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IN THE VADOSE ZONE COMBINING  
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WITH MOISTURE AND NUTRIENT ADDITION

by

Ross N. Miller

A dissertation submitted in partial fulfillment  
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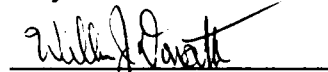
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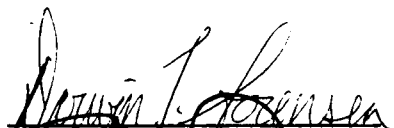
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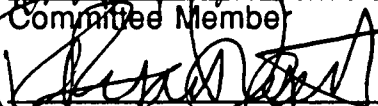
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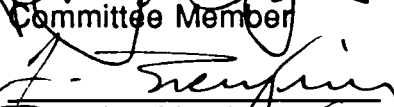
  
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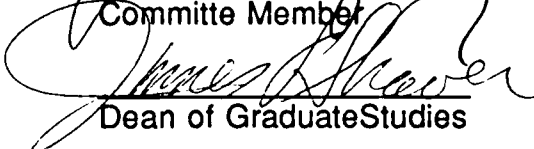
  
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Ross N. Miller

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## ABSTRACT

A Field Scale Investigation of Enhanced Petroleum Hydrocarbon  
Biodegradation in the Vadose Zone Combining Soil Venting  
as an Oxygen Source with Moisture and Nutrient Addition

by

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Soil venting is effective for the physical removal of volatile hydrocarbons from unsaturated soils, and is also effective as a source of oxygen for biological degradation of the volatile and non-volatile fractions of hydrocarbons in contaminated soil. Treatment of soil venting off-gas is expensive, constituting a minimum of 50% of soil venting remediation costs. In this research, methods for enhancing biodegradation through soil venting were investigated, with the goal of eliminating the need for expensive off-gas treatment.

A seven-month field investigation was conducted at Tyndall Air Force Base (AFB), Florida, where past jet fuel storage had resulted in contamination of a sandy soil. The contaminated area was dewatered to maintain approximately 1.6 meters of unsaturated soil. Soil hydrocarbon concentrations ranged from 30 to 23,000 mg/kg. Contaminated and uncontaminated test plots were vented for 188 days. Venting was interrupted five times during operation to allow for measurement of biological activity ( $\text{CO}_2$  production and  $\text{O}_2$  consumption) under varying moisture and nutrient conditions. JSJL

Moisture addition had no significant effect on soil moisture content or biodegradation rate. Soil moisture content ranged from 6.5 to 9.8%, by weight, throughout the field test. Nutrient addition was also shown to have no statistically significant effect on biodegradation rate. Initial soil sampling results indicated that naturally occurring nutrients were adequate for the amount of biodegradation observed. Acetylene reduction studies, conducted in the laboratory, indicated a biological nitrogen fixation potential capable of fixing the organic nitrogen, which was observed in initial soil samples, in five to eight years under anaerobic conditions. Biodegradation rate constants were shown to be affected by soil temperature and followed predicted values based on the van't Hoff-Arrhenius Equation.

In one treatment cell, approximately 26 kg of hydrocarbons volatilized and 32 kg biodegraded over the seven-month field test. Although this equates to 55% removal attributed to biodegradation, a series of flow rate tests showed that biodegradation could be increased to 85% by managing air flow rate. Off-gas from one treatment cell was injected into clean soil to assess the potential for complete biological remediation. Biodegradation rate data collected at this field site indicated that a soil volume ratio of approximately 4 to 1, uncontaminated to contaminated soil, would have been required to completely biodegrade the off-gas from the contaminated soil.

This research indicates that proper ratios of uncontaminated to contaminated soil and air flow management are important factors in influencing total biodegradation of jet fuel and can substantially reduce remediation costs associated with treatment of soil venting off-gas. (403 pages)

## INTRODUCTION

### Background Information

Approximately  $3.6 \times 10^{12}$  kg (4 billion tons) of hazardous materials are transported annually in the United States, and of this amount about 90% consists of gasoline, fuel oil, and jet fuel. Massachusetts officials report that in 1984 58% of reported spills in their northeast region were petroleum products, of which 28% were gasoline, diesel, or fuel oil. If it is assumed that Massachusetts is representative of the rest of the United States, transportation and transfer of petroleum products, particularly fuels, pose a major risk to the environment (Calabrese et al., 1988a).

