BIODEGRADATION OF JET FUEL IN VENTED COLUMNS OF WATER-UNSATURATED SANDY SOIL

By

JOHN W. COHO

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OF WATER UNSATURATED SANDY SOIL
By

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The effect of soil water content on the rate of jet fuel (JP-4) biodegradation in air-vented, water-unsaturated columns of sandy soil was investigated. The contaminated soil was obtained from a spill site located on Tyndall Air Force Base, Florida. The initial soil loading was 4590 milligrams of JP-4 per kilogram of dry soil. Three laboratory columns were packed with the contaminated soil, saturated and drained for periods of 81 to 89 days. Two of the columns were continuously vented with air, and the third, intended to provide an anaerobic control, was vented with nitrogen. The venting gas flows were maintained between 1 and 2.5 soil pore volume changeouts per day.

The total JP-4 removal in the air-vented columns averaged 44 percent of the mass originally present. Biodegradation and volatilization accounted for 93 percent

and 7 percent of the total removal, respectively. A maximum biodegradation rate of 14.3 milligrams of JP-4 per kilogram of moist soil per day was observed at a soil water content of approximately 72 percent saturation. Soil drainage characteristics indicated that this water content may have corresponded to 100 percent of the *in situ* field capacity water content.

CHAPTER 1

INTRODUCTION

Through seepage from natural sources, petroleum hydrocarbons have entered the terrestrial environment for millions of years. These natural sources are generally small, and they release petroleum hydrocarbons very slowly over a long period of time (Bartha, 1986). In contrast to these natural sources, manmade petroleum hydrocarbon sources such as oil spills and leakage from underground storage vessels continually threaten the environment with large, rapid and potentially damaging releases (Schwendinger, 1968).

The need to mitigate the environmental damage caused by such releases has resulted in many research projects, field studies and field applications of methods to remove petroleum hydrocarbons from the groundwater. Among these groundwater remediation methods are physical containment, various pump-and-treat technologies, and *in situ* chemical and biological treatment.

Considering the hazards posed by groundwater contamination, it is understandable that much emphasis has been placed on groundwater remediation. Dissolution of

leum hydrocarbons in groundwater vastly increases the
nt of contamination and the threat to public health
ting from a terrestrial spill (Hoag et al., 1984).

While groundwater remediations are essential to
.ect and restore groundwater quality, much of the time,
.y and effort put into groundwater restoration may result
/ in relatively short-term improvements in groundwater
ity.

The reason for the possible, or even likely, failure of
groundwater remediation schemes to provide long term
undwater quality improvement is that much of the
troleum present in the subsurface after free product
overy is in the soil above the water table that is
sidually saturated with hydrocarbons (Brown and Norris,
6; Hinchee et al., 1987).

Because most of the petroleum hydrocarbon remaining in
ie subsurface after free product recovery remains in the
il above the water table, many groundwater remediation
echniques fail to remove it. As a result, the petroleum
drocarbons in the soil can serve as a long term source of
ydrocarbon contamination of groundwater. Infiltrating
ater will slowly dissolve and carry hydrocarbons to the
ter table where they become highly mobile and can
contaminate large volumes of groundwater. Hence,
roundwater contamination problems are perpetuated by the

petroleum hydrocarbons adsorbed in the soil above the water table (Hoag and Marley, 1986).

A relatively small amount of information is available on soil decontamination with comparison to that available on groundwater decontamination (Mackay and Hoag, 1986). Many of the methods employed for soil decontamination involve excavating, transporting and incinerating or landfilling the contaminated soil. The cost of these methods is often prohibitive (Hinchee et al., 1987).

Cost effective soil treatment methods should minimize or eliminate the excavation and transportation of contaminated soils. Mackay and Hoag (1986) proposed a hierarchy of options for soil decontamination. In order of increasing difficulty of implementation, and increasing cost, they presented the following options:

(1) leave the soil alone to decontaminate naturally,

(2) intervene by in situ enhancement of natural processes of decontamination,

(3) intervene by in situ treatment involving introduction of an artificial decontamination process,

(4) remove the soil, treat it and return it to the site.

The first option obviously involves the lowest direct costs, but it may result in a long-term threat to groundwater underlying a spill site. The second option addresses the enhancement of natural processes to

decontaminate soil *in situ*. This is the option selected for study in this thesis. Specifically, this thesis will address enhancement of the biodegradation of jet fuel (JP-4) by the natural microbial population in an unsaturated soil obtained from a spill site.

Biodegradation of petroleum hydrocarbons in unsaturated soil was first reported around the turn of the century (Kaserer, 1906; Sohngen, 1906). Since then, many studies have focused on the use of soil microorganisms to remove petroleum hydrocarbons from the soil. Methods to enhance the naturally slow process of hydrocarbon biodegradation in soil have been sought (Atlas, 1977).

One means of enhancing hydrocarbon biodegradation in soil is to improve the soil environment to render it more conducive to microbial activity. Many variables in the soil environment can affect the ability of microorganisms to biodegrade petroleum hydrocarbons. Among these are pH, nutrient availability, substrate availability, chemical toxicity, oxygen availability and water availability.

This study involved improvement of the soil environment in laboratory soil columns containing JP-4 contaminated soil. The environmental variables to be studied in this project are oxygen and water availability. Specifically, the availability of oxygen to soil microorganisms will be improved by the process of soil venting, and the

availability of water will be varied by draining the soil from an initially saturated state.

Soil venting is a process in which air flow is induced through a body of soil by applying a pressure differential. Many previous investigations of this process have focused on in situ stripping of volatile organics, but few have discussed the aspect of enhancement of biodegradation using the process of soil venting.

The primary objective of this research is to determine the impact of soil water content on the rate of JP-4 biodegradation in a soil column under the influence of soil venting, and to note the water content at which the maximum biodegradation rate occurs. Additional objectives include construction of a JP-4 mass balance for the soil columns, and determination of the relative influence of volatilization versus biodegradation in a vented soil column.

CHAPTER 2

LITERATURE REVIEW

Hydrocarbon Residual Saturation in Water-Unsaturated Soil

Before a discussion of the removal of petroleum hydrocarbons from soil through biodegradation, it is appropriate to discuss briefly the means by which these contaminants are entrapped in the water-unsaturated soil.

When a petroleum hydrocarbon (PHC) spill occurs in soil, gravitational and capillary forces cause the free product to travel downward toward the water table. As the free product passes through the soil, some of it is retained in the porous matrix as residual saturation. At shallow depths in a uniform soil column initially hydrocarbon saturated and then drained to equilibrium, the residual saturation is present as discrete masses of the liquid at contact points between adjacent soil particles. At greater depths in the soil column, these discrete masses gradually coalesce into larger liquid masses and finally into a capillary surface. If the spill volume is greater than the residual saturation capacity of the soil, the free product may reach the water table and spread laterally. The final distribution of the free product retained in the soil as

residual saturation depends upon the balance of gravitational and capillary forces (Hoag and Marley, 1986).

As the free product is distributed in the soil, sorption, dissolution and volatilization occur. As a result, a petroleum hydrocarbon spill can result in a complex contamination problem consisting of 4 phases which vary in mobility. The phases include

(1) vapor phase contamination,

(2) free product, or separated phase contamination,

(3) soil-water dissolved phase contamination, and

(4) residual saturation, or sorbed phase contamination.

The transport of hydrocarbons through water-unsaturated soil is a multiphase process involving the 4 phases listed above. Excellent overviews of the transport of chemicals spilled in soil are provided by Mackay and Hoag (1986), and Johnson et al. (1987).

PHC Biodegradation in Water-Unsaturated Soil

The first recorded studies of hydrocarbon biodegradation by soil microorganisms were conducted in Germany in the early 1900's (Sohngen, 1906; Kaserer, 1906). These early studies reported that various petroleum distillates could be oxidized to carbon dioxide, water and organic acids by microorganisms found in common, water-unsaturated, garden soil (Bushnell and Haas, 1941).

The natural process of biodegradation of petroleum hydrocarbons (PHCs) in the soil occurs relatively slowly. Several methods have been employed in attempts to stimulate, or enhance, the rate of PHC biodegradation in soils. These methods include changing the microbial population (seeding), changing the composition of the PHC, and the method to be discussed in this review, changing the soil environment (Atlas, 1977).

Factors Influencing PHC Biodegradation in Soil

A recent general review of PHC biodegradation in soil lists several environmental variables that affect or constrain the biodegradation process. The variables include PHC composition, concentration and physical state, soil temperature, nutrient availability, pH, the presence of PHC degrading microorganisms, water content and aeration (Bartha, 1986). Earlier papers on this topic present similar, but less comprehensive, lists of environmental variables influencing PHC biodegradation (Brown and Donnelly, 1983; Atlas, 1977; Odu, 1972; Schwendinger, 1968; Stone et al., 1942).

Water content and aeration, will be discussed in subsequent sections of this review. Each of the remaining variables will be discussed briefly below.

The influence of PHC composition on biodegradability has been studied extensively (Bushell and Haas, 1941; Stone et

al., 1942; Jobson et al., 1972; Atlas, 1975; Raymond et al., 1976). PHC biodegradability depends primarily on chemical structure, but it is also strongly influenced by the physical state and toxicity of the compound (Bartha, 1986). In general, of the common classes of hydrocarbons, straight chain alkanes are most easily biodegraded. Branched alkanes and aromatics, while biodegradable, are utilized at a much slower rate than unbranched alkanes. The petroleum distillates most easily attacked by microorganisms would include kerosene, a petroleum distillate similar to JP-4, up to medium weight lubricating oils (Stone et al., 1941).

The concentration and physical state of PHCs in soil affects the availability of the PHCs to the microorganisms. PHC concentration below a threshold value can limit biodegradation rate by limiting substrate availability. A mathematical model presented by Schmidt et al. (1985) can be used to calculate this threshold value for organic substrates. The physical state of PHCs in soil (dispersed, adsorbed, or aggregated) determines the initial surface area available for microbial attack. Increasing the surface area increases the rate of biodegradation (Bartha, 1986).

The rate of biodegradation of PHCs in soil has been shown to increase with increasing temperature in the range from 5°C to 37°C (Dibble and Bartha, 1979b; Brown and Donnelly, 1983). However Dibble and Bartha reported a

levelling-off of hydrocarbon biodegradation rate above 20°C and only a slight increase up to 37°C.

The affect of nutrient availability on biodegradation of PHCs in soil has been studied extensively (Jobson et al., 1974; Kincannon, 1972; Raymond et al., 1976; Stotzky and Norman, 1963). Nitrogen, phosphorus, sulfur, iron, magnesium, calcium, sodium and other elements are required for microbial growth (Atlas, 1977). Dibble and Bartha (1979b) present a discussion of carbon:nitrogen (C:N) and carbon:phosphorus (C:P) ratios appropriate for biodegradation in soils. They reported theoretical optimal values of 10:1 and 100:1 for the C:N and C:P ratios, respectively. However, their experimental data showed that C:N and C:P values of 60:1 and 800:1, respectively, resulted in the highest hydrocarbon biodegradation rates.

Hydrocarbon degrading microorganisms are not extremely sensitive to changes in hydrogen ion concentration within the range of pH 6.0 to 9.5 (Zobell, 1946). However, the process of hydrocarbon biodegradation itself may lower the pH of the soil from 0.2 to 2 units (Zobell, 1950). Compensation for this effect was provided by lime addition in a study by Dibble and Bartha (1979b).

Microorganisms capable of degrading PHCs are found in most soils (Stone et al., 1942). Although the numbers of such organisms may be low in soils with low hydrocarbon

concentrations, a favorable soil environment can cause rapid population growth (Bartha, 1986).

Soil Water Content

Before a discussion of the literature concerning the effect of soil water content on PHC biodegradation in soil, it is necessary to discuss briefly the topic of water availability. Soil water status is usually described by both soil water content and soil water pressure. Soil water content is typically expressed as a volume (cm^3 water/cm^3 soil) or mass (g water/g soil) value. While such values are easily measured, they fail to completely describe the free-energy status or actual availability of water to soil microorganisms. Water availability is commonly expressed as soil water suction or water tension with typical units being the bar.

Increasing the soil water suction tends to decrease the water content causing the remaining soil water to be less available to the microorganisms living in the soil, and it can limit their biological activity. The ability of microorganisms to thrive under conditions of decreasing water availability varies widely with the species. In general, bacteria tolerate a more narrow range of water availability than do fungi and actinomycetes (Dommergues et al., 1978).

Water availability is one of the most important environmental variables influencing the fate of PHCs in soil. Not only does water availability influence microbial activity directly but it also influences the availability of PHCs to the microorganisms through its effects on adsorption, desorption and diffusion of PHCs in soil (Klecka, 1985).

Soil Water Content and PHC Biodegradation

In water-unsaturated soil, the predominant PHC biodegradation reactions occur at the soil-water interface (Marshall and Devinny, 1988). Both the hydrocarbon and the oxygen necessary for its biodegradation reach microorganisms by diffusion through the thin film of water on the soil particle which provides the habitat in which the soil microorganisms live (McGill et al., 1985; Schmidt and Alexander, 1985; Greenwood, 1961). Although soil-water is essential for soil microorganisms to survive, the excessive amount of soil-water in saturated or nearly saturated soils can hinder aeration and thereby inhibit aerobic respiration (Greenwood, 1961). Clearly, water is essential for microbial activity in soil; however, variations in soil water content can both enhance and inhibit biodegradation of petroleum hydrocarbons.

That soil water content is an important factor in microbial degradation of PHCs in soil was first reported by

Tauson in 1928. Lacking a complete translation of Tauson's work, a summary listed the presence of water with mineral salts as one condition necessary for attack on oil by microorganisms (Stone et al., 1942). Although other authors have studied PHC biodegradation in soil, only brief and infrequent references have been made concerning the influence of water content on this process.

Schwendinger (1968) cited a "dearth of information" concerning the cleanup of soil contaminated by oil spillage as an indication that basic research was needed in this area. He measured carbon dioxide (CO_2) evolution from beakers containing oil-contaminated soil. He determined the effect of different soil-water conditions on the rate of PHC biodegradation by comparing two batches of soil wet to 60 percent of field capacity and allowed to drain for one day and 14 days, respectively, prior to adding oil. Field capacity is defined as the amount of water remaining in a soil two or three days after having been wetted and after drainage is negligible (Cassel and Nielsen, 1982). Schwendinger reported that the soil drained for two weeks prior to oil addition consistently exhibited a higher CO_2 evolution rate than soil wetted one day prior to oil addition. He concluded that the effect of soil-water conditions on the decomposition of oil is large, and that reclamation of contaminated soil can be greatly influenced

by the degree of saturation and aeration in the soil-water system at the time of a spill.

In 1972, Pramer and Bartha reported, in a more quantitative fashion than Schwendinger, that the rate of aerobic biodegradation of simple or complex organic material in soil is greatest in the range of 50 to 70 percent of the soil water-holding capacity.

In a separate study lasting about three years, a soil water content equivalent to 60 percent by mass of the water holding capacity was maintained in an attempt to accelerate PHC biodegradation (Lehtomaki and Niemela, 1975). Selection of water content in the study appears to support Pramer and Bartha's optimal water range. However, the results of this study showed no statistically significant difference in the rate of oil biodegradation between a drier control soil and the soil maintained at 60 percent of the water-holding capacity.

Dibble and Bartha (1979b) conducted a study of oil sludge biodegradation in soils with water contents of 30, 60 and 90 percent of the water-holding capacity. In this study, they employed biometer flasks charged with 10 grams of sieved soil mixed with 10 grams of sand and 2 grams of dried oil sludge. They reported identical CO_2 evolution rates at all three water contents. The expected inhibition of biological activity at the extremes of water content did not show up. They offered as a possible explanation of

their data that the moisture requirements for maximum microbial activity may differ for hydrophobic (petroleum) and hydrophilic substrates. They discussed the likelihood that hydrocarbons reduce the water holding capacity of the soil by rendering some surfaces hydrophobic and thereby increase the availability of the water that is present. In a related study, Dibble and Bartha (1979a) reported an inhibition of biological activity at high, but not quantified, water content.

In 1983, Brown and Donnelly reported on a study of the influence of soil environment on the biodegradation of a petrochemical sludge and a refinery sludge. They found, for both sludges, that water content had a greater influence on the rate of biodegradation at a temperature of 10°C than at higher temperatures. Maximum CO_2 evolution from the soil treated with the refinery sludge occurred at a water content of 18 percent by weight (55 percent saturation). The maximum CO_2 evolution for the petrochemical sludge varied with temperature. At 30°C the maximum occurred at a water content of 11 percent by weight (33 percent saturation) and at 40°C, it occurred at a water content of 33 percent by weight (100 percent saturation). The refinery sludge contained seven percent carbon, and the petrochemical sludge contained 42 percent carbon on a weight basis. The authors concluded that there was a broad range of water contents,

both wetter and drier than field capacity, that had minimal influence on the rate of biodegradation of these sludges.

A 1989 report on jet fuel (JP-4) biodegradation in soil reported that the rate of CO_2 evolution was significantly influenced by water content (Hinchee, 1989). Soil columns were set up to maintain unsaturated water contents of 25, 50 and 75 percent of field capacity. Some of the columns were amended with nutrient solutions while others received no nutrient amendments. All columns were set up to allow air to pass through the soil in an upflow direction. The results of this study clearly showed an increase in cumulative CO_2 evolution with increasing water content in nutrient amended soils; however, in soils which were not amended with nutrients, CO_2 evolution was not significantly affected by increasing water content.

Soil Water Content and Pesticide Biodegradation

While petroleum hydrocarbons and pesticides may differ considerably in chemical composition and structure, they share at least one common trait: both can be biodegraded by soil microorganisms.

Potential routes of pesticide loss from soil include chemical degradation, photodegradation, volatilization and microbial degradation; however, microbial degradation is the most significant process by which many pesticides are degraded in soil (Meikle et al., 1973). Many researchers

have shown that microbial degradation can substantially reduce pesticide persistence in soil, and that one of the primary environmental variables controlling microbial degradation of pesticides is soil water content (Hurle and Walker, 1989; Getzin, 1981; Menn et al., 1965).

The degradation of an organophosphate insecticide (Imidan) in soil was shown to increase with water content (Menn et al., 1965). The half-life of the insecticide in a soil with a two percent water content was 18.4 days, while in the same soil at a ten percent water content, it was 4.9 days. The authors concluded that a portion of this difference in insecticide persistence was a result of a moisture-induced change in microbial activity.

The actual degree of pesticide degradation attributable to soil microorganisms was investigated using the pesticide Zinophos (Getzin, 1968). Autoclaved and non-autoclaved soils were treated with Zinophos and maintained at a water content of 20 percent by weight. At the end of a 16-week incubation at 25°C, only six percent of the initial mass of pesticide remained in the non-autoclaved soil, while 37 percent remained in the autoclaved soil. The difference in mass of Zinophos degraded was attributed to microbial degradation. Getzin also showed that Zinophos degraded more rapidly at a water content of 30 percent than it did at a water content of two percent.

Another study showing a close relationship between pesticide biodegradation and soil water content used the substituted urea herbicide Linuron (Usoroh and Hance, 1974). The results of this study showed that the rate of Linuron degradation was increased by 50 percent by increasing the water content from 25 percent to 100 percent of the soil water holding capacity. The authors attributed much of this degradation rate increase to increased microbiological activity.

While water content may be a critical environmental variable in the degradation of many pesticides, some researchers have shown that soil water content has no effect on the degradation of pesticide Chlorpyrifos (Tashiro and Kuhr, 1978; Getzin, 1981). Although Getzin reports that Chlorpyrifos is subject to microbial degradation, his data confirm Tashiro and Kuhr's earlier work in that soil water contents ranging from three to 20 percent by weight did not affect the pesticide's overall degradation rate. Getzin does mention, however, that the process of drying the soils prior to pesticide addition may have disrupted the activity of some of the pesticide degrading microorganisms.

Aeration

Oxygen availability may be the primary environmental variable controlling biodegradation of PHCs in soil (Bartha, 1986). With respect to PHC biodegradation, soil aeration is

the mechanism which provides oxygen to microorganisms in the soil. Under natural conditions, soil aeration involves the exchange of gases in the soil pore spaces with gases from the atmosphere. The primary mechanisms effecting this exchange are gaseous diffusion and variations in temperature and pressure which can cause bulk movement of atmospheric air into and out of the soil (Batchelder et al., 1986).

Air and water share the available pore space in water-unsaturated soils, and air moves freely in open pore space until it encounters water-filled pores. As the degree of water-saturation increases, soil aeration is increasingly limited because more of the soil pores become water-filled. Under water-saturated conditions, the oxygen supply to soil microorganisms is limited by the diffusion of oxygen through water, which is approximately 10,000 times slower than through air (Greenwood, 1961).

This great difference in the oxygen diffusion rates in air and water serves to inhibit aerobic biodegradation of PHCs, because in-soil oxygen diffusion tends to set an upper limit on PHC biodegradation rates when other conditions in the soil environment are near optimal (Bartha, 1986). Water saturated soils quickly approach anaerobic conditions as a result of chemical and biological processes which utilize oxygen (Greenwood, 1961).

A lack of sufficient aeration has been cited as a contributing factor in the persistence of PHCs in soil

(Atlas, 1981). Several methods have been employed to overcome this lack of oxygen. Among the most common are application of hydrogen peroxide, air, oxygen and ozone sparging, and soil venting (Lee et al., 1988). With the exception of soil venting, each of these methods has its primary influence in the delivery of oxygen to the saturated zone. In efforts to stimulate PHC biodegradation and volatilization in the water-unsaturated zone, soil venting has been getting increased attention in recent years.

Soil venting is a process designed to induce air flow through water-unsaturated soils. It normally involves a series of air inlet and recovery wells and blowers installed to establish an air pressure gradient across a zone of soil that is contaminated with hydrocarbons (Thornton and Wootan, 1982; Crow et al., 1987; Wilson and Ward, 1987; Hoag et al., 1987; Hinchee et al., 1987; Massmann, 1989). Some authors, however, have reported the use of soil venting systems employing vapor extraction wells and no air inlet wells (Batchelder et al., 1986; Agrelot et al., 1985). Although they may not be required at all spill remediation sites, the advantage of using air inlet wells lies in the enhancement of air flow deeper into soil profiles (Singh et al., 1987; Zenobia et al., 1987).

The induced air flow through the soil volatilizes some PHC components while providing the oxygen necessary for aerobic biodegradation of any remaining PHC components. For

relatively light PHCs such as gasoline, the mass of hydrocarbon volatilized may exceed that metabolized by microorganisms (Wilson and Ward, 1987).

Both the PHC volatilization and the biodegradation enhancing aspects of the soil venting process have been studied in recent years.

Soil Venting and Enhancement of PHC Biodegradation

The earliest discussion of soil venting as a means of increasing the availability of oxygen and enhancing PHC biodegradation in soil was published in 1982. The Texas Research Institute was searching for a method capable of providing aeration to deep soils which could not be aerated by rototilling (TRI, 1982). After reviewing a vapor extraction process in which liquid nitrogen was swept through water-unsaturated soil, the possibility of supplying oxygen or air through a similar process became apparent.

This early reference to soil venting lead to further study of the process at the Texas Research Institute. Thornton and Wootan (1982) set up a containment in which they simulated a gasoline spill in soil. The containment was designed to facilitate study of the influence of soil venting on gasoline removal by both volatilization and biodegradation. They reported that over an 11-day venting period, approximately 59 percent of the original 75-gallon spill was removed. Volatilization accounted for

approximately 97 percent of the total removal, while biodegradation accounted for approximately three percent.

The soil venting process was employed in the remediation of a jet fuel (JP-4) spill at Hill Air Force Base in Utah (Hinchee et al., 1989). They reported changes in the composition of the gases in the soil pore spaces resulting from soil venting. Soil venting was reported to greatly improve oxygen availability in water-unsaturated soil. Biodegradation was reported to account for 18.7 to 24.8 percent of the total jet fuel removal at the site, while volatilization accounted for the largest portion (75.2 to 81.3 percent) of the total observed removal.

The reports above indicate wide variation in the relative importance of biodegradation and volatilization as PHC removal mechanisms in soil venting. This variation may be explained in part by the variation in physical and chemical properties of the fuels involved, i.e., gasoline and jet fuel (Hinchee et al., 1987). Nyer and Skladany (1989) also report that physical and chemical properties will have a large effect on the soil venting process.

Soil Venting and PHC Volatilization

The suitability of soil venting as a means of stripping various petroleum distillates from contaminated soils is dependent upon the components of the distillate (Nyer and Skladany, 1989). The rate at which a specific hydrocarbon

will volatilize is related to its vapor pressure. Bennedsen et al. (1987) reports that contaminants with a vapor pressure of 0.5 milliliters of mercury or greater, or with a Henry's Law constant greater than 10 atmospheres are likely to be removed by soil venting.

Gasoline is possibly the lightest petroleum distillate that is spilled or released on a widespread basis. Even among different gasolines, however, vapor pressures can differ by an order of magnitude (Wilson and Ward, 1987), and a significant fraction of heavier distillates may remain in the soil (Johnson et al., 1987). Therefore the effectiveness of the soil venting process for remediation of spills of heavier distillates such as diesel fuel, fuel oil and jet fuel has been reported to be limited (Nyer and Skladany, 1989; Hinchee et al., 1987; Johnson et al., 1985).

The effectiveness of the soil venting process for remediation of gasoline spills has been widely investigated in the past eight to ten years (Thornton and Wootan, 1982; Hoag et al., 1984; Hoag et al., 1987; Crow et al., 1987). Thornton and Wootan (1982) used induced air loading rates ranging from 2.5 to 4.0 $cm^3 \cdot cm^{-2} \cdot min^{-1}$, and they achieved 57 percent removal by volatilization of an initial 75-gallon gasoline spill in 11 days of venting. This study was conducted in a simulated sandy soil and aquifer in a containment measuring 40 feet in length, 20 feet in width and 4 feet in depth.

Hoag et al. (1984) studied the soil venting process in laboratory soil columns. Sandy soils of various water contents were employed to characterize the variation of gasoline-holding capacity (residual saturation) with water content, and to determine the effectiveness of soil venting. Hoag used air loading rates from 16.1 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ to 161 $cm^3 \cdot cm^{-2} \cdot min^{-1}$. A typical result of this experiment was approximately 100 percent removal of an initial 93 grams of gasoline from 5 to 6 kilograms of soil after venting for approximately one day. The removal efficiency was determined by GC/FID analysis of the effluent venting air and confirmed by gravimetric techniques.

Hoag et al. (1987) reported on an in-situ gasoline spill recovery employing soil venting. Approximately 400 to 500 gallons of gasoline were spilled into water-unsaturated soil at a service station. A soil venting system was installed, and it operated at an air loading rate of 31 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ for 90 days. This process removed approximately 364 gallons of gasoline, while approximately 80 gallons of the free product were removed by bailing from the recovery well. The ratio of air used to gasoline removed was 62 liters of air per gram of gasoline. This value was three times higher than that measured under ideal laboratory conditions (Mackay and Hoag, 1986).

Crow et al. (1987) reported on soil venting experiments performed at a five-year old gasoline spill site. The site

soil was sand and gravel, and, therefore, quite porous and conducive to evaluating the effectiveness of soil venting to eliminate hydrocarbon vapors in the soil. This study attempted to quantify the radial influence of the venting system. It was determined that the greatest reduction in hydrocarbon vapor concentrations occurred on the centerlines between the vapor recovery and air inlet wells and that the effectiveness of the air inlet wells decreased as the distance from the vapor recovery well increased. Furthermore, static pressure measurements of vacuum in the soil indicated that the vapor recovery wells had radii of influence of 50 to 110 feet at flow rates of approximately 20 and 40 standard cubic feet per minute, respectively. These radii of influence measurements were made during the first four hours of venting, indicating that hydrocarbon vapors may migrate quickly in porous soils under the influence of soil venting. Crow et al., also reported that the time required to draw down the gaseous hydrocarbon concentration in the water-unsaturated soil was much shorter than the time required to reestablish the initial concentrations upon ceasing venting operations. They concluded that a pulsed venting operation would be a more cost-effective means of achieving vapor control. This conclusion was also reported by Johnson et al. (1987). Neither report provided a quantitative discussion concerning the affect of soil venting on biodegradation.

