8 to subsurface soil. Dissolved fraction will move with the groundwater in the direction, based on hydrostatic pressure potential (i.e. high to low). When JP-8 is released in large quantities, continuously, the plume will push the capillary fringe as well as groundwater table (Newell et al., 1995). After the release is stopped, groundwater table and capillary fringe will come back to original state. Any downward (e.g. rainfall, irrigation) and upward (e.g. evaporation, evapotranspiration) water movement and volatilization will alter the course of JP-8 movement in the subsurface. For

example, the soluble JP-8 fraction may move along transpiration stream and may never reach groundwater table or heavy rainfall may move JP-8 to groundwater faster.

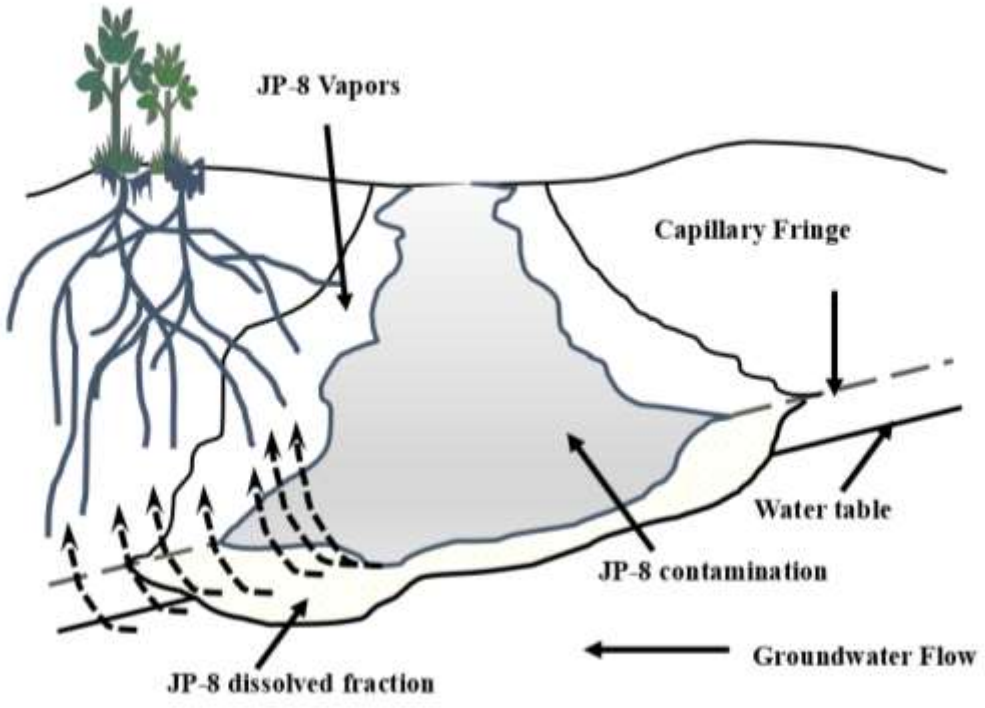

Figure 2.1. Simplified conceptual model for jet fuel release and migration in soil (Modified after Mercer and Cohen, 1990 and Newell et al., 1995).

Volatilization

Volatilization of JP-8 can occur from its NAPL phase and from water-dissolved aqueous phase. Henry's law is applicable to dilute solutions while Raoult's law is applicable to concentrated solutions (Newell et al., 1995). Partitioning of JP-8 between water and gaseous phase can be predicted by Henry's law. Henry's law states that "tendency of a molecule to move from aqueous phase to vapor phase is proportional to its aqueous phase concentration" (Newell et al., 1995). Here, Henry's coefficient for JP-8 can be used to determine its potential fate in aqueous phase (Mendoza and McAlary, 1989). According to Raoult's law, "the partial vapor pressure of each constituent of an ideal mixture of liquids is equal to the product of the mole fraction of the solute and the vapor pressure of the pure-phase liquid" (Newell et al., 1995). Here, Raoult's law will be helpful to predict JP-8 fate in the NAPL phase (Johnson et al., 1990).

Dissolution

When JP-8 is in physical contact with groundwater and soil pore water, fractions of JP-8 will dissolve and become part of aqueous phase. Solubility of JP-8 in the subsurface is dependent on several environmental factors, particularly temperature and hydrostatic pressure (Newell et al., 1995). Typically, solubility of JP-8 can be defined as the maximum concentration of JP-8 in water for the temperature and pressure. Other factors that might affect solubility of JP-8 include pH of water, salinity, presence of any cosolvents, and dissolved organic matter (Newell et al., 1995).

Feenstra et al. (1991) present a method for determining residual NAPL in the subsurface. This method is applicable to find maximum solubility of a compound (termed as "effective solubility") in a mixture under equilibrium conditions. JP-8 is a NAPL mixture and aqueous solubility of a particular compound in JP-8 can be found using the method presented by Feenstra et al. (1991). The maximum concentration, termed as "effective solubility", of a compound (e.g. decane) in JP-8 mixture can be determined using Equation 2.1 (Newell, et al., 1995).

$$S^e_i = X_i S_i \qquad [2.1]$$

where,

S^e_i, = effective aqueous solubility of compound i in JP-8 mixture, mg/L

X_i = mole fraction of compound i in JP-8 mixture, and

S_i = aqueous solubility of the pure phase compound, mg/L.

Equation 2.1 may over or under estimate effective solubility of a compound. However, it should be noted that the effective solubility concept is based on the assumption that equilibrium exists under ideal conditions. This equation is found to provide reasonable estimates for mixtures of hydrophobic compounds with very low aqueous solubilities (Leinonen and Mackay, 1973; Newell et al., 1995).

Typically, once dissolved, NAPL constituents will be transported by groundwater velocities. Mass transfer, particularly dissolution, can occur during transport (Newell, et al., 1995; Mercer and Cohen, 1990; Miller et al., 1990). While the dissolution can be increased by higher groundwater velocities, complete dissolution can take years if not decades under field conditions (Borden and Kao, 1992; Geller and Hunt, 1993; Powers et al., 1991). The rate of dissolution can depend on several mass transfer and transport parameters, other than advection velocity (Powers et al., 1992). Contact time, contact area, solubilities of JP-8 constituents, and JP-8 saturation will also play a major role in JP-8 dissolution in the subsurface. Immediately after an instantaneous release and contact with groundwater, JP-8 concentrations in water (aqueous) will be high. The concentration will decrease sharply if the JP-8 source is removed and reach a steady state concentration which will decline slowly over a period of time. For a continuous JP-8 release, the aqueous phase concentration will increase, remain the same, and slowly decline over the period of time. Other fate processes, particularly sorption and degradation, will govern the NAPL concentration decline in the subsurface (Newell et al., 1995).

Sorption

Sorption is a physio-chemical process by which a substance is fixed or attached to another substance. Desorption is an opposite process – detachment of a substance from another. Sorption-desorption mechanisms play a critical role in the environmental fate of a chemical. Contaminants interact with porous media in the subsurface; soils and aquifer materials (Karickhoff et al., 1979; Newell, et al., 1995; Piwoni and Keeley, 1990; Rao, 1990). JP-8 will interact with porous media while in three phases; gaseous, NAPL, and aqueous. The major sorption pathway for JP-8 in the subsurface will be from aqueous phase. Sorption of JP-8 is governed both by its physical and chemical properties; solubility (i.e. aqueous phase concentration), polarity of JP-8 constituents, and octanol-water partition coefficient, and environmental factors; pH of pore water, presence of other contaminants (that may compete for sorption spaces in porous media), temperature, dissolved organic carbon, soil organic matter, clay content, and aquifer mineral content. Under saturated conditions, sorbed-phase concentration will not be a significant fraction as compared to aqueous or NAPL phase concentrations. Once sorbed, mass transfer of JP-8 from porous media to groundwater (desorption process) will be slow. Desorption is usually a rate-limiting step, resulting in asymptotic effect seen in remediation projects (Newell et al., 1995).

Biodegradation

Biodegradation is a process by which biota, particularly microorganisms in the subsurface, degrade contaminants (Newell et al., 1995). NAPL compounds, here JP-8, are hydrocarbons that can serve as electron donors (food source) for microorganisms. Biodegradation can happen under both aerobic and anaerobic conditions (Atlas, 1981; Atlas and Bartha, 1992). Oxygen will serve as terminal electron acceptor in case of aerobic degradation and nitrate, Fe (III), sulfate, and other organic compounds can serve as terminal electron acceptors in case of anoxic, anaerobic, and fermentation situations. Degradation of JP-8 may result either in complete mineralization or in partial oxidation. The end products will be microbial biomass, water, and carbon dioxide (complete mineralization) or microbial biomass and intermediate organic compounds (partial oxidation) (Atlas and Bartha, 1993; Autry and Ellis, 1992). The biodegradation can happen *in situ* by native microorganisms or enhanced by bioaugmentation

(introduction of microorganisms). Sometimes addition of external nutrients, electron donors, and acceptors may be required (biostimulation) (Alexander, 1985; Anderson and Coats, 1995).

2.1.5. Microbial degradation of petroleum hydrocarbons

Bacteria are the principal microbiota that mineralize petroleum hydrocarbons. There have been several studies on bacterial degradation of petroleum hydrocarbons (Bossert and Bartha, 1986; Chainaeau et al., 1995; Ellis et al., 1990; Erickson et al., 1991; Gibson and Subramanian, 1984; Gibson et al., 1975; Grosser et a1.,1991; Heitkamp and Cerniglia, 1988; 1989; Heitkamp et al., 1988; Kelley and Cerniglia, 1995; Leahy and Colwell, 1990; Lee and Banks, 1993; Mahaffey et al., 1988; Morgan and Watkinson, 1990; 1993; Pradhan et al., 1997). The predominant microorganisms are *Pseudomonas, Mycobacterium, Acinetobacter, Flavobacterium, Arthrobacter, Bacillus,* and *Nocardia* (Atlas and Bartha, 1992; Autry and Ellis, 1992; Walton et al., 1994). Aerobic biodegradation of n-alkanes is the most rapid of all petroleum hydrocarbons. The initial step involves a mono-terminal attack with a primary alcohol being formed. Then an aldehyde and monocarboxylic acid are formed, and further degradation proceeds by β-oxidation. There is subsequent formation of acetyl coenzyme A and release of acetate into the tricarboxylic acid cycle. Fatty acids are found to be accumulated during this degradation pathway, and some of these byproducts could be toxic (Atlas, 1981; McKenna and Kallio, 1965).

Usually, branched alkanes undergo Ω-oxidation resulting in the formation of dicarboxylic acids. This is considered as the major degradation pathway. Hydrocarbons with methyl branching are resistant to microbial attack, and intermediary steps are required to decompose the methyl group (Atlas, 1981; Schaeffer et al., 1979). Cycloalkanes also are resistant to microbial attack, and degradation of substituted and unsubstituted cycloalkanes is through oxidation and cooxidation. Once oxygenated, rings are cleaved to initiate degradation. Substituted cycloalkanes are degraded more readily than unsubstituted alkanes because the microorganisms preferentially attack the first substituted position. Alternatively, an aromatic intermediate can be formed and the ring cleaving can be

followed (Atlas, 1981). Under aerobic conditions, a diol is formed which is cleaved to form a diacid during biodegradation of aromatic hydrocarbons in soils (Cerniglia et al., 1980).

2.1.6. Factors affecting microbial degradation

The soil system is the most integral part of the biosphere. A complex interconnected solid, liquid, and gas phases make up the soil matrix. Particles of varying sizes, array of minerals, complex organic matter, and diverse biota constitute the soil ecosystem. Biodegradation of petroleum hydrocarbons in soil ultimately results in CO_2, H_2O, and microbial biomass. Some hydrocarbons may become part of the soil humus via microbial biomass or by more direct incorporation (Brock, 1966; Gray and Parkinson, 1968; Manilal and Alexander, 1991; Volkering et al., 1992; Walter et al., 1991; Weissenfels et al., 1990; Westgate et al., 1995; Wodzinski and Coyle, 1974). The physiochemical factors of soils that determine the suitability of soil environment as microbial habitats and sites of hydrocarbon biodegradation are given in Table 2.1.

Initial contaminant concentration and acclimation period affect the overall biodegradation. If the initial hydrocarbon concentrations are very high, they may be toxic to native biota. Microorganisms exist in soils and sediments previously exposed to petroleum compounds can degrade hydrocarbons at greater rates than microorganisms isolated from soils with no contamination history. Once hydrocarbon contamination occurs, *in situ* microbial communities require certain acclimation period before metabolizing the hydrocarbons. During this acclimation period, favorable conditions (e.g. oxygen availability, soil moisture, and nutrients) will facilitate microbial growth and growth-associated hydrocarbon degradation (Rathbone et al., 1998).

Table 2.1. Physical and chemical characteristics of soils as microbial habitats (Bossert and Bartha, 1984).

Parameters	**Soils**
Expanse	21% of the global surface
Temperature	-40°C to 65°C
pH	2.5 to 11.0; most soils are slightly acidic
Water potential	-100 MPa to -0.001 MPa
Salinity	From near zero to salt saturation, but low in majority of soils
Oxygen availability	Adequately oxygenated except when water logged
Inorganic nutrients	N and P frequently are limiting
Organic matter	Relatively abundant but consisting mostly of refractory humic substances
Attachment surfaces	Great abundance of inorganic and organic surfaces

Oxygen availability

The initial steps in hydrocarbon degradation are oxygen dependent (Paul and Clark, 1996). Studies on the oxygen requirement for hydrocarbon degradation are many and they are supportive of an absolute oxygen requirement for significant biodegradation activity (Grady et al., 1989; Jobson et al., 1972). Oxygen depletion leads to reduced hydrocarbon degradation in soils. Oxygen consumption of oil-amended soils was found to be a reliable measure of oil degradation (Grady et al., 1989). Studies on oil-impregnated soils consistently showed the highest rates of oil degradation when aeration was maximized (Bouchez et al., 1995; Dunn, 1968; Goswami and Singh, 1991).

The oxygen present in soil depends on the total amount of air-filled pore space, the size of the pores, the rate of oxygen consumption, and the geometric distribution of oxygen-consuming soil layer. Large amounts of air-filled pore space and large pores insure high oxygen reserves and a rapid replacement of oxygen by diffusion. Elimination of air-filled pore space, for instance, by water logging, reduces soil-oxygen reserves to a small amount dissolved in the soil solution. In fine-textured heavy clay soils, the small size of the pores slows oxygen diffusion. Large amounts of rapidly utilizable organic substrates, including hydrocarbons, tend to deplete the oxygen reserve of the soil, especially if small pore spaces or a high degree of water saturation slows oxygen replacement by diffusion. The rate of oxygen diffusion to deeper part of the layers decreases as the thickness of overlying oxygen-consuming soil layers increases. The upper few centimeters of a hydrocarbon-contaminated soil may remain aerobic while its deeper layers become anoxic.

Moisture availability

Moisture is essential to active life processes, but too much moisture in soil interferes with the availability of oxygen (Griffin, 1980; Harris, 1980; Sommers et al., 1980; van Gestel et al., 1993; West et al., 1992; Wilson and Griffin, 1974). In general, the moisture status of a soil is expressed as a percentage of its moisture-holding capacity. At 100% saturation, all available pore spaces are filled with water. At 10% of the soil water-holding capacity, osmotic and matric forces reduce the availability of water to microorganisms to a degree that metabolic activity becomes marginal. However, oxygen transfer is enhanced when soil moisture is low. Moisture content between 50 and 80% of the water-holding capacity is considered optimal for aerobic microbial activities (Paul and Clark, 1996). The partial coating of soil surfaces by hydrophobic hydrocarbons reduces the water-holding capacity of the soil. Moreover, methods to measure soil moisture may be less accurate because of the hydrocarbons that are present. The presence of vegetation may decrease the moisture content

because the roots take up water and transpire it. In general, there is a significant moisture gradient with respect to soil depth (Davidson et al., 1963; Green et al., 1970; Holmes and Colville, 1970). However, it is difficult to trace moisture gradient in soil columns contaminated with petroleum hydrocarbons because of the presence of two different liquid phases: *nonaqueous phase* and *aqueous phase.*

Diversity and activity of microorganisms

Comprehensive knowledge of the diversity of indigenous microbial communities and their activities is considered important when assessing the strategy and outcome of bioremediation; yet little is known about the components of functional diversity responsible for degradation of hydrocarbons in field situations. The degradation of hydrocarbons is facilitated by communities of numerous functional microbial populations, and therefore, microbial composition determines the degradative potential and success of any bioremediation project. A wide range of techniques that examine morphological and physiological properties of isolated pure cultures are available to identify components of microbial communities, but these methods are not definitive in terms of description of functional diversity (Paul and Clark, 1996; Rathbone et al., 1998).

Diversity measures in the terrestrial environment are limited by taxonomy and methods. Microbial communities can be considered functional units that can be characterized by the sum of their metabolic properties. Therefore, substrate utilization patterns of the entire community should result from the taxonomic diversity and the abundance of each taxon. The Automated Microbial Identification System, developed by Biolog® Inc. (Hayward, CA) for rapid identification of pure cultures, has been shown to be useful in the characterization and classification of heterotrophic microbial soil communities (Garland and Mills, 1991; Rathbone et al., 1998).

Soil organic matter

Microbial growth in the soil environment usually is limited by organic carbon. Some of the organic carbon in soil is humified and not readily available for mineralization (Haines and Alexander, 1974; Herbes and Schwall, 1978). In case of soils contaminated with petroleum hydrocarbons, a nitrogen-free carbon source, nitrogen and eventually phosphorus become limiting in the buildup of microbial biomass, and thus limit biodegradation (Bossert and Bartha, 1984). Hydrocarbons partition to soil organic matter, and once they are sorbed their degradation may be dependent on the rate at which these chemicals desorb into the aqueous phase (Banwart et al., 1982; Carmichael and Pfaender, 1997; Karami-Lotfabad et al., 1996; Liu and Amy, 1993; Means et al., 1980; Sposito, 1989). Hence, soil organic matter plays an important role in hydrocarbon degradation. The presence of vegetation may increase the soil organic matter content by releasing root exudates.

2.1.7. Fate and transport of jet fuel in soils: Previous studies

The US Air Force is now in the process of changing operations at its installations within the continental US to use JP-8 in place of JP-4. This changeover has required the alteration of many environment-impact estimates. There are few studies conducted on fate and environmental effects of JP-4 and JP-8. Results of experiments conducted in aquatic systems indicate that evaporation was the major loss for low molecular weight hydrocarbons in JP-4 and JP-8 (Spain and Somerville, 1985; Dean-Ross et al., 1992). An experimental study on fate of JP-8 in soil showed that higher molecular-weight hydrocarbons were removed significantly faster in soils with indigenous microbial populations than in sterile soil (Dean-Ross et al., 1992). Similar study on fate of JP-4 in soil concluded that biodegradation contributed to the removal of the higher molecular-weight fraction of JP-4 from soil (Dean-Ross, 1993). The above two studies suggest that for the less-volatile hydrocarbons, manipulation of conditions to enhance biodegradation may increase their rate of removal

from the terrestrial environment. Results of a study on the biodegradation of JP-4 in a contaminated aquifer indicate that biodegradation was compound-specific (Aelion and Bradley, 1991).

2.2. OBJECTIVES

The overall objective of this research project was to assess the fate and transport of jet fuel, JP-8, in laboratory soil systems with plants. Specific objectives of this portion of the project were to

1. differentiate between abiotic and biotic removal of JP-8 in soils and
2. determine the effects of plant-induced water movement on fate and transport of JP-8 in soils.

2.3. EXPERIMENTAL SECTION

An accidental spill/leakage of JP-8 near the soil surface (unsaturated zone) and near the water table (subsurface, saturated zone) were simulated. Three vegetated systems were used to study the fate of JP-8 in the presence of vegetation: a two-channel system, a four-column system, and a nine-column system. Two unvegetated systems were used as control systems to study the fate of JP-8: one-column system:1 and one-column system:2. The soil systems were contaminated with jet fuel (JP-8). The two-channel and four-column systems were used as preliminary study systems to assess the fate of JP-8 near the soil surface and the toxic effects of JP-8 on vegetation. One-column system:1 was used as a control to assess the abiotic fate of JP-8 in soils without vegetation. The nine-column system was used to study plant transpiration effects on fate and transport of JP-8. One-column system:2 was used as a control to assess the transport and fate of JP-8 in soils without vegetation. The physical properties of JP-8 are presented in Table 2.2.

Table 2.2. Properties of jet fuel (JP-8) (Mayfield, 1996).

Property	
Specific Gravity	0.775 to 0.840
Color	Light Yellow
pH	~ 7.0
Vapor Pressure	5 mm of Hg (at 20°C)
Hydrocarbon Grouping	
Aromatics	25% (by volume)
Distillation Boiling Point	
Initial (°C)	159.5
Final (°C)	263.5
Average (°C)	215.2
Freezing Point (°C)	-48
Flash Point (°C)	56
Kinematic viscosity (mm^2/sec)	8 (at -20°C)

2.3.1. Two-channel system

For this experimental study, a large chamber with 25-mm-thick slate walls used in a previous biodegradation experiments was chosen. The chamber was 40 cm wide, 90 cm long, and 35 cm deep. The chamber was divided along the axial length into two equal halves, each with a width of 20 cm. Each half was divided further by a 78-cm long wall into two halves, each with a width of 10 cm. Thus, the chamber consisted of two U-shaped channels with dimensions 10 cm in width, 35 cm in depth, and 180 cm in axial length with inlet and outlet holes at 5 cm from the bottom (Figure 2.2). The chamber was equipped with eight 40-W fluorescent lights 35 cm from the soil surface and maintained at room temperature (~25°C). The chamber construction and schematic details can be found elsewhere (Narayanan, 1994;

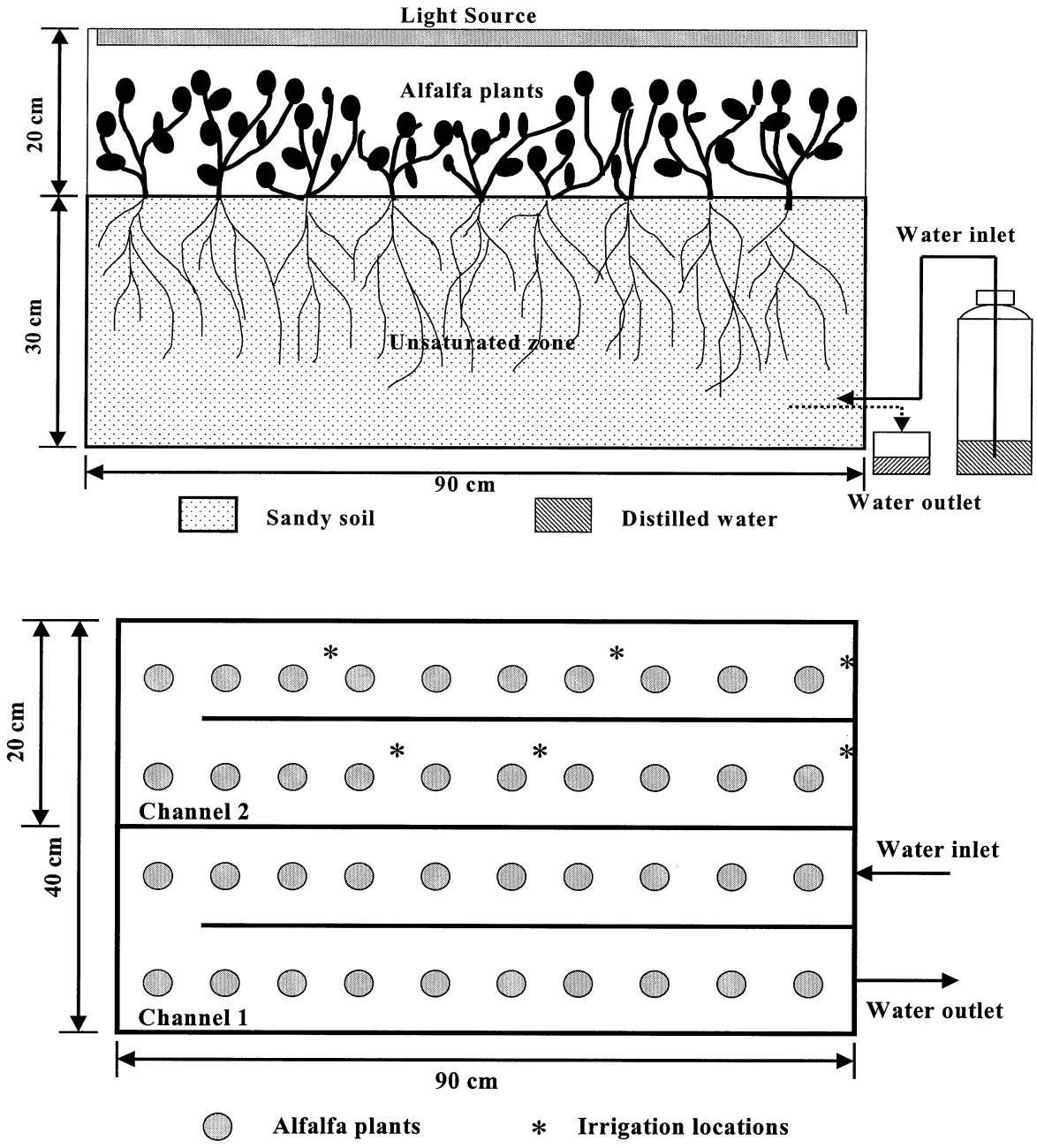

Figure 2.2. Schematic of two-channel system.