In addition to transportation of fuels, leakage of stored fuel has proven to be a serious environmental problem, particularly as a source of ground water contamination. The United States Environmental Protection Agency (EPA) estimates that there are three million underground storage tanks in the United States, of which, 78% (2.3 million) are used to store fuel products. Based on a random sampling, EPA estimates that 35%, or approximately 820,000 of the underground fuel tanks are leaking (Calabrese et al., 1988a).

A recent report indicates that there are three to five million underground storage tanks used to store liquid petroleum and chemical substances and that EPA estimates 100,000 to 400,000 of these tanks may be or have been leaking. The majority of these tanks contain gasoline or other petroleum distillates (Camp, Dresser, and McKee, 1988). Based on the percentages quoted above, the estimate for leaking underground fuel tanks could go as high as 1.4 million. The disparity in estimating the number of leaking underground fuel tanks underscores our inability, to date, to accurately quantify the magnitude of the

problem. Even using minimum estimates, leaking underground fuel tanks pose a significant threat to the environment.

The American public and news media seem less concerned with fuels than with industrial chemicals. This may be the result of widespread familiarity with fuel and the fact that fuels have not generally been categorized as "toxic" by regulatory agencies. This seems somewhat odd because of the magnitude of effects resulting from underground fuel leakage. In a 2.5-year period, over 200 hydrocarbon spills were documented in Pennsylvania alone. One spill discharged 1 million L (270,000 gallons) of fuel to the subsurface. As a result of these spills, eight homes were destroyed by fire or explosion, resulting in 17 personal injuries. In addition to these catastrophic incidents, 115 homes were either abandoned or otherwise adversely affected. In total, 800,000 people were affected by pollution of 104 wells and 14 public water supplies (Osgood, 1974).

Other states have reported similar situations. For example, over 60 cases of petroleum-derived ground water contamination were identified during a 2-year period from 1969 to 1970 in Maryland alone (Matis, 1971).

### **Hazards Associated With Fuel**

Although the general public appears less concerned with fuels than with industrial chemicals, regulatory agencies have long been aware of the threat to public health that these fuels pose. The U.S. Coast Guard and EPA have attempted to characterize the toxicological hazards associated with petroleum contamination. They concluded that exposure to petroleum products from contaminated soils may occur via the following routes: inhalation, dermal absorption, ingestion of contaminated soil, consumption of plants and animals

that have assimilated petroleum products, and consumption of contaminated drinking water (Calabrese et al., 1988b).

A combination of U. S. Coast Guard and EPA ranking systems resulted in a list of 25 priority contaminants found in petroleum products that are of public health concern (Table 1). Hoag's findings support the U. S. Coast Guard and EPA. He reports finding at least eight constituents in gasoline that are listed as hazardous by EPA (Hoag et al., 1984).

Table 1. Priority contaminants identified in petroleum products.

| <b>Heavy Metals</b> | <b>Halogenated Hydrocarbons</b> | <b>Nonhalogenated Aromatic Hydrocarbons</b> | <b>Nonhalogenated Aliphatic Hydrocarbons</b> |
|---------------------|---------------------------------|---------------------------------------------|----------------------------------------------|
| Cadmium             | 1,2,-dibromoethane              | Benzene                                     | Heptane                                      |
| Chromium            | Dichloroethane                  | Benzo (alpha) anthracene                    | Hexane                                       |
| Tetraethyl lead     | Dichlorobenzene                 | Benzo (beta) pyrene                         | Isobutane                                    |
| Tetramethyl lead    | Tetrachloroethylene             | Phenol                                      | Isopentane                                   |
| Zinc                | Trichloroethylene               | Toluene                                     | 1- Pentene                                   |
|                     | PCBs                            | Xylene                                      |                                              |

Adapted from Calabrese et al. (1988b).

Jet fuels have received less attention in the literature than has gasoline. The reason for this is unknown but may be related to the circumstances under which jet fuel is transported and used. Millions of liters of jet fuel are transported daily. However, most jet fuel is delivered by underground pipeline or by rail car directly from the refinery to the user. There have been major jet fuel releases, although most have not been described in published literature. Approximately half of the chemically contaminated sites on Air Force installations are associated with fuels, most of which are JP-4 (Downey and Elliot, 1990).