Some other aspects of soil venting have been studied in the past few years. Johnson et al. (1987) discussed mass transfer of organics between solid, liquid and vapor phases in the soil and related his findings to the effectiveness of the soil venting process. Massmann (1989) described a process for engineering and design of a vapor-extraction system. Specifically, he discussed methods to predict the numbers of air inlet and vapor extraction wells required as well as methods to determine required flow rates. Finally, Hinchee et al. (1987) presented a cost analysis and feasibility comparison of hydrogen peroxide-enhanced bioreclamation, soil venting and ground water extraction for fuel hydrocarbon spill site remediation. They reported costs of $230, $201, and $285 per gallon of fuel removed for enhanced bioreclamation, soil venting and ground water extraction, respectively. The cost cited for the soil venting system includes $130 per gallon of fuel removed for activated carbon treatment of the vent gas effluent. Other methods of effluent venting gas treatment such as catalytic conversion and burning may be employed; however, treatment of the effluent venting gas may not be required in all remediations.

CHAPTER 3

MATERIALS AND METHODOLOGY

Sampling and Setup

The soil used in this study was collected from a jet fuel (JP-4) spill site on Tyndall Air Force Base (AFB), Florida. Specifically, the soil was obtained from a previous fuel storage area located in Area B of Tyndall AFB and designated "Zone 9--POL Area B." The clean soil at the site has been described as very fine to fine grained, poorly graded unconsolidated quartz sand with trace occurrences of organic material (IRP Phase II, 1988).

Sample Collection

Three separate bulk soil samples were collected from this site. All soil samples were taken from the water-unsaturated zone at approximately the same location at the spill site. The actual depth at which the samples were collected was largely determined by the presence or absence of JP-4 in the soil. The goal was to collect soil heavily contaminated with JP-4.

The first two samples, each approximately 20 liters in volume, were collected on 26 May 1989 and 19 July 1989,

respectively. These samples were obtained with a post-hole digger from a depth of approximately 60 - 80 centimeters, which was approximately the top of the capillary water zone. The third sample was collected on 12 November 1989. This sample was also collected with a post-hole digger; however, dewatering activities at the site had lowered the water table to a depth of approximately 200 centimeters. Therefore, this soil sample was collected over a depth from 60 to 180 centimeters below the surface.

Sample Handling

Once retrieved from the bore hole, the soil was placed in clean plastic bags. Excess air was pressed out of the bags, and they were sealed. The soil was mixed by inverting and agitating the bags. This mixing process was used to increase the uniformity of the physical and chemical properties of the soil sample. The bags containing the samples were placed inside a second bag and iced in a sealed cooler for transport to the University of Florida, Gainesville, Florida.

Upon arrival at the University, the samples were placed in a walk-in cooler at a temperature of approximately 4°C. The samples were kept in the cooler pending further processing. The duration of storage for those samples used in biodegradation testing was less than five days.

Description of Apparatus

Columns

A total of three soil columns were used during this investigation. The first column was used in all preliminary work and as an anaerobic control column during biodegradation testing. The other two columns, which will be referred to as columns 1 and 2, were used only in the biodegradation testing phase of this project. A schematic of the columns used in biodegradation testing is shown in Figure 3-1.

The basic design of the soil columns used in this study was obtained from a report by R. S. Mansell et al. (1968). The soil columns were constructed of 3.5 inch outside diameter clear acrylic tubing with a wall thickness of 0.125 inch, and a length of 19.68 inches. To ensure uniformity of column construction, a wrap-around column template was used to position the sampling, tensiometer and venting ports on all three columns.

The single column used during the preliminary phase of this experiment was constructed with nine 0.5-inch diameter soil sampling ports and six 0.375-inch diameter tensiometer ports. The two columns used during the biodegradation testing had no soil sampling ports and only three water tensiometer ports. Each column had air inlet and outlet venting ports 180° opposite one another. Each port consisted of three lines of 0.0625-inch holes separated by

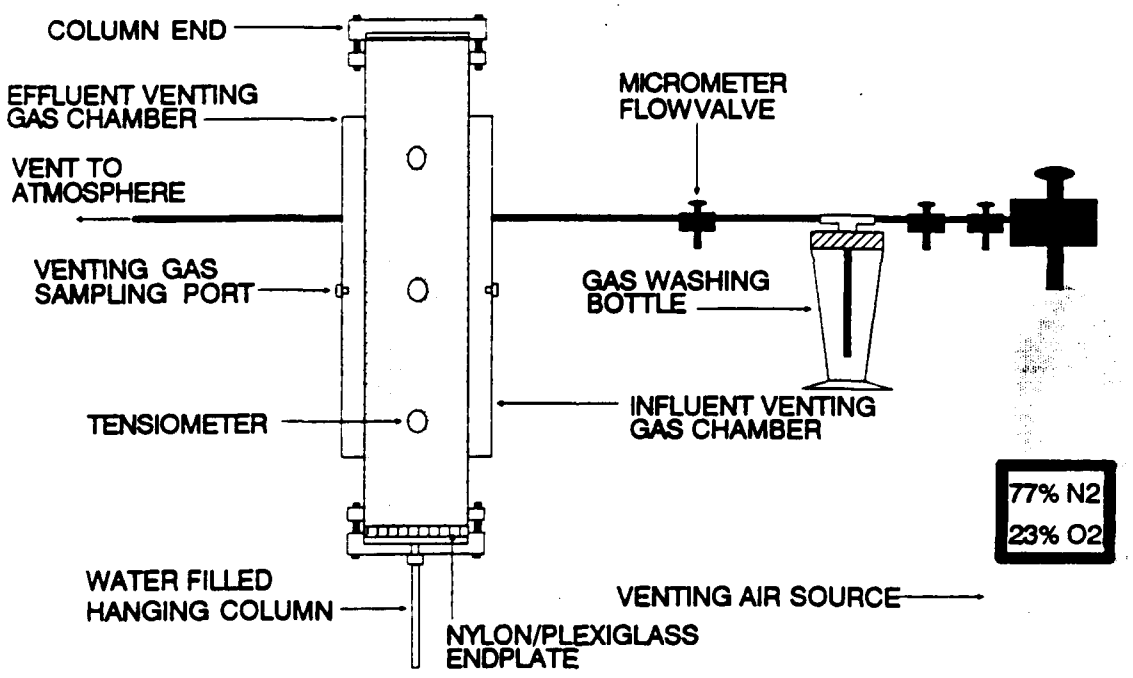

Figure 3-1. Schematic of the Biodegradation Soil Column

0.75-inch around the circumference of the column and by 0.39-inch along the length of the column. A total of 105 holes was used in each inlet and outlet venting port.

Inlet and outlet venting chambers enclosed the venting ports. Each venting chamber was half of a 2.0-inch outside diameter clear acrylic tube split longitudinally. Each chamber was 13.8 inches long, and capped on the ends with plexiglass plates. The venting chambers were held in place with silicon sealant and were leak tested periodically throughout this study. Each chamber had a syringe sampling port sealed with a teflon lined septum and a venting gas inlet/outlet port. Each outlet port was vented to the atmosphere with a 50-centimeter Tygon tubing extension plugged at both ends with glass wool. The extension was used to limit diffusion of ambient air into the effluent chamber.

The column endplates consisted of a woven nylon fabric disk backed by a 0.25-inch thick, 3.50-inch diameter, plexiglas plate perforated with 0.0625-inch holes. These endplates were used in lieu of more common porous ceramic or fritted glass endplates to facilitate more rapid column drainage.

The column ends were machined at the University of Florida machine shop. They were constructed of clear acrylic and machined to seal the ends of the soil columns. The dimensions and basic design of the column ends were the

same as the base of a Model 1450 Tempe Pressure Cell (Soilmoisture Equipment Corporation, Santa Barbara, CA). Each column end had two O-ring seals, a water inflow/outflow port and two syringe ports to permit periodic removal of air bubbles from the column ends.

Water drainage system

The water drainage system originally proposed for this study was designed to use a peristaltic pump to recirculate effluent water from the column water outflow port back into the inflow port on the top of the column. This design was intended to slow the drainage of the column in order to maintain approximately constant soil water suction with depth in the column. However, it was determined during preliminary runs that the required control of drainage could be obtained by utilizing a hanging column on the water outflow port to control the suction applied to the column endplates. With the hanging columns, the suction applied to the endplates could be adjusted to modify the rate and extent of drainage. Thus, the need for recirculating the column water was negated. This matter is discussed further in Chapter 4.

The water drainage system used throughout this study employed hanging columns constructed of water filled Tygon tubing attached to a fitting in the water outflow port. After a hanging column was attached to a soil column, the column was allowed to drain until the soil water suction had

increased to the desired level. The hanging column was then clamped to stop drainage and to allow the soil water suction values to stabilize and remain approximately constant with depth. The time required to achieve this approximately stable condition varied from 7 to 14 days. The column was considered to be stable when the soil water suction readings indicated a change in degree of water saturation of less than one percent over a period of 7 to 10 days.

After achieving and maintaining the approximately stable condition described above, the hanging column was extended by 10 centimeters and the drainage and stabilization process repeated. In this manner, the soil water content in the columns was stepped down from 100 percent saturation to approximately 66 percent saturation in column 2 and 63 percent saturation in column 1.

The water that drained from the columns was collected in 40 milliliter vials for use in determining the mass of JP-4 lost in the aqueous effluent from the columns.

Soil-water monitoring system

A total of six Soilmoisture Corporation Model 2100 tensiometers were used to measure soil water suction throughout this study. The Model 2100 tensiometers incorporate 1 bar porous ceramic cups 0.25 inches in diameter and 1.125 inches in length. The porous cups are attached to a pressure measuring device by a 0.125-inch diameter length of pressure tubing. The pressure measuring

device supplied by the manufacturer was not sufficiently sensitive for this experiment which required a resolution of +/- 0.1 centimeters of water on soil water suction values. The required resolution was obtained by constructing and calibrating six water filled, U-tube manometers, each 100 centimeters in length. Each manometer was connected to one porous cup, and the porous cups were inserted into the soil columns. The tensiometer ports were sealed around the pressure tubing using cored and split rubber stoppers and silicon sealant.

The single column used to develop a soil water characteristic curve (a plot of volumetric degree of water saturation versus suction) during the preliminary phase of this study was instrumented with six tensiometers located 90° from the centers of the influent and effluent venting ports. The porous cups were inserted radially inward into the soil column through the tensiometer ports at levels of 5, 10, 15, 25, 35 and 45 centimeters above the column bottom.

The two columns used during the biodegradation testing were each instrumented with three tensiometers. The tensiometers were installed and sealed in the same manner as described above for the preliminary phase of this study. In each column, the tensiometers were installed at 15, 25 and 35 centimeters above the column bottom.

Venting system

The venting gas used in this study was a high purity mixture containing 22.85 percent O_2 and approximately 77.15 percent N_2. This gas mixture, which will be referred to as venting air throughout this thesis, was very similar to atmospheric air, but it contained no detectable CO_2 when analyzed using the gas chromatograph and chromatographic column employed throughout this study.

The venting air source was a single pressurized cylinder containing approximately 200 cubic feet (STP) of compressed gas. A two-stage regulator, regulator flow valve, and a fine metering valve were used to coarsely adjust the venting air flow into a Fisher-Milligan gas-washing bottle through approximately a 10-foot length of 0.125-inch diameter Teflon tubing. The gas-washing bottle was filled with deaerated distilled water to humidify the venting air. The air path through the gas washing bottle was 36 inches in length.

The humidified venting air from the gas washing bottle flowed through Tygon tubing, was split by a glass "T" and was controlled by a separate micrometer flow valve at the inlet to each column. The venting air flow was checked daily using an electronic Tekmar Digital Flowmeter and adjusted as necessary to maintain a flow rate of 0.75 to 1.5 milliliters per minute. These flow rates correspond to approximately 1 to 2.5 pore volume changeouts per day.

The entire venting air flow system was periodically checked for air tightness by closing and pressurizing the system to check for leakage.

Control column

The single soil column used during the preliminary phase of this study was modified to act as an anaerobic control column during the biodegradation testing. The purpose of this column was to provide JP-4 volatilization data from a soil column free of a significant level of aerobic biodegradation. All tensiometer and sample ports in the column were sealed, and the column was set up and drained in the same manner as the aerobic biodegradation columns. The control column was vented with humidified nitrogen gas through a venting system identical to that described above for the aerobic columns. The nitrogen gas flow rate was maintained between 0.75 and 1.5 milliliters per minute.

Soil Column Packing

A soil column packing procedure was developed to reproducibly pack moist soil into the columns and ensure a uniform wet bulk density approximately equal to the soil wet bulk density at the sample site.

Prior to development of this packing procedure, the wet and dry bulk densities of the soil at the sampling location were determined. A core sampler designed to take

undisturbed cores 3.0 centimeters in depth and 5.38 centimeters in diameter was used to collect the cores for bulk density determinations. A total of 17 cores were taken from depths between 20 and 70 centimeters below the surface. The cores were weighed using a Mettler Tara 0-2500 gram electronic balance, dried in a oven at 105°C for 48 hours, and then reweighed. The wet and dry bulk densities were then calculated based on the known wet and dry soil masses and the volume of each core. For future reference, the average wet and dry bulk densities determined from the field core samples were 1.86 +/- 0.06 and 1.59 +/- 0.06 grams per cubic centimeter, respectively.

After determining the wet bulk density of the field soil, a soil column was packed, analyzed and repacked ten times in succession. The analyses included extracting core samples 8.5 cubic centimeters in volume through the sample ports in the column side and determining the wet and dry bulk densities. These determinations checked the uniformity of packed soil density with depth. The entire column was also weighed after each packing to ensure that the overall wet bulk density of the soil in the column was similar to that of the soil at the field site. The actual step-by-step packing procedure developed for this study is provided in Appendix A.

The single column used in the preliminary phase of this study was packed on 9 August 1989 using soil obtained from

the Tyndall AFB sample site on 19 July 1989. The column was packed in increments one inch in depth and with a soil mass of 255 grams per increment.

The two aerobic biodegradation columns and the control column were packed on 16 and 17 November 1989 using soil collected on 12 November 1989. These columns were packed in increments one inch in depth and with a moist soil mass of 255.5 grams per increment.

Soil Water Characteristic Curves

Equilibrium Soil Water Characteristic Curve

During the preliminary phase of this study, a soil water characteristic curve was developed using a column packed with JP-4 contaminated soil from the field site. Once the column was packed, the tensiometers were installed as previously described, and the column was saturated using deaerated tap water applied under a head of approximately six to twelve inches of water. The water was applied through the bottom column end in an upflow direction. The elevation of the source water reservoir was increased on a day-to-day basis to maintain a head of approximately 6 to 12 inches of water above the surface of the saturated zone in the soil column. This process took place from 24 to 28 August 1989.

After all six tensiometers indicated positive hydrostatic pressures, the column was assumed to be

saturated. At this point, the source water reservoir was removed, and a 10-centimeter hanging column was connected to allow gravity drainage to begin.

On 29 August 1989, the venting air source supplying the column was turned on, and venting continued until the experiment was terminated on 3 November 1989. The soil water suction at each tensiometer was periodically recorded from 29 August through 3 November 1989, at which time the soil water suction at each tensiometer was essentially constant.

The final soil water suction value at each tensiometer was recorded and verified to be approximately equal to the height of that tensiometer above the end of the hanging column. The tensiometer height and soil water suction values were the criteria used to determine whether the soil water in the column was in a state of hydrodynamic equilibrium. The column was assumed to be at equilibrium when these values were approximately equal.

The dry weight basis water content and dry bulk density at each tensiometer were determined by taking soil core samples 8.5 cubic centimeters in volume from the column through sample ports directly opposite and equal in height to the tensiometer ports. The soil samples were weighed using a Mettler PR1200 electronic balance, dried for 24 hours at 105°C and reweighed. The volumetric water content was calculated using the following equation in which the

density of water is assumed to be 1 gram per cubic centimeter:

$$V_{H2O} = W_{H2O} \times D_{dry},$$

where

V_{H2O} = volumetric water content, cm^3 water/cm^3 soil,

W_{H2O} = dry weight basis water content, g water/g soil,

D_{dry} = packed soil dry bulk density, g/cm^3.

The volumetric water content values were plotted against the soil water suction values to develop an equilibrium soil water characteristic curve. This curve was then used during biodegradation testing to estimate soil water content from the soil water suction values.

Non-equilibrium Soil Water Characteristic Curve

A non-equilibrium soil water characteristic curve was developed after the completion of the biodegradation testing phase of this study. This curve was constructed by analyzing the actual biodegradation columns in the same manner described above for the preliminary column. The data from the two columns were then combined to construct a single, non-equilibrium, soil water characteristic curve. The non-equilibrium soil water characteristic curve was used to determine all soil water contents reported in this thesis, as hydrodynamic equilibrium was not established during biodegradation testing. A complete discussion of the

equilibrium and non-equilibrium soil water characteristic curves used in this study is presented in Chapter 4.

Initial Soil Testing

Prior to the packing of the soil columns to be used in the biodegradation testing, a representative soil sample was removed from the original bulk mixed soil sample. This sample was used for initial JP-4 extractions, water content and soil dehydrogenase activity determinations.

JP-4 Extractions and Analyses

The extraction procedure used to remove JP-4 from the soil in this study was similar to that presented by Vandegrift and Kampbell (1988). The method involved placing approximately 10 grams of moist soil in a tared 40 milliliter vial with a teflon lined septum cap. 10.0 milliliters of optima grade methylene chloride was added, and the vial was shaken until soil fines were observed to separate and settle. The vial was then placed in a Branson Ultrasonic Cleaner (Model B-22-4) and sonicated for 60 minutes. After removal from the ultrasonic bath, the vial was allowed to settle, and approximately 3 to 5 milliliters of the methylene chloride were pipetted from the soil. The methylene chloride extract was dried by passing it through a microcolumn of anhydrous sodium sulfate prior to sealing it in a crimp seal vial. The average percent recovery of JP-4

spikes obtained using this extraction procedure and the bulk mixed soil sample was 101 +/- 3 percent.

The JP-4 extraction procedure described above was used in the determination of the mass loading of JP-4 in the soil employed in the biodegradation testing. Eight mixed soil samples, two unmixed soil samples, and two clean soil samples from the Tyndall AFB sample site were analyzed.

A Perkin Elmer Sigma 2000 gas chromatograph equipped with a flame ionization detector (FID) was used for essentially all JP-4 analyses. The gas chromatographic column used was a 15-meter DB-5 0.53-millimeter diameter capillary column with a 1.5 micron film thickness. The carrier gas was ultrahigh purity helium at a flow rate of approximately 10 milliliters per minute. The injection port temperature used 300°C and the detector temperature was 300°C. The oven temperature was programmed as follows:

1. 45°C, three minute hold,
2. 10°C/min up to 150°C, one minute hold,
3. 30°C/min up to 225°C, one minute hold.

Sample volumes of two microliters were injected for all JP-4 samples.

Figure 3-2 shows the JP-4 calibration curve used to determine tne mass of JP-4 in the samples. The curve was developed using standard solutions of JP-4 in methylene chloride. The amount of JP-4 present in the standards and samples was quantified using the sum of the chromatogram

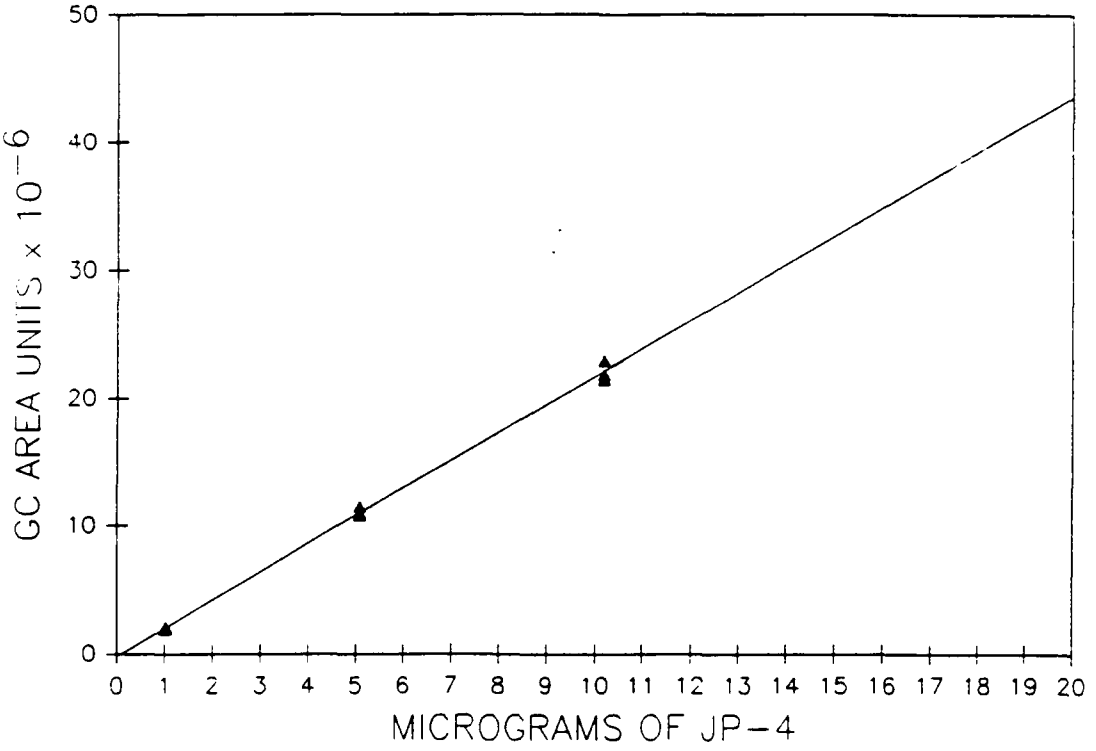

Figure 3-2. GC/FID JP-4 Calibration Curve

area under seven major peaks. Five of these peaks were tentatively identified by matching retention times with standard solutions of isooctane, nonane, decane, dodecane, and tetradecane. The remaining two peaks, undecane and tridecane, were tentatively identified by matching the elution order of the major peaks in a JP-4 chromatogram published by Vandegrift and Kampbell (1988).

Soil Water Content Determinations

Gravimetric soil water content determinations were run on 9 sub-samples from the bulk mixed soil sample prior to packing columns 1 and 2 and the control column. These tests were conducted using sample sizes of approximately 50 grams of moist soil. Each sample was placed in a tared drying dish and dried in an oven at 105°C for 24 hours. The average value of the dry weight basis water content was used to determine the mass of soil to be packed into the soil column per packing increment. The equation used in this determination is presented in Appendix A.

Soil Dehydrogenase Activity Determinations

Stevenson (1959) showed that there is a direct positive correlation between dehydrogenase activity and microbial respiration in soil. In order to determine the impact of the soil venting process on the microbial activity in the test soil, a soil dehydrogenase activity test was performed

before and after the biodegradation testing. The bulk mixed soil was used for the initial determination.

The soil dehydrogenase test employed was a combination of methods presented by Lopez et al. (1986) and Casida (1977). The test used 20 grams of soil mixed with 0.2 grams of calcium carbonate which were mixed and dispensed in 6 gram aliquots into 3, 40 milliliter vials. Each vial of soil received 3.5 milliliters of a sterilized aqueous solution of 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetrazolium chloride (INT), made up by adding 200 milligrams of INT to 100 milliliters distilled water. The contents were then mixed, and the capped vials were incubated for 24 hours at 37°C.

Following incubation, each sample was transferred with methanol to a funnel containing Whatman #5 filter paper. The soil was rinsed with a known volume of methanol until no additional red color was obtained upon rinsing. The filtrate was then refiltered and the absorbance of the red-tinted methanol was read at a wavelength of 485 nanometers against a non-INT soil blank using a Bausch and Lomb Spectronic 21 Ultraviolet-Visible Spectrophotometer. Figure 3-3 presents the calibration curve for the absorbance measurements. Dehydrogenase activity was expressed as micrograms of INT-formazan produced per gram of oven dried soil per 24 hours. These units are commonly found in the

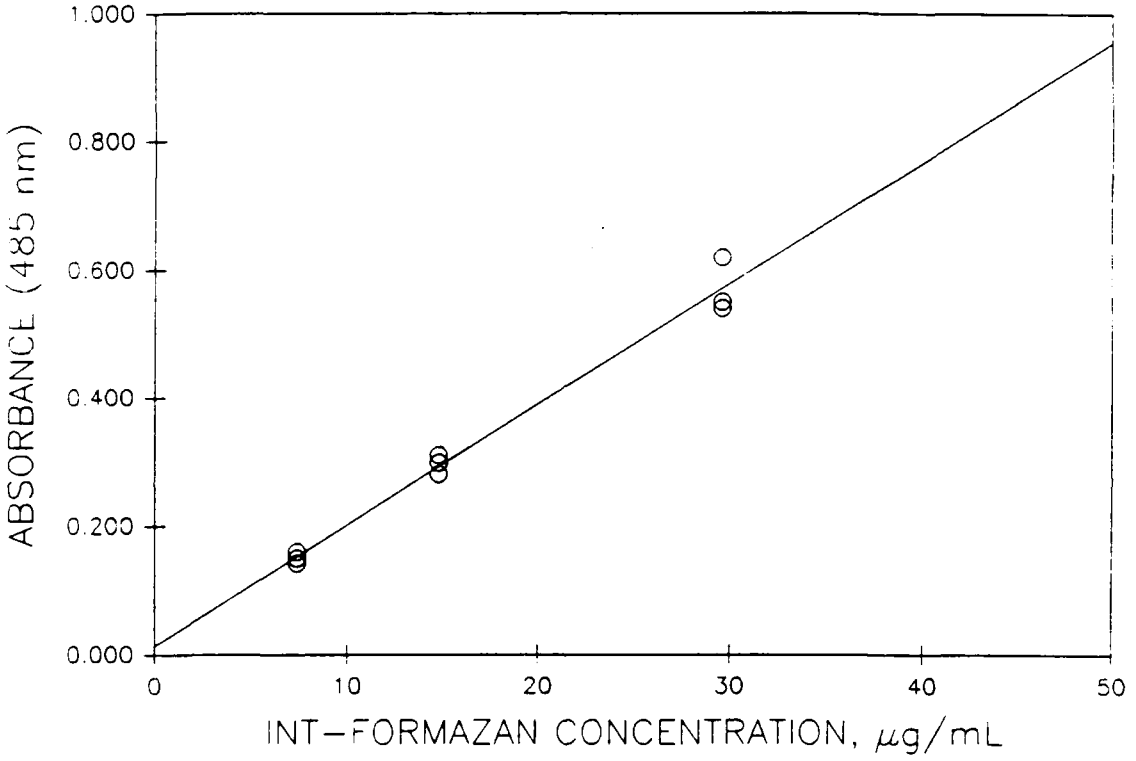

Figure 3-3. INT-formazan in Methanol Calibration Curve for UV/Visible Spectrophotometer

literature for comparison of soil dehydrogenase activities (Frankenberger and Johanson, 1982; Casida, 1977).

Biodegradation Testing

Preparation of Biodegradation Columns

After packing and instrumenting two soil columns for aerobic biodegradation testing, both columns were saturated by flowing deaerated tap water in an upflow direction into the columns under a head of approximately 6 to 12 inches of water. At the same time, the anaerobic control column was set up and saturated using the same water source and hydrostatic pressure head.

Water was added to all three columns until the tensiometers indicated that the aerobic biodegradation columns were saturated. On 26 November 1989, the columns were configured to begin draining by disconnecting the water source and connecting a 10 centimeter hanging column to each soil column. The columns drained for four days prior to the initiation of the venting air flow. The four day delay was required to allow the soil to drain sufficiently to prevent seepage of water through the venting ports into the venting chambers.

Biodegradation Testing Sequence of Events

30 November 1989 was recorded as "day zero" for the biodegradation testing phase of this study. Venting and

drainage of biodegradation column 1 and the control column continued through day 81 (19 February 1990), while biodegradation column 2 was vented and drained through day 58 (27 January 1990). After day 58, column 2 was partially resaturated and subsequently drained and vented through day 89 (27 February 1990). The resaturation process required interruption of the venting air flow to column 2 which was stopped on day 58 and restarted on day 78. Column 2 was rewetted to help confirm whether the recorded trend in biodegradation rate was a result of limited water availability.

Determination of Biodegradation Rate

Biodegradation data was gathered from the aerobic columns on a daily basis through most of the 89 days of biodegradation testing. Biodegradation data consisted of gaseous oxygen uptake and carbon dioxide production measurements. The daily sampling routine involved running oxygen and carbon dioxide standards (Supelco standard gases), and recording the temperature, venting air flow rate, and soil water suction values at the sampling time. The soil water suction values from the three tensiometers in each column were averaged to determine the average value of water content in the venting zone.