Narayanan et al., 1995; 1999). The channels were filled with sandy soil collected from near a landfill in Riley County, Kansas. The depth of soil in the channels was 30 cm. The soil physical and chemical properties are given in Table 2.3.

Table 2.3. Physical and chemical properties of soil in two-channel system. The bulk density of soil was 1.3 g/cm^3 (Narayanan, 1994).

Soil Property	**Top soil (0-10 cm)**		**Middle Soil (10-20 cm)**		**Bottom Soil (20-30 cm)**	
	Channel		**Channel**		**Channel**	
	1	**2**	**1**	**2**	**1**	**2**
pH	7.4	6.6	6.7	5.9	6.6	6
Texture						
Sand (%)	82	90	88	90	90	90
Silt (%)	16	8	10	8	8	8
Clay (%)	2	2	2	2	2	2
Extractable						
NO_3^--N (mg/kg)	4.3	1.4	0.4	0.4	0.3	0.4
Extractable						
NH_4^+-N (mg/kg)	8.1	4.9	1.8	2.1	1.0	5.3
Bray P (mg/kg)	35	26	51	33	37	27
Organic Carbon (g/kg)	11	10	6	7	6	6

[Data from samples taken in March 1999]

The soil had been contaminated with toluene, phenol, and trichloroethylene (TCE) in earlier studies (Narayanan, 1994; Narayanan et al., 1995; 1999). Channel 1 was fed with water

contaminated with 260 μmol of TCE and channel 2 was fed with water contaminated with 105 μmol of TCE. After a long period of drying to volatilize TCE, gas and soil TCE measurements were made. The soil water TCE concentration was <10 μmol/L in October 1998. The gas and soil monitoring indicated that 99% of TCE was gone by December 1998. Alfalfa (*Medicago sativa*) plants (nine plants in each row) were established in the two-channel system five years before the experiment started.

Irrigation for channel 1 entered at 5 cm from the bottom of the inlet end of the U-shaped channel. A graduated reservoir with a capacity of 5 L was used to supply water. The water level in the reservoir was raised to allow natural flow of water through a nylon tube. Occasional plugging at the inlet was observed and rectified daily as needed. Leachate, if any, was collected from the outlet. The total amount of leachate collected was 350 mL over seven-month period that occurred only four times. Channel 2 was irrigated by four open-ended drip tubes along with one each at inlet and outlet ports. The open-ended tubes at inlet and outlet ports discharged water at 20 cm below soil surface and the other four tubes discharged water at 10 cm below soil surface. Each drip tube system consisted of two 50 mL syringes connected with a Y tube and tubing to a glass tube inserted 20 cm into the soil.

For channel 1, a siphon was set up from the 5 L reservoir such that there was a small head (approximately 3 cm) from channel inlet to outlet. The level of the 5 L reservoir was designed to create a water table at 27 cm below ground surface (~ 3 cm deep saturated zone). After the first day, the level had decreased to 3 L which was the static point of the outlet (no outflow). Water was added regularly, initially at 1 L/d, then at 2 L/d to produce a small amount of outflow and moisten the entire soil system. Water was added according to the water consumption rate by alfalfa plants with the goal of maintaining little or no saturated

zone. The wells in the channel were monitored to maintain this condition. Water consumption in two-channel system is provided in Table 2.4.

Table 2.4. Average daily water consumption in two-channel system for seven-month duration.

Month, 1999	Water Consumption, g/day	
	Channel 1	Channel 2
January	1020	1040
February	1340	950
March	1030	880
April	1100	1050
May	1000	980
June	960	1050
July	1000	1000

For the two-channel system, 3 ± 0.1 mL of JP-8 was added at 20 locations in each channel in December 1998 and again in January 1999. Approximate locations were near plants. Holes were pre-drilled in channels with a screwdriver. An 18 gage (1.4 mm, internal diameter) cannula was used to inject JP-8 starting at about 30 cm depth from the soil surface and gradually withdrawing to 5 cm. The holes were filled with the same soil to avoid any volatilization. After injection, both channels were surface irrigated with 2 L distilled water to assure a moist surface that would limit volatilization of JP-8. The jet fuel was assumed to be uniformly distributed with respect to depth from 5 to 30 cm.

2.3.2. Four-column system

Four glass cylinders 40 cm deep and 15 cm diameter were used in the study. The cylinders were filled with sandy soil, collected near the Riley County landfill, to a depth of 30 cm. The soil physical and chemical properties are given in Table 2.5. The soil was contaminated previously with TNT and then watered with toluene, and most recently had been exposed to jet fuel for several months. A graduated reservoir with a capacity of 5 L was used to supply water from the bottom to columns 1 and 2; columns 3 and 4 were surface irrigated. Water was added according to the water consumption rate by horseradish plants with the goal of maintaining little or no saturated zone. Columns 1 and 4 were kept unvegetated and columns 2 and 3 were planted with four horseradish plants in each. The columns were kept beneath eight 40-W fluorescent lights 20 cm from the soil surface and maintained at room temperature (~25°C).

Columns 1 and 4 received approximately 10 ± 0.1 mL of JP-8 in December 1998. Holes were pre-drilled in columns with a screwdriver and then an 18 gage (1.4 mm) cannula was used to inject 5 mL of JP-8 at two different locations. Injection began at about 30 cm depth from the soil surface and continued evenly while the cannula was withdrawn gradually to 5 cm. Another 10 ± 0.1 mL of JP-8 was injected using the same procedure into Columns 1 and 4 in January 1999. The jet fuel was assumed to be uniformly distributed with respect to depth from 5 to 30 cm.

The holes were filled with the same soil to minimize volatilization. Following the fuel injection in January, columns 1 and 4 were surface irrigated with 330 mL distilled water, equivalent to 2 cm depth over the entire surface. Columns 2 and 3 received about 20 ± 0.1 mL of JP-8 in January 1999. The method described above was repeated at four different locations in each column. Four horseradish (*Armoracia rusticana*) roots, cut to about 30 g

Table 2.5. Physical and chemical properties of soil in four-column system[1]. The bulk density of soil was 1.3 g/cm^3.

Soil Property	Top soil (0-10 cm)				Middle Soil (10-20 cm)				Bottom Soil (20-30 cm)			
	1	2	3	4	1	2	3	4	1	2	3	4
pH	5.7	5.8	5.3	6.3	6.1	5.9	5.6	6.5	5.9	5.7	5.8	6.7
Texture												
Sand (%)	90	88	88	88	90	92	92	90	94	94	94	96
Silt (%)	8	10	10	10	8	6	6	8	4	4	4	2
Clay (%)	2	2	2	2	2	2	2	2	2	2	2	2
Extractable												
NO_3^--N (mg/kg)	2.4	0.8	0.6	1.3	0.0	0.4	0.5	0.4	0.4	0.0	0.6	0.4
Extractable												
NH_4^+-N (mg/kg)	5.5	4.5	7.1	7.0	2.5	4.6	3.5	4.9	1.6	3.5	2.4	3.0
Bray P (mg/kg)	23	14	19	25	23	13	15	19	12	12	12	7
Organic Carbon (g/kg)	7	9	7	11	4	6	4	7	2	2	1	2
Water Content (g/g)	0.115	0.173	0.165	0.178	0.121	0.197	0.142	0.190	0.169	0.161	0.154	0.143

[1, 2, 3, 4 = column 1, 2, 3, and 4, respectively]

[1]Data from samples taken in May 1999.

wet weight were planted in column 2 and 3 on the same day of soil contamination. Following this, columns 2 and 3 were surface irrigated with 330 mL distilled water. Water consumption in four-column system is provided in Table 2.6.

Table 2.6. Average daily water consumption in four-column system for five-month duration.

Month, 1999	Water Consumption, g/day			
	Column 1	Column 2	Column 3	Column 4
January	45	70	80	80
February	15	75	85	75
March	40	85	80	80
April	25	50	80	85
May	10	50	80	80

2.3.3. Nine-column system

Nine polyethylene cylinders 50 cm deep and 15 cm diameter were used in the study. The cylinders were filled with sandy soil, collected near the Riley County landfill in Kansas, to a depth of 50 cm. The soil physical and chemical properties are given in Table 2.7. A graduated reservoir with a capacity of 1 L was used to supply water from the bottom to all columns. A constant water table was maintained at 10 cm from bottom.

Columns 1, 2, 3, 7, 8, and 9 were planted with eight alfalfa plants in each column. Columns 4, 5, and 6 were kept unvegetated. After three months, alfalfa (*Medicago sativa*) plants were infested by spider mites and died. The contaminated columns were planted with tall fescue grass (*Festuca arundinacea*) cuttings and uncontaminated columns were planted with shattercane sorghum seedlings. These uncontaminated columns were not experimental treatments but instead were used to minimize edge effects. The average water consumption

over the 12-month experimental duration was 140 mL/day in vegetated columns and 25 mL/day in unvegetated columns. These water consumption rates were used to calculate water velocity in vegetated and unvegetated columns. The surface of each column was 50 cm beneath the center of a 1000-W metal-halide lamp with a 120 cm wide 30 cm deep segmented parabolic reflector. Average irradiance at canopy level was 285 ± 25 W/m^2 (n = 9). Air was maintained at room temperature (-20°C). A fan (3400 rpm; 240 cfm) was used to provide gentle air circulation.

Table 2.7. Physical and chemical properties of soil in nine-column system. The bulk density of soil in each column was approximately 1.75 g/cm^3.

Soil Property	**Top Soil (0-10 cm)**	**Middle Soil (10-20 cm)**	**Bottom Soil (20-30 cm)**
pH	7.2	6.8	6.5
Texture			
Sand (%)	80	90	92
Silt (%)	18	8	6
Clay (%)	2	2	2
Extractable			
NO3 -N (mg/kg)	2.8	3.8	0.4
Extractable			
NH_4^+ -N (mg/kg)	1.5	1.4	0.5
Bray P (mg/kg)	30	24	42
Organic Carbon (g/kg)	12	11	6

[Data from samples taken in November, 1999]

A contaminated zone, 5 cm deep, was created in columns 1, 2, 3, 4, 5, and 6. The soil was contaminated with approximately 25,000 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in November 1999. The bottom of the contaminated zone initially was 10 cm from the bottom of the column. In each column, 10 cm below and 35 cm above the contaminated layer was packed with clean soil. Approximately 500 g of soil was added in increments to the column and the column was tapped gently to allow uniform packing. Columns 7, 8, and 9 were filled with clean soil. Each column was saturated to field capacity initially, after which a 10 cm saturated zone was maintained at the bottom by adding water according to the water consumption rate by plants. A schematic of an experimental column is shown in Figure 2.3.

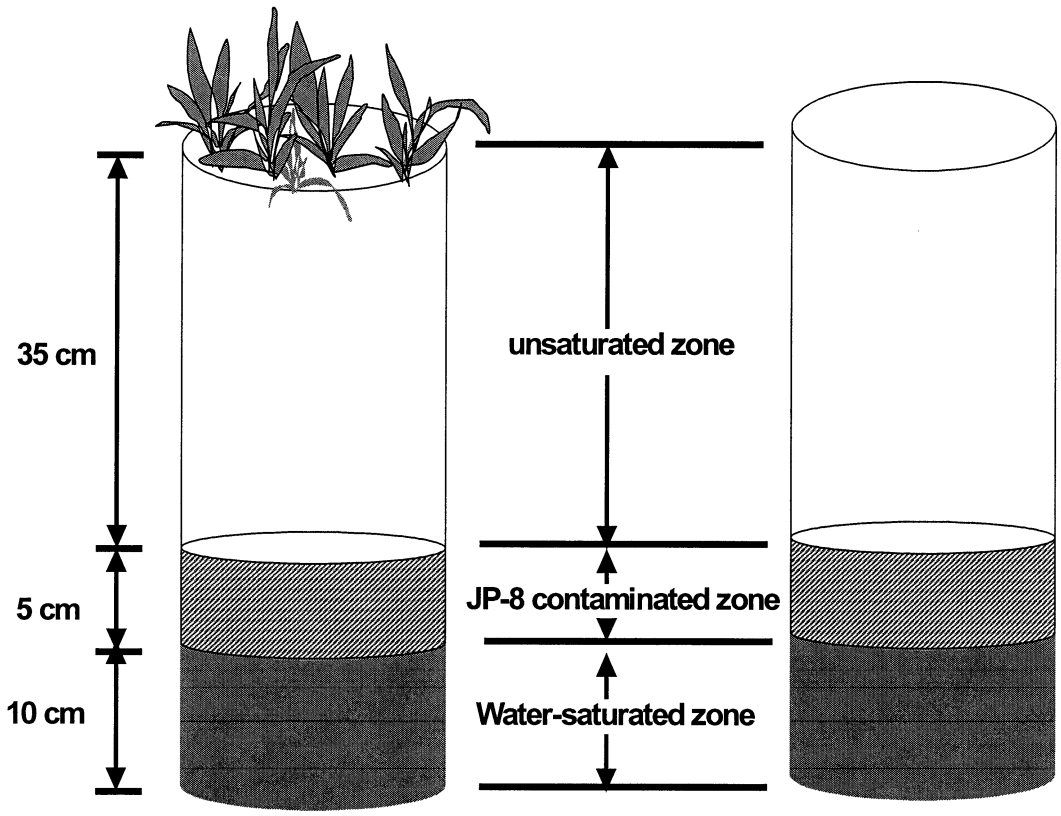

Figure 2.3. Schematic of experimental set up for nine-column system. Initial jet fuel concentration in the contaminated zone was 26,875 ± 1900 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (n=3).

2.3.4. One-column system:1

A 250-mL glass measuring cylinder cut off at 210 mL was used to conduct a separate study on the fate of JP-8 in air-dried soil. A known amount of JP-8 (10 ± 0.01 mL) was added at the bottom of the cylinder. The same soil as that used in the two-channel and four-column systems (Table 2.3) was packed uniformly to fill the cylinder to the 200 mL mark. The bulk density of the soil in this column was 1.43 g/cm^3. This column was kept in the laboratory for about 18 months, and the weight loss was recorded periodically. This column was treated as a control column to study the abiotic fate of JP-8, since microbial activity was minimized by maintaining an air-dry soil water content. The schematic of one-column system:1 is shown in Figure 2.4.

2.3.5. One-column system:2

A glass cylinder of 5 cm diameter and 60 cm height was used to conduct a separate study on the transport and fate of JP-8 in soil. A contaminated zone, 5 cm deep, was created such that the bottom of the contaminated zone was initially at 10 cm from the bottom of the column. The soil was contaminated with approximately 25,000 $mg_{JP\text{-}8}/kg_{dry\ soil}$. In the column, 10 cm below and 35 cm above the contaminated layer was packed with clean soil at an initial moisture content approximately at field capacity. The bulk density of the soil in this column was 1.65 g/cm^3. The column was wrapped in aluminum foil to avoid any algae growth and kept under ambient conditions. No water was added during the experiment. The schematic of one-column system:2 is shown in Figure 2.4.

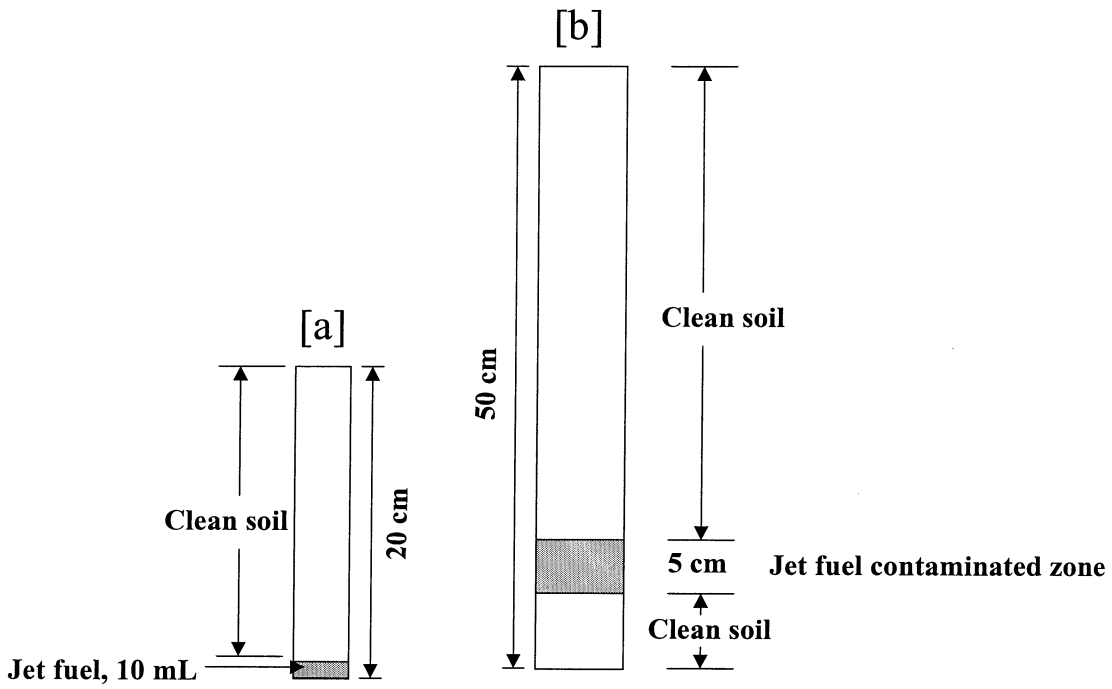

Figure 2.4. Schematic of (a) one-column system:1 and (b) one-column system: 2.

2.3.6. Sampling and analysis

For the two-channel system, plant tops were harvested every month and dry biomass was determined. In 1999, soil samples were collected in March (after three months), May (after five months), and July (after seven months). During the March sampling, a 0.9 cm diameter, 9 cm long brass cylinder was used to collect soil cores and a wooden plunger used to remove soil from the tube. Soil cores were taken at eight different locations in each row of each channel at three depths (from top): 0-10, 10-20, and 20-30 cm. A composite sample of the eight locations was made for each of three depths and two rows of the two channels. For the May sampling, a different sampling procedure was used. A 10 × 10 × 10 cm box was used to take soil cores at one location in only one row per channel at three depths: 0-10, 10-20, and 20-30 cm. Box samples were taken from the front row of each channel because of

convenience of taking samples. Composite samples were made for each depth and each channel. During the July sampling, a 0.9 cm diameter, 9 cm long brass cylinder with a wooden plunger was used. Soil cores were taken at nine different locations in each row of each channel. Three samples were taken at each depth, 0-10, 10-20, and 20-30 cm. A composite sample of the 18 locations was made for each channel. All samples were stored in a freezer at -4°C until analysis by gas chromatography (GC) in May 1999 and August 1999. Approximately 3 g of subsample was taken from the composite and used in total petroleum hydrocarbon (TPH) extraction procedure described later. The analysis was done in triplicate. Approximately 3 g of subsample was taken from the composite and used to determine gravimetric water content.

For the four-column system, a destructive sampling was done in May 1999 (after five months). Each column was divided into three segments (from top): 0-10, 10-20, and 20-30 cm. Soil from each segment was thoroughly mixed and a composite sample of about 500 g was taken and stored in a freezer at -4°C until analysis. Approximately 200 g of soil out of 500 g was sent to the soil testing lab for physical and chemical analysis. Approximately 3 g of sub sample (in triplicate) was taken from each composite and used in the TPH extraction. Approximately 3 g of subsample was taken from the composite and used to determine gravimetric water content.

For the nine-column system, plants were harvested every month and dry biomass was determined. A destructive soil sampling was done after three, eight, and twelve months. A column of each treatment and one control was sacrificed for destructive sampling for the first sampling and a column of each treatment was sacrificed for the second and third sampling. Each column was divided into 10 segments (from top): 0-5, 5-10, 10-15, 15-20, 20-25, 25-30, 30-35, 35-40, 40-45, and 45-50 cm. Soil from each segment was mixed thoroughly and

a composite sample of about 500 g was taken and stored in a freezer at -4°C until analysis. Approximately 3 g of three subsamples were taken from each composite and used in the TPH extraction. Approximately 3 g of subsample was taken from the composite and used to determine gravimetric water content.

For the one-column system:1, a destructive sampling was done after 18 months. The column was divided into four segments (from top): 0-5, 5-10, 10-15, 15-20 cm. Soil from each segment was mixed thoroughly and a 3 g subsample was taken from each segment and used in the TPH extraction. Approximately 3 g of subsample was taken from the composite and used to determine gravimetric water content.

For the one-column system:2, a destructive sampling was done after 12 months. The column was divided into 10 segments (from top): 0-5, 5-10, 10-15, 15-20, 20-25, 25-30, 30-35, 35-40, 40-45, and 45-50 cm. Soil from each segment was thoroughly mixed and a composite sample of about 50 g was taken and stored in a freezer until analysis. Approximately 3 g of three subsamples were taken from each composite and used in the TPH extraction. Approximately 3 g of subsample was taken from the composite and used to determine gravimetric water content.