Lead is not added to jet fuels for octane enhancement, but one analysis revealed 0.09 ppm lead and 0.5 ppm arsenic in these fuels (Riser, 1988). All other metals were below detectable levels, and no halogenated compounds were found. Normal hexane and heptane were measured at 2.21% and 3.67 % by weight, respectively, and the benzene, toluene, ethylbenzene, and xylenes (BTEX) fraction constituted 4.5 % by weight. Aromatics totaled 17.6% of the mixture by weight (Riser, 1988). Seventy-six major components of JP-4 were identified in this analysis, but as many as 270 different components have been reported in other studies (Mason et al., 1985).

There may be significant environmental health and safety hazards associated with subsurface fuel spills. Pathways for human exposure are through ground water contamination, resulting from solubilization of normal and substituted alkane, alkene, and aromatic hydrocarbons, and through exposure to toxic levels of vapors trapped in occupied, confined spaces. Explosion from vapors, which move by advection and diffusion to a confined space containing a source of ignition (i.e., basements), is the greatest potential safety hazard resulting from subsurface fuel spills (Hoag and Cliff, 1988).

### **BTEX Contamination of Ground Water**

BTEX are the contaminants in fuels which most often result in contamination and abandonment of subsurface drinking water supplies. This is due to the relatively high solubility of these aromatics in water coupled with the low aqueous-phase maximum contaminant levels (MCLs) allowed by EPA because of their known or suspected carcinogenicity.

Dissolved benzene, toluene, and xylene resulting from gasoline contamination have been reported in domestic water wells at concentrations of

14, 10, and 10 mg/L, respectively (Hoag and Cliff, 1988). A 38,000 L (10,000 gallon) release from a gasoline station in Bellview, Florida, caused the abandonment of the entire Bellview drinking water well field because of the BTEX fraction found in water samples. BTEX concentrations in soils collected during construction of monitoring wells ranged from 894 to 388 mg/kg (Camp, Dresser, and McKee, 1988).

Conner (1988) indicated that fuel leaks as large as 1 million L (270,000 gallons) have occurred, but that leaks in the 75,000 to 200,000 L (20,000 to 50,000 gallon) range are more common. Considering the damage resulting from the 38,000-L (10,000-gallon) release at Bellview, Florida, the typical 75,000 to 200,000 L (20,000 to 50,000 gallon) spill is environmentally significant. He also stated that soil can hold up to 70 L of gasoline/m<sup>3</sup> (0.5 gallons of gasoline/ft<sup>3</sup>) and that 3.8 L (1 gallon) of gasoline can render 3.8 million L (1 million gallons) of water unsuitable for consumption. This conclusion results from the fact that if 3.8 L (1 gallon) of gasoline containing 1% benzene were added to 3.8 million L (1 million gallons) of water, the benzene concentration would be approximately 7 µg/L (ppb) and would be unfit for human consumption based on the current MCL of 5 µg/L (ppb) (Pontius, 1990). However, this analysis assumes complete benzene solubilization and ignores partitioning and kinetics.

One percent benzene in fuel is not uncommon, and much higher levels have been measured. In fact, benzene generated from the coking operation at Geneva Steel in Utah was used as blending stock at a Utah refinery because it is less expensive than gasoline refined from crude oil. The American Petroleum Institute (API)/EPA reference fuel, PS-6, contains 1.7% benzene, 4% toluene, and 9.8% ethylbenzene and o- m- p- xylene by volume. The total aromatic

fraction was measured at 26.08% by volume (Calabrese et al., 1988b). The BTEX and total aromatic concentration in gasoline varies significantly from refinery to refinery and batch to batch. The fraction of BTEX in gasoline has been reported to range from 6.4 to 36.4% by weight (Riser, 1988).

Additional research indicates that the Bellview well field and others affected by fuel spills will be closed for long periods of time unless remediation of the unsaturated-(vadose-) zone is successful. Work by Wilson and Conrad (1984) shows that 15 to 40% of the pore space can hold fuel. This means that 38,000 L (10,000 gallons) of gasoline can be held in a cube 9mx12mx9m (30ftx40ftx30ft). Malot and Wood (1985) describe a multi-phase transport model by Baehr and Corapcioglu that predicts benzene from a typical gasoline spill will be leached into water for about 20 years, and other components would take several decades longer to be removed through water flushing. Although natural biodegradation may eventually mineralize most fuel contamination, the process is frequently too slow to prevent ground water contamination. High-risk sites require rapid removal of the contaminants to protect drinking water supplies and public health.