The effluent gas from the anaerobic control column was analyzed approximately once every seven days to determine the rate of carbon dioxide production.

Expected optimum soil water content range

The soil water contents cited in the literature as being optimal for microbial degradation of hydrocarbons ranged up to 100 percent of the soil water holding capacity (Pramer and Bartha, 1972; Usoroh and Hance, 1974). It was assumed by this author that the term "soil water holding capacity," as referenced in the literature is equivalent to the term "in situ field capacity" which is defined as the amount of water remaining in a soil two or three days after having been wetted and after drainage is negligible (Cassel and Nielson, 1982). With this in mind, it was expected that a maximum rate of biodegradation might be observed after the soil columns had drained to between 50 and 80 percent saturation.

Oxygen mass utilization rate

The oxygen mass utilization rate (O_2 MUR) was determined by subtracting the mass of oxygen in a 500 microliter effluent gas sample from the initial mass of oxygen in 500 microliters of influent venting air. All gaseous samples were taken with gas tight syringes. The separation and quantification of the oxygen in the effluent venting air was performed using a Perkin Elmer Sigma 2000 Gas Chromatograph equipped with a thermal conductivity

detector. The oxygen was separated from other gases using a 45/60 mesh Molecular Sieve 5A stainless steel packed column 12 feet in length and 0.25 inches in diameter. The analyses were run at 45°C (isothermal) with a flow rate of 60 milliliters per minute of ultrahigh purity helium as the carrier gas. The thermal conductivity detector was set at 175°C.

The O_2 MUR was calculated using the difference in oxygen concentration across the soil column and the average venting air flow rate since the previous sample time. The equation used in this calculation is presented below:

$$O_2 \text{ MUR} = \frac{([O_2]_{IN} - [O_2]_{OUT})}{1000} \times Q \times 1440 \text{ min/day}$$

where

O_2MUR = Oxygen Mass Utilization Rate, mg O_2/day,

$[O_2]_{IN}$ = Influent venting air oxygen concentration, 304.41 mg O_2/L (at 20°C),

$[O_2]_{OUT}$ = Effluent venting air oxygen concentration, mg O_2/L,

Q = Average venting air flow rate since the previous sample time.

Figure 3-4 shows the oxygen calibration curve used to determine the mass of oxygen in the venting air samples. The curve was developed using Supelco calibration gas standards. For biodegradation rate determinations, the mass of oxygen taken up across each column was converted to an equivalent mass of JP-4 using the stoichiometric mass ratio for mineralization of dodecane ($C_{12}H_{26}$) to carbon dioxide and

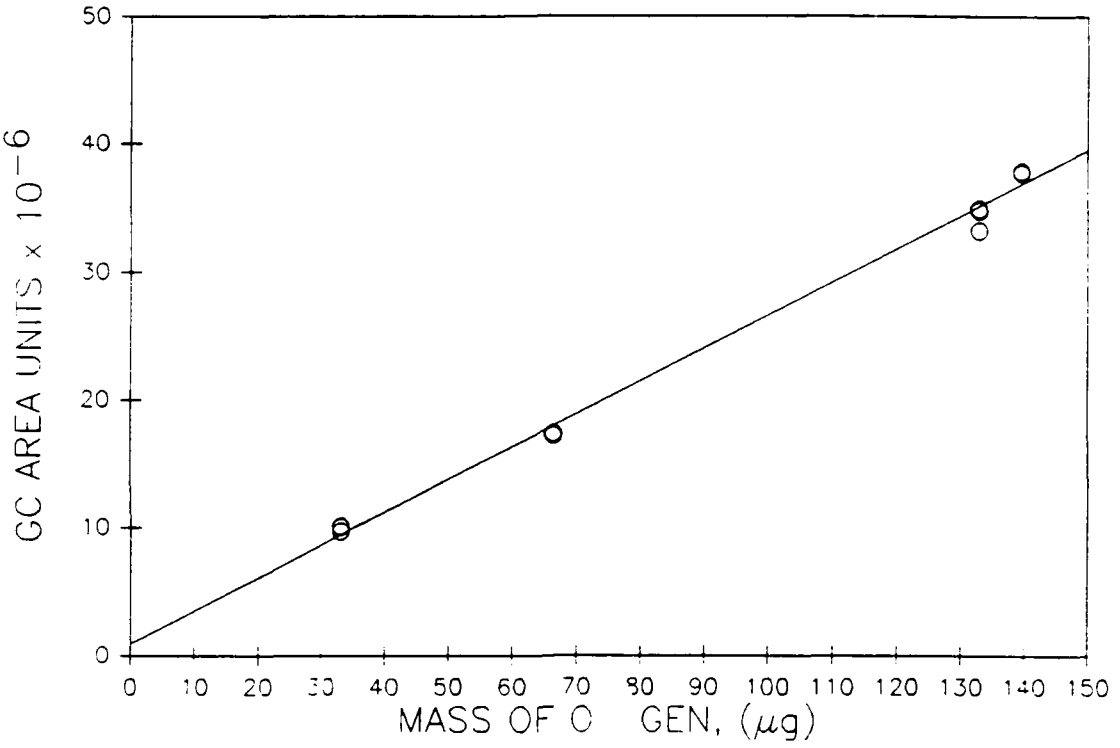

Figure 3-4. GC/TCD Oxygen Calibration Curve

water. The chemical equation for this mineralization reaction is presented below:

$$C_{12}H_{26} + 18.5\ O_2 \text{ ----> } 12\ CO_2 + 13\ H_2O$$

Dodecane was taken as a model compound in JP-4. Based on this assumption and the chemical equation presented above, the ratio of the mass of JP-4 biodegraded to the mass of oxygen used was calculated to be 1:3.48. This assumption is good for the more abundant alkanes in JP-4 for which the ratios vary from 1:3.51 to 1:3.47. The mass of the aromatic compounds degraded may be underestimated as the stoichiometric ratio of the mass of hydrocarbon degraded to mass of oxygen consumed averages about 1:3.10 for benzene, toluene, xylene and naphthalene. However, because alkanes comprise the larger and more biodegradable fraction of JP-4, the use of dodecane as a model compound should provide a reasonable prediction of the mass of JP-4 biodegraded.

The equation used to convert from oxygen uptake to mass of JP-4 biodegraded is presented below:

$$\text{JP-4} = \frac{[(O_2\ \text{MUR})_n + (O_2\ \text{MUR})_{n-1}]}{2} \times \frac{1\ \text{mg JP-4}}{3.48\ \text{mg}\ O_2} \times T$$

where

JP-4 = Mass of JP-4 biodegraded based on O_2 uptake, mg JP-4,

$[(O_2\ \text{MUR})_n + (O_2\ \text{MUR})_{n-1}]/2$ = Average O_2 MUR since the previous sample time,

T = number of days since the previous sample time.

Carbon dioxide mass production rate

The carbon dioxide mass production rate (CO_2 MPR) was determined by measuring the mass of carbon dioxide in a 500 microliter sample collected from the effluent venting chamber using a 1000 microliter gas tight syringe. The separation and quantification of the carbon dioxide in the effluent venting air was performed using a Perkin Elmer Sigma 2000 Gas Chromatograph and a thermal conductivity detector. The carbon dioxide was separated from the other gases using a 80/100 mesh Chromosorb 102 stainless steel packed column six feet in length and 0.25 inches in diameter. The analyses were run at 45°C (isothermal) with a flow rate of 30 milliliters per minute of ultrahigh purity helium as the carrier gas. The thermal conductivity detector was set at 175°C.

The CO_2 MPR was calculated using the carbon dioxide concentration in the effluent venting chamber and the average venting air flow rate since the previous sample time. The equation used in this calculation is presented below:

$$CO_2 \text{ MPR} = \{[CO_2]_{OUT}/1000\} \times Q \times 1440 \text{ min/day}$$

where

CO_2 MPR = Carbon Dioxide Mass Production Rate, mg CO_2/day,

$[CO_2]_{OUT}$ = Effluent venting air CO_2 concentration, mg CO_2/L,

Q = Average venting air flow rate since the previous sample time.

Figure 3-5 shows the carbon dioxide calibration curve used to determine the mass of carbon dioxide in the venting air samples. This curve was developed using Supelco calibration gas standards.

The process of converting from carbon dioxide produced to JP-4 biodegraded involved additional assumptions. Foremost amoung these, was that JP-4 was assumed to contain 85 percent carbon by weight. This assumption is based on a report by Bushnell and Haas (1941) stating that the percentage of carbon in hydrocarbons varies from 80 to 89 percent. Furthermore, the assumed value of 85 percent carbon by weight is consistent with the use of dodecane as a model compound for JP-4. The equation used for the conversion of mass of carbon dioxide to mass of JP-4 is presented below:

$$JP\text{-}4 = \frac{[(CO_2\ MPR)_n + (CO_2\ MPR)_{n-1}]}{2} \times \frac{12\ mg\ C}{44\ mg\ CO_2} \times \frac{1\ mg\ JP\text{-}4}{0.85\ mg\ C} \times T$$

where

JP-4 = Mass of JP-4 biodegraded based on CO_2 production, mg JP-4,

$[(CO_2\ MPR)_n + (CO_2\ MPR)_{n-1}]/2$ = Average CO_2 MPR since the previous sample time,

T = number of days since the previous sample time.

The equation presented above considers only the JP-4 carbon evolved as carbon dioxide. It does not account for JP-4 carbon assimilated into microbial cell mass, which may be assumed to be an approximately equal quantity.

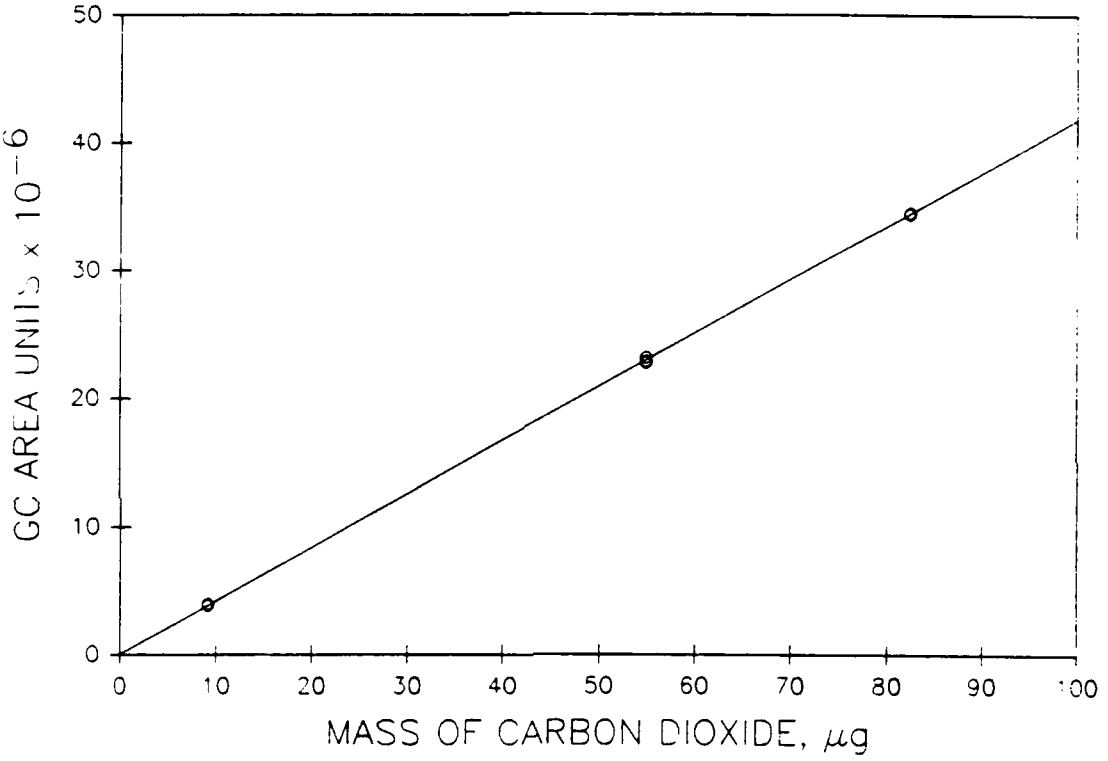

Figure 3-5. GC/TCD Carbon Dioxide Calibration Curve

JP-4 Losses Other Than Biodegradation

Aside from biodegradation, volatilization and water flushing were potential pathways for JP-4 loss from the soil columns. Methods of analysis for each of these additional pathways are discussed below.

JP-4 Mass Volatilization Rate

Measurement of the mass of JP-4 in the effluent gases from the columns was performed on a daily basis for the first ten days of biodegradation testing, and on approximately a weekly basis thereafter. Initially, a total carbon analyzer calibrated with potassium acid phthalate (KHP) as a carbon source was used to determine the mass of JP-4 in the column effluent gases; however, increasing carbon dioxide production and decreasing JP-4 volatilization made total carbon analysis unreliable after day 5 of the biodegradation testing period. Therefore, from day 5 through the end of biodegradation testing, a Perkin Elmer gas chromatograph equipped with a flame ionization detection (FID) was used for all JP-4 analyses.

All JP-4 volatilization analyses (TOC and GC) were done with ten microliter samples of the effluent vent.[illegible]g air. The GC/FID was calibrated using standard solutions of JP-4 in methylene chloride. The instrumentation and methodology employed in JP-4 analyses are described in this chapter under a previous section entitled "JP-4 Extractions and

Analyses". The mass of JP-4 volatilized per day was calculated using the equation presented below:

$$\text{JP-4 MVR} = [\text{JP-4}] \times \frac{1\ \text{mg}}{1000\ \text{ug}} \times \frac{1000\ \text{ul}}{1\ \text{mL}} \times Q \times \frac{1440\ \text{min}}{\text{day}}$$

where

JP-4 MVR = JP-4 Mass Volatilization Rate, mg JP-4/day,

[JP-4] = Effluent venting air JP-4 concentration, ug JP-4/uL venting air,

Q = Average venting air flow rate since the previous sample time, L/day.

JP-4 in the Aqueous Effluent

The water draining from each of the columns was collected in 40 milliliter vials. The hanging columns were inserted into the vials, and Parafilm was used to close the openings around the hanging columns. This closure did not provide an air tight seal, so volatile compounds in the effluent water may have been lost as the water drained from the column. The liquid effluent was collected and stored as a composite sample for the duration of the experiment. At the end of the biodegradation testing, the composite water sample from each column was tested for JP-4 content.

The JP-4 in the aqueous effluent was extracted by adding 10 milliliters of methylene chloride, shaking vigorously, and, after allowing time for the phases to separate, pipetting the methylene chloride from the vial. The methylene chloride was then dried by filtering it through a

microcolumn of anhydrous sodium sulfate and sealed in crimp seal vials.

The concentration of volatile organics in the effluent water from column 2 was determined by drawing a 10 milliliter sample of water directly from the sealed column base. To avoid disturbing the soil columns, this procedure was used only after the biodegradation testing was complete. The 10 milliliter sample was run on a purge and trap and analyzed using a gas chromatograph/mass spectrometer. The results from this sample were assumed to be representative of the aqueous effluent from each of the columns.

The instrumentation and methodology employed in JP-4 analyses are described in this chapter under a previous section entitled "JP-4 Extractions and Analyses."

Procedures After Biodegradation Testing

After completion of the biodegradation testing, the soil cores were removed from the columns and cut into five sections, each approximately 10 centimeters in length. Each of the three sections from the middle 30 centimeters of the aerobic columns was centered on one of the tensiometers. Each 10-centimeter section was sealed in a small, clean plastic bag and thoroughly mixed. The following analyses were performed on the soil from the columns after the biodegradation testing phase of this study: JP-4 soil

extractions and analyses, soil water content determinations and soil dehydrogenase determinations.

JP-4 Extractions and Analyses

Two 10-gram samples were removed from each bag to be used for JP-4 extractions and analyses. The procedures employed are the same as those described in this chapter under the section entitled "Initial Soil Testing."

Soil Water Content Determinations

Gravimetric soil water content determinations were run on soil samples removed from the columns through the tensiometer ports as well as bulk samples taken from each column section. The analyses were used to provide gravimetrically measured water content values to compare with the water contents determined using the soil water characteristic curve. The gravimetric analyses were conducted as described in this chapter under the section entitled "Soil Water Characteristic Curves."

In addition to the moisture determinations described above, one inch of soil from the bottom of column 2 was specifically removed to determine the dry bulk density and 100 percent saturation volumetric water content of the packed soil. These values are presented in this chapter because they were used in the calculation of all volumetric

water contents throughout this study. For future reference, they are listed below:

100% saturation water content = 0.36 cm^3 water/cm^3 soil,

Packed soil dry bulk density = 1.54 g/cm^3.

A theoretical porosity for the packed soil can be estimated with the data given above and the equation presented below:

$$n = 100 \times [1 - (D/2.65)]$$

where

n = theoretical porosity,

D = packed soil dry bulk density, and

2.65 = theoretical sand grain density (density of crystalline quartz, g/cm^3).

The porosity value calculated using the equation and data given above is approximately 42 percent. This value is higher than expected based on the 100 percent saturation volumetric water content. This discrepancy is most likely a result of air entrapment in the pores of the soil sample combined with a high estimate of the average grain density. Although the contaminated soil from the site was not tested to determine its organic content, its black color - compared with the white color of the non-contaminated soil - indicates that the soil may be high in organic content. Therefore, one would expect the average grain density to be lower than that of crystalline quartz.

Soil Dehydrogenase Activity Determinations

Soil dehydrogenase activity determinations were run on soil samples from the top, middle and bottom core sections from each column. These tests were conducted as described in this chapter under the section entitled "Initial Soil Testing."

CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes the results of the laboratory work completed for this thesis. All of the experimental data gathered is presented in tabular form in Appendix B, while graphs and tables are used in this chapter to summarize findings.

Soil Water Characteristic Curves

To provide a means to monitor soil water content during subsequent biodegradation testing, a soil water characteristic curve was developed using a preliminary column packed with JP-4 contaminated soil from the spill site. Work with this column resulted in development of an equilibrium soil water characteristic curve as discussed below.

Equilibrium Soil Water Characteristic Curve

The soil water characteristic curve presented in Figure 4-1 is the equilibrium soil water characteristic curve developed during the preliminary phase of this study. The soil column was considered to be at equilibrium when the soil water suction value in centimeters of water at each

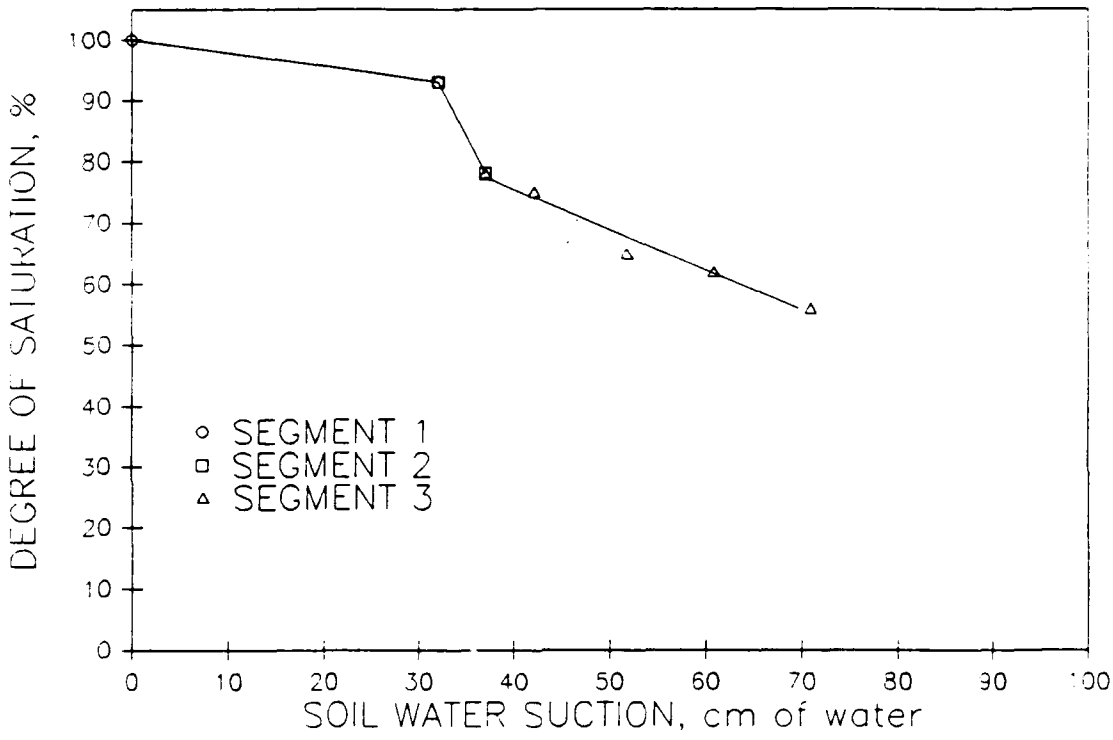

Figure 4-1. Equilibrium Soil Water Characteristic Curve

tensiometer was equal to the height of the tensiometer above the end of the hanging column. The data point plotted at 32 centimeters of suction on Figure 4-1 deviates from the straight line plotted through the 5 data points from 35 through 70 centimeters of suction. At true equilibrium, the soil water characteristic curve for a homogeneous soil could be a straight line with the suction values equal to the height of the tensiometers above the end of the hanging column. The 5 data points from 35 to 70 centimeters of soil water suction meet this criterion. The data point at 32 centimeters of soil water suction also appears to be an equilibrium data point, as the suction value is equal to the height of the tensiometer above the end of the hanging column. However, the degree of saturation (93%) at this suction value is higher than expected. A local non-uniformity of the packed soil is the most likely cause for this point to deviate from the line predicted by the remaining 5 data points.

The non-uniformity appears to have been small and localized, because the overall wet bulk density of the soil column was 1.89 grams per cubic centimeter - a value very similar to the desired density of 1.86 grams per cubic centimeter. Furthermore, all density samples taken from the column were uniform to +/- 0.03 grams per cubic centimeter.

The soil column drained for approximately 67 days before reaching equilibrium. This long drainage period was

required to establish equilibrium in the soil column because the rate of soil drainage decreases as the soil dries. This slowing in the drainage rate is caused by a reduction in both the hydraulic conductivity and the hydraulic gradient which accompanies a reduction in the soil water content (Bouma et al., 1982).

The single soil column used to develop this soil water characteristic curve was packed to an overall wet bulk density of 1.89 grams per cubic centimeter. The dry bulk density determined after development of the soil water characteristic curve ranged from 1.56 to 1.59 grams per cubic centimeter with an average value of 1.58 grams per cubic centimeter. These values compare very well with the 1.86 grams per cubic centimeter wet bulk density and 1.59 grams per cubic centimeter dry bulk density determined from the undisturbed soil cores from the field site.

The curve was plotted in three linear segments. Using linear regressions, the segments can be described by the following equations:

Segment 1, 0 to 30 cm of water suction:

% Saturation = -0.22 x (Suction, cm of water) + 100

Segment 2, 30 to 35 cm of water suction:

% Saturation = -3.0 x (Suction, cm of water) + 189

Segment 3, 35 to 70 cm of water suction:

% Saturation = -0.66 x (Suction, cm of water) + 102

The percent saturation values were calculated on the basis of volumetric water content which was determined from analysis of core samples from the soil column. The 100 percent saturation volumetric water content was found to be 0.35 cubic centimeters of water per cubic centimeter of soil. A calculation of the theoretical porosity using the equation presented in Chapter 3 yields a porosity value of 40 percent. This value is higher than would be expected when compared to the 100 percent saturation water content. Both the theoretical porosity equation and a possible explanation for this discrepancy are presented in the section entitled "Procedures After Biodegradation Testing" in Chapter 3.

Changes Resulting from Preliminary Column Testing

Work done with the preliminary column provided not only an equilibrium soil water characteristic curve, but also additional insight into the soil and soil column behavior that would substantially modify the proposed course of the biodegradation testing. Specifically, it was noted that the rate of unrestricted column drainage was relatively rapid through the first one to two weeks of drainage. During this period, the overall water content decreased at a rate of about one percent saturation per day from 100 to 90 percent saturation. After the second week, however, the rate of drainage had slowed to 0.5 percent saturation per day, and

it declined to a rate of less than 0.1 percent saturation per day as the column approached equilibrium, and an average water content of 70 percent saturation. The slowing of the soil drainage rate, as discussed earlier, is a result of gradually decreasing hydraulic conductivity and hydraulic gradient in the soil column.

The slow drainage rate observed for the preliminary column when the water content was less than 80 percent saturation brought up a concern that an excessively long biodegradation test period might be required to reach 50 percent saturation. If the rate of biodegradation during this period was high, then limited JP-4 or nutrient availability may inhibit microbial activity before any impact of limited water availability could be observed.

To minimize the potential for JP-4 or nutrient limitations, it was decided that the biodegradation columns should be drained in as short a time period as possible. Therefore, the recirculation of the column effluent water was eliminated to facilitate more rapid drainage. In lieu of water recirculation, the water content in the biodegradation columns was slowed, albeit to a limited extent, using the previously described method of restricting drainage by clamping the hanging columns.

The decision to drain the columns as rapidly as possible precluded the establishment of equilibria at discreet soil-water distributions in the biodegradation

columns. Therefore, the equilibrium soil water characteristic curve could not be used to accurately predict the soil water contents from the soil water suction readings. To accurately predict the soil water contents in the biodegradation columns, it was necessary to develop a non-equilibrium soil water characteristic curve.

Non-Equilibrium Soil Water Characteristic Curve

Data from biodegradation columns 1 and 2 were combined to construct the non-equilibrium curve. Figure 4-2 is a plot of the non-equilibrium soil water characteristic curve. The non-equilibrium curve was developed by plotting the final soil water suction values taken from the biodegradation columns against the volumetric percent saturation values of core samples taken after the completion of biodegradation testing.

Table 4-1 summarizes the data used to plot the non-equilibrium soil water characteristic curve. To clarify the tensiometer notation in Table 4-1, tensiometer 1-1 is the top tensiometer in column 1, and tensiometer 2-3 is the bottom tensiometer in column 2. The last entry in Table 4-1 is the saturation water content which was determined from the bottom 1 inch of soil from column 2. The soil water suction value was 0.0 centimeters of water when the soil was at 100 percent water saturation.

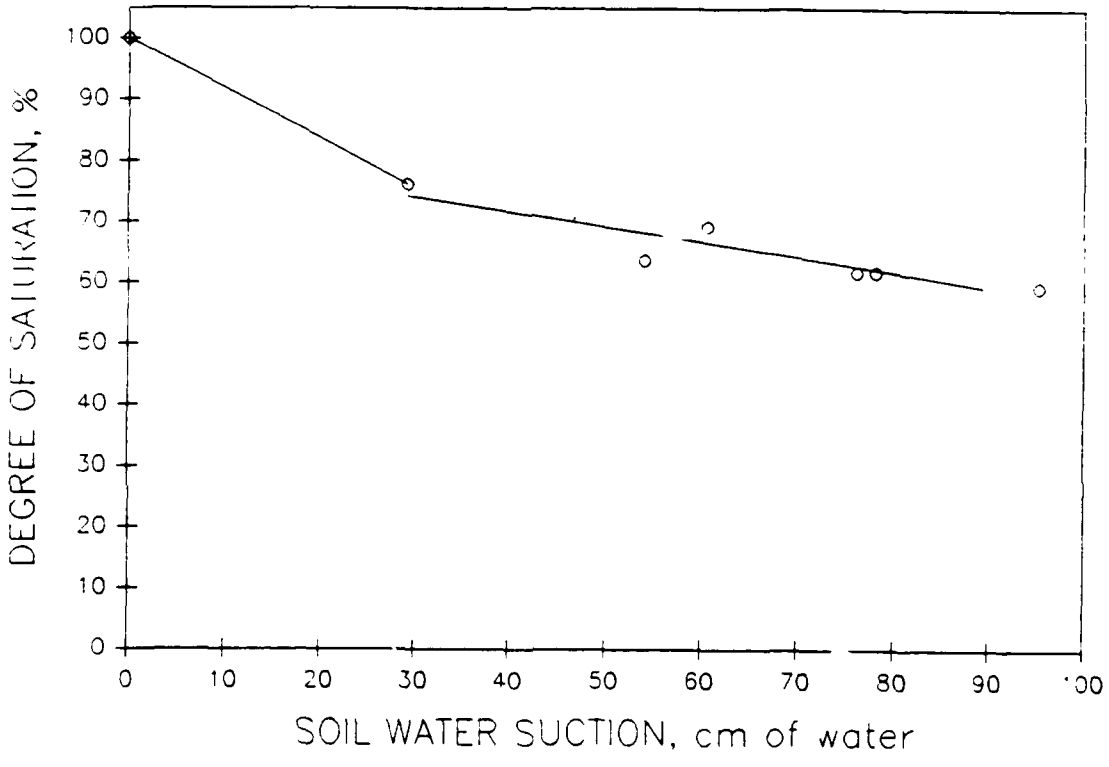

Figure 4-2. Non-equilibrium Soil Water Characteristic Curve

Table 4-1. Non-Equilibrium Soil Water Suction and Water Content Data

Tensiometer # and Depth (cm)	Final Suction (cm water)	Water Content (cm^3/cm^3)	% Saturation
1-1, 15	95.2	0.214	59.4
1-2, 25	78.1	0.222	61.7
1-3, 35	54.1	0.229	63.6
2-1, 15	76.2	0.222	61.7
2-2, 25	60.7	0.249	69.2
2-3, 35	29.2	0.274	76.1
	0.0	0.360	100.0

The linear regression equations for the two segments of the non-equilibrium soil water characteristic curve are presented below:

Segment 1, 0 to 30 cm of water suction:

% Saturation = -0.82 x (Suction, cm of water)+ 100

Segment 2, 30 to 95 cm of water suction:

% Saturation = -0.25 x (Suction, cm of water)+ 81.5

Interpretation of Water Content Data

Since the non-equilibrium soil water characteristic curve was not developed until the biodegradation testing had been completed, the equilibrium curve was used during the biodegradation testing to determine approximate water contents. Once the non-equilibrium curve was developed, all water contents were recalculated using the new curve.