Extraction of petroleum hydrocarbons from soil was done by a mechanical shaking procedure, developed by Schwab et al. (1999). The procedure involved weighing approximately 3 g of soil in 20 mL scintillation vial with foil-lined cap, adding 10 mL of optima©-grade acetone (Fisher Scientific, St. Louis, MO) and a matrix recovery standard (tetracosane) (Fisher Scientific, St. Louis, MO), shaking for 30 min in a reciprocating platform shaker at 120 cycles/min, centrifuging for 10 min at 2100 rpm, and collecting supernatant in a 60 mL foil-lined cap bottle. This was repeated three times. The combined

extract was weighed and 1 mL of extract was transferred to a 2 mL GC vial along with an internal standard, androstane (Fisher Scientific, St. Louis, MO). A set of JP-8 standards were prepared with the same matrix and all GC vials were stored in the freezer at -4°C until analysis.

Analysis of the sample was performed on a 5890A gas chromatograph (Hewlett-Packard, Avondale, PA) with chemstation© integration software and HP7673A auto sampler. The 5890A GC was equipped with a flame ionization detector (FID). The GC utilized a DB-TPH column (J & W Scientific, Folsom, CA). The column was designed specifically for analysis of total petroleum hydrocarbons, had dimensions of 0.32 mm inside diameter, a 30 m length, and 0.25 μm film thickness. The fuel and carrier gas was H_2 (99.999%). The carrier gas was delivered at 4.0 mL/min and the fuel gas at 40 mL/min. The make-up gas was N_2 (99.999%) at a flow rate of 32 mL/min. A support gas of zero-grade air was delivered at 420 mL/min. The temperature program began at 40°C for 2 minutes, increased at 12°C/min to 320°C, and was held at 320°C for a minute. The injection port and detector temperatures were 250°C and 350°C, respectively. The injection volume was 2 μL splitless. The detection limit of the method was 100 $mg_{TPH}/kg_{dry\ soil}$. Values below the detection limit were assigned a value of 50 $mg_{TPH}/kg_{dry\ soil}$ in finding the mean value.

Gravimetric water content of a sample was measured by weighing the moist sample, drying it in an oven at 105°C for 24 h to remove the water, and reweighing it. The water content was expressed as g of water/g of dry soil.

2.4. RESULTS AND DISCUSSION

2.4.1. Plant production in the contaminated soil

In general, alfalfa growth was not affected by jet fuel contamination. The above-ground dry biomass production in the two-channel system varied from 70-110 $g/m^2/30$ days which corresponds to 7-11 Mg/ha/yr. The above-ground dry alfalfa production in the nine-column system varied from 30-50 $g/m^2/30$ days. In Kansas, alfalfa production of 20 Mg/ha/yr is considered to be a good yield under field conditions. The plants were grown under growth chamber conditions and lighted by artificial lights with relatively lower irradiance, which resulted in the lower yield. The growth of fescue grass also was not affected by JP-8. The above-ground dry grass production in the nine-column system varied from 15-25 $g/m^2/30$ days. The dry-matter production was reasonable and grass and alfalfa plant conditions showed no visible effect from JP-8 in soil.

2.4.2. Total petroleum hydrocarbons: One-column system:1

For the column with air-dried soil, the JP-8 concentration measured in each segment after 18 months was converted to mass of JP-8 for each segment by multiplying the concentration by weight of each segment. Then the mass of JP-8 in each segment was added up for the whole column, which was about 3900 mg. This amount of JP-8 corresponds to about 4.8 mL JP-8 present after 18 months. This corresponds to a 52% reduction in JP-8 over a period of 18 months. The mean gravimetric water content of soil in this system after 18 months was 0.0665 ± 0.001 g/g. If air-dried soil was assumed not to facilitate microbial growth, this dry-soil system can be considered as a control that facilitated minimal microbial activity. This implies that about 52% of jet fuel was lost by abiotic processes such as volatilization and diffusion and biotic losses such as biodegradation over 18 month period. Periodic weight measurements also indicated 25% losses in five months, which will be used for comparison with other study systems. We can conclude that if the JP-8 reduction in the other soil

columns was more than 52% after 18 months or 25% after five months, other than abiotic processes are responsible; that is, biodegradation has occurred.

2.4.3. Total petroleum hydrocarbons: One-column system:2

Initially, the overall mass of JP-8 and natural hydrocarbons in one-column system:2 was 4230 mg. The mass of JP-8 after twelve months was 3160 mg. The overall reduction in JP-8 based on initial JP-8 mass was only 25%. The contaminated zone of this column was measured to be 4020 mg of JP-8. After twelve months, the mass of JP-8 in the contaminated zone was 1115 mg. The loss of 2915 mg from the contaminated zone included 1830 mg that moved downwards, 210 mg of JP-8 that moved upwards, and 865 mg that was lost due to abiotic and biotic losses. This column initially was saturated with water to field capacity, and after that, water was not added. The average gravimetric water content of soil in this system after 12 month was 0.105 ± 0.004 g/g. Initially, biodegradation could be facilitated by water present in the column. So, this column cannot be treated as an abiotic control column. However, this column could be treated as no-maintenance column. The total loss in this no-maintenance column was about 25%. Volatilization losses were minimized as the column was saturated initially. About 45% of JP-8 was transported downwards and only 5% was recovered above the contaminated zone. The JP-8 transported upwards was due to diffusion and capillary rise of JP-8 in soil. The amount could be higher than 5% as the biotic and abiotic losses are not included here.

2.4.4. Total petroleum hydrocarbons: Two-channel system

Channel 1: bottom-irrigated

After three months, the mean concentration in the front row of channel 1 was 215 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in top 10 cm, 1250 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 10-20 cm, and 400 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 20-30 cm (Figure 2.5). The jet-fuel concentration estimated at the beginning of the experiment was

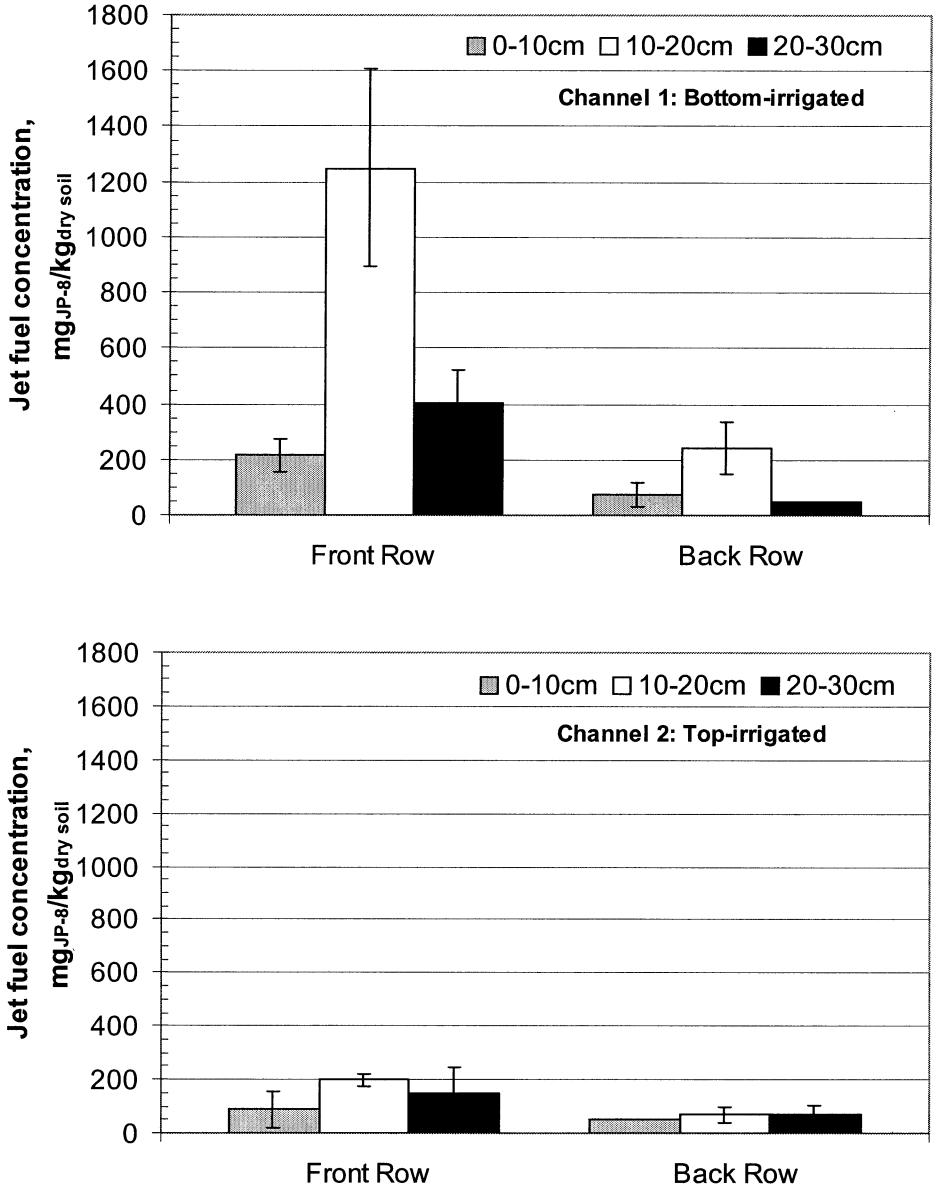

Figure 2.5. Total petroleum hydrocarbon concentration in two-channel system during March 1999 (after three months) for different depths from the soil surface. Error bars represent ± standard deviation, from the mean (n=3).

approximately 820 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in top 10 cm and 1650 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in the middle and bottom 10 cm soil layers. The reduction in jet-fuel concentration in the front row of channel 1 varied from 76% (20-30 cm) to 24% (10-20 cm). The back row of channel 1 had 75 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 0-10 cm, 240 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 10-20 cm, and 50 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 20-30 cm. The reduction in jet-fuel concentration in the back row of channel 1 varied from 97% (20-30 cm) to 85% (10-20 cm). The gravimetric water content was higher in the back row of channel 1 than that of the front row during this sampling period (Table 2.8). This higher moisture content was caused by the back row being closer to the subsurface water inlet might have facilitated microbial degradation of jet-fuel compounds. After five months, the reduction in the front row of channel 1 varied from 93% (20-30 cm) to 55% (10-20 cm) (Table 2.9).

Table 2.8. Gravimetric water content in two-channel system after three months.

	Gravimetric water content (g of water/g of dry soil)		
	0-10 cm	**10-20 cm**	**20-30 cm**
Channel 1 (front row)	0.116	0.166	0.187
Channel 1 (back row)	0.183	0.199	0.187
Channel 2 (front row)	0.121	0.149	0.151
Channel 2 (back row)	0.114	0.138	0.140

Table 2.9. Total petroleum hydrocarbon concentration in the two-channel system after five months. Presented are means and standard deviations of three samples.

	Total Petroleum Hydrocarbons ($mg_{JP\text{-}8}/kg_{dry\ soil}$)		
	0-10 cm	**10-20 cm**	**20-30 cm**
Channel 1 (front row)	75 ± 30	735 ± 115	110 ± 50
Channel 2 (front row)	50 ± 0	130 ± 70	80 ± 35

Channel 2: top-irrigated

The jet-fuel concentration estimated at the beginning of the experiment was approximately 820 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in top 10 cm and 1650 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in the middle and bottom 10 cm soil layers. After three months, the mean jet-fuel concentration in the front row was 90 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in the top 10 cm, 200 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 10-20 cm, and 150 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in 20-30 cm (Figure 2.5). The reduction in jet-fuel concentration in the front row of channel 2 varied from 91% (20-30 cm) to 88% (10-20 cm), and 96% (10-20 cm; 20-30 cm) to 94% (0-10 cm) in the back row (Figure 2.5). The relative uniformity between JP-8 reduction of the front and back rows may be explained by the more uniform application of irrigation water by the subsurface drip system. After five months, the reduction in jet fuel concentration from the concentration at the beginning of the experiment in the front row of channel 2 varied from 95% (20-30 cm) to 92% (10-20 cm). Almost all JP-8 reduction occurred in the first three months.

2.4.5. Total petroleum hydrocarbons: Four-column system

The jet-fuel concentration estimated at the beginning of the experiment was approximately 1390 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in top 10 cm and 2780 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in the middle and bottom 10 cm soil layers. The jet-fuel concentration after five months was 100 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in top 10 cm, 180 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in middle 10 cm, and 525 $mg_{JP\text{-}8}/kg_{dry\ soil}$ in bottom 10 cm of column 1 (Figure 2.6). Similar results were found in column 4. In general, the jet-fuel concentrations in the top 10 cm were below method detection limits (Figure 2.6).

Columns 2 and 3 had the highest jet-fuel concentration in the middle 10 cm. Plant degradative enzymes such as peroxidases can be found external to the horseradish plants (Dec and Bollag, 1994). A greater variety of active plant enzymes has been found in sediments far away from their plant source (Schnoor et al., 1995). The result of the action

of oxidoreductases such as peroxidases on jet-fuel contaminants is often the polymerization of the compounds either onto the root surface or into the soil humic fraction. These polymeric complexes are often referred to as bound residues that are not available for microbial degradation. This might have resulted in higher measured total petroleum hydrocarbon concentrations in the middle 10 cm.

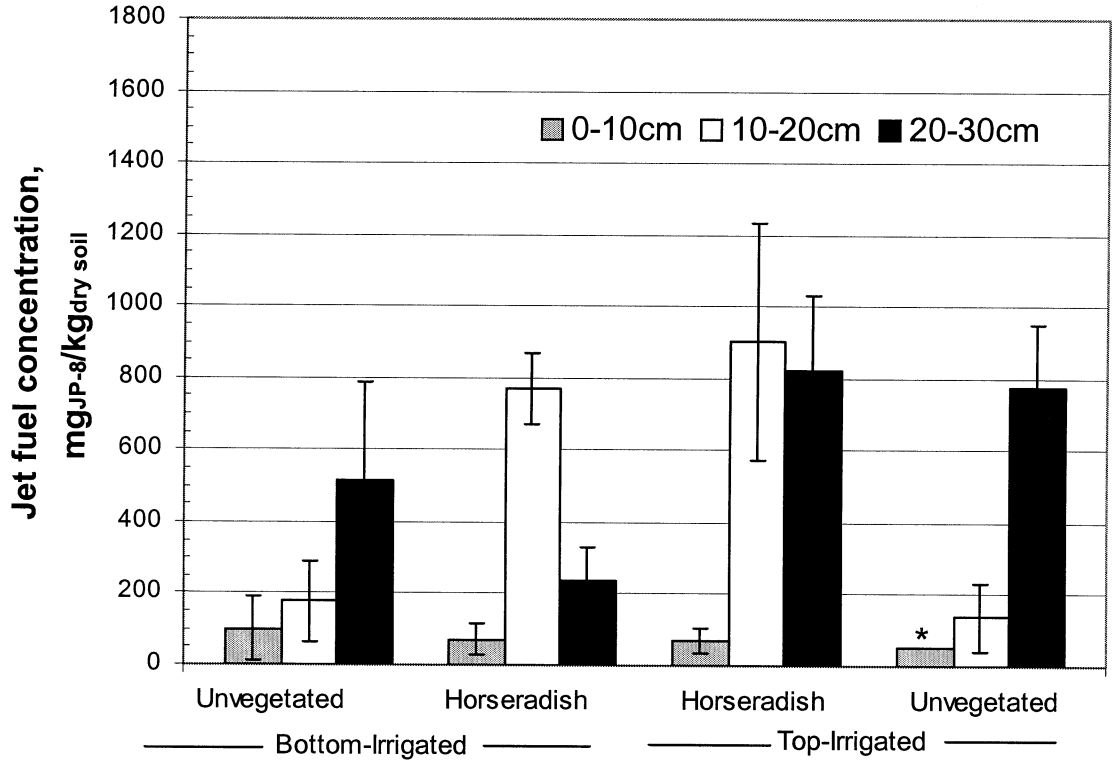

Figure 2.6. Total petroleum hydrocarbon concentration in four-column system during May 1999 (after five months) for different depths from the soil surface. Error bars represent ± standard deviation, from the mean (n=3). [Note: the error bar is not shown where all concentrations were nondetectable].

The jet-fuel concentration increased with depth for columns 1 and 4 that were unvegetated. In all cases, jet-fuel concentrations at the deeper soil profile were higher than the top 10 cm. This might be due to unfavorable conditions, such as low oxygen levels at deeper soil profiles, that may not facilitate biodegradation and/or other losses of jet fuel from the soil system. Unfortunately, most of the leaking of jet fuel and other petroleum hydrocarbons reaches deeper soil profiles, which makes cleaning those soils very difficult. Plants can create favorable root environments for microbial degradation in those zones by enhancing oxygen supply, providing other nutrients, and altering the soil-water environment via water uptake.

2.4.6. Analysis: JP-8 surface spills (unsaturated conditions)

The two-channel system and four-column system used to study JP-8 surface spills were different from one another in size, shape, and irrigation method. Also, facilities were not available for treatment replication. Hence, statistical comparisons among the treatments cannot be made. However, comparisons can be made by relating measured JP-8 losses to the observed conditions of each system without testing for statistical significance. On this basis, conclusions made from this portion of the study are observational.

Abiotic vs. biotic

Reduction of JP-8 (expressed as a percentage from initial contamination concentration after five months) for two-channel system and four-column system was compared with the "abiotic" control which had a 25% reduction after five months and a 52% reduction after 18 month (one-column system:1). The two-channel system included two treatments: 1) alfalfa, drip-irrigated and 2) alfalfa, bottom-irrigated, and the four-column system included four treatments: 3) horseradish, top-irrigated; 4) horseradish, bottom-irrigated; 5) unvegetated, top-irrigated; and 6) unvegetated, bottom-irrigated. The drip-irrigated treatment was

considered to be top-irrigated. All these six treatments were considered biotic treatments (Figure 2.7). The mean reduction calculated for all biotic treatments after five months was 86% ± 6%. The mean of managed biotic treatments (86%) was approximately 10 standard deviations greater than the abiotic treatment (25%). Biotic treatments received water throughout the five-month duration according to either evaporation or evapotranspiration demand. The air-dried treatment did not receive any liquid water, only water vapor from ambient air. Clearly, biotic removal processes occurred in the two-channels and the four columns.

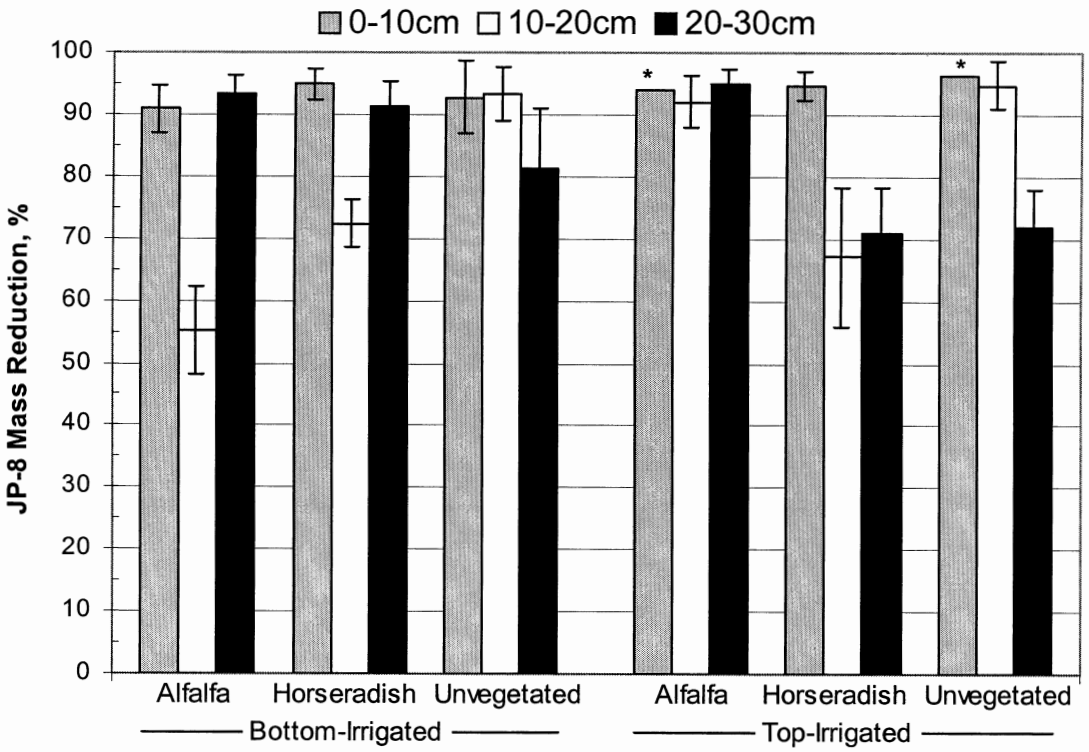

Figure 2.7. Jet fuel mass reduction in two-channel and four-column systems after five months. Error bars represent ± standard deviation, from the mean (n=3). [Note: the error bar is not shown where all concentrations were nondetectable].

Top-irrigated vs. bottom-irrigated

Reduction of JP-8 (expressed as a percentage from initial contaminant concentration after five months) was compared for top-irrigated and bottom-irrigated treatments in the two-channel and four-column systems (Figure 2.7). Six treatments of irrigation and plant cover were studied: 1) top-irrigated, alfalfa; 2) top-irrigated, horseradish; 3) top-irrigated, unvegetated; 4) bottom-irrigated, alfalfa; 5) bottom-irrigated, horseradish; and 6) bottom-irrigated, unvegetated. The mean percent reduction for top-irrigated treatments was 86% ± 8% compared to 85% ± 5% for bottom-irrigated treatments. Irrigation method did not appear to affect overall levels of JP-8 removal.

Vegetated vs. unvegetated

To make comparisons with vegetated and unvegetated treatments, reduction percentage from initial contaminant concentration after five months for two-channel and four-column system was calculated (Figure 2.7). Vegetated treatments included four treatments: 1) alfalfa, top-irrigated; 2) alfalfa, bottom-irrigated; 3) horseradish, top-irrigated; and 4) horseradish, bottom-irrigated. Unvegetated treatment included two treatments: 5) unvegetated: top-irrigated and 6) unvegetated, bottom-irrigated. The mean percent reduction for unvegetated treatments was 88% ± 1% compared to 84% ± 7% for vegetated treatments. Vegetation appears to have no effects on overall levels of removal in this study, but more-controlled study would be necessary to determine if this difference is significant.

Alfalfa vs. horseradish

Reduction of JP-8 (expressed as percentage from initial contaminant concentration after five months) for alfalfa was compared against horseradish treatments in the two-channel and four-column systems (Figure 2.7). Alfalfa treatment included two treatments: 1) alfalfa,

top-irrigated and 2) alfalfa, bottom-irrigated. Horseradish treatment included two treatments: 3) horseradish, top-irrigated and 4) horseradish, bottom-irrigated. The mean percent reduction for alfalfa treatments was 87% ± 10% compared to 82% ± 6% for horseradish treatments. The mean of alfalfa treatments was greater than the mean of horseradish treatments. The relative difference among vegetation types appears not to be significant; more-controlled study would be necessary to determine if this difference is significant.