### **Vadose-Zone Remediation**

The realization that contaminated soil is a long-term source of ground water contamination has shifted the focus of remediation from treating contaminated ground water (pump and treat) to treating the source of the contamination in the vadose-zone. The initial remediation method employed by consulting firms was excavation of contaminated soil which was then placed in landfills or used in asphalt plants. Fuel-contaminated soil is not a listed or characteristic hazardous waste, and disposal in sanitary landfills is often

recommended to reduce disposal costs (Rollins, Brown, and Gunnel, 1985). The cost of this alternative ranges from \$400 to \$660 per  $\text{m}^3$  (\$300 - \$500 per  $\text{yd}^3$ ) of contaminated material (Clarke, 1987). This type of recommendation has been made without consideration of the listed hazardous waste components in fuels and of the future costs associated with being identified as a potentially responsible party (PRP) in the cleanup of a hazardous waste or sanitary landfill. Increased restrictions by EPA on landfill disposal of hazardous waste and the risk of being identified as a PRP in a hazardous waste or sanitary landfill cleanup have led to the emergence, as a preferred remediation method, of excavation coupled with incineration technology. However, this approach is extremely expensive at \$1300 to \$2600 per  $\text{m}^3$  (\$1000 to \$2000 per  $\text{yd}^3$ ), making it cost-prohibitive for large volumes of contaminated soil (Clarke, 1987).

Excavation is not only expensive but may be impossible if contamination extends beneath buildings or across property lines. If contamination is deep, the size of safe excavations may be prohibitive (Bennedsen et al., 1987). Numerous failures at hazardous waste landfills together with the inability to excavate many sites has sparked increased emphasis on on-site cleanup technologies. In many cases, on-site treatment technologies have proven to be less expensive than off-site alternatives, and, if feasible, they are usually preferred by EPA (U.S. EPA, 1989). Technologies for *in situ* remediation of vadose-zone fuel contamination include soil washing, radio frequency (RF) heating of soil, soil venting, and enhanced microbial degradation.

Soil venting is a technology that has been proven effective for the physical removal of volatile compounds such as gasoline and TCE from the unsaturated-zone. However, as will be demonstrated in the Literature Review, soil venting produces an effluent which may require expensive treatment prior

to discharge. This off-gas treatment step frequently constitutes a minimum of 50% of total remediation costs. In addition, volatilization of contaminants through soil venting alone is not effective in the removal of nonvolatile or low volatility components of jet fuel. This research explores the possibility of reducing or eliminating expensive off-gas treatment while remediating low volatility jet fuel contamination of vadose-zone soils through enhancing *in situ* biodegradation.

## RESEARCH OBJECTIVES

### Air Force Research Objectives

The Air Force stores and transports  $11 \times 10^9$  L ( $3 \times 10^9$  gallons) of JP-4 jet fuel annually (Downey and Elliot, 1990). JP-4 is less volatile than gasoline and contains a considerable nonvolatile fraction (Mason et al., 1985). This research, funded by the Air Force, builds upon earlier work with enhanced bioreclamation through soil venting at Hill Air Force Base (AFB), Utah (Hinchee et al. 1989a). This research direction resulted from the apparent failure of hydrogen peroxide ( $H_2O_2$ ) to adequately deliver oxygen at JP-4-contaminated sites studied at Kelly AFB, Texas, and Eglin AFB, Florida (Downey and Elliot, 1990). As an alternative approach, Air Force research is presently concerned with evaluating soil venting as an economical process for supplying oxygen for enhanced biodegradation in the subsurface.

The objective of this project was to investigate the potential for enhanced biodegradation of JP-4 jet fuel in the vadose-zone by providing oxygen through soil venting combined with moisture and nutrient addition. This project is a field evaluation and demonstration of this *in situ* technology. Soils at the field site have been classified as Urban Land by the Soil Conservation Service (U.S. DA, 1984) and were not physically described. However, soils near the field site were surveyed and classified as the Mandarin series which is a member of the sandy, siliceous, thermic family of Typic Haplohumods. Soils at the site resembled the Mandarin series classification. Specific objectives were:

1. to evaluate the potential for enhanced biodegradation of JP-4 in the vadose-zone (Mandarin series soil) as the result of soil venting and

incremental effectiveness observed with addition of nutrients and moisture,

2. to evaluate the relationships among air flow rate, biodegradation, and volatilization to determine minimal aeration rates required to maintain aerobic conditions for maximizing biodegradation and minimizing volatilization, and
3. to evaluate the potential for biodegradation of hydrocarbon vapors (off-gas) in uncontaminated or less contaminated vadose-zone soil as an alternative to expensive above-ground off-gas treatment.