As discussed in Chapter 3, the three tensiometer readings in each column were averaged to obtain a single average soil water suction value each time data was

collected. Typical data are presented in Table 4-2 to illustrate the actual variation in water content across the venting zone during the biodegradation testing.

The data in Table 4-2 show that the range of water content across the venting zone widens as drainage continues from day 20 to day 81. If the columns were allowed to reach equilibrium, the suction values would differ by only 20 centimeters of water between the top and the bottom of the venting zone. This would correspond to a difference of about five percent saturation. However, the columns were not allowed to reach equilibrium. Rather, the hanging columns were extended throughout the course of biodegradation testing in order to increase the rate and extent of drainage. By extending the hanging columns, the soil columns were drained to a greater extent, but the range of water content across the venting zones was widened.

As shown in Table 4-2 for day 81, there is a difference of about 10 percent saturation across the venting zone. This wide range of water content across the venting zone made it possible for microorganisms at different locations in the venting zone to experience significantly different soil-water conditions. Therefore, it is critical to understand that any correlations between water content data and biodegradation data presented in this thesis are based on the average water content in the venting zone.

Table 4-2. Typical Soil-water Distribution Across the Venting Zone

Day	Tensiometer # and Depth (cm)	Suction (cm of water)	% Saturation
20	1-1, 15	48.0	69.6
	1-2, 25	43.0	70.8
	1-3, 35	39.5	71.7
	Average	43.5	70.7
48	2-1, 15	70.0	64.1
	2-2, 25	62.8	65.9
	2-3, 35	46.5	70.0
	Average	59.8	66.7
81	1-1, 15	95.2	57.9
	1-2, 25	78.1	62.1
	1-3, 35	54.1	68.1
	Average	75.8	62.7

Note: The percent saturation values presented in this table were determined using the non-equilibrium soil water characteristic curve.

Initial Soil Test Results

Before the biodegradation columns were packed, the mixed soil sample was analyzed for JP-4 content, water content and dehydrogenase activity. The results of these tests are presented below.

Initial JP-4 Determinations

A total of eight soil sub-samples were taken from the bulk mixed soil sample. The JP-4 was extracted from these samples as previously described. Table 4-3 presents the results of these initial extractions along with the results of two extractions that were run on non-contaminated soil

from the spill site. Based on the data in Table 4-3, the average JP-4 loading in the mixed soil prior to packing into the biodegradation columns was approximately 3560 milligrams of JP-4 per kilogram of moist soil, or 4590 milligrams of JP-4 per kilogram of dry soil.

Table 4-3. Results of Initial Soil JP-4 Analyses

Sample	Soil Loading (mg JP-4/kg Moist Soil)	Mass of JP-4, mg Column 1	Column 2
1	3353	17800	17600
2	3283		
3	3391		
4	3792		
5	3749		
6	3943		
7	3485		
8	3521		
Clean 1	0		
Clean 2	0		

Initial Water Content Determinations

The raw soil samples from the field had dry weight basis water contents ranging from 0.172 grams of water per gram of dry soil to 0.265 grams of water per gram of dry soil. When these samples were mixed together, the bulk mixed soil had an average dry weight basis water content of 0.225 grams of water per gram of dry soil. The initial overall wet bulk densities of columns 1 and 2 were 1.87 and 1.86 grams per cubic centimeter, respectively. These values compare very well with the 1.86 grams per cubic centimeter

wet bulk density determined from undisturbed field core samples. This close agreement of the densities of the packed soil columns to the soil in the field indicates that the physical conditions in the columns should be similar to those in the soil at the field site.

Initial Dehydrogenase Activity

The initial dehydrogenase activity of the mixed JP-4 contaminated soil was determined by testing four samples prior to packing the biodegradation columns. The results showed a range of dehydrogenase activity from 108 to 147 micrograms of INT-formazan produced per gram of dry soil per 24 hours. The average value was 123 micrograms of INT-formazan produced per gram of dry soil per 24 hours. Figure 3-3 presented the calibration curve used to determine INT-formazan concentration from the sample absorbance at 485 nanometers. The equation used for this calculation is presented below:

$$\text{INT-formazan (ug/mL)} = \frac{\text{Absorbance} - 1.367 \times 10^{-2}}{1.884 \times 10^{-2}}$$

Frankenberger and Johanson (1982) reported soil dehydrogenase activities of 32 and 56 micrograms of formazan produced per gram of dry soil per 24 hours at 37°C for soil contaminated with kerosene and diesel fuel, respectively. Their testing employed initially clean soil samples to which petroleum fractions were added at the start of the 30-day

test period. The tetrazolium salt used by Frankenberger and Johanson was 2,3,5-triphenyltetrazolium chloride (TTC). Lopez et al., reported that both TTC and INT are converted to the colored formazan species when they act as an electron acceptor during dehydrogenation. However, unless steps are taken to exclude oxygen from the soil during the TTC test, oxygen will be the preferred electron acceptor, and formazan production will be lower than otherwise expected.

Frankenberger and Johanson do not mention any effort to exclude oxygen from the test soils in their 1982 article. Therefore it is possible that their data provide low estimates of the dehydrogenase activity in hydrocarbon contaminated soils.

The average dehydrogenase activity determined during the initial testing in this thesis was about 2.5 to 4 times greater than that reported by Frankenberger and Johanson. However, better agreement might have been attained had oxygen been excluded during the cited study.

Biodegradation Test Results

The length of the biodegradation testing phase during which the columns were continuously vented was 81 days for column 1 and the control column, and 70 days for column 2. During this phase, oxygen uptake, carbon dioxide production and soil water suction (water content) were measured on nearly a daily basis, and JP-4 volatilization was measured

on approximately a weekly basis. In addition to these tests, the liquid effluent from each of the columns was accumulated and analyzed for JP-4 content at the end of the biodegradation testing. The results of these tests are discussed below.

Biodegradation Rate

Oxygen uptake and carbon dioxide production were used as indicators of the JP-4 biodegradation rate in the aerobic soil columns. Figures 4-3 and 4-4 summarize the variation of the biodegradation rate with time for column 1 and column 2, respectively. The data plotted in these figures are the actual data gathered on a day to day basis over the duration of the biodegradation testing.

Table 4-4 presents the maximum and average biodegradation rates observed during this study.

Table 4-4. Overall JP-4 Biodegradation Rates

Basis of Calculation	Column	Maximum Biodegradation Rate mg JP-4/kg Soil/Day	Average Biodegradation Rate mg JP-4/kg Soil/Day
O_2 Uptake	1	16.7	11.9
CO_2 Production	1	14.3	10.6
O_2 Uptake	2	15.9	10.7
CO_2 Production	2	13.6	9.6

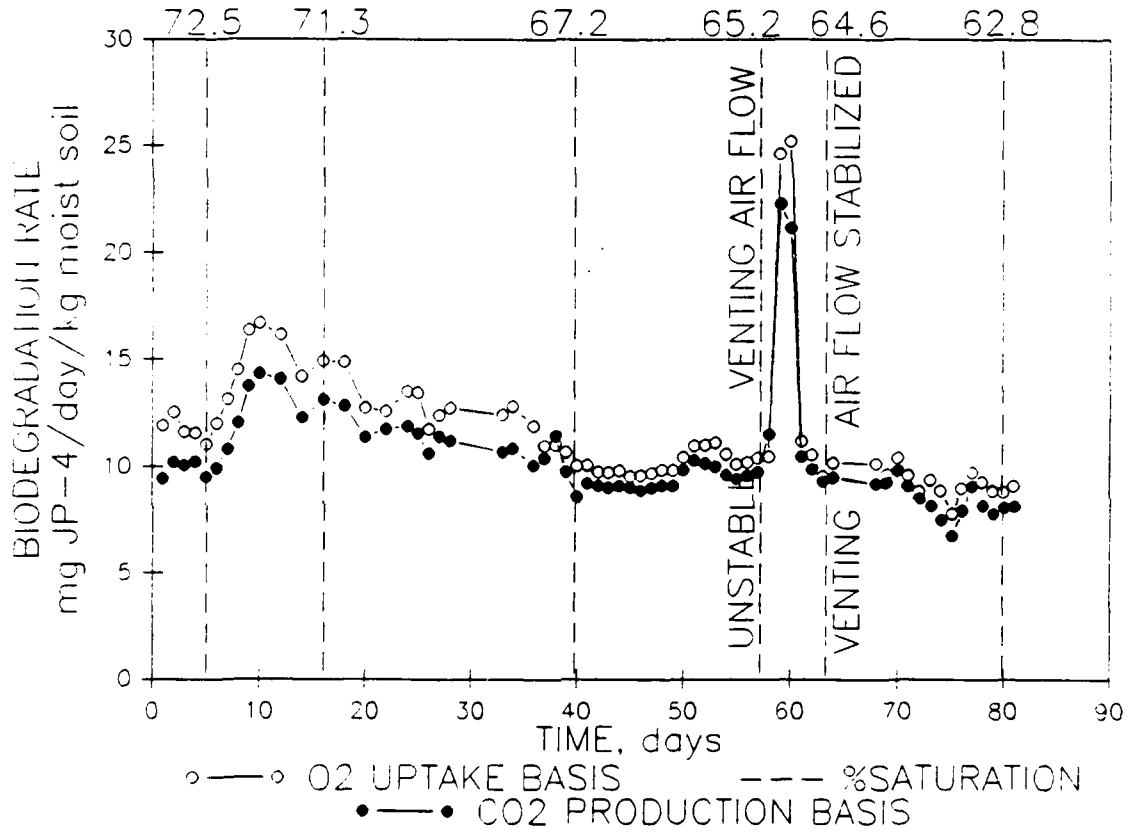

Figure 4-3. Variation of Biodegradation Rate with Time, Column 1

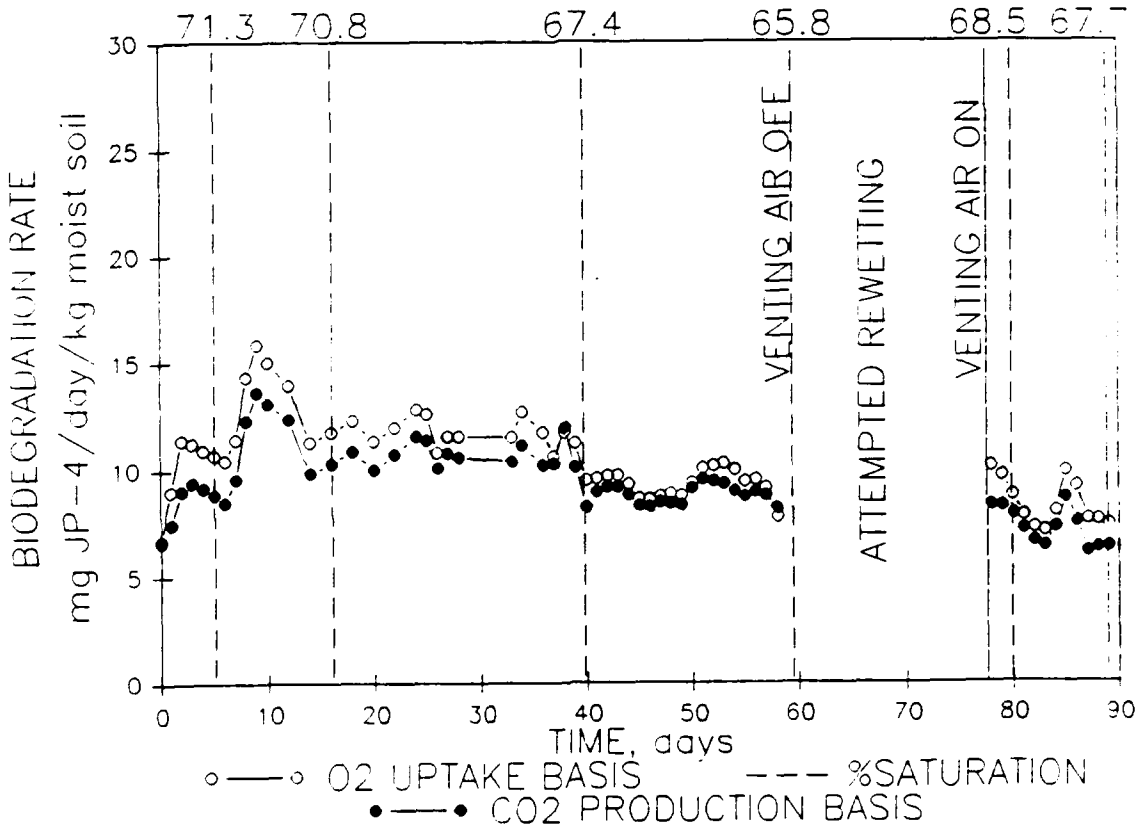

Figure 4-4. Variation of Biodegradation Rate with Time, Column 2

The maximum biodegradation rates were observed on day 10 in column 1 and on day 9 in column 2. A quick comparison of Figures 4-3 and 4-4 shows that with respect to biodegradation rate, these columns were virtually identical.

Comparison of the biodegradation rates observed during this study with those presented in the literature provides an indication of the degree to which the soil environments in the columns were optimized.

Watts et al. (1989) reported biodegradation rates of 4 to 8 milligrams of JP-5 per kilogram of soil per day. His study involved soils with various JP-5 loadings to which nutrients and hydrogen peroxide were added. Watts found that the observed biodegradation rate increased with JP-5 loading up to a loading of 487 milligrams of JP-5 per kilogram of soil. At loadings higher than 825 milligrams per kilogram, however, biodegradation ceased. He attributed this to the possible presence of water insoluble films and globules of JP-5 when the fuel was present in high loadings.

The initial JP-4 loading in the soil employed in this study was 3560 milligrams of JP-4 per kilogram of soil. Unlike the data produced by Watts et al., data gathered during this study show that biodegradation was indeed going on at this loading.

Bartha (1986) reported biodegradation rates ranging from 34 to 425 milligrams of PHC per kilogram of soil per day for soils under partially optimized conditions. The

term "partially optimized" is taken to mean that the conditions in the microbial environment had been improved by some combination of pH adjustment, nutrient addition, oxygen addition and other means to enhance biodegradation.

Bartha's range of biodegradation rates came from many studies reported in the literature over the years. Relative to the range reported by Bartha, the biodegradation rates observed in this study are somewhat low. These relatively low biodegradation rates could be a result of poor nutrient availability or some other non-optimized condition in the microbial environment.

Variation of Biodegradation Rate with Water Content

The primary objective of this study was to determine the impact of variation in soil water content on the rate of JP-4 biodegradation while supplying oxygen through soil venting. The soil used in this study was not amended with nutrient solutions or additional carbon sources.

During the actual biodegradation phase of this study, the soil water content decreased from approximately 100 percent saturation to 63 percent saturation in column 1 and to 65 percent saturation in column 2. These water contents were determined using the non-equilibrium soil water characteristic curve. The range of water contents in which a maximum biodegradation rate was expected was between 50 and 80 percent saturation, as discussed earlier.

Figures 4-3 and 4-4 show the variation in biodegradation rate with time and water content for column 1 and column 2, respectively. Including the data from both columns, the range of soil water contents in which this maximum occurs is 70.8 to 72.5 percent saturation.

Table 4-5 summarizes the average biodegradation rates during the time and water content periods marked on Figures 4-3 and 4-4.

Table 4-5. Average Biodegradation Rates at Times and Water Contents Shown on Figures 4-4 and 4-5

	Column 1		Column 2	
Time Range (Days)	Saturation Range (% Sat)	Biodegradation Rate (mg JP-4/kg Soil/d)	Saturation Range (% Sat)	Biodegradation Rate (mg JP-4/kg Soil/d)
0-5	100-72.5	9.6	100-71.3	8.4
5-16	72.5-71.3	12.2	71.3-70.8	10.9
16-40	71.3-67.2	11.1	70.8-67.4	10.5
40-57	67.2-65.2	9.4	67.4-65.8	8.8
62-80	64.6-62.8	8.6	N/A	N/A
80-90	N/A	N/A	68.5-65.3	7.0

N/A = Data not available or not collected.

In each column, the biodegradation rate gradually declines after reaching a maximum at an average 71.6 percent saturation. Linear regressions of the data gathered between day 10 and the end of biodegradation testing yield lines with slopes of 0.061 and 0.062 for columns 1 and 2, respectively. The equations for these lines are presented below:

Column 1: Rate = -0.061 x (Time, days) + 13.85

Column 2: Rate = -0.062 x (Time, days) + 12.62

These equations indicate that the biodegradation rate in both columns decreased over time at a single, approximately constant rate.

This consistent trend in biodegradation rate in columns 1 and 2 indicates that some environmental variable, or some combination of environmental variables, was gradually changing and thereby slowing the biodegradation rate. This slowing could be attributed to the gradually decreasing soil water content in the columns. However, because JP-4 was being degraded, substrate availability was also decreasing with time. Changes in other environmental variables such as pH and nutrient availability may also have influenced the observed trend in biodegradation rate.

Based on the data gathered during this study, it cannot be determined how changes in soil water content, substrate availability, soil pH or nutrient availability may have influenced the observed trend in biodegradation rate. Therefore, although a maximum biodegradation rate was observed at an average water content of 71.6 percent saturation, it is unclear whether this maximum, or the observed decreasing trend after the maximum, occurred as a result of optimal soil-water conditions, or simply as an artifact resulting from variations in other environmental variables.

One observation that may support the role of water content as a major influence in the observed biodegradation trend involves the field capacity of the test soil. Although the field capacity of this soil was not specifically determined, the columns met the conditions of field capacity as cited in the definition of *in situ* field capacity at approximately 71.6 percent saturation. Specifically, column drainage, as indicated by increasing soil water suction, was very rapid from day 0 to day 3, at which time drainage effectively ceased until day 12. From the definition of *in situ* field capacity, an initially saturated soil will drain rapidly for two to three days, and drainage will become negligible at the field capacity (Cassel and Nielson, 1982). Therefore, based on the definition of *in situ* field capacity, it appears that the field capacity water content of columns 1 and 2 coincides with the observed maximum biodegradation rate.

Hydrocarbon biodegradation rates have been reported to increase with water content up to 100 percent of the field capacity and to decrease above 100 percent of the field capacity due to insufficient aeration (Hurle and Walker, 1981; Walker, 1976; Usoroh and Hance, 1973). Clearly, if the field capacity of the soil in this study falls in the range of 70.8 to 72.5 percent saturation, these results would be consistent with those reported in the literature cited above.

To provide additional support for the hypothesis that variation of water content was a major factor in the observed trend of biodegradation rate, an attempt was made to increase the water content of column 2. This process is discussed below.

Attempted Rewetting of Column 2

The original plan for this study involved draining both columns to approximately 50 percent saturation. On the basis of the equilibrium soil water characteristic curve used during biodegradation testing, columns 1 and 2 were drained from 100 percent saturation to 52 percent and 60 percent saturation, respectively.

During this drainage period for column 2, it was observed that there had been a continuous, gradual decrease in biodegradation rate since a water content of approximately 71 percent saturation (based on the non-equilibrium soil water characteristic curve) was recorded on day 9. On the basis of this observation, a decision was made to rewet column 2 in an attempt to reestablish the previous, apparently optimal, water content of approximately 71 percent saturation, while allowing column 1 to continue draining as planned. If the biodegradation rate was observed in increase to some higher level as a result of water addition, such a finding would support the conclusion

that the observed gradual decrease in biodegradation rate was a result of decreasing water content.

Figure 4-4 is annotated to indicate the time frame during which column 2 was rewetted. Also indicated on Figure 4-4, as well as on Figure 4-3, are the water content values at days 5, 16, 40 and 80.

The rewetting of column 2 was attempted in the same manner as the original saturation of the soil columns prior to biodegradation testing. Specifically, water was applied through the column base under a pressure head that was increased from approximately 12 inches to 36 inches of water.

For an undetermined reason, only about the bottom one-third of column 2 could be resaturated by this process. It is suspected that partial clogging of the soil pores by precipitated inorganic compounds and/or by microbial biomass may have contributed to this problem. As a result of this inability to resaturate column 2 by the normal process, it was decided that water would be injected into the venting zone through the top end of the column.

Inherent to the process of injecting water through the top of the column were several problems. The worst of these problems involved partial air entrapment during the wetting process. As a uniform wetting front moves downward through a soil column, air can be entrapped in the soil pores and hinder or stop any further water flow through the column.

Air entrapment and the resultant non-uniform distribution of water in the soil column could affect the soil venting process by preferentially diverting air through the drier soil in the venting zone.

If air became entrapped in the column, it was questionable whether any further useful biodegradation data could be gathered. Therefore, in order to avoid creating a downward moving uniform wetting front in the soil column, water was injected into the soil near the top of the venting zone using a long, sterile glass Pasteur pipette. As shown in Figure 4-4, this method of rewetting column 2 resulted in only a partial and non-uniform resaturation, but no evidence of air entrapment was observed following the addition of water.

The biodegradation data gathered after the attempted rewetting indicated that there was a decrease in the biodegradation rate. Some possible reasons for this apparent decrease include altered air flow patterns through the soil in the venting zone and possibly a shorter average venting air residence time in the soil. Another possible cause of the observed decrease in biodegradation rate would be that the microbial population in column 2 was adversely affected by the 19-day interruption in venting air flow.

The attempted rewetting of column 2 failed to provide experimental confirmation that water content was a major factor influencing biodegradation rate. However, because

the rewetting was only partial and non-uniform, one cannot conclude that the increased water content was the primary cause in the observed decrease in biodegradation rate following the attempted rewetting.

Mass of JP-4 Biodegraded

Based on the biodegradation rate data discussed above and summarized in Tables 4-4 and 4-5, the resulting total mass of JP-4 biodegraded in each column is presented below in Table 4-6.

The data in Table 4-6 indicate that the mass of JP-4 biodegraded in column 1 was significantly higher than that biodegraded in column 2. However, column 1 was vented for a period 11 days longer than column 2. Had column 2 been vented for 11 additional days at the same average biodegradation rate, the total mass of JP-4 biodegraded would have been 4235 milligrams and 3795 milligrams on the basis of oxygen uptake and carbon dioxide production,

Table 4-6. Mass of JP-4 Biodegraded

Basis of Calculation	Column	Mass of JP-4 Biodegraded, mg	% of Initial Mass	Number of Days Vented
O_2 Uptake	1	4670	26.2	81
CO_2 Production	1	4160	23.4	81
O_2 Uptake	2	3660	20.8	70
CO_2 Production	2	3280	18.6	70

respectively. Clearly, biodegradation was occurring at similar rates in both columns.

Mass of JP-4 Volatilized

The low range of venting air flow rates used throughout this study was intended to minimize JP-4 losses through volatilization while still providing an excess of oxygen for microbial use. The flow rates in both columns ranged from 0.75 to 1.50 milliliters per minute. The average flow in column 1 was 1.15 milliliters per minute, and in column 2 the average flow was 1.09 milliliters per minute.

The average air loading rate was approximately 3.9×10^{-3} cubic centimeters of air per minute per square centimeter of soil, assuming that only the venting zone in each column was effectively vented. Venting system air loading rates reported in the literature range from 3 to 5 orders of magnitude above those used in this study. Most of the venting systems reported in the literature, however, were designed to maximize hydrocarbon volatilization.

Figures 4-5 and 4-6 show the variation of JP-4 mass volatilization rate with time. The concentration of JP-4 in the effluent venting gas was measured approximately once every 7 to 10 days, with the exception of days 0 through 9, when it was measured on a daily basis. The data for days when JP-4 was not directly measured were calculated assuming

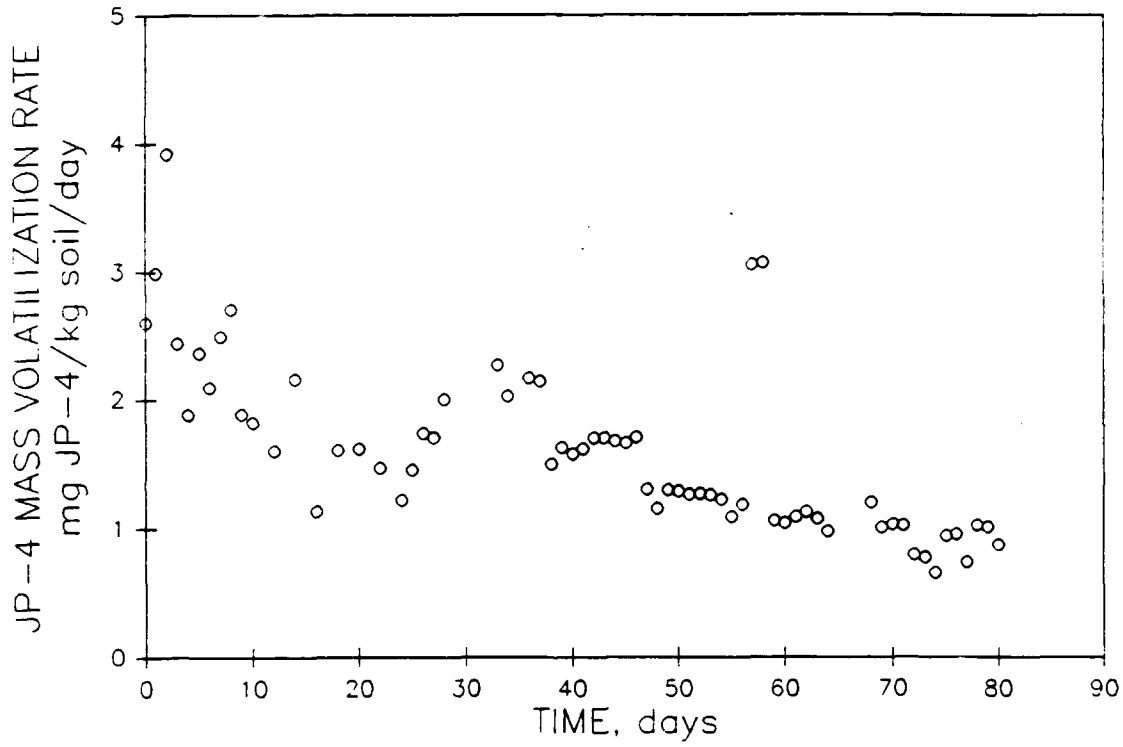

Figure 4-5. Variation of JP-4 Mass Volatilization Rate with Time, Column 1

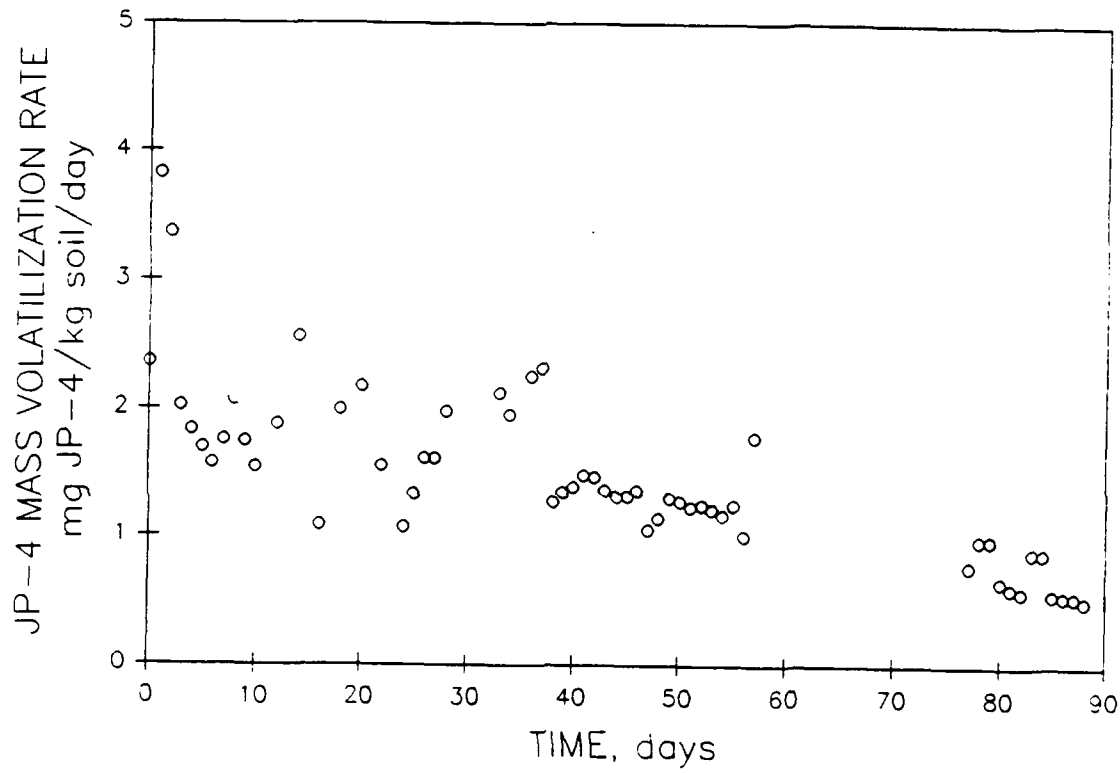

Figure 4-6. Variation of JP-4 Mass Volatilization Rate with Time, Column 2

the average JP-4 concentration from the nearest actual samples preceding and following the given day.