2.4.7. Total petroleum hydrocarbons: Nine-column system

Jet-fuel concentration profile

Figure 2.8 shows the concentration profile in the vegetated column after three, eight, and twelve months. Initial concentration measured in the contaminated soil used for the contaminate zone was 26,875 ± 1900 $mg_{JP\text{-}8}/kg_{dry\ soil}$. The concentration in the contaminated zone was 10,120 ± 2145 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (62% reduction) after three months and was further decreased to 9650 ± 1650 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (64% overall reduction) in the next five months. After a year, the concentration in the contaminated zone was decreased to 9040 ± 875 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (66% overall reduction). The concentration in the contaminated zone of unvegetated column was 9715 ± 980 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (64% reduction) after three months (Figure 2.9). The concentration in the contaminated zone further decreased to 9280 ± 745 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (65% overall reduction) in the next nine months (Figure 2.9).

It is evident that JP-8 was transported both upwards and downwards from the contaminated zone in both the vegetated and unvegetated columns (Figures 2.8 and 2.9). The upward movement of JP-8 could be due to capillary rise of JP-8 in soil pores as well as due to advection. The downward movement of JP-8 could be a result of gravitational forces and advection as well. Advection could have caused the transport of dissolved fraction of JP-8 upwards and downwards.

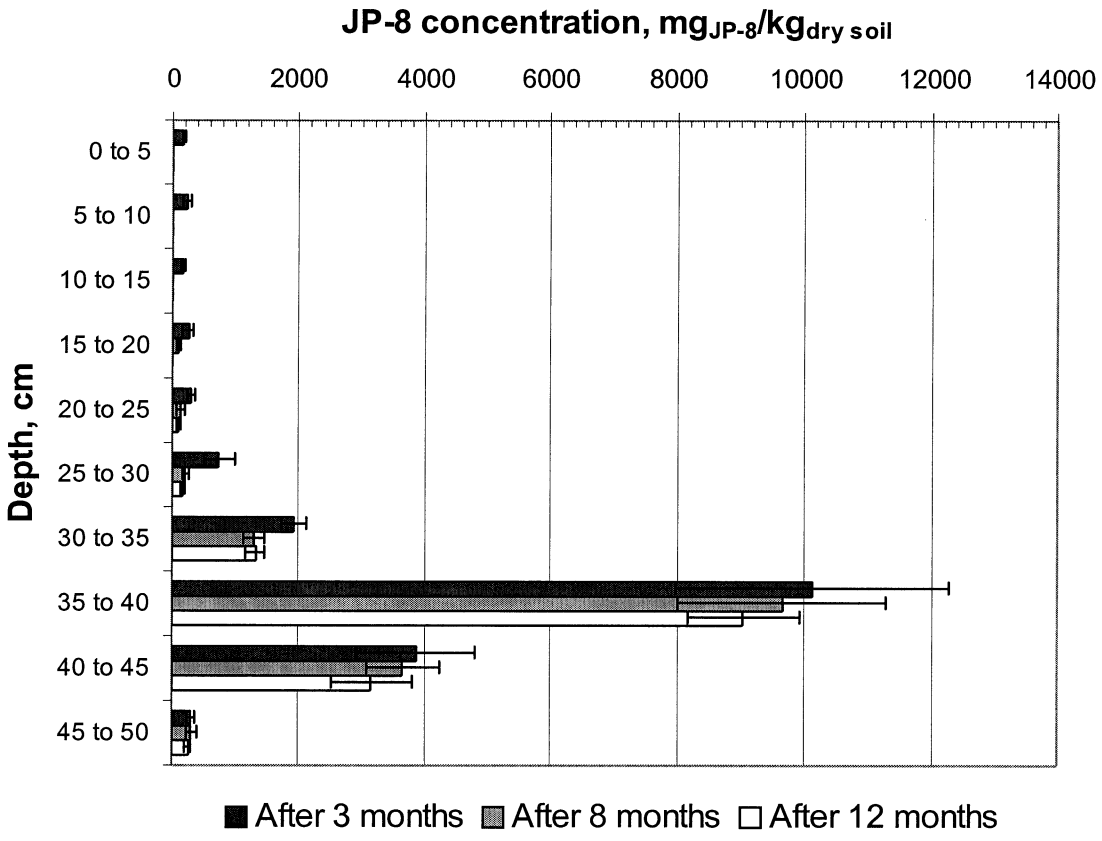

Figure 2.8. Jet-fuel concentration profile in the vegetated treatment (nine-column system) after three, eight, and 12 months. Initial contamination was 26,875 ± 1900 $mg_{JP-8}/kg_{dry\ soil}$ (n=3) in the 35-40 cm layer. Error bars represent ± standard deviation, from the mean (n=3).

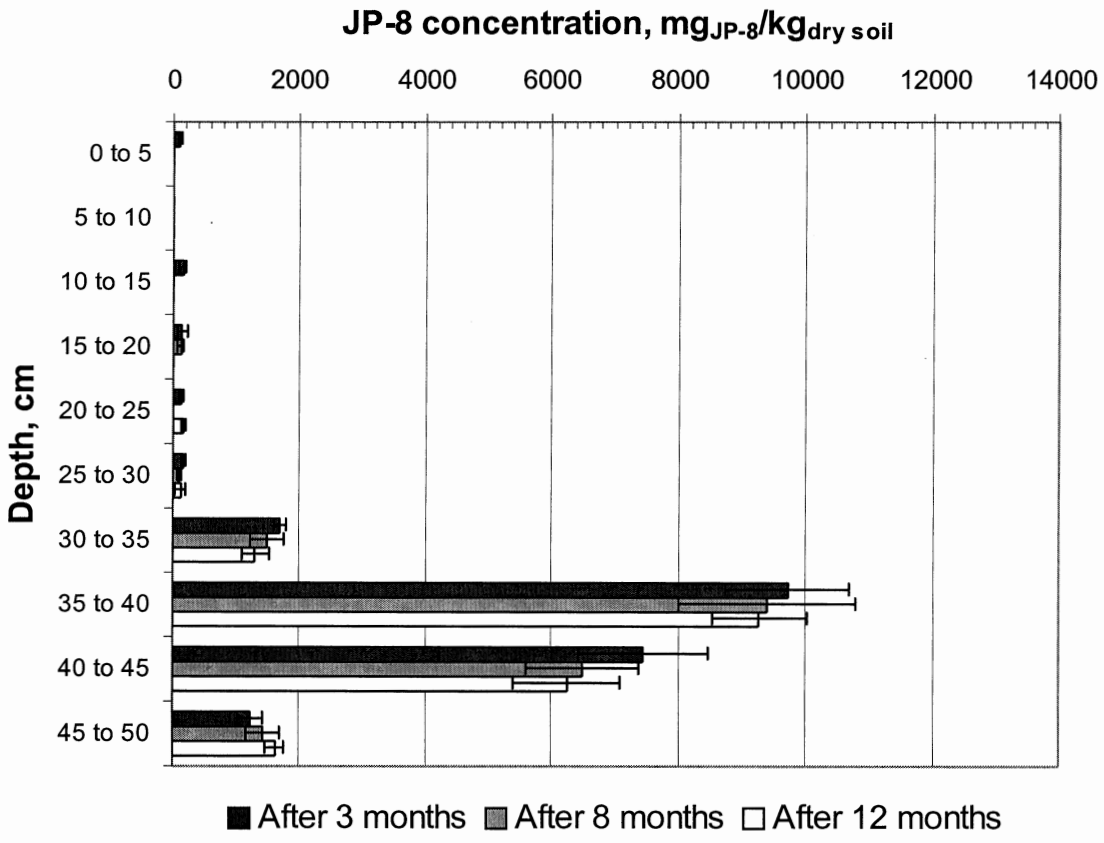

Figure 2.9. Jet-fuel concentration profile in the unvegetated treatment (nine-column system) after three, eight, and 12 months. Initial contamination was 26,875 ± 1900 $mg_{JP-8}/kg_{dry\ soil}$ (n=3) in the 35-40 cm layer. Error bars represent ± standard deviation, from the mean (n=3).

Jet-fuel mass reduction

Initial jet-fuel concentration in the contaminated zone was 26,875 ± 1930 $mg_{JP\text{-}8}/kg_{dry\ soil}$ (n=3). The clean soil also was extracted for hydrocarbon concentrations and the mean background concentration was 150 ± 50 $mg_{TPH}/kg_{dry\ soil}$. The concentration of jet fuel in each 5 cm layer, except the contaminated layer, was calculated by subtracting the background TPH concentration of clean soil from the observed GC results. Initially, the overall mass of JP-8 in each column was 42,350 mg. In the vegetated column, the mass of JP-8 was reduced to 27,100 mg (36% reduction) after the first three months, 23,000 mg (46% reduction) in the next five months, and 21,100 mg (50% reduction) in the next four months (Figure 2.10). In the unvegetated column, the mass of JP-8 was reduced to 31,100 mg (26% reduction) after three months, 28,550 mg (33% reduction) after eight months, and 28,100 mg (34% reduction) after 12 months (Figure 2.10).

In this study, there was a rapid reduction of JP-8 for the first three months followed by a slower decline for the next nine months (Figure 2.10). Mass transfer of contaminants from the NAPL phase to aqueous phase often is a rate-limiting step and is partially responsible for the tailing effect. Previous laboratory studies indicated that complete dissolution of an LNAPL pool may require hundreds or thousands of pore volumes of water (Borden and Kao, 1992; Hatfield and Stauffer, 1993; Hatfield et al., 1993; Powers et al., 1991; 1994a; 1994b; Whelan et al., 1994). Also, those studies observed high aqueous LNAPL concentrations during the initial period of time that included rapid decline of aqueous LNAPL concentrations later on (Anderson et al., 1992; Brusseau, 1992; Geller and Hunt, 1993; Imhoff et al., 1990; 1994; Pearce et al., 1994; Powers et al., 1991; Szlag and Illangasekare, 1992; 1993; 1994a; 1994b; Voudrias and Yeh, 1994). When NAPL is present, soil-phase (sorbed) contaminants may represent a small fraction of the total contaminant mass in soil and aquifer material (Borden and Piwoni, 1992; Johnson and Pankow, 1992; Malone et al.,

1993; Mayer and Miller, 1990; 1992; 1996). The majority of the contaminant mass in these systems typically is present in the NAPL phase. It is likely that the soluble fraction of NAPL pool was readily degraded in the first three months and subsequent degradation was limited by the rate of NAPL dissolution.

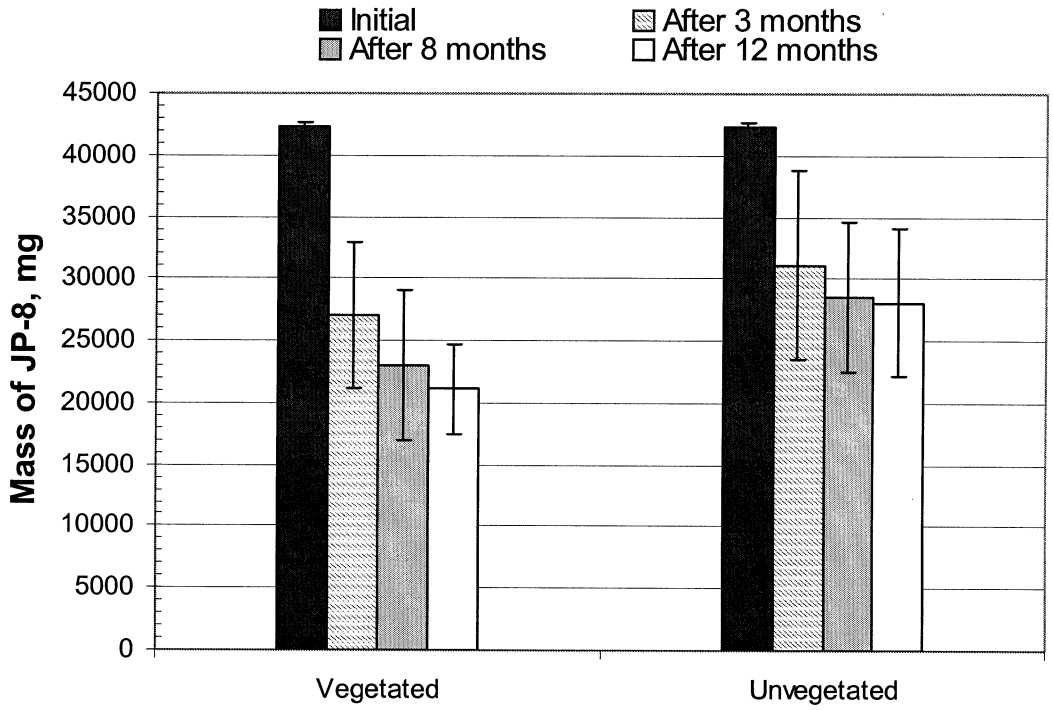

Figure 2.10. Mass of jet fuel reduction in the nine-column system during the 12 month period. Error bars represent weighted average standard deviations of 3 measures at each of 10 depths.

Jet-fuel mass movement from the contaminated zone: Vegetated column

Initially, the mass of JP-8 in the contaminated zone was 40,310 mg in both vegetated and unvegetated columns. The vegetated column had 15,180 mg in the contaminated zone after three months. This 25,130 mg loss of mass from the contaminated zone included 6240 mg of JP-8 contained in soils below this zone and 5660 mg in soils above this zone. The rest (13,230 mg) was lost from the whole column. The JP-8 mass in the vegetated column further decreased to 14,475 mg in the contaminated zone after eight months and 13,560 mg after 12 months. After eight months, 5930 mg of JP-8 was below and 2590 mg was above the contaminated zone, and 17,315 mg was lost due to abiotic and biotic losses from the column. After 12 months, 5115 mg of JP-8 was below and 2385 mg was above the contaminated zone, and 19,250 mg was lost due to abiotic and biotic losses from the column.

Jet-fuel mass movement from the contaminated zone: Unvegetated column

The unvegetated column had 14,570 mg in the contaminated zone after three months. The loss of mass from the contaminated zone, 25,740 mg, included 12,980 mg of JP-8 contained in soils below this zone, 3560 mg of JP-8 in soils above this zone, the rest, 9200 mg was lost from the whole column. The JP-8 mass in the unvegetated column further decreased to14,100 mg in the contaminated zone after eight months and 13,390 after 12 months. After eight months, 11,870 mg of JP-8 was below and 2560 mg was above the contaminated zone, and 11,780 mg was lost due to abiotic and biotic losses from the column. The overall loss from the column was almost equal to the mass of JP-8 contained below the contaminated zone. After 12 months, 11,775 mg of JP-8 was below and 2380 mg was above the contaminated zone, and 12,765 mg was lost due to abiotic and biotic losses from the whole column.

Jet-fuel mass movement from the contaminated zone: Discussion

In general, JP-8 concentration below the contaminated zone was higher in unvegetated column compared to vegetated column (Figures 2.8 and 2.9). The mass of JP-8 below the initial contaminated zone in the unvegetated column was almost twice the amount contained below the contaminated zone of the vegetated column. The development of black soil layer below the contaminated zone accompanied by noxious odors was experienced during destructive soil sampling. This is an indication of anaerobic zones in the soil profile (Paul and Clark, 1996). The biotic fate of JP-8 below the contaminated zone depends on the degradative capability of anaerobic organisms that dominate that water-saturated zone. In general, these organisms have slower hydrocarbon-degradation rates compared to aerobic organisms (Erickson and Fan, 1988; Healy and Young, 1979; Heider et al., 1998; Hutchins et al., 1991; Karthikeyan and Bhandari, 2001; Sleat and Robinson, 1984). Increased JP-8 concentration in that zone could either be toxic to those organisms or those organisms may require longer acclimation periods to degrade JP-8 constituents (Song and Bartha, 1990; Dean-Ross, 1993). The anaerobic microorganisms once adapted to the JP-8 contamination would start utilizing JP-8 constituents as carbon/energy source.

The loss of JP-8 was higher in vegetated column compared to unvegetated column at any sampling time. This loss may include abiotic losses such as volatilization and biotic losses such as biodegradation. This loss might have occurred in the contaminated zone itself or have occurred after it was transported upwards or downwards from the contaminated zone. However, the aerobic degradation of jet-fuel constituents generally is more predominant than that of anaerobic degradation (Aelion and Bradley, 1991; Atlas and Bartha, 1992; Bossert and Bartha, 1986; Spain and Somerville, 1985) suggesting that these losses occurred after upward movement into the more aerobic surface layers. Direct uptake of JP-8 constituents, BTEX type compounds and short-chain aliphatic chemicals, by plants could be a possible

mechanism that moved the JP-8 fractions away from the contaminated zone. The translocated fractions of JP-8 may be stored in plant structures or volatilized or metabolized (Shimp et al., 1993; Trapp and McFarlane, 1995). The JP-8 fractions transported inside the plant can diffuse out of the plant roots and stems to the more aerobic portions of the soil. However, mixtures of petroleum hydrocarbons similar to jet-fuels were not translocated inside plants via direct plant-uptake (Reilley et al., 1996; Schwab and Banks, 1994; Wetzel et al., 1997). Also, plants enhance the microbial activity in the aerobic zones due to the presence of organisms in the rhizosphere. Root exudates provide substrates that might facilitate cometabolism of jet fuel constituents (Kruger et al., 1997; Schwab and Banks, 1994).

The abiotic losses including volatilization was about 52% in air-dried soils used in one-column system:1 over 18 month period. The abiotic losses were minimized in the one-column system:2 because the soil was saturated initially. The total loss in that column was about 25% over a 12 month period. It is evident that volatilization of JP-8 in air-dried soils is more predominant than in wet soils. Similar results were observed in unsaturated soils with jet-fuel mixtures (Li and Voudrias, 1994a; 1994b). Water was added to nine-column system according to evapotranspiration losses to maintain saturated conditions at the bottom of the columns. Thus the volatilization losses were minimized to a greater extent above the saturated zone. Most of the losses that occurred in this system should be due to biodegradation. Two-channel and four-column systems showed about 86% reduction in the aerobic, top 10 cm soil layer. This layer was relatively dry and hence losses could have been due to volatilization as well. The top 10 cm soil layer of nine-column system was also relatively dry and hence the losses in this layer could be due to biodegradation and volatilization as well. However, JP-8 reduction in the middle and deeper soil layers of the columns and chamber was lower than the reduction near the soil surface (Figures 2.5 and 2.6; Table 2.9). The soluble fractions of JP-8 should be moved upwards in order to get degraded

in the soil. After 12 months, the vegetated column had lost 6500 mg more JP-8 compared to unvegetated column. Plants moved soluble fractions of JP-8 upwards or at least decreased the downward movement of JP-8 (Figure 2.8), whereas in unplanted columns, more mass of JP-8 moved downwards to anaerobic zones (Figure 2.9). This could be a major reason for lower overall reduction of JP-8 in the unvegetated columns compared to vegetated columns.

JP-8 concentration was higher in downward direction compared to upward direction against gravity in both vegetated and unvegetated columns. Water flux through the contaminated zone could carry soluble fractions of JP-8 and transport them upwards. The volume of water moved through the contaminated zone in a 12-month period was approximately 51 L for the vegetated column and 9 L for unvegetated column. The maximum soluble fraction of JP-8 that could have been carried by water flux above the contaminated zone in 12 months would be 61,200 mg in the vegetated column and 10,800 mg in the unvegetated column, assuming solubility of JP-8 fractions as 1200 mg/L. This compares to 21,635 mg lost or transported upward in the vegetated columns and 15,145 mg in the unvegetated columns. However, there are limitations such as saturation of water with soluble JP-8 constituents and slow upward water velocity (Mayer and Miller, 1996; Szlag and Illangasekare, 1992; 1993; 1994a; 1994b). JP-8 transported above the contaminated zone could be degraded rapidly by aerobic organisms that harbor in these zones. Previous studies showed that aerobic degradation of jet fuel and kerosene constituents was rapid in soils with or without plants (Aelion and Bradley, 1991; Dean-Ross et al., 1992; Dror et al., 2001; Spain and Somerville, 1985). The observation that degradation in the unplanted column exceeded 10,800 mg suggests that some degradation occurred independent of transport to the near surface. The observation that 9000 mg remained in the initially contaminated zone of the vegetated column shows that water could not effectively mobilize as much as 1200 mg/L but more likely only a few hundred mg/L.

2.5. CONCLUSIONS

The overall JP-8 mass reduction in two-channel system was 83% after three months, 93% after five months, and 96% after seven months. Almost 86% of JP-8 disappeared in the simulated surface spill experiments (two-channel and four-column systems) during the five month period. The losses were not just due to volatilization but also due to biodegradation. The biotic losses were higher compared to abiotic losses for the soil systems with simulated surface jet-fuel spills. This is a promising result that shows manipulating the JP-8 contaminated soils, either by adding nutrients and water (by favoring microbial growth) could result in faster restoration of those soils contaminated by JP-8 spills. Growing plants in JP-8 contaminated soils could favor microbial growth indirectly. However, data from this study do not support that plants significantly increase the JP-8 removal from soils compared to unvegetated systems. More-controlled study is required to determine if plants contribute a significant difference in removing JP-8 from soils either by direct uptake or by indirectly stimulating microbial activity.

The reduction in JP-8 concentration in planted soil systems where subsurface leakages were simulated was only 50% after twelve months. This shows that JP-8 leakages that occur near the groundwater table could persist for longer duration than those that occur near the soil surface. Also, downward movement of JP-8 was higher in unplanted columns compared to columns with plants. This could pose a potential threat to a nearby groundwater source. Plants could decrease this threat by decreasing the downward movement and also facilitating upward movement of dissolved fractions of JP-8. JP-8 transported upwards could be degraded faster by aerobic organisms. JP-8 transported downwards could persist in the environment for longer duration if anaerobic conditions prevail. Plant-assisted bioremediation or intrinsic bioremediation may be an inexpensive and effective technology to clean up subsurface soil contaminated with JP-8.

CHAPTER 3

MODELING FATE AND TRANSPORT OF JET FUELS (JP-8) IN SOILS WITH PLANTS

3.1. INTRODUCTION

Recently plant-based *in situ* remediation of organic contaminants has been studied extensively (Chang and Corapcioglu, 1998; Shimp et al., 1993; Davis et al., 1998; Fiorenza et al., 2000). Plants grown in soils contaminated with organic contaminants, either naturally or by design, offer their aesthetic value and a stabilizing medium (Chang and Corapcioglu, 1998). These plants also may stimulate remediation of soils contaminated with organic contaminants at low soil concentrations, and represent a potential low-cost and effective alternative for managing contaminated sites (Jones, 1991). Plant remediation has been applied at the field scale to capture the downgradient plume and control leachate at landfill sites (Matso, 1995). Applications of various plants to soils contaminated with various organic contaminants has been summarized for both laboratory and field studies (Corapcioglu, 1992; Matso, 1995; Shimp et al., 1993). Several steps are necessary before actual field implementation of a remediation strategy with plants. One of the most widely used techniques for determining the optimal design and management strategy is the development of mathematical models to quantify the fate processes in soils with plants.

Mathematical models are quantitative representation of reality. These models can provide relationships between cause and effects (Keely, 1987). A process or phenomenon, either natural or manmade, can be presented by simple or complex mathematical formulations. To represent a process occurring in nature, a set of governing equations can be derived by assuming a control volume of uniform properties. The accuracy of a mathematical model will depend largely on the fundamental assumptions made to represent a system and the variability in the system. Any contaminant fate and transport can be simulated by mathematical models provided the fate and transport processes are well represented by rigorous mathematical formulations (Keely, 1987). Once a model is formulated, it can be used as a powerful tool to generate various transport scenarios in the subsurface. Consequently, conducting costly and time consuming experiments can be minimized. In the subsurface, JP-8 transport is a complex phenomenon; physical, chemical, and biological

processes interacting among each other and varying spatially and with time (Keely, 1987). In this study, release of JP-8 in the subsurface, near the groundwater table is simulated by mathematical formulations. This section briefly discusses JP-8 transport parameters that govern the migration, transport of JP-8 in the subsurface, and previous mathematical modeling studies conducted on fate and transport of LNAPLs in soils.