The intended result is to develop sufficient information to allow the Air Force and/or other large users of similar fuel mixtures to progress to full-scale implementation of the technology.

## LITERATURE REVIEW

### Literature Review Objectives

This literature review addresses technologies for *in situ* remediation of vadose-zone fuel hydrocarbon contamination including soil washing, radio frequency (RF) heating of soil, soil venting, and microbial degradation. Soil washing and RF heating are only briefly addressed as they do not directly apply to this research. However, they are included to provide the reader an overview of vadose-zone *in situ* treatment alternatives. A review of soil venting literature was conducted to identify costs, efficiencies, and any connections between soil venting and biodegradation. Although aerobic and anaerobic biodegradation of hydrocarbons is well documented, enough literature is cited here to provide the reader with a working knowledge of applicable terms and mechanisms. Literature addressing conventional enhanced biodegradation is reviewed as an introduction and justification for enhanced biodegradation through soil venting. The literature review and introductory material, originally presented in English units, has been metricized.

### Soil Washing

Soil washing is the flushing of contaminants from the vadose-zone combined with pump and treat technology. Although this method may be successful for water soluble compounds, it is of limited value for water insoluble material. Fuel as a whole has a low aqueous solubility and although the BTEX fraction is more soluble, removal is dependent upon partitioning from the low solubility or oily fraction of the fuel into the water. Surfactants and solvents have been used successfully to flush contaminants from the soil but their use has

been hindered by the toxicity of commercially available products. Also, this technology is hindered by the inability to hydraulically trap and pump all of the solubilized contaminant and solvent (Hoag and Cliff, 1988). It has been estimated that flushing with surfactants requires 30 to 40 pore volume exchanges of water to extract contaminants (Clarke, 1987).

Column studies using a 4% surfactant solution resulted in 86 and 98% removal of crude oil and polychlorinated biphenyls (PCBs), respectively, after passing 10 pore volumes through the soil (Downey and Elliot, 1990). However, field scale research at Volk Field Air National Guard Base, Wisconsin, showed no significant removal of oil and grease after passing 14 pore volumes of surfactant solution through the soil (Downey and Elliot, 1990). Because of the problems described, *in situ* soil washing has received less attention for fuel hydrocarbon remediation than either soil venting or microbial degradation.

### **Radio Frequency Heating of Soil**

This emerging technology involves the heating of soil by radio frequency energy emitted through a network of soil probes. Absorbed RF energy is capable of heating soil to a range of 150 to 400°C. The high temperature effectively drives off contaminants due to their substantially increased vapor pressures. Vapors are collected at the surface or through vented electrodes that are also used for heating.

A field demonstration project of this technology was conducted at Volk Air National Guard Base, Camp Douglas, Wisconsin. Fourteen m<sup>3</sup> (500 ft<sup>3</sup>) of soil were heated for 12.5 days with maximum temperatures reaching 150 to 160°C. Ninety-nine % of volatile and semi-volatile aromatics and volatile aliphatics, and 94% of semi-volatile aliphatics were removed. Costs were estimated at \$33

to \$64 per Mg (\$1.5 to \$2.9 per 100 lbs) or approximately \$52 to \$104 per m<sup>3</sup> (\$40 to \$80 per yd<sup>3</sup>) of treated soil (IIT Research Institute, 1989). This technology is just emerging and little published literature is available. A full scale demonstration project has not yet been conducted, however, one sponsored by the U.S. Air Force, is currently planned for Kelly AFB, Texas.

### **Soil Venting**

Soil venting is the process whereby a vacuum is applied to a well or wells installed in the vadose-zone in an area contaminated with volatile organics. Clean air is drawn through the subsurface along natural flow lines from the surface or through wells installed to allow preferential introduction or forced injection. The technology has the dual effect of reducing organic vapor concentrations within the vadose-zone and accelerating evaporation and removal of volatile organic materials.