As shown in Figures 4-5 and 4-6, the maximum JP-4 volatilization rates occurred during the first several days of venting. The JP-4 volatilization rates drop quickly from the initially high rates, and then they gradually approach some lower value, possibly zero. A similar trend was reported by Marley and Hoag (1984) based on laboratory soil column venting studies. Marley and Hoag, however, used air loading rates of approximately 3 to 11 cubic centimeters of air per square centimeter of soil per minute, and they observed maximum gasoline volatilization rates during the first several hours of venting rather than the first several days of venting.

The total masses of JP-4 volatilized from column 1 and column 2 were 625 milligrams and 530 milligrams, respectively. Therefore, the mass of JP-4 volatilized from each column is approximately 3 to 4 percent of the mass of JP-4 originally present in the columns. Contrasting this finding with that of Thornton and Wootan (1982) provides an illustration of how different venting air loading rates and different petroleum fractions can influence the relative effectiveness of volatilization and biodegradation in a soil venting system. Thornton and Wootan reported that 57 percent of the gasoline originally present was volatilized and only two percent was biodegraded during their 11-day

soil venting experiment. Using an air loading rate three orders of magnitude lower, and with a heavier petroleum fraction, the volatilization loss of JP-4 in this study was 3 to 4 percent and the mass biodegraded based on carbon dioxide production was 18 to 26 percent of the mass originally present. It is interesting to note that the gasoline biodegradation rate calculated using Thorton and Wootan's data is approximately 9 milligrams of gasoline per kilogram of soil per day - a value very similar to those determined in this study for JP-4 biodegradation.

Mass of JP-4 Lost Through Column Drainage

The volumes of water drained from column 1 and column 2 over the course of this study were 113 and 107 milliliters, respectively. The rate at which water drained from the columns varied from approximately 8 milliliters per day for the first three days, to a value of approximately 1 milliliter per day by day 10. The drainage rate after day 10 ranged from 0.8 to 0.0 milliliters per day for the duration of the biodegradation testing.

These small volumes and slow rates of drainage did not allow for routine collection and analysis of column water samples for JP-4 content. As a result, the water drained from each column over time was accumulated as a composite sample and analyzed at the end of the biodegradation testing. The concentration of volatile organics in the

effluent water from the columns was estimated from a single 5 milliliter sample of water drawn directly from the sealed base of column 2 on the last day of biodegradation testing.

Extraction and GC/FID analysis of the composite water samples and GC/MS analysis of the 5-milliliter sample for volatile organics (EPA Method 624) yielded results showing that less than 1 milligram of JP-4 was lost through water drainage from each column.

This result is only an estimate of the mass of JP-4 lost through column drainage. It is likely that some of the JP-4 originally dissolved in the water effluent from the columns was volatilized or biodegraded during the long collection and storage times. However, even if this estimate is low by an order of magnitude, the mass of JP-4 lost through column drainage would be insignificant in comparison to the mass biodegraded.

Total JP-4 Removal

The total mass of JP-4 removed from each column during biodegradation testing was determined by performing initial and final soil extractions and analyses to quantify the initial and final JP-4 loadings. The initial JP-4 loading in the test soil was 3560 milligrams of JP-4 per kilogram of soil, as discussed earlier. Soil with this average loading was packed into each column prior to biodegradation testing.

As discussed in Chapter 3, each of the soil columns was divided into five sections, each approximately 10 centimeters in length, prior to beginning post-biodegradation analytical procedures. Table 4-7 summarizes the results of the final JP-4 soil extractions.

Table 4-7. Final JP-4 Loadings and JP-4 Removals

Section of Column	Depth of Section (cm)	Final Loading (mg JP-4/kg Moist Soil) Column 1	Column 2	Mass Removed (mg JP-4) Column 1	Column 2
1	0-10	1670	1450	1840	1900
2	10-20	1400	1440	2110	2180
3	20-30	1490	2310	2050	1310
4	30-40	1570	1870	1700	1490
5	40-50	3300	2870	270	710

In Table 4-7, column section 1 corresponds to the top and column section 5 to the bottom 10 centimeters of the columns. Based on the data presented in Table 4-7, the total masses of JP-4 removed from columns 1 and 2 were 7970 and 7590 milligrams of JP-4, respectively. These values are equivalent to approximately 45 percent removal in column 1 and 43 percent removal in column 2.

To determine whether any of the chemical compounds in JP-4 were preferentially removed during the soil venting process, the fractional removals of seven selected peaks were calculated using the initial and final chromatograms. Each selected peak was tentatively identified as discussed in Chapter 3. The peaks represent alkanes from C-8 to C-

14, inclusively. Figure 4-7 shows the fractional removal of these C-8 to C-14 alkanes.

The soil venting process, overall, appears to favor removal of the compounds with a smaller carbon number. Nearly 90 percent removal is obtained at carbon number C-8, and less than 10 percent removal is obtained at carbon number C-14.

Similar results were reported by Lehtomaki and Niemela (1975). They found that compounds in the range C-8 to C-12 were almost completely removed from an oily waste land treatment site within one year after waste application. This report, however, did not differentiate between biodegradation and volatilization. Bartha (1986), and Stone et al. (1941) reported that biodegradation of compounds in the range from C-5 to C-10 is inhibited, as these compounds act as solvents disrupting cellular structures. Stone also reported that alkanes from C-10 to C-16 are readily biodegraded.

These earlier reports indicate that much of the JP-4 removal in the C-8 to C-10 range shown in Figure 4-7 is a result of volatilization, while the removal from C-10 to C-14 can be increasingly attributed to biodegradation.

The results presented in Table 4-7 will be discussed with respect to location or depth in the column, final water content and final microbial activity in the following sections. Please note that the mass of soil in each section

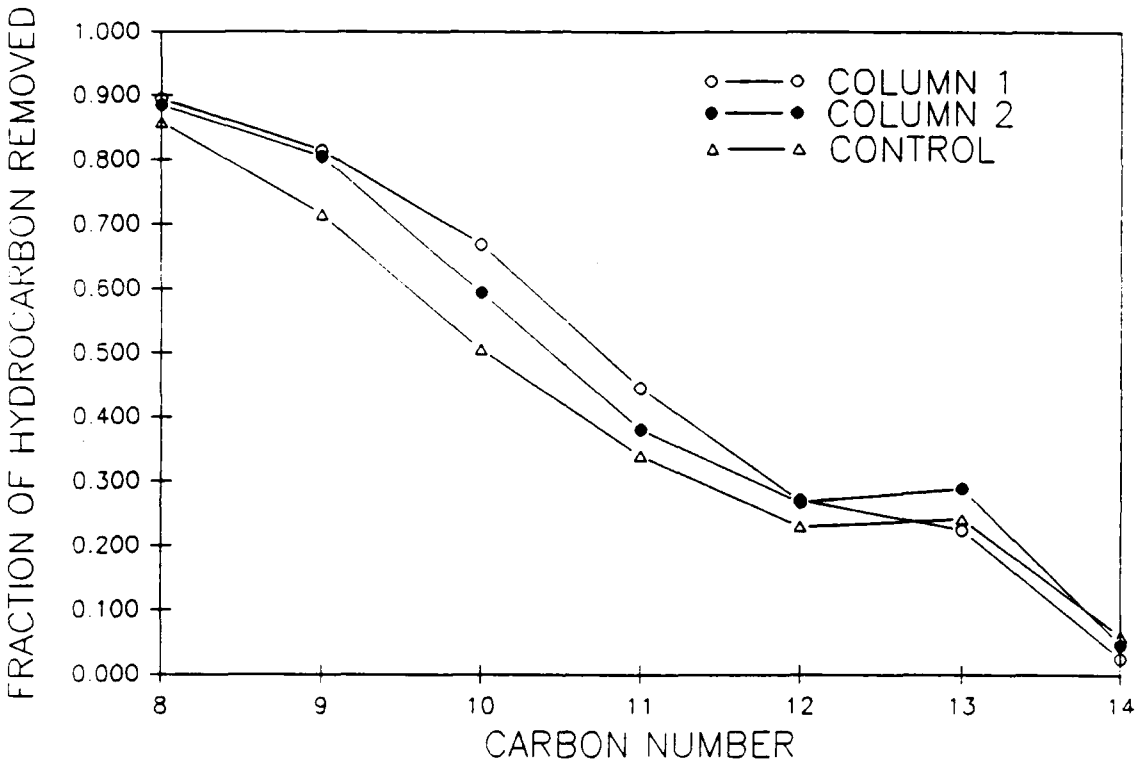

Figure 4-7. Variation of Hydrocarbon Removal with Alkane Chain Length

varied from approximately 800 to 1100 grams. To present the total JP-4 removal results graphically, it was necessary to divide the total mass removed per section by the mass of that section. Each of the figures presented in the subsequent sections plots JP-4 removal per kilogram of moist soil.

Variation of JP-4 removal with depth in the column

A discussion of JP-4 removal with depth in the column will provide information concerning the impact of soil venting on total JP-4 removal.

Both columns 1 and 2 were approximately 50 centimeters in length, and the venting zone was 35 centimeters in length and centered on the column. With reference to the column section numbers on Table 4-7, only about 25 percent of the soil in sections 1 and 5 is located in the venting zone. The zone of soil receiving direct venting air flow is largely encompassed by sections 2, 3 and 4.

Figure 4-8 shows the variation of JP-4 removal with depth from the column top. The greatest JP-4 removal occurs in the venting zone. There seems to be a general trend favoring greater removal near the top of the venting zone, with gradually decreasing removal toward the bottom of the venting zone. Only the data point from section 3 of column 2 seems to deviate from this trend, as the removal in that section is much lower than that in sections 2 or 4. The average removal in the top sections of the columns is nearly

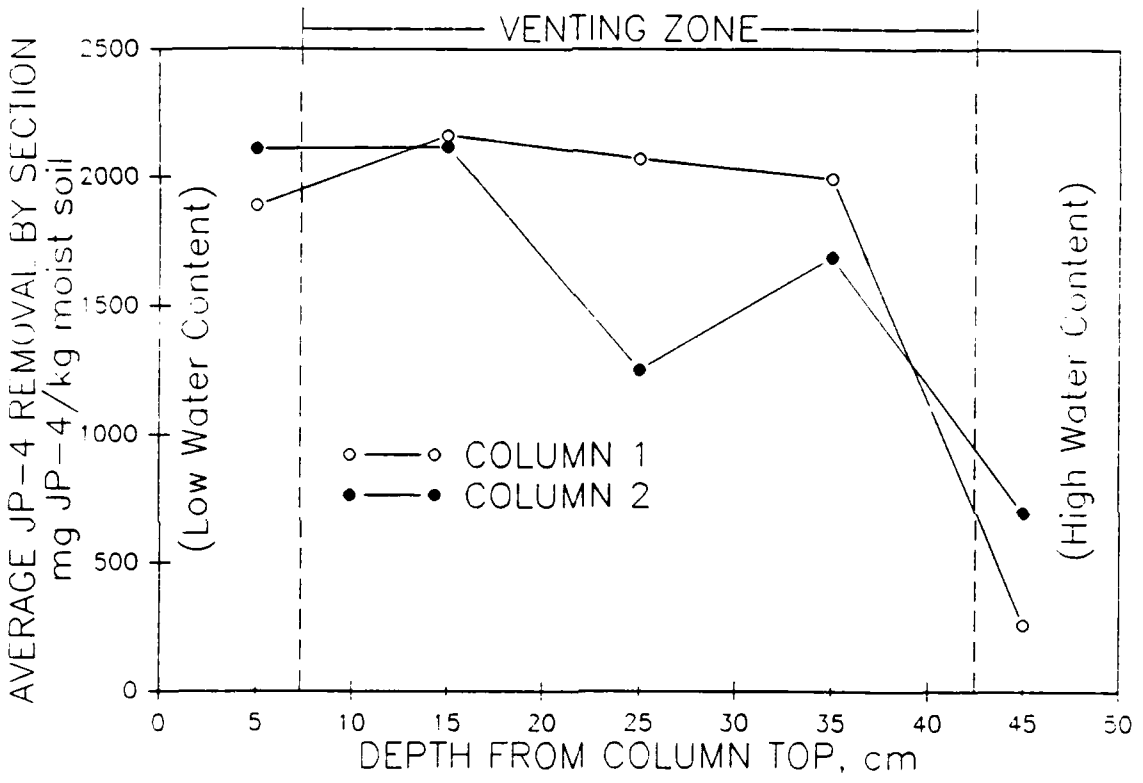

Figure 4-8. Variation of JP-4 Removal with Depth in Column, Data for Columns 1 and 2

as high as that in the top of the venting zone, while the average removal in the bottom sections is relatively low.

The general trend of decreasing removal across the venting zone might be explained by the extent to which each section was drained. The more completely drained sections near the column top could have received a somewhat larger fraction of the venting air flow leading to increased removal by volatilization. Furthermore, the drier sections of the columns had more air filled pore spaces and, hence, more complete contact between the air, soil particles and water films. This would increase the surface area available for aerobic microbial degradation of JP-4.

The most poorly drained section of each column, section 5, consistently showed the lowest JP-4 removal of all sections. This is probably a result of reduced volatilization and biodegradation of JP-4 related to poor soil aeration. The high water content in section 5 would have restricted venting air flow through the soil in that section. A lack of venting air flow through the soil in section 5 would have resulted in less JP-4 being lost through volatilization. Furthermore, poor soil aeration would have reduced the amount of JP-4 biodegraded because the amount of oxygen available to the microorganisms in section 5 would have been limited by the rate of oxygen diffusion through the soil-water. As discussed earlier, the

diffusion of oxygen through water is approximately 10,000 times slower than it is through air.

Variation of JP-4 removal with final water content

An examination of the variation of JP-4 removal with final water content will indicate whether the total removal of JP-4 during soil venting is enhanced by wetter or drier soil conditions.

Figure 4-9 shows the variation of soil water content over the depth of the columns. Keeping in mind that column 2 was partially rewetted, Figure 4-9 shows that the soil venting process dries the soil in the venting zone. The observed drying of the soil in the venting zone occurred even though the venting air was humidified as described in Chapter 3.

Drying of the soil in the venting zone could be a problem at field sites where soil venting is employed to enhance biodegradation of hydrocarbons in the soil. Excessive drying and possible limitation of microbial activity would be most likely to occur in arid regions where both soil water content and atmospheric relative humidity are low. Similar problems could be experienced in sandy soils in regions with humid climates, as sandy soils drain very rapidly. The results of this study, however, indicate that the reduction of soil water content down to approximately 60 percent saturation leads to greater total JP-4 removal in a soil that was initially saturated.

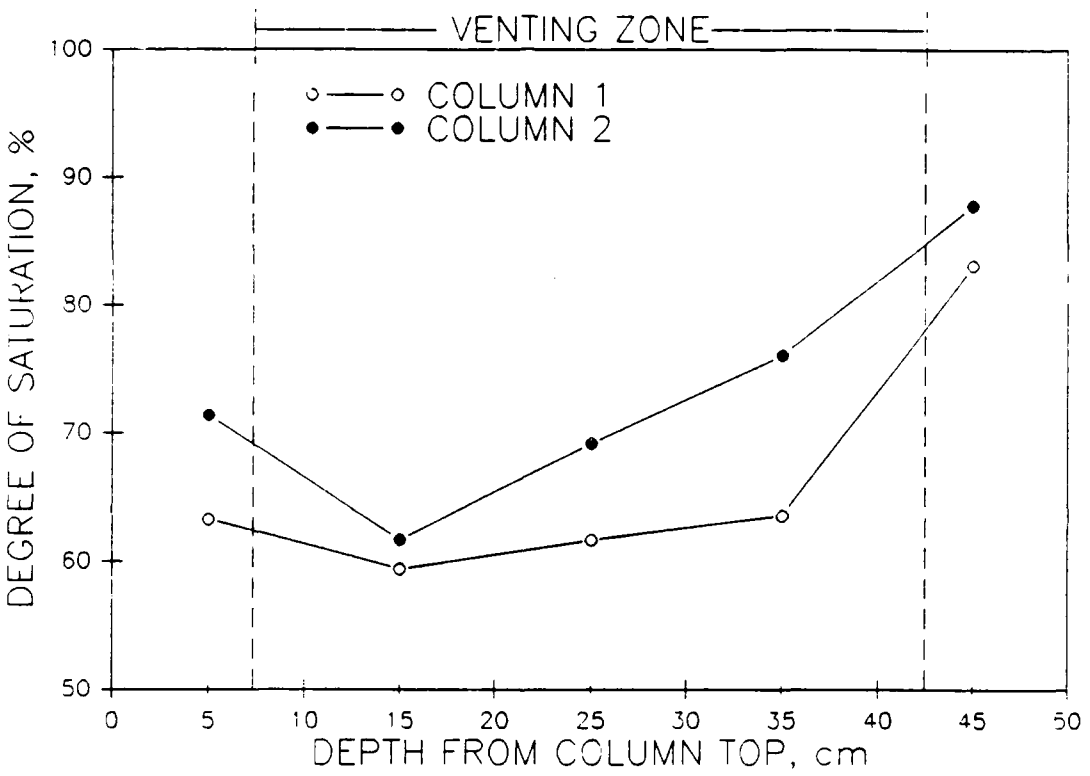

Figure 4-9. Final Water Distribution in Columns 1 and 2

Figure 4-10 shows that total JP-4 removal decreases as final water content increases from approximately 60 to 90 percent saturation. Because the soil in the columns was initially saturated, these results indicate that better removal can be obtained during soil venting by draining a soil from 100 percent to 60 percent saturation than can be obtained by draining from 100 percent to only 85 percent saturation. As discussed earlier with respect to Figure 4-8, poor aeration in the column sections with higher water content would have reduced both volatilization and biodegradation thereby leading to the observed lower total JP-4 removal.

Variation of soil dehydrogenase activity with water content

The soil dehydrogenase activity was determined before and after biodegradation testing. The purpose of these tests was to determine the impact of the soil venting process on the microbial activity in the venting soil.

As mentioned earlier, the initial soil dehydrogenase activity of the test soil averaged 123 micrograms of INT-formazan produced per gram of dry soil per 24 hours. The initial soil water content was approximately 96 percent saturation.

Tables 4-8 and 4-9 summarize the results of the final soil dehydrogenase determinations, final JP-4 soil loadings and final soil water contents from columns 1 and 2, respectively.

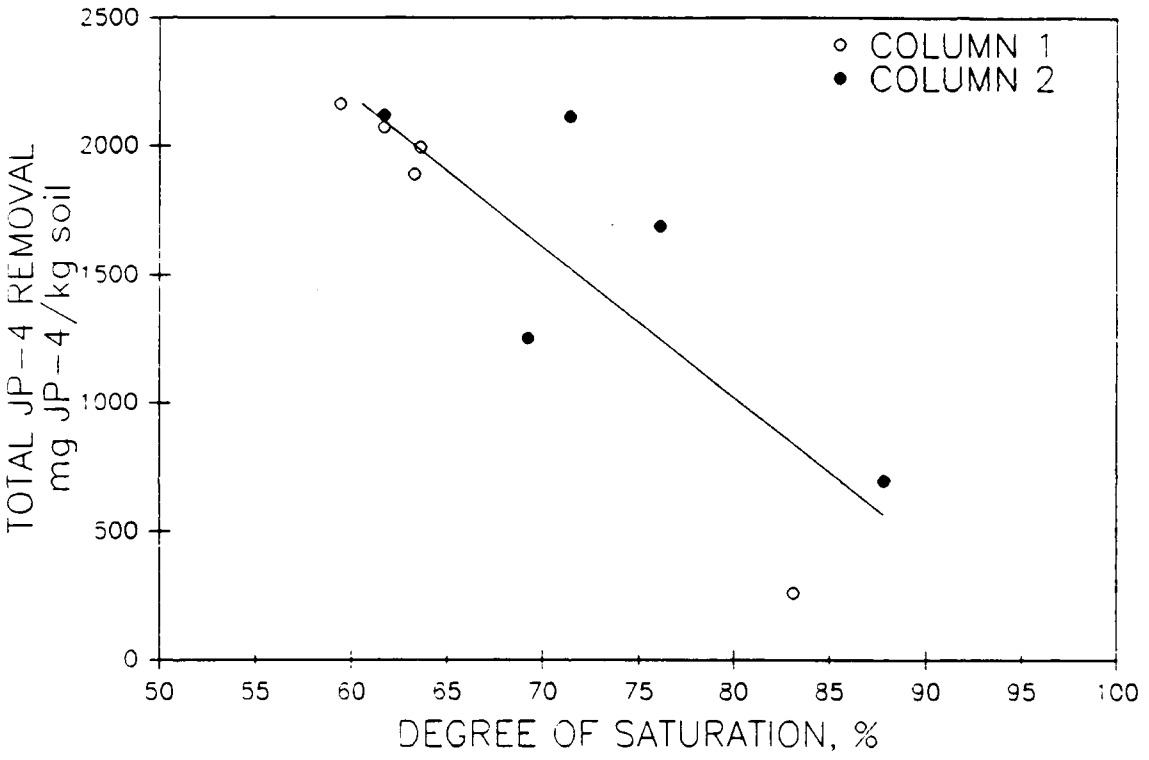

Figure 4-10. Variation of JP-4 Removal with Final Water Content, Columns 1 and 2 (R = 0.88)

Table 4-8. Column 1 Final Soil Dehydrogenase Activity (DHA), JP-4 Loading and Soil Water Content

Column Section	DHA (mg INT-F/g Dry Soil/ 24 Hrs)	JP-4 Loading (mg JP-4/kg Soil)	Water Content (%Saturation)
1	326	1670	63.3
3	245	1490	61.7
5	719	3300	83.1

Table 4-9. Column 2 Final Soil Dehydrogenase Activity (DHA), JP-4 Loading and Soil Water Content

Column Section	DHA (mg INT-F/g Dry Soil/ 24 Hrs)	JP-4 Loading (mg JP-4/kg Soil)	Water Content (%Saturation)
1	299	1450	71.4
3	502	2310	69.2
5	787	2870	87.8

The data presented in Tables 4-8 and 4-9 show that the soil venting process increases the soil dehydrogenase activity. The minimum final dehydrogenase activity is nearly double the initial value.

The final JP-4 loading and final water content data are included in the tables above, as both substrate and water availability may influence microbial activity. Figure 4-11 shows that the soil microbial activity, as indicated by INT-formazan production, increases as water content increases. The R value of the regression line in Figure 4-11 is 0.94. This indicates that there is a reasonably good correlation

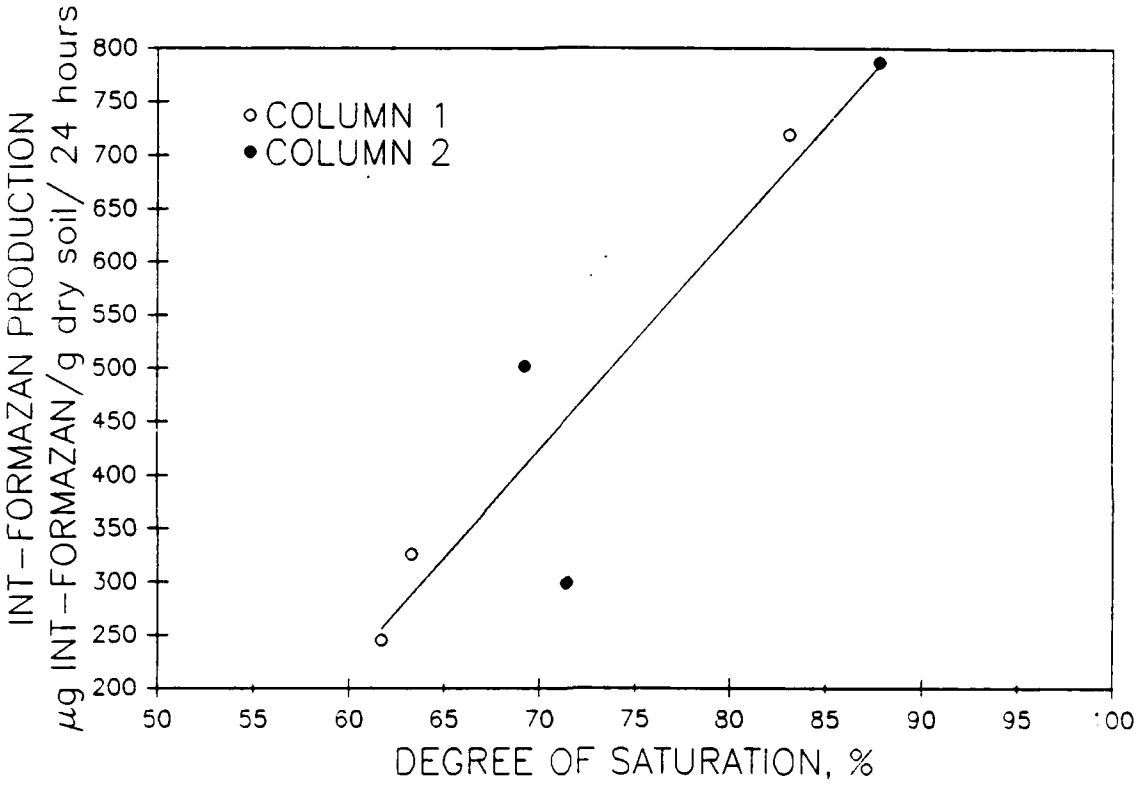

Figure 4-11. Variation of INT-formazan Production with Final Water Content, Columns 1 and 2 (R = 0.94)

between increasing water content and increasing microbial activity.

A similar relationship is apparent in Figure 4-12 which shows that INT-formazan production increases as final JP-4 loading increases. The R value of the regression line in Figure 4-12 is 0.96, indicating that this correlation may be slightly better than that presented in Figure 4-11.

Because microbial activity increases at a similar rate with both water content and final JP-4 loading, it is difficult to say whether water or substrate availability is more limiting in the microbial environment. This issue is further clouded by the possibility that other environmental variables, such as pH and nutrient availability which were not measured during this study, may be influencing the microbial activities in these final results. At best, one may interpret these results to indicate that since the greatest JP-4 removal occurred in the driest sections of the columns, water availability, at least over the 60 to 100 percent saturation range, does not severely limit microbial activity.