3.1.1. JP-8 transport parameters

Aquifer characteristics and JP-8 properties govern the transport of JP-8 in the subsurface (Newell et al., 1995). The properties of JP-8 used in the study are presented in Table 2.2. Even though NAPL movement is controlled by several complex factors that are highly unpredictable in nature, it is necessary to understand the processes at the pore-scale. Newell et al. (1995) describe various pore-scale properties that control transport of NAPL in the subsurface. The following parameters play a significant role in JP-8 transport in the subsurface; capillary pressure, density, diffusivity, interfacial tension, relative permeability, saturation and residual saturation, solubility, viscosity, and wettability. For a detailed discussion on NAPL transport and parameters that control the groundwater transport, refer to Newell et al. (1995) and Chapter 6 in Bedient et al. (1999).

Capillary pressure

Pressure difference between two immiscible fluids in a thin tube is defined as capillary pressure. Usually it is represented as the height of equivalent water column (Newell et al., 1995). Capillary pressure is an indirect measure of adhesive and cohesive forces that exist at the interfaces (Miller and Miller, 1956). In the subsurface the wetting fluid (water) and non-wetting fluid (here, JP-8) will compete to enter the capillaries. In order to enter the porous medium, the non-wetting fluid should overcome the capillary pressure exerted by the largest pores (Bear, 1972; 1979; Newell et al., 1995).

Capillary pressure and the capillary size are inversely proportional: smaller capillaries lead to larger pressures (Miller and Miller, 1956). Soil matric potential plays a crucial role in governing the capillary pressure as well: drier subsurface (more negative matric potential) leads to higher capillary pressures (Newell et al., 1995; Mercer and Cohen, 1990). Capillary size, arrangement, geometry, and connectivity also determine the physical movement and trapping of JP-8 in the subsurface.

Once trapped in small capillaries, JP-8 may remain in the subsurface for a longer period of time. Biotic and abiotic degradation also get restricted due to this trapping. Fibrous roots and fungal hyphae can reach trapped JP-8 and potentially degrade *in situ* or translocate. Groundwater flow can release some of the trapped JP-8 by modulating the viscosity and solubility. Sometimes hydro-flushing by injecting water at very high velocities and air sparging can be employed to mobilize trapped JP-8. It should be noted that complete removal of trapped JP-8 from micro capillaries is highly impractical to achieve (Newell et al., 1995).

Density

Density of a substance is defined as mass per unit volume. Alternatively, fluid density can be represented as specific gravity: mass of a liquid at a given volume to mass of water at the same volume at standard temperature and pressure. Density of a substance is influenced by temperature. For most fluids, density is inversely proportional to temperature (Newell et al., 1995). Specific gravity of JP-8 is less than 1.0 (Table 2.2) and hence it is a LNAPL; floating on water. In the subsurface, JP-8 density controls the extent and direction of movement. Dissolution of different constituents of JP-8 in water will alter the molecular weight and specific gravity of JP-8.

Diffusivity

Movement of a substance from higher concentration to lower concentration may occur by diffusion (Bedient et al., 1999). The rate parameter at which a liquid diffuses is known as diffusivity. Diffusion occurs in liquids and gases. At molecular scale, molecules move randomly due to concentration gradients. In the subsurface, dissolution of JP-8 in water and then movement of dissolved JP-8 fractions in the presence or absence of water in porous media are examples of diffusion processes (Bedient et al., 1999; Newell et al., 1995). Typically, diffusion is very slow when water moves slowly in the subsurface (Bedient et al., 1999). Low groundwater velocities may be due to a barrier (i.e. presence of tight clay liner or rock) in the subsurface. Diffusivity of JP-8 in water plays a major role in diffusion of JP-8 in the subsurface under saturated conditions.

Interfacial tension

When a hydrophobic liquid (e.g. JP-8) and hydrophilic liquid (e.g. water) are in contact, a physical interface is established. This is due to the interfacial energy between the liquids (Bear, 1972; 1979; Dullien, 1991; Newell et al., 1995). Each liquid, here JP-8 and water, will have internal molecular forces. Differences in the internal forces will result in energy difference at the interface. The surface energy difference at the interface is known as interfacial tension (Newell et al., 1995). Higher energy differences in case of immiscible liquids (e.g. JP-8 and water) will result in higher interfacial tension, and highly stable interface. Temperature, pH changes, salinity, and the presence of surfactants in the subsurface will lower the interfacial tension and destabilize the interface (Newell et al., 1995).

Relative permeability

Relative permeability is defined as "the ratio of the effective permeability of the medium to a fluid at specified degree of saturation and the permeability of the medium to the fluid

at 100% saturation" (Newell et al., 1995). It is a unitless fraction with range between 0 and 1. Newell et al. (1995) present a simplified relative permeability diagram for a hypothetical LNAPL/water system in a porous medium (after Williams and Wilder, 1971). This diagram can be used to demonstrate how JP-8 and water interfere with each other to reduce mobility in the subsurface (Figure 3.1). This illustration is for two-phase systems under saturated conditions. Ferrand et al (1989) present similar diagram for a three-phase system (NAPL, water, and air) under unsaturated conditions.

Saturation and residual saturation

In a given pore volume, the fraction of pore space filled by a flowing liquid is known as its degree of saturation (Newell et al., 1995). The mobility of the liquid is highly dependent on the degree of saturation: a higher saturation leads to higher mobility. This mobility vs. degree of saturation can be determined from the relative permeability curves (Figure 3.1). It is evident that when the saturation decreases mobility of NAPL also decreases and ceases in the subsurface. At residual saturation, NAPL becomes immobile and gets trapped in pores. This residual NAPL phase will be a prolonged threat to groundwater contamination and it is hard to remove completely. The magnitude and severity of residual saturation is affected by interconnectivity of pores, pore size, interfacial tension, density, and viscosity of the liquid (Anderson et al., 1992; Demond and Roberts, 1991; Mercer and Cohen, 1990; Newell et al., 1995).

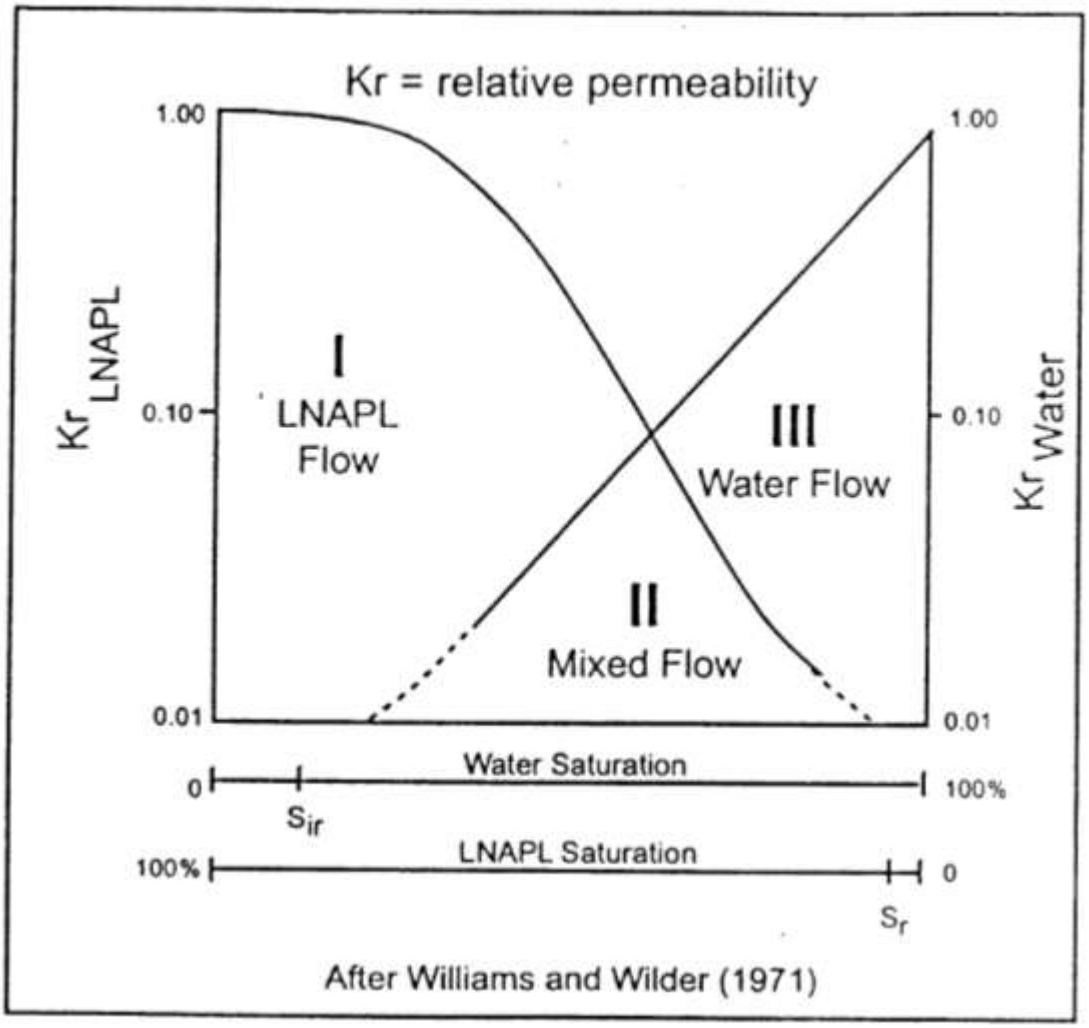

Figure 3.1. Hypothetical relative permeability curves for water and an LNAPL in a porous medium (After Newell et al., 1995 and Williams and Wilder, 1971).

Solubility

"Solubility is the dissolution of a compound into the aqueous phase" (Newell et al., 1995). Several compounds in JP-8 mixture will dissolve in water controlled by various environmental factors including temperature and pressure (Newell et al., 1995). It should be noted that JP-8 is a mixture of several compounds of varying solubilities and an "effective solubility" of JP-8 can be estimated theoretically by Equation [2.1] (Newell et al., 1995). This can be a better approximation of JP-8 solubility under field conditions.

Viscosity

"Viscosity is the resistance of a fluid to flow" (Newell et al., 1995) due to its internal frictional forces. This can be informally described as "thickness" of a liquid or "affinity to flow". Viscosity is highly variable with temperature. As the temperature increases, viscosity of most fluids decreases (Newell et al., 1995). When a liquid is less viscous, the energy required for the liquid to flow is low. In the subsurface, highly viscous liquids (e.g. crude oil) flow slowly while less viscous liquids flow faster (e.g. water).

Wettability

When two immiscible fluids are present, one fluid will smear on or stick to solid surfaces. This tendency is called wettability (Newell et al., 1995). Wettability is a pore-scale phenomenon; as the scale increases, it is hard to illustrate wettability. In the subsurface, when multi-phase system exists, wetting liquid will preferentially occupy smaller pores (due to capillary adhesion) while non-wetting liquid will occupy larger pores. When water and JP-8 are present in porous medium, water will migrate to smaller pores due to its wettability. In case of JP-8 and air system (unsaturated zone), JP-8 will preferentially wet soil solid surfaces and occupy small pores (Newell et al., 1995). Wettability can be influenced by soil clay, minerals, presence of surfactants, and JP-8 composition (Newell et al., 1995).

3.1.2. JP-8 migration

Darcy's law

Darcy's law governs both groundwater flow and JP-8 migration in the subsurface. Darcy's velocity (for water) depends on hydraulic conductivity and hydraulic gradient. Similar relationship exists for LNAPL (here, JP-8) movement as well (Newell et al., 1995):

$$v = -\ [k\rho g/\mu]\ dh/dL \quad \text{..... [3.1]}$$

where,

v = Darcy velocity (LT^{-1}),

k = intrinsic permeability (L^2),

ρ = density of NAPL (ML^{-3}),

g = acceleration due to gravity (LT^{-2}),

μ = dynamic viscosity of NAPL ($ML^{-1}T^{-1}$), and

dh/dL = hydraulic gradient of NAPL mass (LL^{-1}).

Darcy's velocity is inversely proportional to the viscosity of JP-8 and directly proportional to intrinsic permeability and density (Newell et al., 1995). In the subsurface, due to abiotic and biotic degradation, JP-8 composition might change (Johnson et al., 1990). Consequently, viscosity and density of JP-8 will also change. This mathematical relationship shows that the mobility of JP-8 can change with respect to time.

Migration through vadose zone

When introduced in the subsurface, JP-8 moves downward in the soil profile due to gravity (Figure 2.1). In the vadose zone, JP-8 will displace air in soil pores and wet the soil surface (Newell et al., 1995). JP-8 will occupy small pores and may get trapped due to capillary pressure. Capillary fringe due to raising groundwater table will dissolve JP-8 in pores,

pick up the soluble constituents, and move them in the soil profile. Infiltration of rainfall and irrigation water will also pick up JP-8 and move it downward.

Accumulation at the water table

Continuous supply of JP-8 in the subsurface will result in further downward movement to saturated zone (Newell et al., 1995). Then, JP-8 will float on top of water and slide with groundwater flow. A fraction of JP-8 will be dissolved at the liquid-liquid interface and that will move in the subsurface due to advection and diffusion. In saturated zone, JP-8 can move in all directions depending on flow conditions and hydraulic head differences. When a huge amount of JP-8 is released, it will ultimately depress the water table to some extent (Newell et al., 1995). Abdul (1988) has shown that LNAPLs could move in all directions in the vadose zone. LNAPL migration within the saturation zone depended on amount of LNAPL released and characteristics of the subsurface (Abdul, 1988).

Smearing due to fluctuating water table

Smearing of JP-8 in the subsurface is a result of molecular diffusion and advection at pore-scale. When JP-8 reaches the capillary fringe, water table fluctuations will pick up JP-8 and some will dissolve (Newell et al., 1995). Due to concentration gradient, dissolved JP-8 will move from higher concentration to lower concentration. Water table fluctuations can result from seasonal effects and anthropogenic activities including pumping. Trapped JP-8 will dissolve due to water table movement and move up and down due to fluctuations, resulting in smearing as well (Newell et al., 1995).

3.1.3. Mathematical modeling of fate and transport processes of jet fuel in soils

Modeling jet fuel transport is complicated because of multiple phases and possible interphase transfer of fluids. Transport of each phase is coupled with capillary pressures and effective saturation of other phases. This approach is described in detail by Abriola (1984) and

Abriola and Pinder (1985a; 1985b). Much effort has been made to simulate NAPL transport and, particularly, fate of residual NAPL in porous media (Hatfield and Stauffer, 1993; Hatfield et al., 1993) and specifically LNAPL transport (Faust et al., 1989; Kaluarchchi and Parker, 1989; Katyal et al., 1991; Seagren et al., 1994; Weaver et al., 1994). Subsurface is a highly complex, heterogeneous environment. Fate and transport of a chemical in the subsurface is a complex phenomenon as well. Multiphase (water and JP-8) liquid system adds another challenging layer to the system to be modeled (Newell et al., 1995). Hence, there is a lot of uncertainties involved in models that predict fate and transport of LNAPL (here JP-8) in the subsurface. The models are highly sensitive to several parameters; porosity, hydraulic conductivity, JP-8 composition, and pore-water velocity are only a few to list. However, as mentioned earlier, these models can generate large amount of data on fate of JP-8 in the subsurface under different scenarios.

To consider health effects, the dissolved fraction of JP-8 is the one that should be considered. Hence modeling the fate and transport of dissolved phase is justified. Once dissolved, aqueous fractions of JP-8 will move with groundwater. Contaminant fate and transport in the subsurface can be described by the advective dispersion equation (ADE) (Anderson and Woessner, 1992; Bedient et al., 1999; Domenico and Schwartz, 1998). ADE includes both mass-transport (advection and diffusion) and mass-transfer (sorption and biotic and abiotic degradation) processes.

Here, movement of dissolved fractions of JP-8 along with groundwater flow is called advection. For all practical purposes, pore velocity is treated as advection velocity in the subsurface. Diffusion, a molecular process, occurs due to JP-8 concentration gradient. Due to velocity variations, JP-8 is mixed in the flowing water. This process is termed as dispersion. Sorption occurs due to partitioning of JP-8 soluble fractions from aqueous phase to soil-solid phase. Abiotic processes (e.g. photolysis, chemical reactions) and microbial

degradation can degrade JP-8 in the subsurface. The mass-transfer processes can be combined and treated as “retardation” (Bedient et al., 1999).

Mathematical derivations of the governing mass-transport equations are provided in this subsection, and have been presented earlier (Bear, 1972; 1979; Bedient et al., 1999; Freeze and Cherry, 1979; Miller and Rabideau, 1993; Ogata, 1970; Trapp and McFarlane, 1995). Domenico and Schwartz (1998) and van Genuchten and Alves (1982) present a number of analytical solutions for the ADE with varying initial and boundary conditions.

3.2. OBJECTIVES

The objective of this research was to develop and verify an 1-D mathematical model that describes the fate and transport of dissolved fraction of jet fuels (JP-8) in soil columns The approach considers the advective and dispersive transport of jet fuels dissolved in groundwater, which may undergo simple first-order decay or linear adsorption. The governing partial differential advection dispersion equation (ADE), is solved in one-dimension (soil columns). The data from an experimental set up (nine-column system) was used to validate the model. The following sections present the development of governing ADE with analytical solutions, model simulations, and comparison with experimental data.

3.3. MODELING SECTION

Mass Conservation Equation

The first step is to establish the mass-conservation equation for the contaminant, jet fuel. This can be achieved by developing the mass balance for the system during an arbitrarily small time period Δt between t and $t + \Delta t$. Over this time period, the mass-conservation equation may be stated in words as follows:

Mass of contaminant entering soil volume during Δt =

mass of contaminant leaving soil volume during Δt

+ increase of contaminant mass stored in soil volume during Δt

+ mass of contaminant that has disappeared from the soil volume by plant root uptake or by microbial degradation (biotic) or by abiotic reactions during Δt [3.2]

For the one-dimensional vertical flow process shown in Figure 3.2,

$$\frac{\partial J_c}{\partial z} + \frac{\partial C_T}{\partial t} + r = 0 \qquad [3.3]$$

where J_c is the contaminant flux, C_T is the total contaminant concentration, and r is rate of contaminant disappearance. Units for all parameters are given in Table 3.1. Equation [3.3] is known as advective dispersion equation (ADE) for a contaminant in one dimension.

The total contaminant concentration in soil is given by,

$$C_T = \theta_w C_w + \theta_a C_a + \rho C_s + \theta_{napl} C_{napl} \qquad [3.4]$$

where θ_w is the volumetric fraction of water, θ_a is the volumetric fraction of air, ρ is the soil bulk density, θ_{napl} is the volumetric fraction of NAPL, C_w is the contaminant concentration in soil-water phase, C_a is the contaminant concentration in soil-air phase, C_s is the contaminant concentration sorbed to the solid phase, and C_{napl} is the contaminant concentration in soil-NAPL phase. Total contaminant concentration (C_T) should be expressed in terms of aqueous phase concentration (C_w) to solve ADE. This can be achieved as follows:

According to Henry's law,

$$H = \frac{C_a}{C_w} \text{ or } C_a = HC_w \qquad [3.5]$$

where H is the Henry's coefficient.

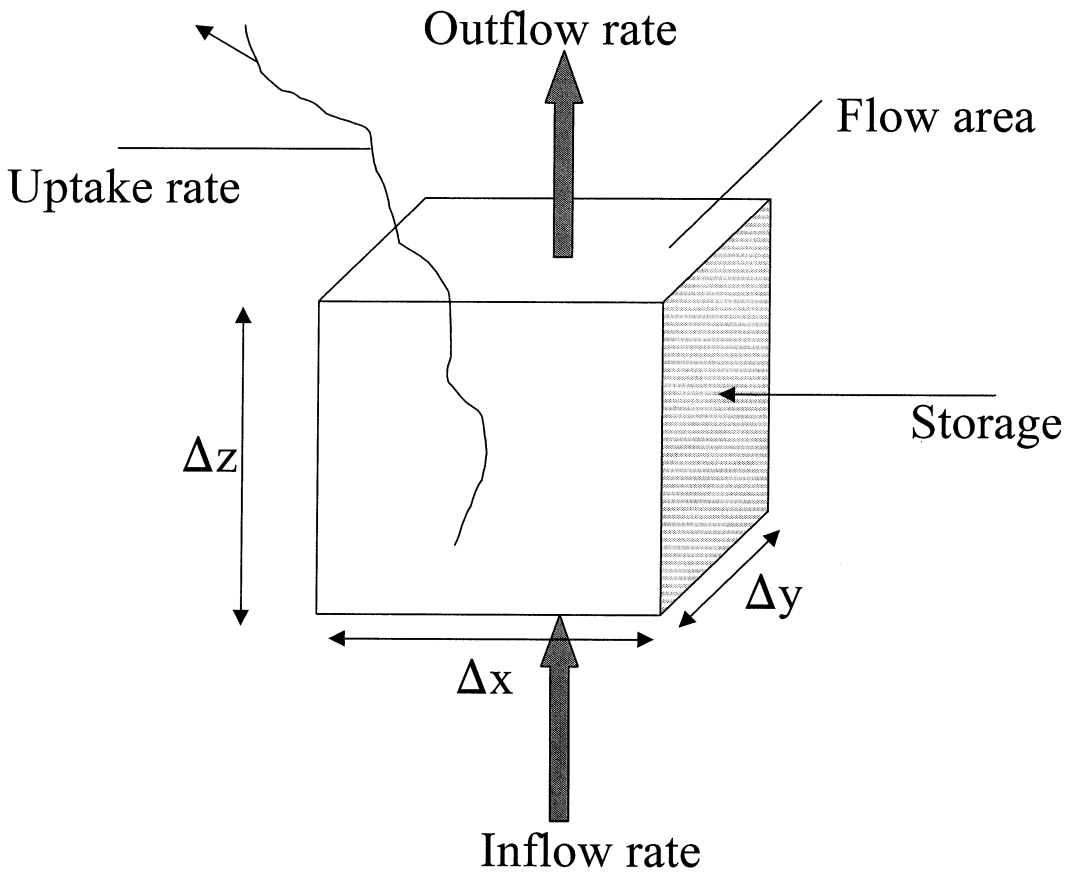

Figure 3.2. Elementary volume of soil used in calculating the contaminant mass balance equation.

Table 3.1. Dimensions of all parameters used in the model development.