Early work on soil venting was accomplished in 1984 by the Texas Research Institute (1984) under contract to the API. Four experiments were conducted to examine forced venting of air through the soil above a gasoline spill in a model aquifer. Various flow rates and geometries for the venting plumbing were used to determine the most cost efficient method of : (a) removing gasoline from the underground environment and (b) lowering gasoline vapor concentrations in the unsaturated-zone above the spill. This laboratory research concluded that forced venting was a worthwhile technique to investigate in the field. Possible techniques for optimizing field use were suggested (Texas Research Institute, 1984). This research also investigated microbial degradation resulting from oxygen supplied by soil venting.

Researchers concluded that biodegradation was insignificant (Texas Research Institute, 1984).

Work by the Texas Research Institute suggested soil venting as a viable *in situ* technology, but did not address mechanisms of removal or prediction of removal rates. Marley and Hoag (1984) measured evaporation rates of over 50 compounds found in gasoline using column studies. The effects of soil density, moisture content, particle size, and induced air flow were determined. They demonstrated that 99% recovery of gasoline was possible using soil venting. A model based on Dalton's and Raoult's laws demonstrated excellent agreement between predicted and observed mass loss rates (Marley and Hoag, 1984; Hoag et al., 1984). Additional laboratory research was conducted by Clarke (1987) to evaluate the effectiveness of soil venting as a function of contaminant and soil type using column studies. Models were developed to assess feasibility and define parameters which would optimize field scale studies.

Numerous field demonstration and full-scale remediation projects involving fuel hydrocarbons have demonstrated the efficacy of the technology. These projects have demonstrated that *in situ* treatment of volatile hydrocarbons by soil venting is not only effective but much less expensive than traditional excavation/reburial or excavation/incineration technologies. A soil venting field demonstration was conducted at a spill site in Granger, Indiana. A ruptured valve at a petroleum fuels marketing terminal resulted in a release of 380,000 L (100,000 gallons) of gasoline. A substantial amount of the gasoline was recovered but the actual amount was not reported. Much of the unrecovered product had migrated 7.6 m (25 ft) to the water table where 50 cm (1.6 ft) of floating product was measured in the monitoring wells. Two parallel test cells were constructed, each with one extraction well and two injection

wells. After approximately 40 days of operational tests, 700 L (186 gallons) of product had been removed and vapor concentrations had been reduced 99.2% at 30 cm (1 ft) above the capillary zone (Hutzler et al., 1988).

A pilot soil venting test at the previously described Bellview, Florida, site measured initial extraction rates ranging from 150 to 980 L (39 to 260 gallons) per day. After 123 days of operation, a total of 11,120 L (2,937 gallons) of the estimated 38,000 L (10,000 gallon) release had been extracted from the site (Camp, Dresser, and McKee, 1988).

Explosive vapors in a manhole discovered by an electrical utility company lead to the discovery of a long term leak at a gasoline station. Soil venting at this site was shown to remove 730 kg (1,600 lbs) of gasoline hydrocarbons from contaminated soil, reducing soil vapor concentrations from the explosive range to less than 5% of the lower explosive limit (LEL). Concentrations remained below 5% LEL following a shut down period of 1 week. During the 8 weeks of soil venting, all traces of free product (originally measured up to 15 cm (6 in) were removed from the shallow water table. Ground water hydrocarbon concentrations were also reduced more than 98% (Malot and Wood, 1985). It is not clear from this article whether ground water movement or soil venting was responsible for apparent cleanup of the ground water. Investigators at another gasoline station spill site reported a removal rate of 15 kg (33.5 lbs) of total gasoline hydrocarbons per day. Regulators are allowing direct emission of volatilized hydrocarbon vapor at this site based on a risk assessment utilizing downwind dispersion modeling (Bliss, 1987).

Soil venting systems are not always vertical and can be modified to match site characteristics. A horizontal soil venting system was designed and operated at a gasoline contaminated site underlain by a shallow water table

(Conner, 1988). Treatment for the evaporated gasoline was carbon adsorption with steam regeneration. The steam generator required 3.8 to 4.9 L (1 to 1.3 gallons) of fuel oil per 3.8 L (gallon) of gasoline removed. The extraction system was constructed on 6 m (20 ft) centers, 1.2 to 1.4 m (4 to 4.5 ft) deep. Injection trenches were later placed between extraction pipes to enhance removal. Investigators found that a polyethylene cover reduced short circuiting and improved removal efficiency. Investigators also found that most fuel was in the area of the fluctuating water table and they considered dewatering to allow cleanup of this zone during winter months when the water table was high. It was concluded that soil venting reduced the concentration of contaminant in ground water as well as soil. They estimate a total cleanup cost of \$144,000 as opposed to \$560,000 for excavation (Conner, 1988).