Mass Balance of JP-4 from Columns 1 and 2

Another major objective of this study was the construction of a mass balance for the JP-4 originally present in the columns. The purpose of constructing a mass balance was to substantiate the JP-4 losses determined by

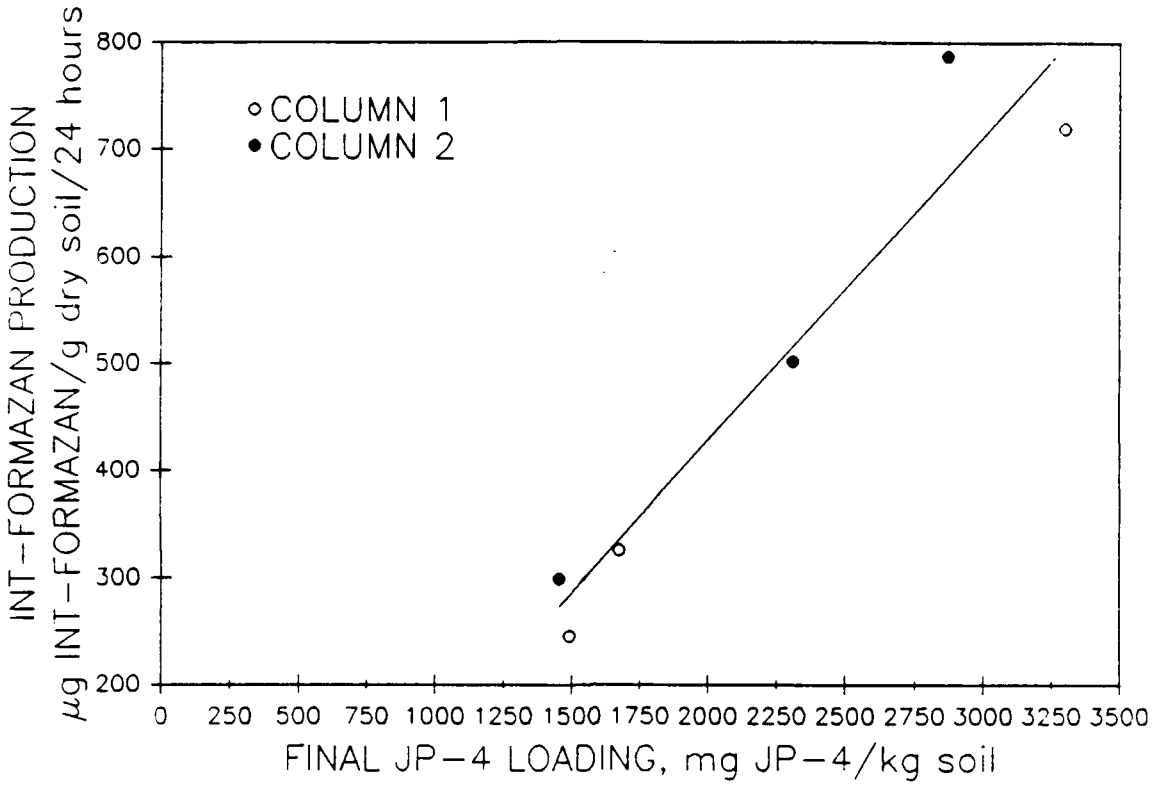

Figure 4-12. Variation of INT-formazan Production with Final JP-4 Loading, Columns 1 and 2 (R = 0.96)

the analytical methods discussed herein. The JP-4 losses through biodegradation, volatilization and column drainage have been summarized and discussed in the text above. Total JP-4 removal as determined by initial and final soil extractions has also been discussed.

From the data presented in previous sections of this chapter, a mass balance of the JP-4 initially present in the soil columns can be constructed. The only significant mechanisms of JP-4 removal have been volatilization and biodegradation. The cumulative contributions of biodegradation based on carbon dioxide evolution and volatilization of JP-4 are shown in Figures 4-13 and 4-14 for columns 1 and 2 respectively. Table 4-10 summarizes the total JP-4 removal for columns 1 and 2.

In Table 4-10, the measured mass of JP-4 remaining in each column was determined by extracting and quantifying JP-4 present after the biodegradation testing.

Table 4-10. Mass Balance of the JP-4 in Columns 1 and 2

Column	Initial Mass (mg)	Mass Biodegraded (mg)	Mass Volatilized (mg)	Calculated Mass Remaining (mg)	Measured Mass Remaining (mg)
1	17800	4160	625	13015	9820
2	17600	3280	530	13790	10010

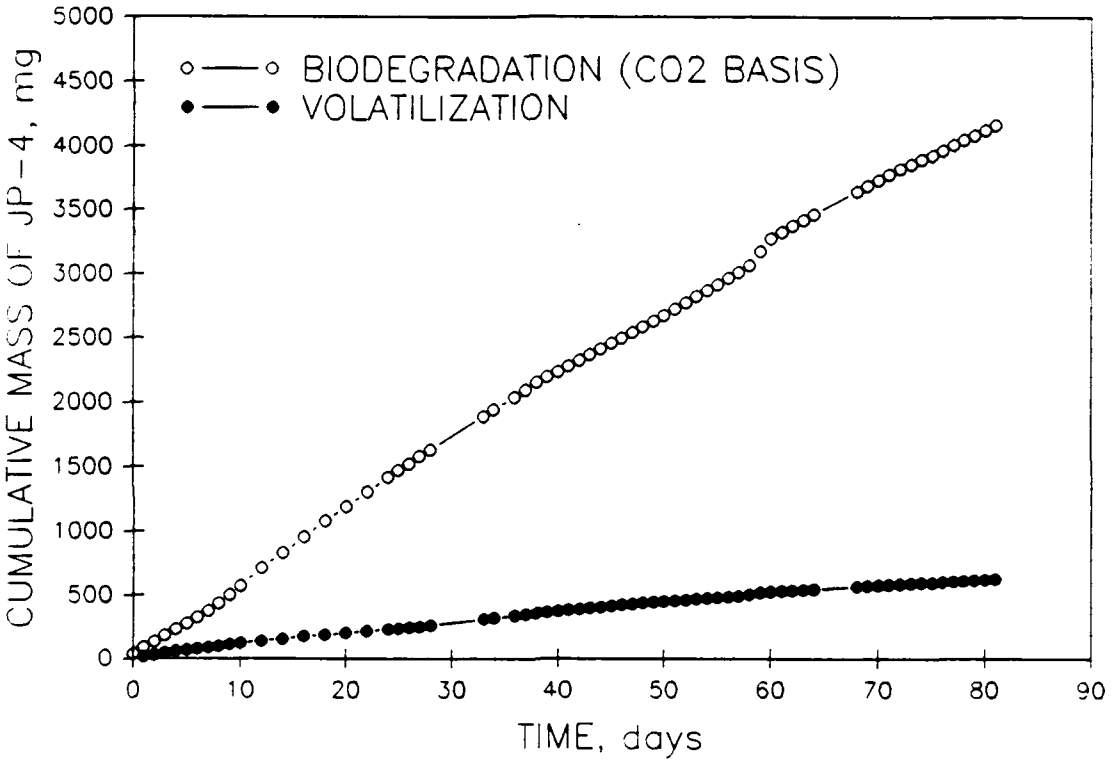

Figure 4-13. Cumulative JP-4 Removal from Column 1, Biodegradation and Volatilization Data

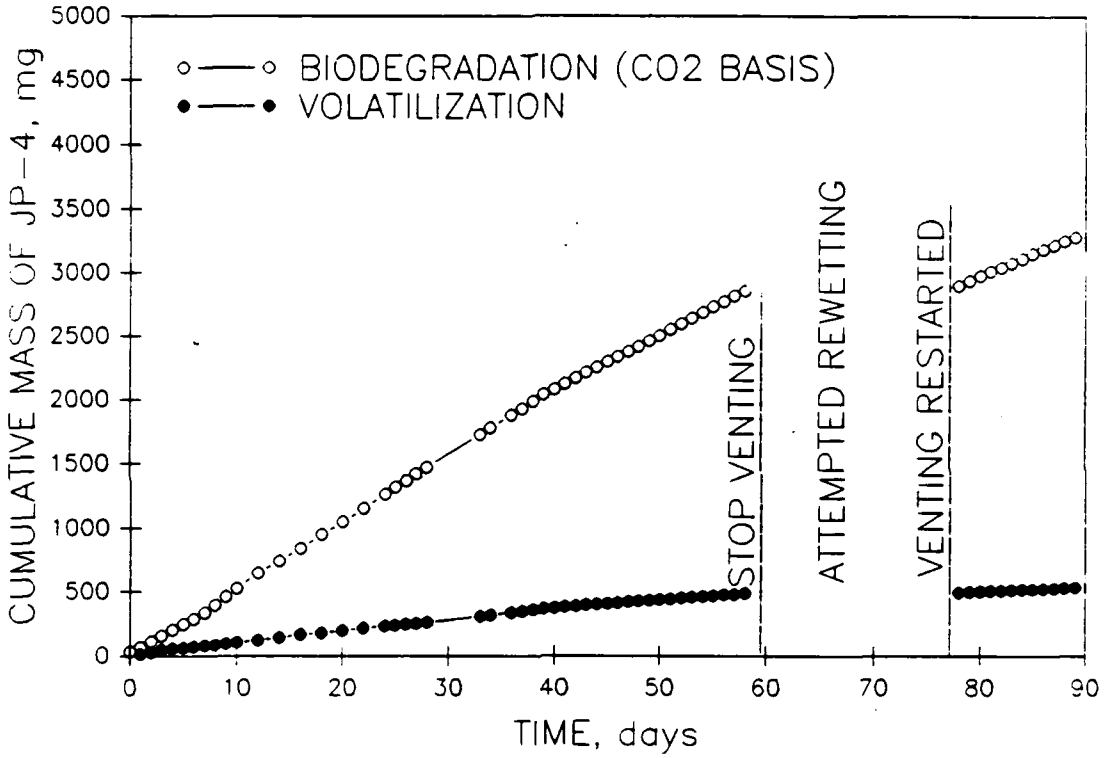

Figure 4-14. Cumulative JP-4 Removal From Column 2, Biodegradation and Volatilization Data

These results show that the calculated mass balance based on carbon dioxide evolution under-predicts the mass of JP-4 removed during soil venting by 40 percent in column 1 and 50 percent in column 2. The masses of JP-4 biodegraded in Table 4-10 are based on carbon dioxide eluted rather than oxygen uptake. Because of the possible presence of anaerobic areas in the soil, carbon dioxide production is a more appropriate measure of biodegradation than is oxygen consumption (Stotzky, 1965). To find a possible explanation for the large discrepancy between the measured and calculated masses of JP-4 remaining, the discussion below will focus on the respiratory quotient of the test soil in this study as well as additional literature findings.

Respiratory quotient

The respiratory quotient is a value cited in the literature as an indicator of the degree of mineralization of hydrocarbons (Stone et al., 1942; Bushnell and Haas, 1941). The respiratory quotient is the ratio of moles of oxygen used to the moles of carbon dioxide produced during biological oxidation processes. Stone et al. (1942) reported respiratory quotients from 0.5 to 0.7 with a typical value of 0.65 resulting from bench-scale light oil biodegradation tests. Based on the chemical equation given previously for the mineralization of dodecane, the theoretical respiratory quotient for JP-4 is approximately 0.65. The respiratory quotients calculated from the oxygen

uptake and carbon dioxide production data from this study were approximately 0.58 for both aerobic columns. This value is only 11 percent lower than the theoretical respiratory quotient. According to Stone et al. (1942) this indicates that a large percentage of the molecules attacked were completely oxidized to carbon dioxide and water.

This finding indicates that the mass of carbon given off as carbon dioxide should be very similar to the observed mass of JP-4 carbon lost during the biodegradation testing process. To determine whether this was true, the ratio of mass of JP-4 biodegraded on a carbon dioxide evolution basis to that biodegraded based on initial and final soil extractions (CO_2 evolved/residual PHC ratio) was determined for each column.

This ratio should not be confused with cell yield. Cell yield is a value often used in discussions of biodegradation systems. It is defined as the mass of microbial cells produced per mass of substrate degraded. The ratio being discussed herein is a ratio of the masses degraded on the basis of two different measurements, i.e., CO_2 evolved and residual hydrocarbon remaining in the soil.

The value of the CO_2 evolved/residual PHC ratio was 0.56 for column 1 and 0.46 for column 2. In other words, the mass of JP-4 biodegraded on the basis of carbon dioxide production differs from that determined by soil extractions by about a factor of two.

JP-4 losses through volatilization, which were discussed earlier, do not account for this difference. However, similar inconsistencies between the total PHC biodegradation predicted by carbon dioxide production and that predicted by initial and final hydrocarbon extractions have been reported in the literature. Dibble and Bartha (1979b) reported CO_2 evolved/residual PHC ratios ranging from 0.52 to 0.62 for oil sludge biodegradation in soils with no nutrients or other amendments added. Addition of nutrients increased these ratios in Dibble and Bartha's work. Brown and Donnelly (1983) reported CO_2 evolved/residual PHC ratios ranging from 0.28 to 0.44 for petrochemical sludge biodegradation in various soils. Finally, ZoBell (1973) reported that an average of about 50 percent of the carbon in hydrocarbons metabolized by bacteria is converted into cell substance or other hydrocarbons. It can be inferred from ZoBell's report that the remaining 50 percent of the metabolized carbon is given off as carbon dioxide.

Because of the inconsistent predictions of the total mass of JP-4 biodegraded based on carbon dioxide production versus that predicted by the difference between the initial and final soil JP-4 loadings, the carbon dioxide production data was reevaluated with the assumption that only 50 percent of the metabolized carbon is given off as carbon

dioxide. Table 4-11 presents the results of this reevaluation in the form of a corrected mass balance.

This corrected mass balance attempts to account for the JP-4 carbon which is metabolized by microorganisms but not completely mineralized to carbon dioxide.

The mass balance based on corrected carbon dioxide evolution over-predicts JP-4 removal by 12 percent in column 1, and under-predicts JP-4 removal by 7 percent in column 2. The close agreement between the values of mass of JP-4 remaining as predicted by the corrected mass balance and by the final soil extractions supports the contention that

Table 4-11. Corrected Mass Balance of JP-4 In Columns 1 and 2 Assuming 50 Percent JP-4 Carbon to CO_2 Conversion

Column	Initial Mass (mg)	Mass Biodegraded (mg)	Mass Volatilized (mg)	Calculated Mass Remaining (mg)	Measured Mass Remaining (mg)
1	17800	8320	625	8855	9820
2	17600	6560	530	10510	10010

about 50 percent of the metabolized JP-4 carbon is converted to carbon dioxide.

The biodegradation rates predicted using the assumed 50 percent conversion of JP-4 carbon to carbon dioxide, as discussed above, would be double the rates presented in Table 4-4 based on carbon dioxide production. Although these adjusted biodegradation rates may more closely

approach the true biodegradation rates, the rates presented in Table 4-4 should be used for comparison with rates presented in the literature, as most of the biodegradation rates presented in the literature are based on actual carbon dioxide evolution.

Control Column

The initial objective of running a control column during the soil venting biodegradation testing was to obtain JP-4 volatilization data from a soil column free of a significant level of aerobic biodegradation. It was anticipated that in a control column vented with high purity nitrogen gas, the total JP-4 removal determined by initial and final soil extractions would be approximately equal to volatilization.

The literature seemed to support the fact that anaerobic biodegradation of PHC's is, at best, very slow in the environment with comparison to aerobic biodegradation. Atlas (1977) reported that hydrocarbons are not degraded in the environment under anaerobic conditions. In 1973, ZoBell reported that, for practical purposes, free or dissolved oxygen was essential for PHC biodegradation. However, ZoBell mentioned that PHC's can be oxidized by sulfate reducing bacteria, albeit at a very slow rate. In 1968, Schwendinger reported that anaerobic organisms utilized PHC's with difficulty, but at a rate about 10 percent that

of aerobes. Finally, in a 1986 report, Bartha discussed PHC biodegradation in oxygen-limited environments. He stated that while the initial attack on a hydrocarbon molecule requires molecular oxygen, subsequent attacks on partially oxygenated intermediate hydrocarbons may be supported by nitrate or sulfate reduction. It can be inferred from Bartha's report that the rate of biodegradation of PHCs in oxygen-limited environments, but not in strictly anaerobic environments, may be significant in comparison with the biodegradation rate in aerobic environments.

Bartha's report addresses the situation actually encountered with the control column during this study. Specifically, the control column was not strictly anaerobic at any time during the 81-day biodegradation run. GC/TCD analyses of the effluent venting gas from the control column showed oxygen concentrations ranging from approximately 100 parts per million to 3400 parts per million throughout this study.

Considering the discussion above, it is clear that the original objective was not fulfilled with the control column. Apparently, leakage of atmospheric oxygen was occurring through the plugged sampling and tensiometer ports. (Note that no unused ports were present on the aerobic biodegradation columns to act as sources of leakage.) The result of having a partially aerobic environment in the control column is that the data gathered

from the column is characteristic of an oxygen-limited environment, i.e. an environment in which both biodegradation and volatilization play significant roles in the total removal of JP-4.

The data from the control column is briefly summarized in subsequent sections of this thesis. The scales used on the axes of all graphs are the same as those used in the corresponding graphs from the aerobic columns. Therefore, comparisons can be made directly between the control column graphs and those from columns 1 and 2.

Biodegradation rate and mass of JP-4 biodegraded

The biodegradation rate based on carbon dioxide evolution was essentially constant with time after the first 15 days of venting. The average biodegradation rate was approximately 2.5 milligrams of JP-4 per kilogram of moist soil per day. This rate is about 25 percent of the average rates observed in the aerobic columns.

Figure 4-15 shows the variation of the control column biodegradation rate with time. The mass of JP-4 biodegraded over the 81 day biodegradation test phase of this study was approximately 780 milligrams on the basis of the data plotted in Figure 4-15. Notice that no data were gathered during the initial 9 days of the biodegradation testing. This was a result of being unable to establish a nitrogen venting flow across the control column with the same pressure drop used in the aerobic columns. For the first 8

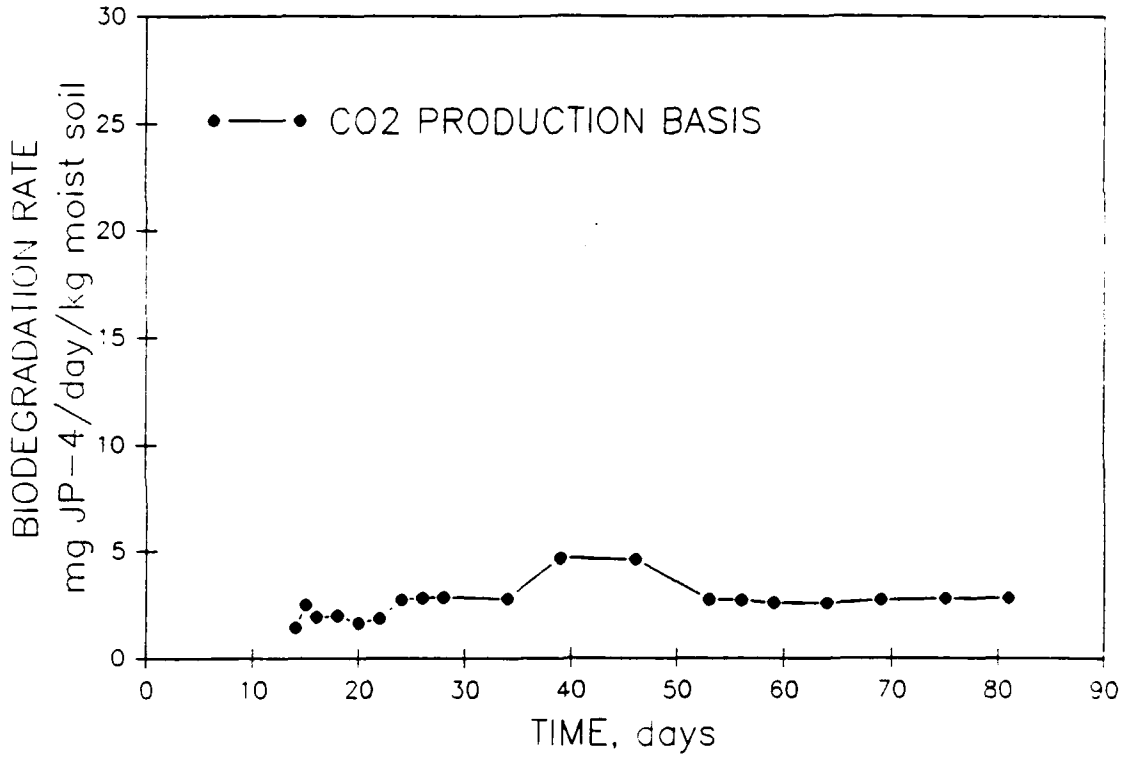

Figure 4-15. Variation of Biodegradation Rate with Time, Control Column Data

days of biodegradation testing, the control column was vented at a pressure of several feet of water rather than the 0.1 to 0.5 inches of water used for the aerobic columns. The failure of the control column to accept a nitrogen flow was apparently a result of air entrapment and the related slow column drainage rate. By pressurizing the control column for eight days, the excess water and entrapped air were forced from the soil pores. After this pretreatment, the control column accepted an average nitrogen flow of approximately 1.05 milliliters per minute at the same pressure used in the aerobic columns.

Figure 4-16 shows the variation of the JP-4 mass volatilization rate with time for the control column. The variation of JP-4 volatilization rate with time is very similar to that observed with the aerobic columns. Had volatilization data been collected during the first eight days of venting, it can be assumed that the trend during this time frame would also have been similar to those observed in columns 1 and 2.

The total mass of JP-4 volatilized from the control column between days eight through 81 was approximately 370 milligrams. If the control column lost JP-4 through volatilization from day 0 through day 8 at the same rate as the aerobic columns, the total mass of JP-4 volatilized would have been 440 milligrams. Considering the difficulties encountered with the control column and the

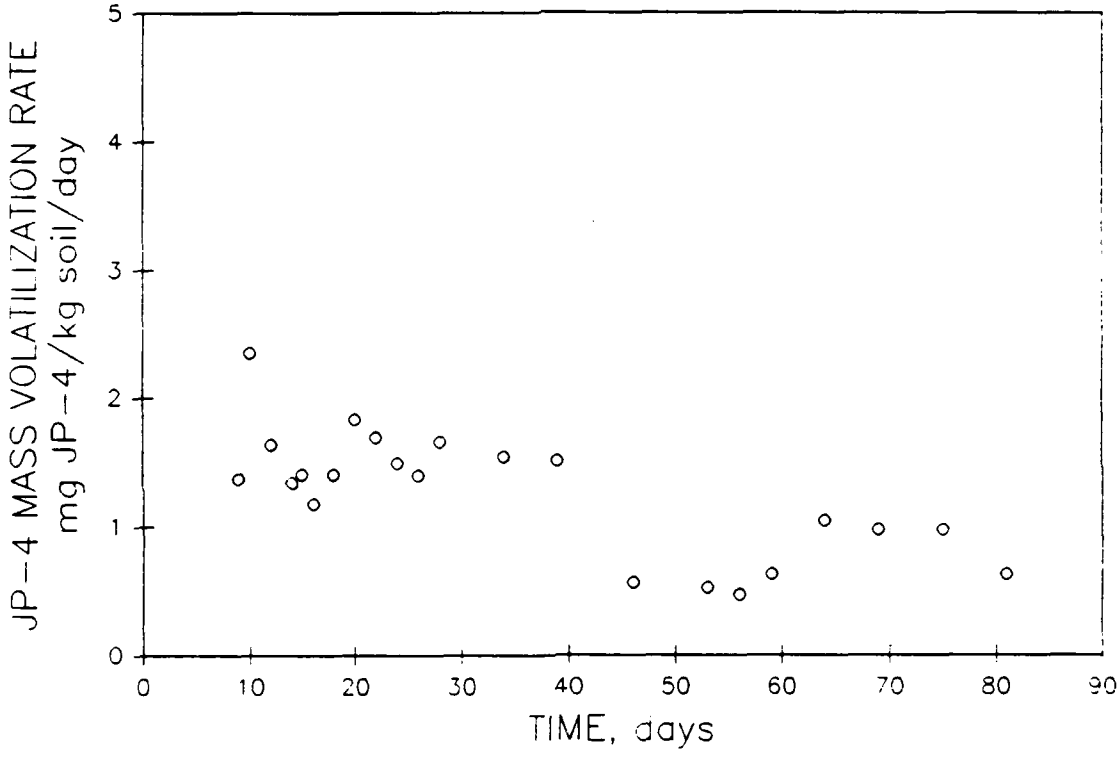

Figure 4-16. Variation of JP-4 Mass Volatilization Rate With Time, Control Column Data

assumptions made above, the value of 440 milligrams of JP-4 volatilized is not significantly different from the data from the aerobic columns.

Total JP-4 removal and mass balance

The total mass of JP-4 removed from the control column as determined by initial and final soil extractions was approximately 7410 milligrams. This value represents a removal of approximately 42 percent of the total 17600 milligrams of JP-4 initially present in the control column.

The total JP-4 removal from the control column compares very well with the average 44 percent removal observed in the aerobic columns. Unfortunately, the mass of carbon dioxide evolved and the mass of JP-4 volatilized do not account for
the observed total removal, and the mass of JP-4 lost through column drainage was negligible, as in the aerobic columns.

Figure 4-17 shows the cumulative contributions of volatilization and biodegradation based on the data collected from the effluent venting gas. Table 4-12 summarizes the total removal of JP-4 from the control column.

The calculated mass of JP-4 remaining over-predicts the measured mass remaining by approximately 127 percent. A possible explanation for this large discrepancy could be that a large fraction of the JP-4 molecules attacked were

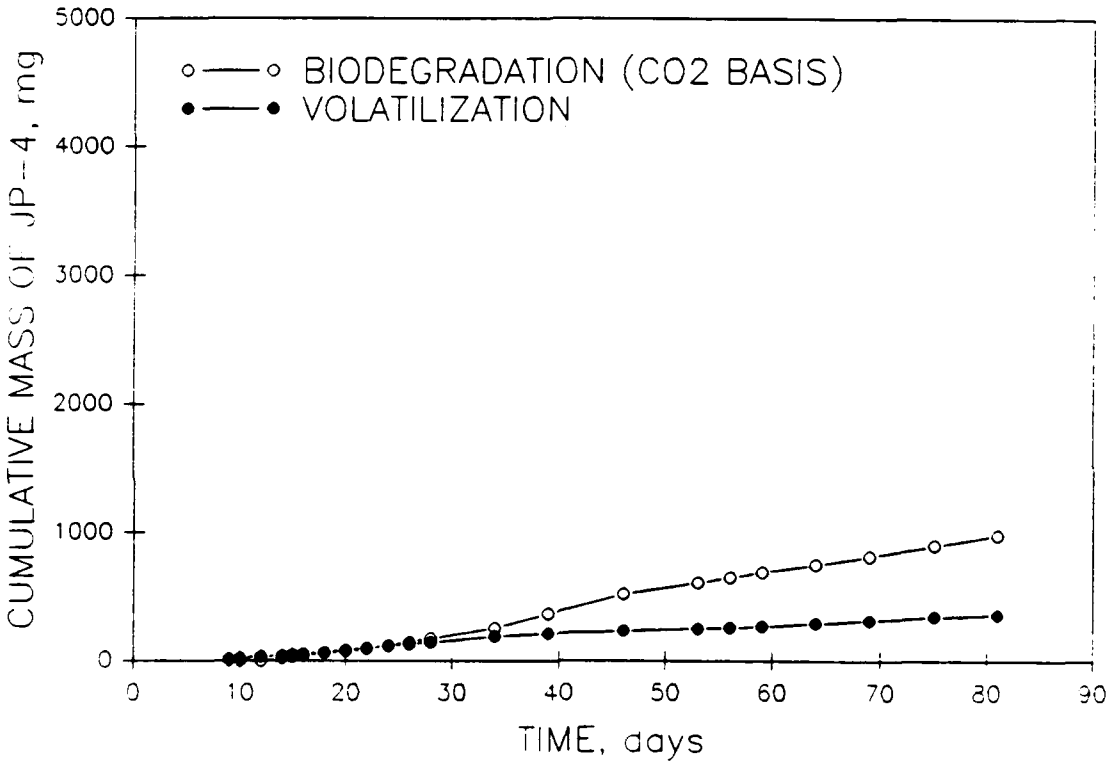

Figure 4-17. Cumulative Removal of JP-4 from the Control Column

Table 4-12. Mass Balance of the JP-4 in the Control Column

Initial Mass (mg)	Mass Biodegraded (mg)	Mass Volatilized (mg)	Calculated Mass Remaining (mg)	Measured Mass Remaining (mg)
17600	780	440	16820	7410

converted into intermediates that remained in the soil and were not accurately quantified by the methods used in this study. Also, it is likely that methane was produced during the venting of the control column. Methane producing microorganisms may have survived in anaerobic microenvironments within the soil column despite the observed oxygen leakage into the system. The loss of JP-4 carbon as methane would account for some of the observed discrepancy.