Parameter	Description	Dimension
Δx	arbitrarily small length in x direction	L
Δy	arbitrarily small length in y direction	L
Δz	arbitrarily small length in z direction	L
Δt	arbitrarily small time period	T
J_c	rate of contaminant mass flow per unit area	$ML^{-2}T^{-1}$
r	rate of contaminant mass disappearance per unit volume	$ML^{-3}T^{-1}$
C_T	total contaminant concentration in different phases	ML^{-3}
C_w	contaminant concentration in soil-water phase	ML^{-3}
C_a	contaminant concentration in soil-air phase	ML^{-3}
C_s	contaminant concentration in soil-solid phase	MM^{-1}
C_{napl}	contaminant concentration in NAPL phase	ML^{-3}
θ_w	volumetric water content	L^3L^{-3}
θ_a	volumetric air content	L^3L^{-3}
θ_{NAPL}	volumetric NAPL content	L^3L^{-3}
ρ	soil bulk density	ML^{-3}
H	Henry's constant	$ML^{-3}M^{-1}L^3$
k_d	soil-water partitioning coefficient	L^3M^{-1}
k_{oc}	soil organic carbon mass fraction	L^3M^{-1}
f_{oc}	fraction of organic carbon in soil	MM^{-1}
v_z (also q_z)	velocity of water moving in z direction	LT^{-1}
D_z (also D)	soil aqueous phase diffusion coefficient	L^2T^{-1}
$\mathcal{D}$	molecular diffusion coefficient	L^2T^{-1}
D_m	mechanical dispersion coefficient	L^2T^{-1}
α	dispersivity	L
β	overall first-order decay coefficient for contaminant	T^{-1}
μ_w	first-order decay coefficient for contaminant (aqueous phase)	T^{-1}
μ_s	first-order decay coefficient for contaminant (sorbed phase)	T^{-1}

According to soil-water partition law,

$$k_d = \frac{C_s}{C_w} \text{ or } C_s = k_d C_w \qquad [3.6]$$

where k_d is the soil-water partition coefficient ($k_d = k_{oc} f_{oc}$).

Now Equation [3.4] becomes

$$C_T = \theta_w C_w + H C_w \theta_a + \rho k_d C_w + \theta_{napl} C_{napl} \qquad [3.7]$$

$$C_T = C_w[\theta_w + \theta_a H + k_d \rho] + \theta_{napl} C_{napl} \qquad [3.8]$$

$$C_T = C_w \kappa + \theta_{napl} C_{napl} \qquad [3.9]$$

where

$$\kappa = \theta_w + \theta_a H + k_d \rho \qquad [3.10]$$

κ is also known as retardation coefficient.

The contaminant flux can be due to advection ($J_c|_{adv}$) and due to diffusion ($J_c|_{diff}$). The flux due to advection ($J_c|_{adv}$) is the flux of dissolved contaminant in aqueous phase, as described by

$$J_c|_{adv} = v_z \theta_w C_w \qquad [3.11]$$

where v_z is the velocity of water moving in z direction, θ_w is the volumetric water content, and C_w is the aqueous phase concentration of the contaminant.

The flux due to diffusion ($J_c|_{diff}$) is the flux of contaminant in vapor phase and in the liquid phase.

According to Fick's first law,

$$J_c|_{diff} = -\theta_w D_z \frac{\partial C_w}{\partial z} - \theta_a D_{za} \frac{\partial C_a}{\partial z} \qquad [3.12]$$

where D_z is the soil aqueous phase diffusion coefficient and D_{za} is the soil gas phase diffusion coefficient. Here, only aqueous phase diffusion is considered. D_z can be given by,

$$D_z = \mathfrak{D} + D_m \qquad [3.13]$$

where $\mathfrak{D}$ is molecular diffusion coefficient and D_m is mechanical dispersion coefficient. D_m can be given by

$$D_m = \alpha v_z \qquad [3.14]$$

where α is dispersivity and v_z is the velocity of water moving in z direction

Now the contaminant flux (J_c) becomes,

$$J_c = v_z \theta_w C_w - \theta_w D_z \frac{\partial C_w}{\partial z} \qquad [3.15]$$

The sink term r is assumed to be due to microbial degradation. Plant uptake of contaminants and abiotic losses such as photodegradation are assumed to be negligible for jet fuels. Microbial degradation could take place in both aqueous and soil sorbed phases. However, microbial degradation of contaminant in NAPL phase is assumed to be negligible.

$$r = \mu_w \theta_w C_w + \mu_s \rho C_s \qquad [3.16]$$

where $C_s = k_d C_w$ and μ_w and μ_s are first order decay constants for the contaminant in aqueous and soil sorbed phase, respectively. Equation [3.16] can be written as

$$r = \beta C_w \qquad [3.17]$$

where

$$\beta = \mu_w \theta_w + \mu_s \rho k_d \qquad [3.18]$$

Now, using Equations [3.8], [3.9], [3.15], and [3.17], Equation [3.3] becomes

$$\frac{\partial \{v_z \theta_w C_w - \theta_w D_z \frac{\partial C_w}{\partial z}\}}{\partial z} + \kappa \frac{\partial C_w}{\partial t} + \frac{\partial [\theta_{napl} C_{napl}]}{\partial t} + \beta C_w = 0 \qquad [3.19]$$

Equation [3.19] is the ADE equation that includes the contaminant present in the NAPL-phase. However, here JP-8-contaminated zone (NAPL-saturated zone) was treated as a continuous source of NAPL that supplied NAPL at concentration equal to C_o (saturated aqueous phase concentration) to the above soil zones. At the boundary of NAPL zone,

$$\frac{\partial[\theta_{napl} C_{napl}]}{\partial t} = \theta_z v_z C_w \qquad [3.20]$$

and above the NAPL zone, $\theta_{napl} = 0$ and only water, soil, and vapor phase exists. Equation [3.19] can then be reduced to the following after rearrangement.

$$\kappa \frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial z^2} - q_z \frac{\partial C_w}{\partial z} - \beta C_w \qquad [3.21]$$

here $v_z \theta_w$ = water velocity in z direction and lumped as q_z and $D = D_z \theta_w$. This equation can be used to simulate transport of the soluble JP-8 constituents.

Initial and Boundary Conditions

This section gives analytical solutions of Equation [3.21] subject to various initial and boundary conditions. The general initial conditions would be

$$C_w(z, 0) = f(z) \quad \text{for } t = 0 \qquad [3.22]$$

f(z) is the contaminant concentration in the aqueous phase at t = 0.

Two different boundary conditions can be applied at z = 0, which is at the upper surface of the NAPL zone: a first- or concentration-type boundary condition (van Genuchten and Alves, 1982) of the form

$$C_w(0, t) = g(t) \qquad \text{for } z = 0 \qquad [3.23]$$

or a third- or flux-type boundary condition (van Genuchten and Alves, 1982) of the form

$$-D\frac{\partial C_w}{\partial z} + q_z C_w = q_z g(t) \quad \text{for } z = 0 \qquad [3.24]$$

Here g(t) can take on several distributions, such as a constant value in time as long as NAPL is present.

For the upper boundary, the following condition can be applied

$$\frac{\partial C_w}{\partial z}(\infty, t) = 0 \qquad [3.25]$$

This condition assumes that the soil column is semi-infinite. An alternative boundary condition, one that is used frequently for displacement studies, is that of a zero concentration gradient at the upper end of the column:

$$\frac{\partial C_w}{\partial z}(L, t) = 0 \qquad [3.26]$$

where L is the length of the column. This condition, which leads to a continuous concentration distribution at z = L, has been used extensively. Equation [3.26] does lead to conservation of mass inside a soil column, whereas Equation [3.25] may lead to mass balance errors.

Assumptions and Limitations

1. Evapotranspiration was at a steady-state condition (In this study, lighting was applied 24-hrs per day and temperature was constant).
2. Water velocity in vertical direction was constant and equal to the evapotranspiration flux in the columns.
3. Phase equilibrium existed among the local solid, water, gas, and NAPL phases.

4. Biodegradation was considered as first-order decay both in solid and aqueous phases.

5. The soil above the contaminated zone was considered as homogenous with uniform and constant volumetric water content.

6. Contaminated NAPL zone was treated as a continuous supply source. Water passing through contaminated zone was considered to be saturated with JP-8 equal to its maximum aqueous solubility as long as NAPL is present.

Analytical Solution

Analytical solutions for Equation [3.21] do exist for initial condition, type 1 and 3 lower boundary conditions, and finite and semi-finite upper boundary conditions. Analytical solutions for ADE (Equation[3.21]) (van Genuchten and Alves, 1982):

1. Initial condition:

$$C_w(z, 0) = f(z) = C_i = 0 \qquad [3.27]$$

2. Lower boundary condition: type 1;

$$C_w(0, t) = g(t) = C_o = 1200 \text{ mg/L}; \text{ for } 0 < t < t_o;$$

$$C_w(0, t) = 0; \text{ for } t > t_o \qquad [3.28]$$

3. Upper boundary condition: semi-infinite;

$$\frac{\partial C_w}{\partial z}(\infty, t) = 0 \qquad [3.29]$$

$$C_w(z, t) = C_i A(z, t) + C_o B(z, t) \qquad \text{for } 0 < t \leq t_o$$

$$C_w(z, t) = C_i A(z, t) + C_o B(z, t) - C_o B(z, t - t_o) \qquad \text{for } t > t_o \qquad [3.30]$$

where

$$A(z, t) = \exp(-\frac{\beta t}{\kappa}) \{1 - \frac{1}{2} \mathrm{erfc}[\frac{\kappa z - q_z t}{2\sqrt{\kappa D t}}] - \frac{1}{2} \exp[\frac{q_z z}{D}] \mathrm{erfc}[\frac{\kappa z + q_z t}{2\sqrt{\kappa D t}}] \} \quad [3.31]$$

$$B(z, t) = \frac{1}{2} \exp[\frac{(q_z - u)z}{2D}] \mathrm{erfc}[\frac{\kappa z - ut}{2\sqrt{\kappa D t}}] + \frac{1}{2} \exp[\frac{(q_z + u)z}{2D}] \mathrm{erfc}[\frac{\kappa z + ut}{2\sqrt{\kappa D t}}] \quad [3.32]$$

where

$$u = q_z (1 + \frac{4\beta D_z}{q_z^2})^{\frac{1}{2}} \quad [3.33]$$

and

$$\mathrm{erfc}(B) = \frac{2}{\sqrt{\pi}} \int_B^{\infty} e^{-t^2} dt \quad [3.34]$$

The product of exp[A] and erfc[B] cannot be handled for very small or very large values of its arguments A, B. Commercial spreadsheet programs can not calculate erfc if argument B is negative. The product of exp[A] and erfc[B] should be calculated using approximate functions defined by van Genuchten and Alves (1982). A separate function EXF(A, B) = exp[a] erfc[b], was defined with approximations and solved using a computer code.

3.4. PARAMETER DETERMINATION AND SELECTION

Parameters that were used in the simulation included soil properties and JP-8 properties (Table 3.2). Experimental data and data from previous literature were used to determine these parameters. Equation [3.10] describes retardation coefficient (κ) that includes

volumetric fraction of water (θ_w), volumetric fraction of air (θ_a), Henry's coefficient (H), soil bulk density (ρ), and soil-water partition coefficient (k_d).

Table 3.2. Parameters used in the simulation.

Parameter	Value	Source
C_w (0,t)	1200 mg L^{-1} (for benzene type compounds)	Heath et al., 1993; Watts, 1997
θ_w	0.223 cm^3cm^{-3} (V); 0.293 cm^3cm^{-3} (U)	Laboratory
θ_a	0.136 cm^3cm^{-3} (V); 0.066 cm^3cm^{-3} (U)	Laboratory
ρ	1.7 g cm^{-3}	Laboratory
k_{oc}	500 cm^3 g^{-1}	Heath et al., 1993; Watts, 1997
f_{oc}	0.005 g g^{-1}	Laboratory
H	8 [dimensionless]	Watts, 1997
q_z	2.01×10^{-6} cm sec^{-1} (V); 4.80×10^{-7} cm sec^{-1} (U)	Laboratory
$\mathcal{D}$	5×10^{-5} cm^2sec^{-1}	Bedient et al., 1999
α	0.09 cm	Bedient et al., 1999
μ_w	3.5×10^{-6} sec^{-1}	Watts, 1997
μ_s	2.3×10^{-6} sec^{-1}	Watts, 1997

V = vegetated column; U = unvegetated column

Water content

Gravimetric water content of a sample was measured by weighing the moist sample, drying it in an oven at 105°C for 24 h to remove the water, and reweighing it. Gravimetric water content was calculated by the following relationship,

$$\theta_g = \frac{W_w - W_d}{W_d} \qquad [3.35]$$

where θ_g is gravimetric water content, w_w is the soil wet-weight, and w_d is the soil dry-weight after 24 h drying in an oven at 105°C.

Gravimetric water content was determined for each 5 cm soil layer and converted to the volumetric fraction of water (θ_w) by multiplying gravimetric water content with bulk density. The θ_w used in the simulation was an average value for the entire 12-month duration. Also, it was assumed that the θ_w remained the same above the contaminated zone.

Bulk density and porosity

Approximately 500 g of soil was added to the soil column and the column was tapped gently to allow uniform packing. The column was filled with clean air-dried soil in 500 g increments up to 50 cm deep. Bulk density of the soil was calculated by the following relationship,

$$\rho = \frac{W}{V} \qquad [3.36]$$

where ρ is the bulk density, W is the weight of the soil occupying 50 cm of the column after packing, and V is the volume of the column (15 cm diameter; 50 cm depth). Porosity of the soil was calculated using the following relationship,

$$\varphi = 1 - \frac{\rho}{\rho_s} \qquad [3.37]$$

where φ is the porosity of soil material, ρ is the bulk density, and ρ_s is the soil particle density. Volume fraction of air (θ_a) was then calculated using the following relationship:

$$\varphi = \theta_w + \theta_a \qquad [3.38]$$

Soil-water partition coefficient

Soil-water partition coefficient (k_d) was calculated as the product of k_{oc} and f_{oc}. Fraction of organic carbon (f_{oc}) was determined in the laboratory (Nelson and Sommers, 1996) and k_{oc} was obtained from literature. There was no published value for k_{oc} and Henry's coefficient (H) for jet fuels as jet fuels are mixture of few hundred compounds in varying properties (Mayfield, 1998). Determining k_{oc} and H of jet fuels is a difficult task, and the published reports on those properties for JP-8 type jet fuels are either unavailable or are often conflicting (Heath et al., 1993; Mayfield, 1998; Watts, 1997). The simulations were done for transport of soluble fractions of JP-8, which are benzene type compounds. The k_{oc} and dimensionless Henry's coefficient (H) of BTEX-type compounds were obtained from literature.

Solubility

JP-8 is a complex mixture of aliphatic and aromatic hydrocarbons and it is very difficult to find accurate physical chemical properties to represent a mixture of hydrocarbons. JP-8 has compounds with solubilities from < 2 mg/L to > 1200 mg/L. The solubility of BTEX compounds (1200 mg/L) was used in the simulation to describe the transport of soluble fractions of JP-8. Diffusion coefficient ($\mathcal{D}$) and dispersivity (α) for BTEX-type compounds was obtained from literature and used in the simulations.

Water velocity

Daily water consumption in both vegetated and unvegetated column was recorded for the entire 12-month duration. The average daily water consumption rate was determined. Water velocity in z direction (v_z) was calculated by the following relationship,

$$v_z = \frac{C}{A} \qquad [3.39]$$

where C is the average daily water consumption rate and A is the cross-sectional area of the column (15 cm diameter).

Decay coefficient

The degradation rate of JP-8 was assumed to follow first-order kinetics. First-order decay constants for BTEX-type compounds in aqueous (μ_w) and soil sorbed phase (μ_s) were obtained from literature.

3.5. RESULTS AND DISCUSSION

The 1-D model was used to simulate the JP-8 profile in the vegetated and unvegetated soil columns (nine-column system). Figures 3.3, 3.4, 3.5, and 3.6 show the simulated JP-8 profiles above the jet-fuel contaminated NAPL zone in the vegetated and unvegetated columns along with the experimental results. The experimental results are reported as mean ± standard deviation (n=3). Initially, soil above the JP-8 contaminated zone was considered to be free of contaminants and was subjected to a continuous supply of 1200 mg/L. Simulated scenarios included advection without retardation, advection with retardation, and advection with retardation and decay. Simulated JP-8 concentrations were converted to mg/kg of dry soil and were compared with experimental results for the three sampling periods of different depths above the JP-8 contaminated zone. Experimental results were much higher than the simulated results after 90 days for both vegetated and unvegetated columns at 5 cm above the contaminated zone (Figure 3.3). This could be due to 'smearing' and capillary rise of jet fuel blobs, as this zone is just 5 cm above the contaminated zone and 10 cm above the watertable. Experimental results were closer to advection results after 240 and 360 days for both vegetated and unvegetated columns (Figure 3.3). This suggests that jet fuel transported to this zone did not go through any decay and the contaminant transport was not influenced by retardation. This zone was in the capillary fringe of the watertable, and anoxic conditions could prevail. The development of black soil layer near this soil zone

accompanied by noxious odors was experienced during destructive soil sampling. This is an indication of anaerobic zones in the soil profile (Paul and Clark, 1996). Jet fuel transported to this zone should either be further transported upwards in order to undergo aerobic degradation or be degraded in that zone itself by anaerobic organisms. Most of the jet fuel compounds do not undergo biodegradation under anoxic conditions (Aelion and Bradley, 1991; Dean-Ross, 1993; Dean-Ross et al., 1992; Lovley, 1997; Spain and Somerville, 1985).

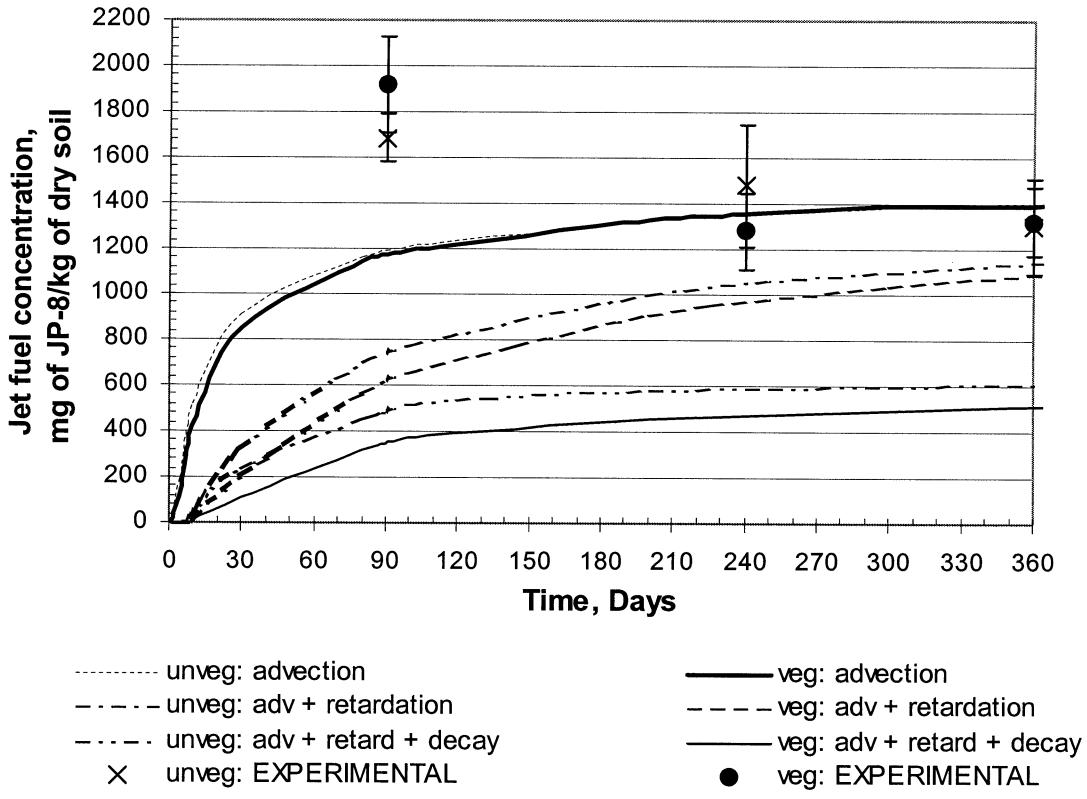

Figure 3.3. Simulated and experimental jet fuel concentration at 5 cm above the jet fuel contaminated zone in vegetated and unvegetated columns.

In Figure 3.4a, the simulated jet fuel concentration after 90 days for advection without retardation is in reasonable agreement with the experimental JP-8 concentration in the vegetated column at 10 cm above the contaminated zone. This shows that advection was the dominant process in this zone for the vegetated column. However, the experimental JP-8 concentration in the unvegetated column coincides with the simulated advection profile with retardation, after 90 days of contamination (Figure 3.4a). This could be due to lower water velocities in this column. After 240 days, the experimental results in both vegetated and unvegetated columns were close to the simulated profile with retardation and decay at 10 cm above the contaminated zone (Figure 3.4a). This could be due to microbial acclimation during the 240 days which resulted in biodegradation. After 360 days, the experimental results were even closer to the simulated profile with retardation and decay, which supports microbial degradation. Similar results were found at 15 cm depth above the contaminated zone (Figure 3.4b).

In Figure 3.5a, the experimental JP-8 concentration after 90 days was close to the simulated advection result and after 240 days was close to the simulated advection with retardation curve at 20 cm above the contaminated zone for both columns. After 360 days, the simulated advection with retardation and decay described the experimental JP-8 concentrations in both the columns very well. At 25 cm above the contaminated zone, the experimental concentration of both the columns was close to the simulated advection result after 90 days, simulated advection with retardation and decay result after 240 and 300 days (Figure 3.5b). Simulated JP-8 concentrations with decay, clearly described the experimental results in both vegetated and unvegetated columns at 30 and 35 cm above the contaminated zone after 240 and 360 days (Figure 3.6).

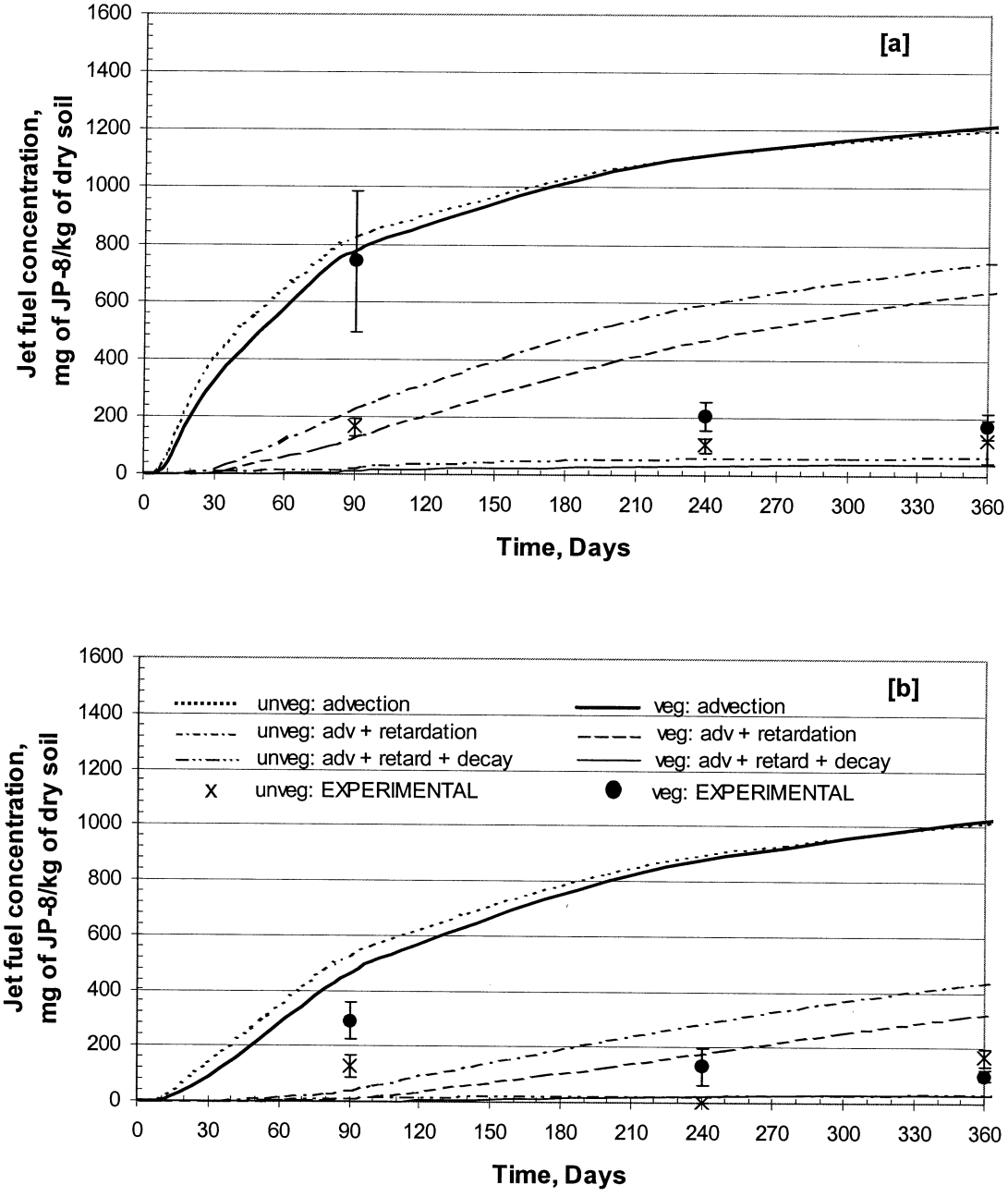

Figure 3.4. Simulated and experimental jet fuel concentration at (a) 10 and (b) 15 cm above the jet fuel contaminated zone in vegetated and unvegetated columns.