One of the largest and best documented fuel hydrocarbon soil venting projects is at Hill AFB, Utah. In January of 1985, an estimated 100,000 L (27,000 gallons) of JP-4 jet fuel was released when an automatic shut-off device for a large fuel storage tank failed. An estimated 14,000 m<sup>3</sup> (18,000 yd<sup>3</sup>) of soil were unevenly contaminated to a depth of 15 m (50 ft). The formation is composed of sand and gravel with occasional clay stringers. A slight amount of perched but discontinuous ground water was found under the site. This demonstration project was designed to test soil venting technology as a potential remediation technology for JP-4 and to produce a design manual for future remediation projects. The work was accomplished by Oakridge National Laboratories (ORNL) under contract to the Air Force Engineering and Services Center (AFESC). Utah State University (USU) was subcontracted by ORNL to operate and monitor the venting and treatment system. Soil venting was initiated on December 18, 1988, and as of September 30, 1989, approximately

51,950 kg or 68,000 L (114,400 lbs or 18,000 gal) of product had been removed (Hinchee, 1989a). Off-gas was initially treated by both fluidized and fixed bed catalytic incineration during the first year of operation. A change in operation modes has allowed the direct discharge of low hydrocarbon concentration off-gas during the second year of the operating period. Microbial degradation, measured by CO<sub>2</sub> production and O<sub>2</sub> consumption, has also been observed at this site. A final project report is expected in September, 1990. In addition to fuel hydrocarbon remediation, soil venting is being successfully applied to the physical removal of chlorinated hydrocarbons from soil. A field demonstration project, designed to determine parameters for trichloroethylene (TCE) soil venting technology, demonstrated cleanup of soils by three orders-of-magnitude at an estimated cost of \$19 to \$26 per m<sup>3</sup> (\$15 to \$20 per yd<sup>3</sup>) (Anastos et al., 1985). Perchloroethylene (PCE) was found in ground water near Stevensville, Michigan at concentrations ranging from 100 to 800 µg/L. The source was surface disposal of PCE tank sludge that had contaminated 800 to 1600 m<sup>3</sup> (1000 to 2000 yd<sup>3</sup>) of soil. After 45 days of soil venting, PCE concentrations declined to 10 mg/m<sup>3</sup> in extracted air and less than 1 mg/kg in soil. Operational costs were estimated at less than 20% of projected excavation costs (Hutzler et al., 1988).

The Twin Cities Army Munitions plant is successfully remediating a site contaminated with TCE and 1,1,1-trichloroethane (TCA) using soil venting technology. Treatment of the gas stream is by carbon adsorption. Regulators are allowing total saturation of carbon or 100% breakthrough. As of September, 1988, 28,600 kg (63,000 lbs) of VOCs had been extracted from the soil and collected on 105,300 kg (232,000 lbs) of carbon (27% by weight). A major complaint has been noise generated by the extraction blowers and noise

control measures have been implemented (Connell, 1988). TCE was also the subject of a case study in California. After 440 days of operation at an air extraction rate of  $2.8 \text{ m}^3/\text{min}$ , the vacuum extraction system had removed 30 kg of the 32 kg of TCE in the soil. Carbon adsorption was used for off-gas treatment. To satisfy a 10 g/day emission limit, 180 kg of activated carbon were used for the removal of 25 kg of TCE (14% by weight) (Ellgas and Marachi, 1984).

The Verona well field supplies drinking water to 50,000 residents of Battle Creek, Michigan. Ten of the city's 30 production wells were contaminated with chlorinated hydrocarbons, aromatics, and ketones traced to the Thomas Solvent Company. Soil venting was selected for site remediation with treatment of the off-gas by carbon adsorption. The project is currently ongoing and costs are projected at \$50 to \$60 per  $\text{m}^3$  with off-gas treatment, and \$20 per  $\text{m}^3$  without off-gas treatment (Guerriero, 1989).