Variation of INT-formazan production with water content

Although no references were found in the literature discussing the applicability of the INT dehydrogenase activity determination for assessing the activity of anaerobic microorganisms, the test was used in this study. Only in a 1972 report by Howard was any mention made of anaerobic dehydrogenases. Howard reported that anaerobic dehydrogenases utilize TTC (a tetrazolium salt discussed previously) as a hydrogen acceptor.

With the questionable applicability of the INT dehydrogenase test in mind, the test results are discussed below.

An average production of approximately 600 micrograms of INT-formazan per gram of dry soil per 24 hours was observed using the soil from the control column. The rate of INT-formazan production was essentially constant over the depth of the column, despite a variation in water content from 84 percent to 68 percent saturation. Samples with similar variations in water content from the aerobic columns resulted in INT-formazan production rates that differed by an average of more than 35 percent.

These results indicate two very interesting possibilities. First, they indicate that the oxygen limited conditions in the control column favored the development of a population of microorganisms that are not as sensitive to differences in soil water content as their counterparts in the aerobic columns. Secondly, if the values of the INT-dehydrogenase determinations can be compared between the aerobic columns and control column, they indicate that the average microbial activity in the control column was somewhat higher than that in either aerobic column. Table 4-13 summarizes the INT-formazan production rates from the three columns.

Once again, the results presented for the control column in Table 4-13 represent the INT-formazan production

in soil from an oxygen limited environment. It is questionable whether meaningful comparisons can be made

Table 4-13. INT-formazan Production Rates

Column Section	INT-formazan Production Rate (ug INT-formazan/g dry soil/24 hrs) Column 1	Column 2	Control
1	326	299	594
2	245	502	591
3	719	787	621

between the INT-formazan production rates from the control column and the predominantly aerobic columns 1 and 2.

With reference to Table 4-13, in each column, the microbial activity is greatest in section 5. As discussed earlier, section 5 also has the highest water content,lowest JP-4 removal, and poorest aeration of all column sections. Therefore, one would expect the microbial environment in section 5 of each column to be the most nearly anaerobic of all column sections.

The observed JP-4 removal in section 5, being the lowest of all column sections, seems to support the contention that biodegradation of PHCs in the absence of oxygen is very slow. However, the high rates of INT-formazan production in section 5 indicate that microbial activity is greatest in this section.

The higher microbial activity and lower JP-4 removal in section 5 seem to be contradictory results. One possible

explanation for this apparent contradiction is that the majority of the microorganisms in this section are not fuel-hydrocarbon degraders. The microorganisms in section 5 of each column may have utilized some other carbon source as their primary growth substrate, and they may, or may not, have used JP-4 hydrocarbons as a secondary carbon source. Regardless of the nature of the carbon source, whether it was a non-fuel hydrocarbon or a by-product hydrocarbon of JP-4 degradation, it seems clear that this carbon source was not accurately quantified by the soil extraction and analytical techniques employed in this study.

CHAPTER 5

SUMMARY AND CONCLUSION

The primary objective of this research was to determine the impact of various levels of soil water content on the rate of biodegradation of JP-4 in a soil column under the influence of soil venting.

The rate of JP-4 biodegradation reached a maximum at a water content of approximately 72 percent saturation, which appeared to be the field capacity of the soil in the experimental packed columns. The observed maximum biodegradation rate was 14.3 milligrams of JP-4 per kilogram of moist soil per day based on the mass of carbon dioxide evolved. The average biodegradation rate was approximately 75 percent of the maximum, and the minimum biodegradation rate observed was approximately 50 percent of the maximum rate.

The biodegradation rate increased as the columns drained from saturation, peaked at 71.6 percent saturation and then decreased at a constant rate with time as drainage continued. It remains unclear whether this trend was solely a result of decreasing soil water content or a combination

of several environmental variables such as soil pH, nutrient availability and substrate availability.

The biodegradation rates observed during this study were low relative to those reported by other investigators from other studies in which soil environmental conditions were partially optimized. This finding indicates that other factors such as pH and nutrient availability in the soil may have limited the rate of biodegradation throughout this study.

The following text presents several additional conclusions concerning the soil venting process as a means of enhancing biodegradation of hydrocarbons in soil.

The soil venting process was most effective at removing the lighter hydrocarbons in JP-4. Overall, approximately 45 percent of the JP-4 initially present in the soil columns was removed by volatilization and biodegradation. An examination of the removal of alkanes from C-8 to C-14 showed that the removal of alkanes is inversely proportional to carbon chain length. The removal of alkanes nearer to C-8 approached 100 percent, while C-14 removal was less than 10 percent. Some of this difference could be attributed to volatilization of the lighter hydrocarbons, but a microbial preference for shorter alkanes appears to be the larger factor. Had this study continued for a longer time period, the continuing depletion of the shorter hydrocarbons may

have forced increased microbial use of the longer hydrocarbons.

Soil venting tended to dry the soil in the venting zone even though the venting air was humidified. This drying appears to have increased the overall removal of JP-4, as the drier sections of the soil columns exhibited the greatest reduction in JP-4 loading. This enhancement of total removal can be attributed to increased aeration and the resultant increases in volatilization and biodegradation. However, the drying effect could be a problem in field applications of soil venting to enhance biodegradation, especially in regions where atmospheric relative humidity and soil water content are low.

Removal of adsorbed hydrocarbons by soil flushing or water drainage was insignificant in comparison with the removal by volatilization and biodegradation during soil venting. Of the total JP-4 removal, on the average, approximately 93 percent was attributed to biodegradation, and approximately 7 percent was attributed to volatilization.

One additional conclusion concerns soil biodegradation studies in general. It appears from the results of this study and others cited in the literature, that the best estimate of the mass of hydrocarbon biodegraded can be obtained by doubling the observed mass of carbon dioxide evolved. This accounts for carbon loss from the PHC that

has been metabolized but not evolved as carbon in carbon dioxide. The use of oxygen uptake data as a means to estimate total biodegradation in soil may produce misleading results, as even vented soil systems may contain anaerobic pockets.

Additional research on the soil venting process should include efforts to more clearly define the optimal rate and means of nutrient addition. Inorganic nutrients are essential to microbial metabolism, but addition of nutrients in solution may lead to excessively wet soil conditions and ineffective venting.

Soil pH may change during soil venting as a result of increased production of microbial metabolic byproducts. Future work with soil venting should address the need for pH measurement and control.

Future studies attempting to assess the impact of soil venting and soil water content on the rate of biodegradation of petroleum hydrocarbons should employ small (3.5-inch diameter and 2 - 3 inches high), individual soil columns, each maintained at a single moisture content. The column design should facilitate a forced, rapid drainage of the soil by increasing the pressure of the gases contained within the soil pores. Such a system is simple and commercially available, and it would allow the investigator to quickly and reproducibly attain a desired water content. The column system used in this study was too large to drain

rapidly, and the time required for drainage was so long that the substrate and nutrient availabilities could not be assumed to be constants. Hence, they became non-quantified variables potentially responsible, in some degree, for the observed changes in the biodegradation rate.

APPENDIX A
SOIL COLUMN PACKING PROCEDURE

1. Thoroughly mix the soil sample in a tightly closed container.

2. Once mixed, take several samples of the soil and determine the water content on a dry mass basis (dw). If the soil is well mixed, the water content should be approximately the same in all samples.

3. Attach a 15-cm extension to the column base and a 45-cm extension to the column top.

4. Pack soil into the column in mass increments equal to the mass contained in one inch of the column depth when the column is packed to the desired wet bulk density. Use the following equation to determine the mass to be packed in each increment:

$$i = I * [(1 + dw,packed)/(1 + dw,field)],$$

where

dw,packed = the dry weight basis water content of the packing soil,
dw, field = the dry weight basis water content of the initial field samples from which the desired wet bulk density was determined,
i = mass of moist packing soil at dw,packed to be packed
into the column per increment,
I = Column volume * field wet bulk density/column length (inches).

5. Weigh out an increment of soil, break up chunks, remove rocks and replace any rocks with an equal mass of soil. (Keep the soil container closed at all times to prevent water loss from the packing soil.)

6. Put soil into the column by sliding it down the side - do not allow it to freefall into the column.

7. Pack the soil by "bumping" the column bottom on the countertop. This should be done lightly enough to prevent dislodging of the soil from the increment below.

8. Continue packing until the soil is packed to the desired height in the column.

9. Measure and record the height of the soil in the column after each increment.

10. Loosen the top surface of the each packed increment prior to adding the soil for the next increment. (This will reduce the likelihood of unwanted soil layering.)

11. Use the following equation to determine the final average wet bulk density of the packed column:

Wet bulk density = total wet mass of packed soil/column volume

This value should be compared to the field wet bulk density to determine whether the packed column density is similar to the field density.

APPENDIX B
SOIL COLUMN DATA

Table B-1. Column 1 Venting Air Flow and Moisture Data

DAY	DATE	VENTING AIR FLOWS INSTANT. (mL/min)	VENTING AIR FLOWS 24 HR AVG (mL/min)	MOISTURE DATA SUCTION (cm H2O)	MOISTURE DATA % SAT
0	30 Nov	0.82	0.82	21.6	95.0
1	1 Dec	0.64	0.73	29.3	74.3
2	2 Dec	0.77	0.7	32.8	73.4
3	3 Dec	1.0	0.88	34.2	73.1
4	4 Dec	1.16	1.08	35.4	72.8
5	5 Dec	1.01	1.09	36.5	72.5
6	6 Dec	1.05	1.03	37.0	72.4
7	7 Dec	1.03	0.89	37.0	72.4
8	8 Dec	0.99	1.0	37.0	72.4
9	9 Dec	1.0	0.99	36.9	72.4
10	10 Dec	0.92	0.96	37.3	72.3
12	12 Dec	0.93	0.93	38.2	72.1
14	14 Dec	1.47	1.2	39.8	71.7
16	16 Dec	1.66	1.57	41.2	71.3
18	18 Dec	0.83	0.83	42.2	71.1
20	20 Dec	1.19	1.17	43.5	70.8
22	22 Dec	1.16	1.18	44.2	70.6
24	24 Dec	0.9	1.03	45.5	70.3
25	25 Dec	0.65	0.78	46.2	70.1
26	26 Dec	1.2	0.93	46.8	69.9
27	27 Dec	1.02	1.11	48.0	69.6
28	28 Dec	1.15	1.09	48.8	69.4
33	2 Jan	1.4	1.27	53.2	68.4
34	3 Jan	1.31	1.35	54.0	68.2
36	5 Jan	1.46	1.39	55.4	67.8
37	6 Jan	1.51	1.49	56.0	67.7
38	7 Jan	1.43	1.47	56.2	67.6
39	8 Jan	1.12	1.02	57.2	67.4
40	9 Jan	1.11	1.11	58.0	67.2
41	10 Jan	1.05	1.08	58.3	67.1
42	11 Jan	1.16	1.11	59.0	66.9
43	12 Jan	1.16	1.16	59.7	66.7
44	13 Jan	1.16	1.16	60.1	66.6
45	14 Jan	1.13	1.15	60.6	66.5
46	15 Jan	1.14	1.14	61.2	66.4

Table B-1. (continued)

DAY	DATE	VENTING AIR FLOWS INSTANT. (mL/min)	VENTING AIR FLOWS 24 HR AVG (mL/min)	MOISTURE DATA SUCTION (cm H2O)	MOISTURE DATA % SAT
47	16 Jan	1.2	1.17	61.9	66.2
48	17 Jan	0.99	1.09	62.6	66.0
49	18 Jan	1.25	1.12	62.8	66.0
50	19 Jan	1.26	1.26	63.2	65.9
51	20 Jan	1.23	1.25	63.7	65.8
52	21 Jan	1.22	1.23	64.1	65.7
53	22 Jan	1.24	1.23	64.4	65.6
54	23 Jan	1.2	1.22	64.5	65.6
55	24 Jan	1.18	1.19	65.0	65.4
56	25 Jan	1.27	1.23	65.7	65.3
57	26 Jan	1.34	1.31	65.9	65.2
58	27 Jan	5.41	3.37	66.3	65.1
59	28 Jan	1.37	3.39	66.6	65.0
60	29 Jan	0.96	1.17	67.2	64.9
61	30 Jan	1.2	1.15	67.5	64.8
62	31 Jan	1.21	1.2	68.0	64.7
63	1 Feb	1.29	1.25	68.3	64.6
64	2 Feb	1.03	1.16	68.9	64.5
68	6 Feb	1.54	1.27	70.4	64.1
69	7 Feb	1.57	1.56	71.2	63.9
70	8 Feb	1.41	1.31	71.4	63.8
71	9 Feb	1.27	1.34	71.9	63.7
72	10 Feb	1.37	1.32	72.2	63.6
73	11 Feb	0.68	1.03	72.5	63.6
74	12 Feb	0.85	1.0	72.8	63.5
75	13 Feb	0.6	0.85	73.2	63.4
76	14 Feb	1.23	1.22	73.7	63.3
77	15 Feb	1.25	1.24	74.2	63.2
78	16 Feb	0.67	0.96	74.4	63.1
79	17 Feb	1.3	1.33	75.1	62.9
80	18 Feb	1.33	1.31	75.5	62.8
81	19 Feb	1.4	1.36	75.8	62.8

Table B-2. Column 1 Mass Rates

DAY	DATE	COLUMN MASS RATES O2 MUR (mg/day)	CO2 MPR (mg/day)	JP-4 MVR (mg/day)
0	30 Nov	171.6	125.2	
1	1 Dec	229.5	158.5	12.7 *
2	2 Dec	192.4	148.4	14.6 *
3	3 Dec	198.7	154.1	19.0 *
4	4 Dec	191.0	153.7	11.9 *
5	5 Dec	180.0	133.3	9.1 *
6	6 Dec	224.0	165.3	11.4 *
7	7 Dec	218.3	160.0	10.1 *
8	8 Dec	269.0	202.8	12.0 *
9	9 Dec	281.4	211.4	13.1 *
10	10 Dec	279.1	219.7	9.1
12	12 Dec	263.9	204.8	8.8
14	14 Dec	214.1	165.2	7.7 *
16	16 Dec	287.5	230.1	10.4
18	18 Dec	212.1	155.9	5.5
20	20 Dec	216.1	186.8	7.8
22	22 Dec	207.7	167.5	7.8
24	24 Dec	246.4	190.9	7.1 *
25	25 Dec	205.8	157.2	5.9
26	26 Dec	189.7	162.6	7.0
27	27 Dec	227.8	180.2	8.4
28	28 Dec	200.2	156.5	8.2
33	2 Jan	217.7	165.1	9.7
34	3 Jan	213.7	162.0	11.0 *
36	5 Jan	186.6	140.9	9.8
37	6 Jan	182.4	173.0	10.5
38	7 Jan	189.2	172.4	10.4
39	8 Jan	170.3	121.3	7.2
40	9 Jan	167.9	137.5	7.9
41	10 Jan	170.7	140.3	7.6
42	11 Jan	157.8	133.8	7.8
43	12 Jan	169.4	137.4	8.2
44	13 Jan	160.5	136.5	8.2
45	14 Jan	160.2	134.9	8.1
46	15 Jan	161.7	131.8	8.0
47	16 Jan	164.7	139.7	8.3
48	17 Jan	166.4	135.4	6.3 *
49	18 Jan	163.8	138.9	5.6
50	19 Jan	187.1	157.8	6.3
51	20 Jan	181.9	152.4	6.2
52	21 Jan	188.6	153.5	6.1
53	22 Jan	185.2	147.5	6.1
54	23 Jan	171.0	141.4	6.1
55	24 Jan	169.4	142.2	5.9

* Denotes day on which JP-4 analysis was conducted.

Table B-2. (continued)

DAY	DATE	COLUMN MASS RATES O2 MUR (mg/day)	CO2 MPR (mg/day)	JP-4 MVR (mg/day)
56	25 Jan	173.9	146.1	5.3 *
57	26 Jan	176.3	147.3	5.7
58	27 Jan	176.1	199.1	14.8
59	28 Jan	650.8	471.6	14.8
60	29 Jan	196.2	164.7	5.1
61	30 Jan	180.5	150.4	5.0
62	31 Jan	175.1	147.4	5.3
63	1 Feb	146.3	133.1	5.5
64	2 Feb	196.3	152.7	5.2 *
68	6 Feb	144.4	124.1	4.7
69	7 Feb	179.7	154.4	5.8
70	8 Feb	170.3	140.9	4.9
71	9 Feb	152.1	132.2	5.0
72	10 Feb	145.1	123.6	4.9
73	11 Feb	170.2	121.8	3.8
74	12 Feb	128.2	103.3	3.7
75	13 Feb	134.1	99.7	3.2
76	14 Feb	167.5	139.3	4.5
77	15 Feb	160.1	133.7	4.6
78	16 Feb	152.0	112.1	3.6
79	17 Feb	145.9	122.1	5.0
80	18 Feb	150.2	121.5	4.9
81	19 Feb	155.4	124.1	4.2 *

* Denotes day on which JP-4 analysis was conducted.

Table B-3. Column 1 Effluent Venting Air Component Gas Concentrations and Biodegradation Rates

DAY	DATE	EFFLUENT VENTING AIR CONCENTRATIONS CO_2 (mg/L)	EFFLUENT VENTING AIR CONCENTRATIONS O_2 (mg/L)	BIODEGRADATION RATE CO_2 BASIS (mg JP-4/kg soil/day)	BIODEGRADATION RATE O_2 BASIS (mg JP-4/kg soil/day)
0	30 Nov	105.89	159.2	8.3	10.2
1	1 Dec	150.39	86.7	9.4	11.9
2	2 Dec	146.28	114.66	10.2	12.5
3	3 Dec	121.41	147.89	10.0	11.6
4	4 Dec	98.72	181.7	10.2	11.6
5	5 Dec	85.17	189.35	9.5	11.0
6	6 Dec	111.34	153.52	9.9	12.0
7	7 Dec	124.77	134.17	10.8	13.2
8	8 Dec	141.05	117.31	12.0	14.5
9	9 Dec	147.93	107.49	13.8	16.4
10	10 Dec	159.08	102.31	14.3	16.7
12	12 Dec	153.57	106.47	14.1	16.1
14	14 Dec	95.37	180.77	12.3	14.2
16	16 Dec	101.9	177.09	13.1	14.9
18	18 Dec	131.08	126.07	12.8	14.9
20	20 Dec	111.05	175.92	11.4	12.7
22	22 Dec	99.0	181.65	11.8	12.6
24	24 Dec	128.58	138.42	11.9	13.5
25	25 Dec	140.62	120.31	11.6	13.4
26	26 Dec	121.95	162.07	10.6	11.8
27	27 Dec	112.88	161.72	11.4	12.4
28	28 Dec	100.02	176.43	11.2	12.7
33	2 Jan	89.92	185.78	10.7	12.4
34	3 Jan	83.21	194.64	10.9	12.8
36	5 Jan	70.61	210.86	10.1	11.9
37	6 Jan	80.9	219.1	10.4	11.0
38	7 Jan	81.51	214.92	11.5	11.1
39	8 Jan	82.18	189.02	9.7	10.7
40	9 Jan	85.67	199.71	8.6	10.1
41	10 Jan	90.12	194.74	9.2	10.1
42	11 Jan	83.8	205.57	9.1	9.8
43	12 Jan	81.95	203.33	9.0	9.7
44	13 Jan	81.45	208.63	9.1	9.8
45	14 Jan	81.62	207.45	9.0	9.5
46	15 Jan	80.53	205.54	8.9	9.6
47	16 Jan	82.95	206.6	9.0	9.7
48	17 Jan	86.1	198.55	9.1	9.8
49	18 Jan	86.15	202.8	9.1	9.8
50	19 Jan	87.09	201.12	9.9	10.4
51	20 Jan	84.86	203.09	10.3	11.0
52	21 Jan	87.02	197.47	10.2	11.0
53	22 Jan	83.26	199.87	10.0	11.1
54	23 Jan	80.54	207.0	9.6	10.6

Table B-3. (continued)

DAY	DATE	EFFLUENT VENTING AIR CONCENTRATIONS CO_2 (mg/L)	O_2 (mg/L)	BIODEGRADATION RATE CO_2 BASIS (mg JP-4/kg soil/day)	O_2 BASIS (mg JP-4/kg soil/day)
55	24 Jan	83.25	205.23	9.4	10.1
56	25 Jan	82.83	205.79	9.6	10.2
57	26 Jan	78.23	210.8	9.7	10.4
58	27 Jan	40.98	268.15	11.5	10.5
59	28 Jan	96.59	171.11	22.3	24.6
60	29 Jan	97.82	187.88	21.1	25.2
61	30 Jan	90.95	195.23	10.5	11.2
62	31 Jan	85.09	203.3	9.9	10.6
63	1 Feb	74.1	222.95	9.3	9.6
64	2 Feb	91.53	186.76	9.5	10.2
68	6 Feb	68.09	225.16	9.2	10.1
69	7 Feb	68.84	224.27	9.2	9.6
70	8 Feb	74.78	214.05	9.8	10.4
71	9 Feb	68.42	225.68	9.1	9.6
72	10 Feb	64.8	228.34	8.5	8.8
73	11 Feb	82.48	189.14	8.1	9.4
74	12 Feb	71.59	215.54	7.5	8.9
75	13 Feb	81.52	194.82	6.7	7.8
76	14 Feb	79.29	209.08	7.9	9.0
77	15 Feb	74.8	214.88	9.1	9.7
78	16 Feb	81.18	194.34	8.2	9.3
79	17 Feb	63.57	228.43	7.8	8.9
80	18 Feb	64.24	224.99	8.1	8.8
81	19 Feb	63.22	225.27	8.2	9.1

Table B-4. Column 2 Venting Air Flow and Moisture Data

DAY	DATE	VENTING AIR FLOWS INSTANT. (mL/min)	VENTING AIR FLOWS 24 HR AVG (mL/min)	MOISTURE DATA SUCTION (cm H2O)	MOISTURE DATA % SAT
0	30 Nov	0.88	0.88	24.4	94.0
1	1 Dec	0.4	0.64	32.3	73.5
2	2 Dec	1.02	1.06	36.8	72.4
3	3 Dec	1.01	1.01	39.0	71.9
4	4 Dec	0.92	0.96	40.1	71.6
5	5 Dec	0.89	0.9	41.3	71.3
6	6 Dec	0.68	0.78	41.3	71.3
7	7 Dec	1.16	0.93	41.2	71.3
8	8 Dec	1.03	1.07	40.6	71.5
9	9 Dec	0.96	1.0	40.0	71.6
10	10 Dec	0.84	0.9	40.1	71.6
12	12 Dec	0.75	0.8	40.4	71.5
14	14 Dec	1.2	0.98	42.7	71.0
16	16 Dec	1.61	1.4	44.2	70.6
18	18 Dec	0.7	0.65	44.7	70.5
20	20 Dec	1.3	1.19	46.2	70.1
22	22 Dec	1.31	1.3	46.7	70.0
24	24 Dec	0.81	1.06	47.6	69.7
25	25 Dec	0.67	0.74	47.9	69.7
26	26 Dec	1.16	0.91	48.3	69.6
27	27 Dec	1.05	1.11	49.4	69.3
28	28 Dec	1.16	1.11	50.3	69.1
33	2 Jan	1.56	1.56	53.4	68.3
34	3 Jan	1.37	1.47	54.3	68.1
36	5 Jan	1.62	1.5	55.1	67.9
37	6 Jan	1.83	1.72	55.3	67.8
38	7 Jan	1.72	1.77	55.8	67.7
39	8 Jan	1.01	0.97	56.2	67.6
40	9 Jan	1.04	1.03	56.9	67.4
41	10 Jan	1.08	1.06	57.0	67.4
42	11 Jan	1.19	1.13	57.4	67.3
43	12 Jan	1.05	1.12	58.0	67.2
44	13 Jan	1.02	1.04	58.2	67.1
45	14 Jan	0.98	1.0	58.4	67.1
46	15 Jan	1.03	1.0	58.7	67.0
47	16 Jan	1.04	1.04	59.1	66.9
48	17 Jan	0.88	0.96	59.8	66.7
49	18 Jan	1.15	1.01	60.2	66.6
50	19 Jan	1.16	1.16	60.8	66.5
51	20 Jan	1.11	1.14	61.4	66.3
52	21 Jan	1.09	1.1	62.1	66.1
53	22 Jan	1.13	1.11	62.6	66.0
54	23 Jan	1.03	1.08	63.1	65.9
55	24 Jan	1.04	1.04	63.4	65.8
56	25 Jan	1.14	1.09	63.5	65.8

Table B-4. (continued)

DAY	DATE	VENTING AIR FLOWS INSTANT. (mL/min)	VENTING AIR FLOWS 24 HR AVG (mL/min)	MOISTURE DATA SUCTION (cm H2O)	MOISTURE DATA % SAT
57	26 Jan	1.22	1.18	62.7	66.0
58	27 Jan	3.03	2.09	60.9	66.4
78	16 Feb	0.61	0.91	50.4	69.0
79	17 Feb	1.03	1.15	52.3	68.6
80	18 Feb	1.14	1.15	52.5	68.5
81	19 Feb	1.15	1.15	51.1	68.9
82	20 Feb	1.03	1.09	49.7	69.2
83	21 Feb	1.05	1.04	50.8	68.9
84	22 Feb	2.11	1.58	50.8	68.9
85	23 Feb	1.02	1.56	51.9	68.7
86	24 Feb	0.98	1.0	52.5	68.5
87	25 Feb	0.98	0.98	53.6	68.3
88	26 Feb	0.96	0.97	54.1	68.1
89	27 Feb	0.98	0.94	55.0	67.9

Table B-5. Column 2 Mass Rates

DAY	DATE	COLUMN MASS RATES O2 MUR (mg/day)	CO2 MPR (mg/day)	JP-4 MVR (mg/day)	
0	30 Nov	114.1	100.8		
1	1 Dec	192.6	125.9	11.5	*
2	2 Dec	195.1	149.1	18.7	*
3	3 Dec	187.0	137.9	16.4	*
4	4 Dec	184.7	140.6	9.9	*
5	5 Dec	178.9	128.4	9.0	*
6	6 Dec	176.5	129.6	8.3	*
7	7 Dec	212.2	161.6	7.7	*
8	8 Dec	274.4	212.9	8.6	*
9	9 Dec	264.8	201.0	10.1	*
10	10 Dec	245.9	197.0	8.5	
12	12 Dec	228.1	179.5	7.5	
14	14 Dec	155.6	119.8	9.2	
16	16 Dec	244.0	194.0	12.5	*
18	18 Dec	173.7	136.4	5.3	
20	20 Dec	211.7	168.1	9.7	
22	22 Dec	195.5	157.6	10.6	
24	24 Dec	240.0	194.2	7.6	*
25	25 Dec	187.9	152.1	5.2	
26	26 Dec	179.9	155.4	6.5	
27	27 Dec	213.0	172.9	7.9	
28	28 Dec	179.4	148.6	7.9	
33	2 Jan	211.8	167.6	9.7	
34	3 Jan	218.8	171.3	10.4	*
36	5 Jan	179.7	139.3	9.6	
37	6 Jan	181.7	174.6	11.0	
38	7 Jan	216.7	188.5	11.3	
39	8 Jan	164.7	118.6	6.2	
40	9 Jan	157.4	132.2	6.6	
41	10 Jan	168.6	140.6	6.8	
42	11 Jan	161.1	139.0	7.2	
43	12 Jan	169.4	140.7	7.2	
44	13 Jan	147.0	127.5	6.6	
45	14 Jan	146.5	125.4	6.4	
46	15 Jan	145.5	124.9	6.4	
47	16 Jan	151.1	133.5	6.6	
48	17 Jan	150.0	123.0	5.1	*
49	18 Jan	148.1	130.2	5.6	
50	19 Jan	170.2	147.4	6.3	
51	20 Jan	172.1	143.4	6.2	
52	21 Jan	173.3	143.2	6.0	
53	22 Jan	175.9	140.2	6.1	
54	23 Jan	162.9	132.6	5.9	
55	24 Jan	157.9	132.4	5.7	

* Denotes day on which JP-4 analysis was conducted.