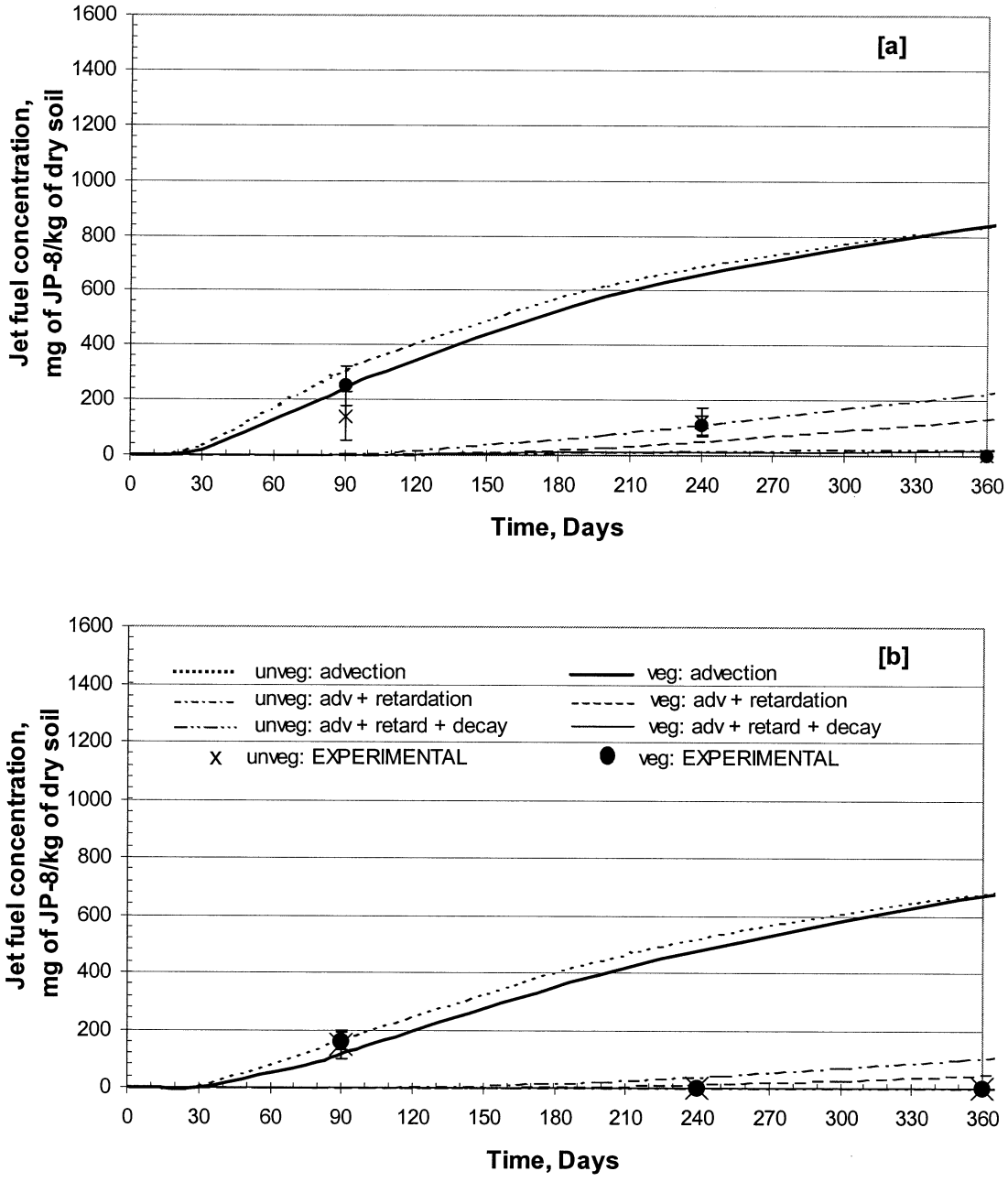

Figure 3.5. Simulated and experimental jet fuel concentration at (a) 20 and (b) 25 cm above the jet fuel contaminated zone in vegetated and unvegetated columns.

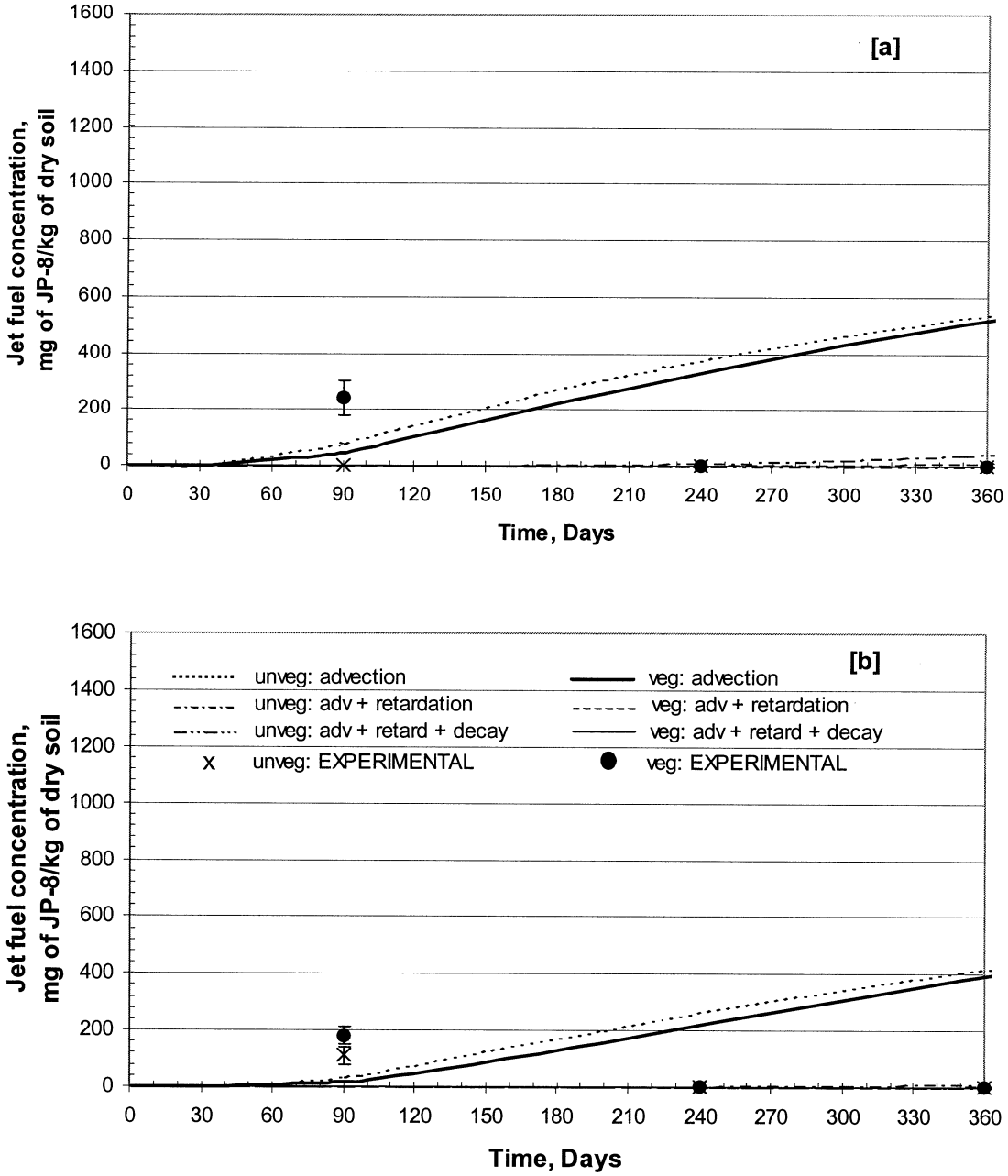

Figure 3.6. Simulated and experimental jet fuel concentration at (a) 30 and (b) 35 cm above the jet fuel contaminated zone in vegetated and unvegetated columns.

In general, advection appears to be a dominant transport mechanism for JP-8 transport in vegetated columns. Vegetation caused the higher water velocity in the vegetated columns; transpiration-induced water movement moved the soluble fractions of JP-8. In a year, the plants in the vegetated column evapotranspired approximately 51 L and the evaporation loss in the unvegetated column was only 9 L. The roots extracted 42 L more from the saturated zone. Soil water is the main agent moving soluble JP-8 fractions in the soil. In a planted soil under controlled irrigation conditions, the fate of soil water is related closely to root-water interaction (Chang and Corapcioglu, 1998). The extent of the effect of root behavior on the interaction depends on the mean daily water uptake rate. Soil water content profile is quite sensitive to changes of mean daily water uptake rate (Georgen et al., 1991; Taylor et al., 1992).

In a phytoremediation study, high mean daily water uptake rate induced a relatively large water potential gradient and resulted in moisture deficiency of upper soil (Chang and Corapcioglu, 1998). Such a moisture deficiency of upper soil layers may greatly limit the plant uptake of water and may encourage growth of deep roots to absorb their moisture from the lower soil layers (Brady, 1990). Roots can have an overall effect of retarding the transport of JP-8 in soil. Roots achieve this by absorbing the contaminant and reducing the soil-water content (Chang and Corapcioglu, 1998). Reduction in soil-water content results in a decrease in advective transport of JP-8 because the hydraulic conductivity of unsaturated soil decreases with decreasing soil-water content, as expressed by Haverkamp et al. (1972). The retardation coefficient κ increases with decreasing soil-water content and corresponding increasing gas phase volume fraction as shown in Equation [3.10]. Plant parameters such as the mean daily water uptake rate have been shown to play an important role in determining the extent of JP-8 and water absorption by the root, which, in turn, is related to the JP-8 retardation. The water content in the vegetated column was lower compared to unvegetated column and hence the retardation coefficient was higher in the vegetated

column. Higher retardation coefficient reduced the advective transport of JP-8 in the vegetated column (Figures 3.3, 3.4, 3.5, and 3.6). Chang and Corapcioglu (1998) found that the variation of the retardation coefficient along the soil profile imitated the variation of water content in response to changes in the mean daily water uptake rate. Higher uptake rates produced higher retardation because of lower water content along the soil profile.

It was assumed in this study that indigenous sources were sufficient for primary substrate utilization in the vegetated vadose zone. Biomass yield as well as endogenous decay in the utilization of JP-8 in low levels was assumed to be inconsequential and the decay was assumed to follow first-order kinetics. Also, it was assumed that the first-order decay coefficient was constant over the time and space above the contaminated zone for both vegetated and unvegetated columns. In this study, the decay constant was assumed to be the same for both vegetated and unvegetated columns. However, most bacteria in the natural subsurface have a tendency to attach to solid particles and form a biofilm. Generally, the biofilm is penetrated fully by substrates (Rittmann, 1993). Therefore, the chemical concentrations in the biofilm can be assumed to be the same as the average bulk aqueous-phase concentrations. This provides an expression for the rate of utilization of JP-8 at low levels in a bulk soil by the use of Monod-type expression (Rittmann, 1993). Because of abundant root releases such as exudates and mucilages, a rapid buildup of a biofilm generally occurs within 50 μm from the root surface, where the microbial population is 50-100 times greater than in bulk soil. As the biofilm becomes sufficiently thick, it may have solute diffusion resistance and subsequent development of a nonlinear concentration profile (Rittmann and McCarty, 1980). When the concentration profile within the biofilm changes rapidly with respect to the biofilm thickness, the rate of utilization of substrates in the biofilm can be described with a steady-state biofilm model elucidated by Rittmann and McCarty (1981). Incorporating this biofilm model in Equation [3.21] would improve the simulation of JP-8 transport with decay.

However, the parameters for the biofilm model, maximum substrate utilization rate in the bulk soil, half-saturation coefficient in the bulk soil, and microbial concentration in the bulk soil were not measured during this study. The biodegradation component of Equation [3.21] was treated as a lumped-sink term, β, described in Equation [3.18] for the entire soil profile. In Equation [3.18], θ_w was the only term that was different for vegetated and unvegetated columns. Unvegetated column had higher θ_w and hence higher β. After 240 days, at 20, 25, 30, and 35 cm above the contaminated zone, biodegradation appears to be important in both vegetated and unvegetated columns (Figures 3.5 and 3.6). The plant roots in this zone harbor microorganisms that can degrade JP-8. Even the unvegetated columns have native microorganisms that can degrade JP-8 once they are acclimated (Karthikeyan et al., 1999; 2001). However, the model does not differentiate the effect of vegetation on microbial activity and ultimately on degradation of JP-8.

This model could be a helpful tool to simulate the transport of JP-8 due to advection and advection with retardation. Incorporating a biofilm model would improve the simulations of JP-8 transport with degradation. This model is very sensitive to soil-water content and, measuring soil-water content accurately improves the accuracy of the model simulations.

3.6. CONCLUSIONS

A mathematical model was developed to simulate soluble fractions of JP-8 transport in 1-D columns. Simulated results with different scenarios described the experimental results well for different depths above the contaminated zone in both vegetated and unvegetated columns. Mathematical modeling of JP-8 movement is a useful tool that can be used before implementing any field scale implementation of vegetation enhanced bioremediation of JP-8 contaminated aquifers. However, the data available in the literature for mixtures of hydrocarbons are sparse and vary a lot. Modeling of four-phase systems with NAPL phase is complex.

CHAPTER 4

VEGETATED TREATMENT OF SEDIMENTS FROM VEHICLE WASH FACILITY

4.1. INTRODUCTION

Bioremediation in the presence of vegetation is an important clean-up method for soils contaminated with petroleum hydrocarbons. The establishment of vegetation in soils contaminated with petroleum hydrocarbons can help stimulate bioremediation (Schwab and Banks, 1994). Establishment of vegetation can be an economic, effective, low maintenance approach to remediation and stabilization of contaminated soils and sediments. The use of plant-based remediation systems is not new; only the name phytoremediation was coined in recent years. Phytoremediation is defined as the "use of green plants and their associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render harmless environmental contaminants" (Anderson and Coats, 1995; Comis, 1996; Cunningham and Berti, 1993; Cunningham and Lee, 1995; Cunningham et al., 1995; Davis et al., 1993; Erickson et al., 1994; Kruger et al., 1997; McInture and Lewis, 1997; Walton et al., 1994). The use of plants in the remediation of groundwater, air, and soil are all receiving significant attention. The first plant-based system was installed over 300 years ago in Germany for treatment of municipal sewage. Since that time, overland-flow systems, spray-irrigation systems, reed-bed filters, and artificial-wetland systems have become common for secondary and tertiary treatment of municipal sewage waters.

Phytoremediation is divided into two broad categories, namely: phyto-decontamination and phyto-stabilization. The naturally occurring processes involved in phyto-decontamination are: phyto-extraction, phyto-volatilization, phyto-degradation, and rhizosphere degradation. Phyto-stabilization consists of humification, lignification, and irreversible binding. Phyto-decontamination aims at total removal of contaminants from the soil and phyto-stabilization focuses more on stabilization and sequestration of contaminants in soil. Bioavailability of contaminants is the driving force in phyto-decontamination and phyto-stabilization. Physical, chemical, and biological properties of soil and aging of contaminants affect bioavailability to a great extent.

Plants have been studied as structures for uptake and translocation of organic contaminants into roots and within plants, respectively (McFarlane, 1995). Effects of crude oil on different field crops have been studied extensively (Amadi et al., 1992; Amakiri and Onofeghara, 1984; Bossert and Bartha, 1985; Bossert et al., 1984; Chainaeau et al., 1996; Oudot et al., 1989). Baker (1970) provides an extensive review on effects of oil on plants. Aprill and Sims (1990) studied the effects of using deep-rooted prairie grasses to remediate soil contaminated with PAHs. They demonstrated that the roots of these perennial grasses may be more effective in stimulating the rhizosphere microflora due to their fibrous roots.

The term "rhizosphere" was first introduced by Hiltner in 1904 to describe the specific interaction between bacteria and the roots of legumes (Anderson and Coats, 1995; Anderson et al., 1993). The term has been refined to regard the rhizosphere as the soil region under the immediate influence of plant roots in which there is an increased microbial population (Anderson et al., 1993; Aprill and Sims, 1990; Banks et al., 2000; Curl and Truelove, 1986; Hsu and Bartha, 1979; Nichols et al., 1997; Paul and Clark, 1996; Reilley et al., 1996; Schwab and Banks, 1994; Shann and Boyle, 1994; Watkins et al., 1994; Wetzel et al., 1997). Generally, the rhizosphere contains significant populations of gram-negative bacteria (Atlas and Bartha, 1993). However, there are several factors, such as root type, plant species, plant growth stage, soil type, and root exudates, that determine the actual composition and diversity of microorganisms in the rhizosphere. The rhizosphere microbial community typically is different than that of the bulk soil as a result of apparent chemical and physical properties.

Microorganisms may cover 4-10% of the root area. The rhizosphere effect is commonly measured as the ratio of microbial numbers per unit weight of rhizosphere soil, R, to the number of microorganisms per unit weight of non-rhizosphere soil, S. Fungi, actinomycetes, protozoa, and algae are not significantly influenced by the presence of roots. The influence

of rhizosphere is selective for type of microorganism rather than the total number of microbes (Alexander, 1977). Plants release nutrients such as amino acids, simple sugars, carbohydrates, and enzymes into the soil that are potential substrates for the microorganisms. Root exudates usually are low molecular weight substances that leak from all plant cells into either intercellular spaces and then into soil via cell junctions, or directly into the soil through the epidermal cell walls. Root secretions and plant hormones are low molecular weight compounds as well as high molecular weight mucilages, both of which are released as a result of metabolic processes (Curl and Truelove, 1986; Radwan et al., 1995).

Vegetated microbial filters were found to increase removal of aromatic and aliphatic compounds (Wolverton et al., 1983). The fibrous root systems of grasses were shown to enhance the bioremediation of PAHs in clay soils. The deep fibrous roots of prairie grasses may improve aeration in soil and provide a means for bringing microbes into contact with PAH compounds through the large surface area of the root-soil interface. Turf grasses, in addition to enhancing degradation of contaminants, also contribute benefits such as providing an erosion-resistant cap to contaminated soil to reduce human exposure. Surface runoff and infiltration to groundwater also are reduced in turf-grass establishments (Qiu et al., 1994).

Gunther et al. (1996) studied the effects of ryegrass on the biodegradation of hydrocarbons in soil. In ryegrass columns, there was 97% reduction of applied hydrocarbon mixture. The hydrocarbon mixture was comprised of decane, tetradecane, hexadecane, docosane, tetracosane, pristine, phenanthrene, and pyrene (Gunther et al., 1996). Schwab and Banks (1994) investigated the degradation of PAHs in the rhizosphere of a variety of plants grown in land-farmed, petroleum-contaminated soils. Their results indicated that PAH compounds dissipated at a faster rate in rhizosphere soil than in unvegetated soil. They found rapid dissipation of pyrene in the presence of vegetation. Concentrations of pyrene were reduced from 100 ppm to 0.16 ppm with switchgrass and 0.15 ppm with fescue after 24 weeks.

Microbial plate counts were increased up to 70-200 times in rhizosphere soils (Schwab and Banks, 1994).

There have been many field and lab studies on species evaluation, bioavailability of PAHs, feasibility of phytoremediation, microbial diversity in rhizosphere, and cometabolism of other compounds during degradation. Studies have shown that aggressive roots of higher plants may enhance degradation of petroleum hydrocarbons in soil (Schwab and Banks, 1994). Typically, denser and more diverse microbial populations are seen in the root zone. The roots also facilitate increasing microbial contact with contaminants. Rhizosphere has been demonstrated to enhance the degradation of PAHs, but the mechanisms of dissipation have not been identified (Wetzel et al., 1997). These researchers conclude that the effect of rhizosphere on PAH degradation is a short-lived phenomenon that requires continued presence of roots. Hydrocarbon-degrading strains of bacteria and fungi were isolated and identified at the generic or specific level (Chaineau et al., 1995). These researchers studied the biodegradation of the fuel-oil hydrocarbons contained in drilling cuttings in soil microcosms during a 270-day experiment and found the decrease in hydrocarbon concentration was logarithmic with time. At the end of their study, the fuel oil was 75% degraded; normal and branched alkanes were almost totally eliminated in 16 days; and 22% of the cycloalkanes were not assimilated. Aromatic fraction was 71% degraded but some polycyclic aromatics were persistent (Chaineau et al., 1995).

Many army-training reservations contain vehicle wash facilities where combat vehicles and other equipment are washed with high-pressure water hoses (Kulakow et al., 1998). During this process, sediments containing significant concentrations of petroleum hydrocarbons accumulate in sedimentation basins. Significant quantities of these sediments are generated at 12 army installations throughout the United States, two of which are located in the Great Plains/Rocky Mountain region. Military vehicles at Fort Riley, Kansas are washed at the

Central Vehicle Wash Facility (CVWF). Washwater from the CVWF flows into an impoundment, where particulate matter settles and light petroleum products are removed (Kulakow et al., 1998). Approximately 765 m^3 of water-saturated sediments are removed from the washwater impoundment every six to nine months and spread on the ground surface in 45 to 105 cm thick layers. Laboratory analysis of representative samples of sediments from the impoundment and land application site indicate measurable Total Petroleum Hydrocarbon (TPH) concentration between 482 and 3800 $mg_{TPH}/kg_{dry\ soil.}$ The Kansas Department of Health and Environment (KDHE) generally considers cleanup goals for TPHs in soils as 100 $mg_{TPH}/kg_{dry\ soil,}$ but grants variances depending on future uses of contaminated soils (Oliver et al., 1996). Conventional treatment methods to manage these sediments include landfill disposal or land application; vegetative remediation systems may offer a cost-effective alternative (Davis et al., 1998; Reilly et al., 1996; Schnoor et al., 1995).

4.2. OBJECTIVES

The main objective of this study was to design an inexpensive plant-based treatment system requiring minimal management to treat petroleum-contaminated sediments generated at the Central Vehicle Wash Facility (CVWF), Fort Riley, Kansas. The specific objective was to determine the effects of vegetation in treating the sediments under field conditions.

4.3. EXPERIMENTAL SECTION: FORT RILEY FIELD TRIAL

Approximately 136 m^3 of sediments from the CVWF were spread on a mowed grassland in July 1997. The sediments were spread approximately 30 cm deep. In September 1997, a vegetative treatment scheme was established with three treatments: (1) an unvegetated control, (2) a grass mixture consisting of tall fescue *(Festuca arundinacea)* and western wheatgrass *(Agropyron smithii),* and (3) a grass-legume mixture consisting of tall fescue with red clover *(Trifolium pratense),* birdsfoot trefoil *(Lotus corniculatus),* and yellow sweet clover *(Melilotus officinalis).* Each plot was 6 × 6 m in size and all the plots were fertilized

with nitrogen and phosphorus. The plots were arranged in a randomized complete block design with four replicates. After seeding the plots in September 1997, management of the trial included 4 fertilizer applications (56 kg/hectare of nitrogen and 27 kg/hectare of phosphorus for each application) on all plots; 3 mechanical clippings of vegetated plots; and 4 herbicide (Roundup©) applications on unvegetated plots.

Sediment samples and native soil samples were collected for preliminary analysis prior to the seeding (July 1997). A composite sample of sediments and the underlying native soil (30 cm total depth) was analyzed for chemical and physical properties. Physical and chemical properties of native soil and sediment samples are given Table 4.1. The experimental plots were sampled seven times (0, 6, 9, 12, 18, 24, and 36 months after seeding) to determine TPH concentration. During each sampling period, samples were taken from 4 random places in each plot and a composite was made. This resulted in four composites for each treatment. The composites were air dried, ground, sieved through a 2 mm sieve, and stored in a cold room at 0°C until analysis. A 3 g subsample was taken from each composite and extracted for TPH. Total petroleum hydrocarbon concentrations have been estimated using a procedure that estimates hydrocarbons in the motor oil range by gas chromatography described in chapter 2 of this dissertation (Schwab et al., 1999).

4.4. RESULTS AND DISCUSSION

Figure 4.1 shows the average TPH concentrations in the soil with a grass mixture during a 36-month period. Initially the TPH concentration was 900 ± 230 $mg_{TPH}/kg_{dry\ soil}$ (mean ± standard deviation of four samples) which declined to 430 ± 80 $mg_{TPH}/kg_{dry\ soil}$ in six months. During the first six months of plant establishment, the reduction was about 52% with continued overall reduction of 73% for the next three months. After 12 months, the TPH had declined to 200 ± 115 $mg_{TPH}/kg_{dry\ soil}$. This amounts to a 78% reduction during the first year after planting. During the second and third year of the trial no further reduction in TPH was

observed. The overall reduction in the grass mixture plots was about 76% in 24 months and was about 77% in 36 months (Figure 4.1).

Table 4.1. Physical and chemical properties of Central Vehicle Wash Facility (CVWF) sediments and native soil (where the sediments were land applied).

Characteristic	Unit	CVWF sediment	Native soil
Texture			
Sand	%	40	20
Silt	%	44	62
Clay	%	16	18
pH		8	6.4
Organic Matter	g/kg	28	38
NH_4^+	mg/kg	6.4	6.9
NO_3^-	mg/kg	5.1	1.8
Bray P	mg/kg	1	6
Total N	mg/kg	1027	703
Total P	mg/kg	255	173
Sulfate	mg/kg	28.2	3.2
Chloride	mg/kg	4	2
Exchangeable Cation			
K	mg/kg	209	301
Ca	mg/kg	4740	3350
Mg	mg/kg	370	605
Na	mg/kg	38.3	13.2
Cation Exchange Capacity (CEC)	mmole/kg	14.3	28.8

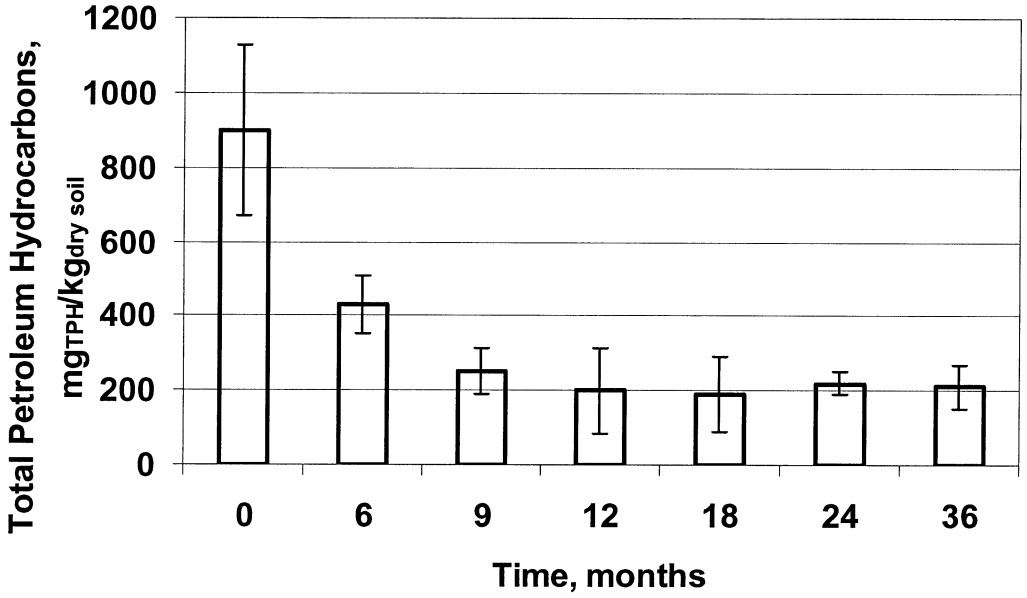

Figure 4.1. Effect of time on total petroleum hydrocarbon concentration for grass mixture.

For the legume treatment, the initial average TPH concentration in the soil was 710 ± 140 $mg_{TPH}/kg_{dry\ soil}$ (Figure 4.2). TPH concentration decreased to 460 ± 140 $mg_{TPH}/kg_{dry\ soil}$ in the first six months (35% reduction). During the next three months, the overall reduction was about 60%, increasing only to 68% in the following three months (Figure 4.2). At the end of first growing season, the TPH concentration was 230 ± 100 $mg_{TPH}/kg_{dry\ soil}$. During the second year, mean TPH values fluctuated between 150 and 290 $mg_{TPH}/kg_{dry\ soil}$. The overall reduction in legume-mixture plots was about 59% in 24 months. After 36 months, the TPH concentration was decreased to 115 ± 50 $mg_{TPH}/kg_{dry\ soil}$ (83% reduction from initial TPH concentration)(Figure 4.2).

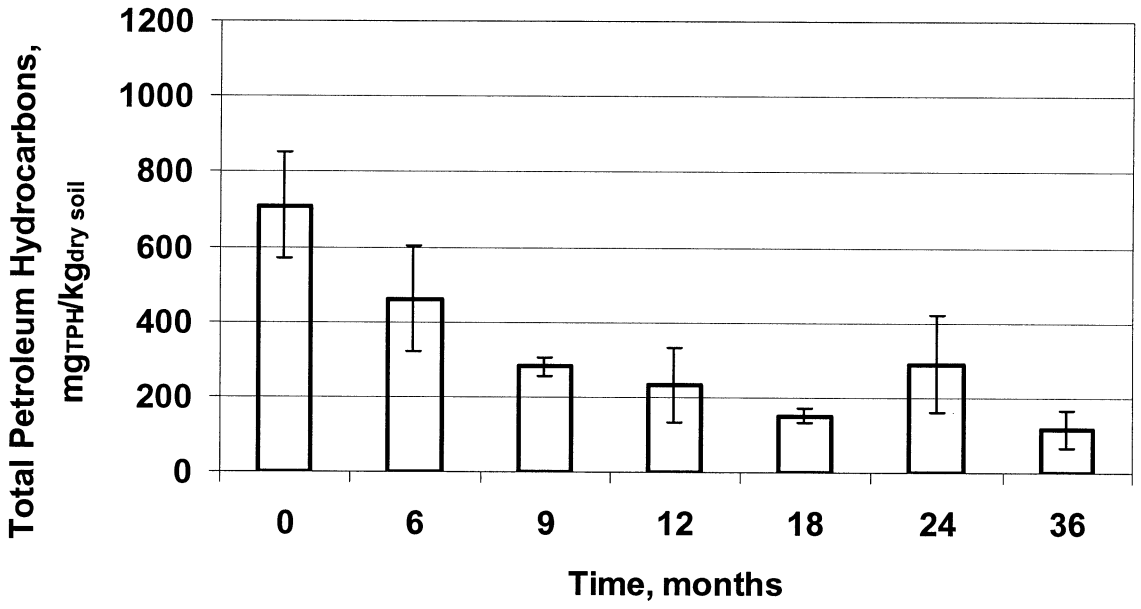

Figure 4.2. Effect of time on total petroleum hydrocarbon concentration for legume mixture.

Figure 4.3 shows the TPH concentration in unvegetated plots over the 36-month period. Initially TPH concentration in the unvegetated plots was 845 ± 210 $mg_{TPH}/kg_{dry\ soil}$ which decreased to 230 ± 100 $mg_{TPH}/kg_{dry\ soil}$ over the 36-month period (overall reduction of 73%). The reduction during the first six months was 42%, and during the first year the cumulative reduction was 78% (Figure 4.3). There was no further reduction during the second and third years of the study.

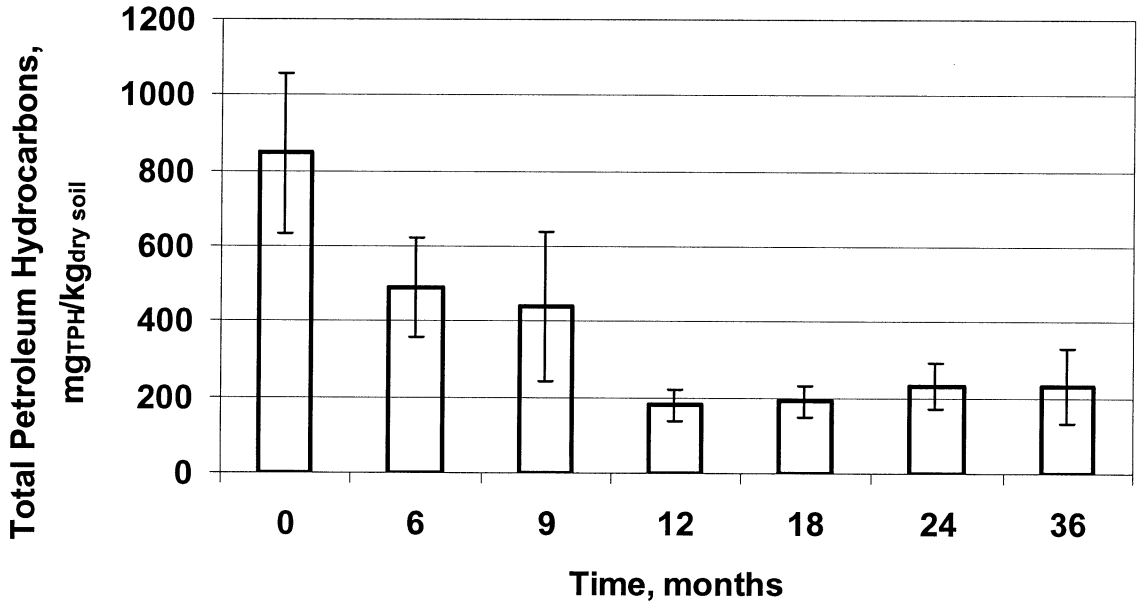

Figure 4.3. Effect of time on total petroleum hydrocarbon concentration for unvegetated treatment.

TPH concentrations at the beginning of the trial, for all plots, averaged 820 $mg_{TPH}/kg_{dry\ soil}$. For all plots the average TPH concentration decreased to 460 $mg_{TPH}/kg_{dry\ soil}$ at six months, 200 $mg_{TPH}/kg_{dry\ soil}$ at 12 months, 250 $mg_{TPH}/kg_{dry\ soil}$ at 24 months, and 185 $mg_{TPH}/kg_{dry\ soil}$ at 36 months. After 36 months of vegetation treatment, the TPH concentrations declined about 75% from the initial values to 185 $mg_{TPH}/kg_{dry\ soil}$. Most of the decrease occurred from 0 to 12 months and the reduction stabilized between 12 and 36 months. It also is important to note TPH has been estimated in the motor oil range in this study. If the TPH were estimated for gasoline or diesel range hydrocarbons, the estimated TPH values would likely be lower because the residual TPH included mostly lubricants and grease range compounds.

No significant differences have been observed between vegetated and unvegetated treatments by analysis of variance for the first 24-months. At 36 month, the mean TPH concentration of one vegetation treatment (grass-legume mixture) was significantly different from unvegetated treatment. It is important to note that both the vegetated and unvegetated treatments were fertilized during the study. Therefore the unvegetated treatment cannot be considered a treatment option that leaves the sediments without management. The mean TPH concentration at the beginning of this trial was low (820 $mg_{TPH}/kg_{dry\ soil}$). Considering this low beginning TPH concentration, we have seen only limited evidence of enhanced dissipation of hydrocarbons with vegetation. Since vegetation helps to hold soil in place and prevent erosion by wind and water, keeping the soil vegetated has value even if there is no significant difference in the rate of biodegradation.

To estimate the concentration of petroleum hydrocarbons in the native soil, a sample of the native soil was taken from outside the trial area during 24-month sampling period. The TPH concentration for this sample was 90 $mg_{TPH}/kg_{dry\ soil}$. Soil samples also have been taken from the native soil at the depth of 30 cm from the ground surface. Estimated TPH for these samples have ranged from 40 $mg_{TPH}/kg_{dry\ soil}$ to 160 $mg_{TPH}/kg_{dry\ soil}$ with most samples near

100 $mg_{TPH}/kg_{dry\ soil}$. At 36-month sampling, soil samples were collected beneath the vegetated and unvegetated plots (at a depth of 40 cm) and outside the treatment plots. The samples were analyzed for TPH. The soil beneath the vegetated plots had 120 $mg_{TPH}/kg_{dry\ soil}$, the soil beneath the unvegetated plots had 160 $mg_{TPH}/kg_{dry\ soil}$, and the soil outside the treatment plots had 110 $mg_{TPH}/kg_{dry\ soil}$. The plant roots extract soil water and decrease deep percolation (Georgen et al., 1991; Taylor et al., 1992). The leaching of petroleum hydrocarbons with percolating water was minimized and hence decreased TPH concentrations contained beneath the sediment layer of vegetated plots.

Two soil samples from the 24-month sampling were split; one set was analyzed in our laboratory and the other submitted to the commercial laboratory that provided analysis for the second field trial (data not reported in this dissertation). One sample was from a grass vegetated treatment. The other sample was from the native soil. These samples were analyzed for TPH and PAH. The TPH estimate of the vegetated treatment was 330 $mg_{TPH}/kg_{dry\ soil}$ (compared against the average grass mixture TPH of 220 ± 30 $mg_{TPH}/kg_{dry\ soil}$, analyzed in our laboratory). For the commercial laboratory, the TPH concentration of the sample from the native soil was 140 $mg_{TPH}/kg_{dry\ soil}$ (compared against the average native soil TPH of 100 $mg_{TPH}/kg_{dry\ soil}$, analyzed in our laboratory). The PAH concentrations for seven probable carcinogenic PAHs were all very low ranging from 0.0041 $mg_{TPH}/kg_{dry\ soil}$ for dibenzo[a, h]anthracene to 0.15 $mg_{TPH}/kg_{dry\ soil}$ for benzo[b]floranthene. The estimated benzo[a]pyrene concentration was 0.0099 $mg_{TPH}/kg_{dry\ soil}$. These PAHs levels were well below concentrations associated with cancer risk levels stipulated by regulatory agencies. A tier 2 risk-based summary stipulated by Kansas Department of Health and Environment (KDHE) is provided in Table 4.2.

While the values from the commercial laboratory are larger than the values from our laboratory, the differences may be associated with the natural variations associated with

Table 4.2. Risk-based standards for carcinogenic PAHs by KDHE.

[Source: Kansas Department of Health and Environment, 1999]

PAH	Residential Conditions	
	Soil Pathway (mg/kg)	**Soil to Groundwater Protection Pathway (mg/kg)**
Naphthalene	100	39
Acenaphthylene	NA*	NA
Acenaphthene	300	190
Fluorene	270	200
Anthracene	13	13
Phenanthrene	NA	NA
Fluoranthene	2700	3800
Pyrene	2000	3000
Benzo[a]anthracene	12	10
Chrysene	1200	1000
Benzo[b]fluranthene	12	22
Benzo[k]fluoranthene	120	240
Benzo[a]pyrene	1.2	40
Indeno[1,2,3,-c,d]pyrene	12	40
Dibenzo[a,h]anthracene	1.2	3.1
Benzo[g,h,i]perylene	NA	NA

* NA = Not Available

sampling and laboratory analysis procedures. Based on the fact that the recent TPH values are only about 100 $mg_{TPH}/kg_{dry\ soil}$ above background levels and the PAH concentrations for the seven probable carcinogenic PAHs are all very low, this remediation process appears to be leading to acceptable results.

4.5. SUMMARY AND CONCLUSIONS

An inexpensive vegetation treatment system was established to treat sediments from the Central Vehicle Wash Facility (CVWF) at Fort Riley, KS. There was a significant reduction in TPH concentration. The overall reduction was about 75%; however, significant differences among treatments were not found until 36 months. Final concentrations approached 185 mg/kg, 85 mg/kg above background levels which is 15 mg/kg below regulatory targets. Sufficient reduction of petroleum hydrocarbons can be reached in fertilized soil with or without vegetation for the batch of sediments we used from CVWF in this field trial. This might be due to the low initial hydrocarbon concentrations. Treatment differences with vegetation may be more likely to be evident for sediments with higher initial hydrocarbon levels. Though treatment differences were small, the presence of vegetation has several specific advantages, such as controlling soil erosion and leaching as well as improved aesthetic appearance, that make vegetation a preferable option to no vegetation.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

Jet fuel spills were simulated in vadose zone soils with plants. Almost 86% of JP-8 disappeared in the simulated surface spill experiments during the five month period. The losses were not just due to abiotic losses such as volatilization but also due to biotic losses such as biodegradation. The biotic losses were higher compared to abiotic losses for the soil systems with simulated surface JP-8 spills. Growing plants in JP-8 contaminated soils could favor microbial growth indirectly. However, data from this study do not demonstrate that plants significantly increase the JP-8 removal from soils compared to unvegetated systems.

Jet fuel leakage was simulated in saturated zone of soils with plants. The reduction in JP-8 concentration in planted soil systems where subsurface leakages were simulated was only 50% after twelve months. This shows that JP-8 leakages that occur near the groundwater table could persist for longer duration than those that occur near the soil surface. Downward movement of JP-8 was higher in unplanted columns compared to columns with plants. This poses a potential threat to groundwater. Plants could decrease this threat by decreasing the downward movement and also facilitating upward movement of dissolved fractions of JP-8. JP-8 transported upwards could be degraded faster by aerobic organisms and JP-8 transported downwards could persist in the environment for longer duration if anaerobic conditions prevail. Plant-assisted bioremediation may be a feasible and inexpensive method to clean up JP-8 contaminated subsurface soils.

A mathematical model was developed to simulate soluble fractions of JP-8 transport in 1-D soil columns with plants. Simulations included advection without retardation, advection with retardation, and advection with retardation and decay. Simulated results with different scenarios described the experimental results well for different depths above the contaminated zone in both vegetated and unvegetated columns. In general advection appeared to be a dominant mechanism for JP-8 transport in vegetated columns. Vegetation caused the higher

water velocity in the vegetated columns; plant-induced water movement moved the soluble fractions of JP-8 above the saturated zone. This model is very sensitive to soil-water content.

An inexpensive vegetation treatment system was established to treat petroleum-contaminated sediments from the Central Vehicle Wash Facility (CVWF) at Fort Riley, KS. There was a significant reduction in petroleum hydrocarbon concentration. The overall reduction was about 75%, and most of the reduction occurred during the first year of the study. Significant differences among treatments were not found until 36 months. Sufficient reduction of petroleum hydrocarbons can be reached in fertilized soil with or without vegetation for the batch of sediments used in this study. Though treatment differences were small, the presence of vegetation has several specific advantages, such as controlling soil erosion and leaching as well as improved aesthetic appearance, that make vegetation a preferable option to no vegetation.

5.2. RECOMMENDATIONS

Jet fuel spills near soil surface could be simulated where the head space above the soil surface is enclosed to trap volatile fractions of jet fuel mixture. Measuring gas phase jet-fuel concentration above the soil surface would help in determining volatilization losses from the soil surface. Rhizosphere and non-rhizosphere soils contaminated with jet fuel should be incubated in laboratory microcosms under aerobic conditions and concentration of jet fuel and aerobic microbial activity be measured periodically. Results from this incubation would determine the biodegradation rate, relationship between microbial activity and biodegradation rate, and the effect of rhizosphere on microbial activity and ultimately biodegradation of jet fuel.

Another laboratory incubation could be conducted with jet fuel contaminated rhizosphere and non-rhizosphere soils under various redox conditions: aerobic, anoxic, and anaerobic.

Measuring concentration of jet fuel and microbial activity periodically would help determine the biodegradation rates of jet fuel under different redox conditions. A separate leaching study could be conducted with soil columns that have jet fuel contaminated zone to determine the pore volumes of water to cause the breakthrough of jet fuel. Another study could be conducted by forcing water at different velocities through soil columns that have jet fuel contaminated zone to determine the effect of water velocity in moving the soluble JP-8 fractions. Soil water and soil should be sampled for jet fuel at different depths from the contaminated zone for both the studies. Soil water content at different depth should also be measured for both the studies.

A biofilm model could be added to the 1-D model developed in this study to simulate biodegradation mechanism. This 1-D model could be numerically solved by finite difference or finite element technique to simulate jet fuel concentration profile at different time and depths. Results from the laboratory incubation and column studies for different time periods could be used to validate the model.

A field study could be conducted to study the effect of fertilizer on dissipation of petroleum hydrocarbons. The treatments could be vegetated-fertilized, vegetated-unfertilized, unvegetated-fertilized, and unvegetated-unfertilized. Petroleum hydrocarbon concentration, plant root biomass, and microbial activity should be determined periodically. Relationships between fertilization and root biomass and fertilization and microbial activity should be determined. Ultimately relationships between root biomass and microbial activity, root biomass and hydrocarbon dissipation, microbial activity and hydrocarbon dissipation should be determined. Degradation rates with and without vegetation and with and without fertilizer should be determined under field conditions.

CHAPTER 6

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6.1. BIBLIOGRAPHY

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