Table B-5. (continued)

DAY	DATE	COLUMN MASS RATES O2 MUR (mg/day)	CO2 MPR (mg/day)	JP-4 MVR (mg/day)	
56	25 Jan	165.4	139.7	6.1	*
57	26 Jan	145.1	127.6	4.9	
58	27 Jan	118.1	121.5	8.7	
78	16 Feb	172.0	126.3	3.8	
79	17 Feb	156.5	124.2	4.8	
80	18 Feb	140.2	114.7	4.8	
81	19 Feb	124.2	103.2	3.2	*
82	20 Feb	121.1	97.9	3.0	
83	21 Feb	119.7	95.2	2.8	
84	22 Feb	152.3	125.5	4.3	
85	23 Feb	183.1	136.7	4.3	
86	24 Feb	128.0	91.3	2.7	
87	25 Feb	130.2	94.2	2.7	
38	26 Feb	127.0	97.5	2.6	
89	27 Feb	123.6	95.9	2.5	*

* Denotes day on which JP-4 analysis was conducted.

Table B-6. Column 2 Effluent Venting Air Component Gas Concentrations and Biodegradation Rates

DAY	DATE	EFFLUENT VENTING AIR CONCENTRATIONS CO_2 (mg/L)	O_2 (mg/L)	BIODEGRADATION RATE CO_2 BASIS (mg JP-4/kg soil/day)	O_2 BASIS (mg JP-4/kg soil/day)
0	30 Nov	79.86	213.97	6.6	6.7
1	1 Dec	137.0	94.8	7.4	9.0
2	2 Dec	98.11	175.98	9.0	11.4
3	3 Dec	94.4	176.44	9.4	11.2
4	4 Dec	101.18	171.44	9.1	10.9
5	5 Dec	98.7	166.95	8.8	10.7
6	6 Dec	115.06	147.64	8.5	10.5
7	7 Dec	121.08	145.43	9.6	11.4
8	8 Dec	138.72	125.59	12.3	14.3
9	9 Dec	139.85	120.17	13.6	15.9
10	10 Dec	151.38	115.49	13.1	15.0
12	12 Dec	156.13	106.05	12.4	13.9
14	14 Dec	85.28	193.66	9.8	11.3
16	16 Dec	96.08	183.55	10.3	11.8
18	18 Dec	145.82	118.71	10.8	12.3
20	20 Dec	97.8	181.23	10.0	11.3
22	22 Dec	84.02	200.2	10.7	12.0
24	24 Dec	127.36	147.03	11.6	12.8
25	25 Dec	143.16	127.56	11.4	12.6
26	26 Dec	117.97	167.82	10.1	10.8
27	27 Dec	108.3	170.97	10.8	11.6
28	28 Dec	93.07	192.07	10.6	11.5
33	2 Jan	85.36	196.52	10.4	11.5
34	3 Jan	81.01	200.94	11.1	12.7
36	5 Jan	64.62	221.01	10.2	11.7
37	6 Jan	70.34	231.19	10.3	10.6
38	7 Jan	73.8	219.56	11.9	11.7
39	8 Jan	84.93	186.41	10.1	11.2
40	9 Jan	89.52	197.81	8.2	9.5
41	10 Jan	92.22	193.83	9.0	9.6
42	11 Jan	85.34	205.48	9.2	9.7
43	12 Jan	87.23	199.39	9.2	9.7
44	13 Jan	85.39	205.94	8.8	9.3
45	14 Jan	87.26	202.47	8.3	8.6
46	15 Jan	86.43	203.69	8.2	8.6
47	16 Jan	89.43	203.19	8.5	8.7
48	17 Jan	89.07	195.79	8.4	8.9
49	18 Jan	89.15	203.01	8.3	8.8
50	19 Jan	88.37	202.37	9.1	9.4
51	20 Jan	87.64	199.27	9.6	10.1
52	21 Jan	90.61	194.8	9.4	10.2
53	22 Jan	87.8	194.23	9.3	10.3
54	23 Jan	85.2	199.77	9.0	10.0

Table B-6. (continued)

DAY	DATE	EFFLUENT VENTING AIR CONCENTRATIONS CO_2 (mg/L)	O_2 (mg/L)	BIODEGRADATION RATE CO_2 BASIS (mg JP-4/kg soil/day)	O_2 BASIS (mg JP-4/kg soil/day)
55	24 Jan	88.67	198.67	8.7	9.4
56	25 Jan	88.86	199.25	8.9	9.5
57	26 Jan	75.07	219.07	8.8	9.1
58	27 Jan	40.41	265.11	8.2	7.7
78	16 Feb	96.39	173.19	8.3	10.1
79	17 Feb	75.27	209.55	8.2	9.7
80	18 Feb	69.49	219.46	7.8	8.7
81	19 Feb	62.47	229.24	7.2	7.8
82	20 Feb	62.23	227.43	6.6	7.2
83	21 Feb	63.41	224.64	6.3	7.1
84	22 Feb	55.17	237.45	7.2	8.0
85	23 Feb	60.76	223.05	8.6	9.9
86	24 Feb	63.51	215.32	7.5	9.2
87	25 Feb	67.02	211.76	6.1	7.6
88	26 Feb	69.82	213.54	6.3	7.6
89	27 Feb	71.03	212.9	6.4	7.4

Table B-7. Control Column Venting Gas Flows and Column Mass Rates

DAY	DATE	VENTING GAS FLOWS N_2 VF (mL/min)	24 HR AVG (mL/min)	CO2 MPR (mg/day)	JP-4 MVR (mg/day)	
9	9 Dec	1.77	1.77	N/A	13.1	*
10	10 Dec	1.34	1.56	N/A	7.6	
12	12 Dec	0.82	1.08	N/A	5.3	
14	14 Dec	0.95	0.89	40.4	4.3	*
15	15 Dec	0.94	0.95	34.1	6.7	
16	16 Dec	0.90	0.92	23.2	5.7	
18	18 Dec	1.30	1.10	36.0	6.7	
20	20 Dec	1.56	1.43	13.3	8.8	
22	22 Dec	1.08	1.32	42.5	8.1	
24	24 Dec	1.55	1.31	39.8	7.2	*
26	26 Dec	1.67	1.61	45.1	6.7	
28	28 Dec	2.15	1.91	40.7	8.0	
34	3 Jan	2.22	2.18	43.2	7.4	*
39	8 Jan	0.82	1.52	96.8	5.1	
46	15 Jan	0.79	0.80	41.4	2.7	
53	22 Jan	0.71	0.75	40.8	2.5	
56	25 Jan	0.70	0.70	N/A	2.2	*
59	28 Jan	0.62	0.66	38.5	3.0	
64	2 Feb	1.15	0.89	N/A	5.0	*
69	7 Feb	1.19	1.17	40.9	4.7	
75	13 Feb	1.15	1.17	43.0	4.7	
81	19 Feb	1.08	1.11	42.0	3.0	*

* Denotes day on which JP-4 analysis was conducted.

Table B-8. Effluent Venting Gas CO_2 Concentration and Biodegradation Rates

DAY	DATE	EFFLUENT CO2 CONC (mg/L)	BIODEGRADATION RATE CO2 BASIS (mg JP-4/kg soil/day)
9	9 Dec	N/A	N/A
10	10 Dec	N/A	N/A
12	12 Dec	N/A	N/A
14	14 Dec	31.59	1.4
15	15 Dec	24.98	2.5
16	16 Dec	17.53	1.9
18	18 Dec	22.80	2.0
20	20 Dec	6.44	1.6
22	22 Dec	22.38	1.9
24	24 Dec	21.04	2.8
26	26 Dec	19.43	2.8
28	28 Dec	14.77	2.9
34	3 Jan	13.76	2.8
39	8 Jan	44.27	4.7
46	15 Jan	35.77	4.6
53	22 Jan	37.81	2.7
56	25 Jan	N/A	2.7
59	28 Jan	40.53	2.6
64	2 Feb	N/A	2.6
69	7 Feb	24.26	2.7
75	13 Feb	25.55	2.8
81	19 Feb	26.17	2.8

APPENDIX C
EXAMPLE BIODEGRADATION CALCULATIONS

This appendix provides examples of the calculations employed to determine biodegradation rates in this study. Below are presented example calculations for: Carbon Dioxide Mass Production Rate (CO_2 MPR), Oxygen Mass Utilization Rate (O_2 MUR), and the CO_2 and O_2 based Biodegradation Rates.

Example Calculation 1. CO_2 MPR (Day 64, Column 1)

$$CO_2 \text{ MPR} = ([CO_2]_{OUT}/1000) \times Q \times 1440 \text{ min/day}$$

where

CO_2 MPR = Carbon Dioxide Mass Production Rate, mg CO_2/day,
$[CO_2]_{OUT}$ = Effluent venting air CO_2 concentration, mg CO_2/L,
Q = Average venting air flow rate since the previous sample time.

Data for Day 64, Column 1: Q = 1.16 mL/min, $[CO_2]_{OUT}$ = 91.53 mg CO_2/L

CO_2 MPR = (91.53/1000) x 1.16 x 1440
CO_2 MPR = 152.9 mg CO_2/day

Example Calculation 2. O_2 MUR (Day 64, Column1)

$$O_2 \text{ MUR} = \frac{([O_2]_{IN} - [O_2]_{OUT})}{1000} \times Q \times 1440 \text{ min/day}$$

where

O_2 MUR = Oxygen Mass Utilization Rate, mg O_2/day,

$[O_2]_{IN}$ = Influent venting air oxygen concentration, 304.41 mg O_2/L (at 20°C),

$[O_2]_{OUT}$ = Effluent venting air oxygen concentration, mg O_2/L,

Q = Average venting air flow rate since the previous sample time.

Data for Day 60, Column 1: Q = 1.16 mL/min,

$[O_2]_{OUT}$ = 186.76 mg O_2/L

$$O_2 \text{ MUR} = \frac{(304.41 - 186.76)}{1000} \times 1.16 \times 1440 \text{ min/day}$$

O_2 MUR = 196.5 mg O_2/day

Example Calculation 3. CO_2 Basis Biodegradation Rate

$$\text{JP-4} = \frac{[(CO_2 \text{ MPR})_n + (CO_2 \text{ MPR})_{n-1}]}{2} \times \frac{12 \text{ mg C}}{44 \text{ mg } CO_2} \times \frac{1 \text{ mg JP-4}}{0.85 \text{ mg C}} \times T$$

where

JP-4 = Mass of JP-4 biodegraded based on CO_2 production, mg JP-4,

$[(CO_2 \text{ MPR})_n + (CO_2 \text{ MPR})_{n-1}]/2$ = Average CO_2 MPR since the previous sample time,

T = number of days since the previous sample time.

$$BIO_{CO2} = \text{JP-4/SOIL/T}$$

where

BIO_{CO2} = Biodegradation rate based on CO_2 evolution, mg JP-4/kg soil/day,
JP-4 = Mass of JP-4 biodegraded based on CO_2 production, mg JP-4,
SOIL = Mass of moist soil in the column, kg,
T = number of days since the previous sample time.

Data for Day 64, Column 1:
$(CO_2\ MPR)_n$ = 152.7 mg CO_2/day
$(CO_2\ MPR)_{n-1}$ = 133.1 mg CO_2/day
T = 1 day
SOIL = 4.832 kg

$$JP\text{-}4 = \frac{[(152.7) + (133.1)]}{2} \times \frac{12\ mg\ C}{44\ mg\ CO_2} \times \frac{1\ mg\ JP\text{-}4}{0.85\ mg\ C} \times T$$

JP-4 = 45.85 mg JP-4

BIO_{CO2} = 45.85/4.832/1

BIO_{CO2} = 9.5 mg JP-4/kg soil/day

Example Calculation 4. O_2 Basis Biodegradation Rate

$$JP\text{-}4 = \frac{[(O_2\ MUR)_n + (O_2\ MUR)_{n-1}]}{2} \times \frac{1\ mg\ JP\text{-}4}{3.48\ mg\ O_2} \times T$$

where

JP-4 = Mass of JP-4 biodegraded based on O_2 uptake, mg JP-4,
$[(O_2\ MUR)_n + (O_2\ MUR)_{n-1}]/2$ = Average O_2 MUR since the previous sample time,
T = number of days since the previous sample time.

$$BIO_{O2} = JP\text{-}4/SOIL/T$$

where

BIO_{O2} = Biodegradation rate based on O_2 evolution, mg JP-4/kg soil/day,
JP-4 = Mass of JP-4 biodegraded based on O_2 production, mg JP-4,
SOIL = Mass of moist soil in the column, kg,
T = number of days since the previous sample time.

Data for Day 64, Column 1:
$(O_2\ MUR)_n$ = 196.3 mg O_2/day
$(O_2\ MUR)_{n-1}$ = 146.3 mg O_2/day
T = 1 day
SOIL = 4.832 kg

$$JP\text{-}4 = \frac{[(196.3) + (146.3)]}{2} \times \frac{1\ mg\ JP\text{-}4}{3.48\ mg\ O_2} \times T$$

JP-4 = 49.22 mg JP-4

BIO_{02} = 49.22/4.832/1

BIO_{02} = 10.2 mg JP-4/kg soil/day

APPENDIX D
EXAMPLE JP-4 CHROMATOGRAMS

The chromatograms presented in this appendix are representative of typical chromatograms from JP-4 standards, initial JP-4 soil extractions, and JP-4 soil extractions following the soil venting biodegradation testing process. Table D-1 presents values for the vapor pressures of the seven hydrocarbons used in quantification of JP-4 throughout this study. These hydrocarbons were tentatively identified by matching GC/FID retention times with hydrocarbon standards.

Table D-1. Retention Times and Approximate Vapor Pressures of the Seven Hydrocarbons Used in JP-4 Quantification

Compound	Figure D-1 Retention Time (min)	Vapor Pressure (mm Hg) at 20°C
Isooctane	3.79	45
Nonane	6.14	3.2
Decane	8.21	2.7
Undecane	10.06	0.9 *
Dodecane	11.72	0.3
Tridecane	13.26	0.3 *
Tetradecane	14.85	0.1 *

* Vapor pressure was estimated by plotting the unknown compound's boiling point on a curve developed by plotting known values of boiling point versus vapor pressure for the straight chain alkanes given above.

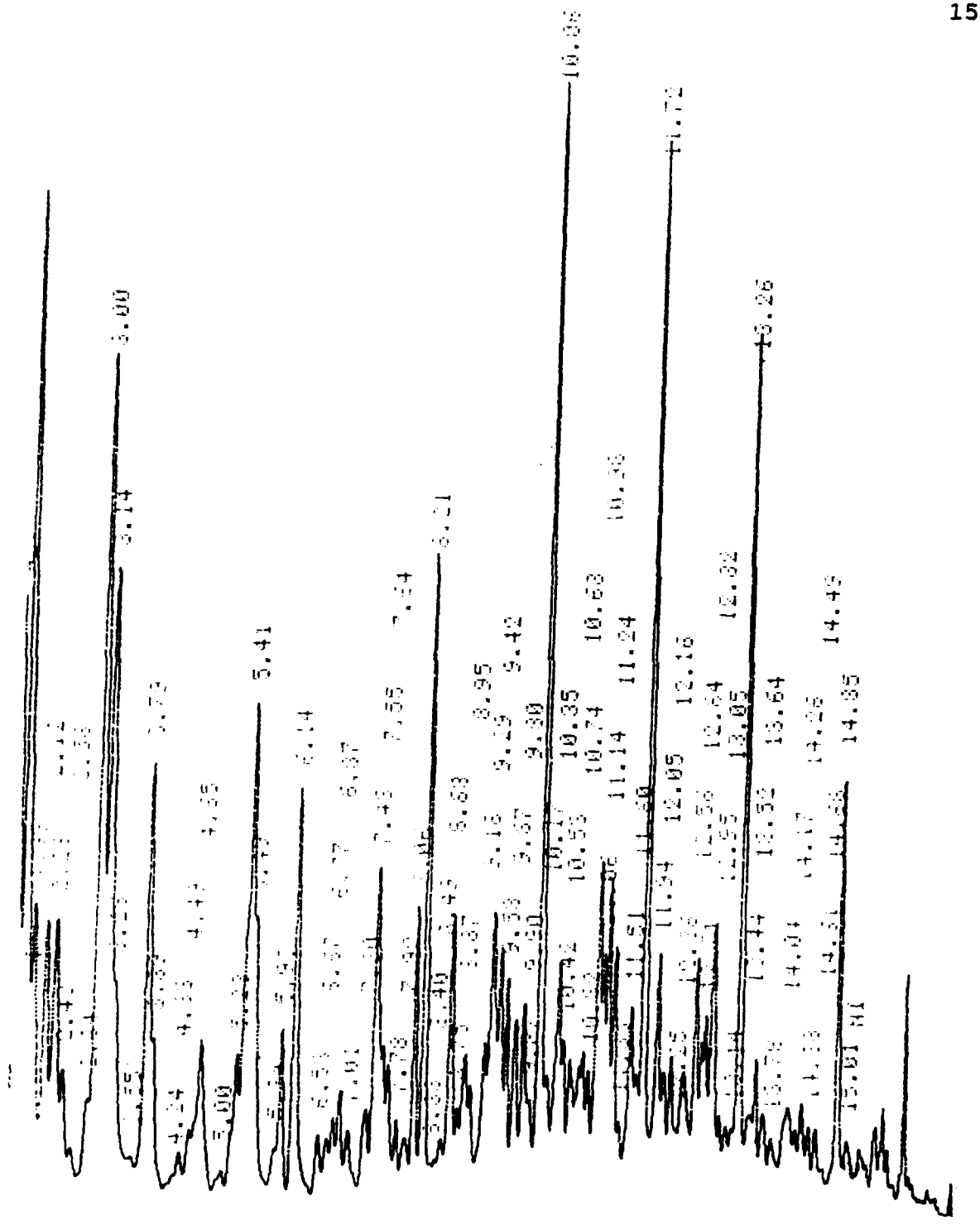

Figure D-1. JP-4 Standard, 5.089 ug/uL; Attenuation = 128

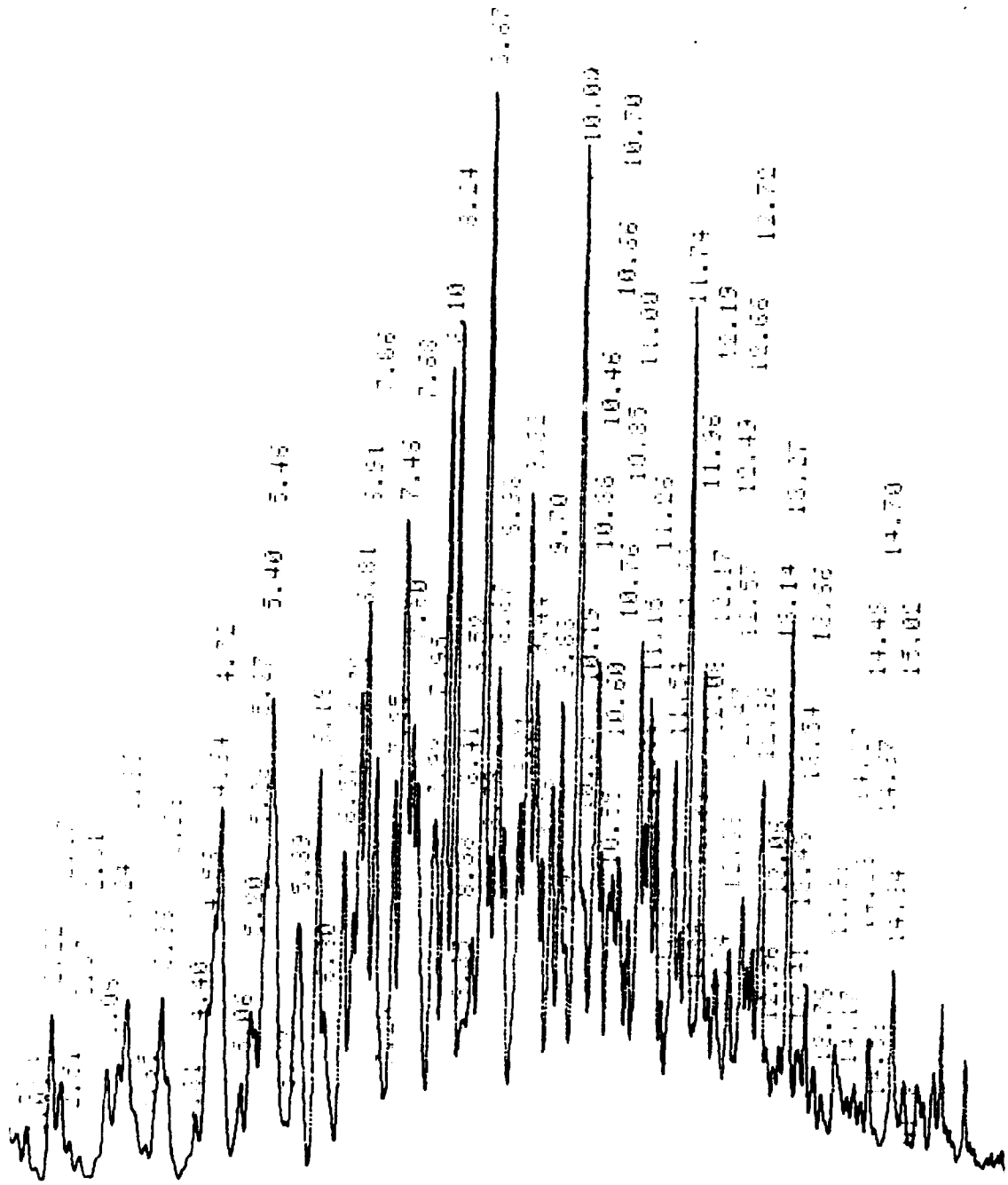

Figure D-2. JP-4 Chromatogram from the Initial Bulk Mixed Soil Sample, Attenuation = 128

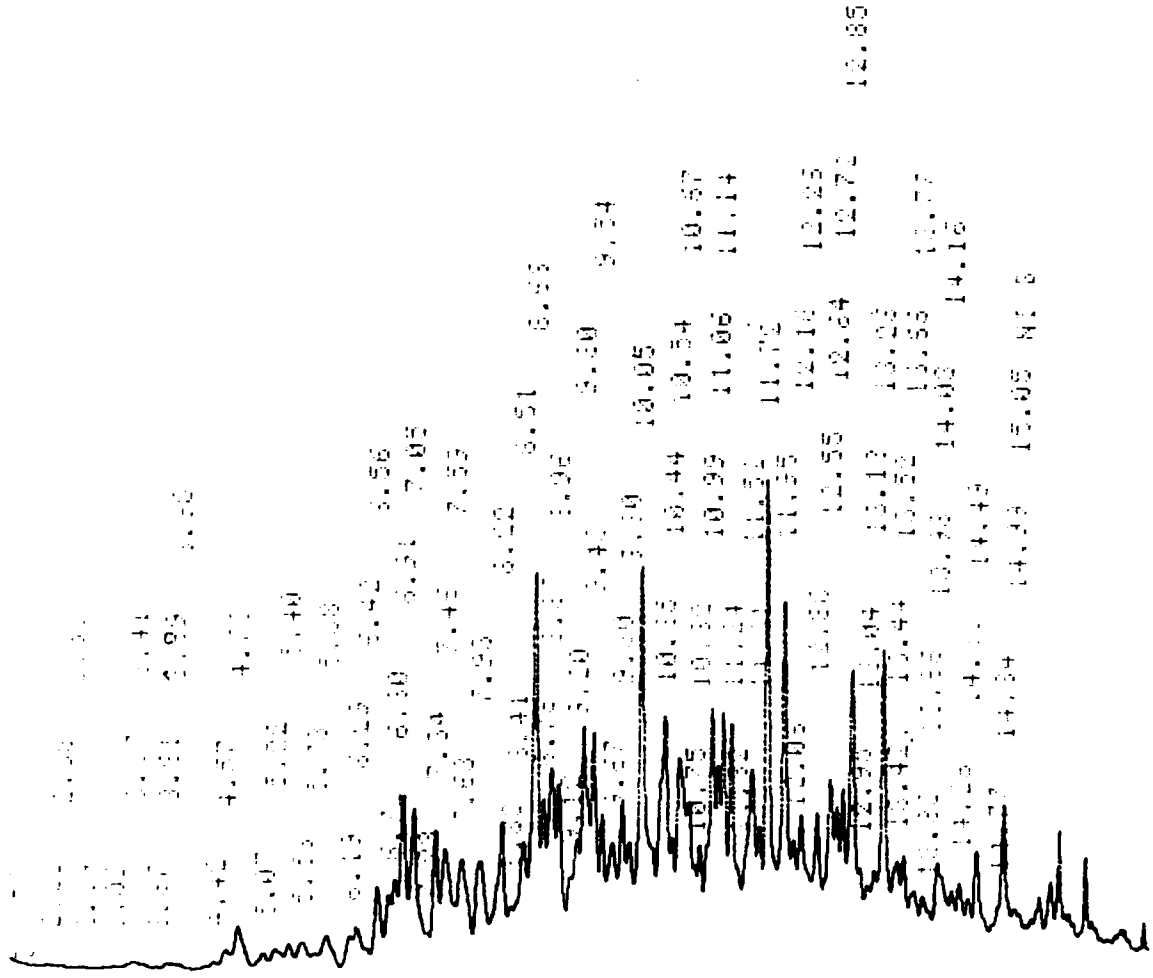

Figure D-3. JP-4 Chromatogram from the Top Section of Column 2 After Biodegradation Testing, Attenuation = 128

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BIOGRAPHICAL SKETCH

John W. Coho [redacted], as the second of four children. His father, Kenneth P. Coho, was employed by the Bell Telephone Company and his mother, Ruth E. Coho, was a registered nurse. Both are still alive, well, retired and living in Pennsylvania.

John attended a catholic elementary school through grade six, and transferred to the public school system in Altoona, Pennsylvania, where he remained through high school graduation. His class ranking upon graduation from Altoona Area High School in June 1977 was 92nd out of 910 students.

After high school, John enlisted in the U.S. Army and worked as a medical laboratory technician for 3 years while on active duty at Fort Knox, Kentucky. John left the active service in September of 1980 to pursue his bachelors degree in environmental engineering at the Pennsylvania State University. He remained active in the U.S. Army reserve throughout his four year stay at Penn State.

In September of 1982, John married Nancy J. Mills, also a native of central Pennsylvania. Nancy assisted John, both morally and financially, through the remaining two years of his undergraduate degree program. John graduated with high distinction (3.72/4.0 GPA) from Penn State in May 1984. His

excellent scholarship was recognized by Tau Beta Pi National Engineering Honor Society, an organization in which John is currently a member.

Immediately after graduating from Penn State, John decided to accept a commission as a second lieutenant in the U.S. Air Force. In his first Air Force position, he worked as an environmental engineer in the U.S. Air Force space program in Southern California. John's day-to-day work involved interfacing with Air Force, NASA, and civilian aerospace corporation engineers, environmental scientists, and administrators. He worked on many space related projects, ranging from the activation of the space shuttle launch site at Vandenberg Air Force Base, California in 1984, through the tragic Challenger launch from Kennedy Space Center, Florida in 1985, and into the Strategic Defense Initiative (SDI) program until August 1988.

Early in 1988, John applied for and was selected by the Air Force to obtain an advanced degree in environmental engineering. He selected the University of Florida for its progressive curriculum dealing with hazardous waste management and hazardous waste site remediation. He felt that the Air Force, and, moreover, the world, needed greater technical support in these areas. He directs his efforts toward achieving a balance between an environmentally sound future for our planet, and economic development and technological advancement.

John, now a captain in the Air Force, is still happily married to Nancy, and he is the father of two beautiful girls: Christina, age 5 and Lauren, age 4 months. In the coming years, John will continue his career in the U.S. Air Force. His next assignment will take him to Kelly Air Force Base, San Antonio, Texas, where he plans to remain for approximately three years.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Engineering.

W. Lamar Miller, Chair
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Engineering.

Paul A. Chadik, Cochair
Assistant Professor of
Environmental Engineering
Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Engineering.

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This thesis was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Master of Engineering.

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