An overturned Southern Pacific rail car near Benson, Arizona, resulted in a spill of 68,000 kg (150,000 lbs) of 1,3-dichloropropene. At the time of cleanup, it was estimated that 20,000 to 41,000 kg (45,000 to 90,000 lbs) remained, contaminating approximately  $460 \text{ m}^3$  ( $600 \text{ yd}^3$ ) of soil. The balance of the spilled product had already volatilized prior to project initiation. Over a period of 7 months, 6,500 kg (14,300 lbs) were extracted at a capital cost of \$25,000 and operational cost of \$50,000. Treatment of the off-gas was not required. Cost of the project was \$1,150 per  $\text{m}^3$  (\$875 per  $\text{yd}^3$ ) which is in the range of costs for excavation/incineration (Hutzler et al., 1988). Operational costs for this project were high due to the remote location and the need to provide power generation. This site was the subject of a Master's thesis which

recommended ways to reduce soil venting operational costs primarily by pulse pumping as opposed to continuous operation (Johnson, 1988).

### Microbial Degradation

The microbial degradation of petroleum hydrocarbons has been extensively studied and well documented in the literature. A review of one computer database (Life Sciences Collection), from January 1978 to June 1989 revealed over 700 citations for the microbiological decomposition of hazardous materials. The compounds described in the literature are primarily saturated and substituted hydrocarbons. Early research into biodegradation of hydrocarbons in soil systems can be traced to the agricultural literature where modified hydrocarbons have been used extensively for pest control. Decomposition of herbicides, insecticides, and fungicides is dependent upon both biotic and abiotic reactions, and the rate of these reactions determines the required frequency of application. The high cost of pest control has been the motivation for conducting research concerning degradation mechanisms and degradation rates for these applied pesticides.

Researchers have long understood mechanisms and even microbial populations responsible for biodegradation of hydrocarbons (Alexander, 1977 ; Atlas, 1981 ; Dragun, 1988 ; Riser, 1988). Hydrocarbon-degrading organisms isolated from soil include 22 strains of bacteria and 31 strains of fungi (Dragun, 1988). A number of strains of hydrocarbon-degrading actinomycetes have also been isolated but do not seem to compete as well as other microorganisms in hydrocarbon contaminated soils. The most commonly isolated species of hydrocarbon degrading bacteria in decreasing order include: *Pseudomonas*, *Arthrobacter*, *Alcaligenes*, *Corynebacterium*, *Flavobacterium*, *Achromobacter*,

*Micrococcus*, *Nocardia*, and *Mycobacterium*. The most commonly isolated hydrocarbon degrading fungi in decreasing order include: *Trichoderma*, *Penicillium*, *Aspergillus*, and *Mortierella* (Dragun, 1988).

Researchers have studied in great detail the relationship between chemical structure and biodegradation. Petroleum hydrocarbons are comprised primarily of alkanes, alkylaromatics, and aromatics. The n-alkanes, n-alkylaromatics, and aromatics in the C<sub>10</sub> to C<sub>22</sub> range are the hydrocarbons least toxic to organisms and the most biodegradable. The n-alkane, alkylaromatic, and aromatic hydrocarbons in the C<sub>5</sub> to C<sub>9</sub> range are biodegradable by a narrower range of species of microorganisms and at lower concentrations (Dragun, 1988). In most soil systems, compounds in the C<sub>5</sub> to C<sub>9</sub> range are removed, to a greater extent, by volatilization than by biodegradation. The species of hydrocarbon degraders responsible for the degradation of the gaseous compounds (n-alkanes C<sub>1</sub> to C<sub>4</sub>) is even narrower although biodegradation of these materials has been documented. Volatilization in this range is more important than biodegradation in typical soil environments. Branched alkanes and cycloalkanes in the C<sub>10</sub> to C<sub>22</sub> are less degradable than n-alkanes and aromatics of equivalent size. Branching hinders beta-oxidation which is the primary mechanism in the degradation of straight chain hydrocarbons, and cycloalkane degradation requires the presence of two or more species for complete metabolism to take place (Dragun, 1988).

Liebig's Law of the Minimum states that the rate of biological processes, such as growth and metabolism, is limited by the factor present at its minimal level (Dragun, 1988). In uncontaminated subsurface soil, the factor that often limits microbial growth is the absence of an available source of energy. Since

most soil microorganisms are heterotrophs, the limiting factor is usually a source of readily degradable organic matter. Soil microbiologists have observed an abundant population of microorganisms whenever an abundant source of carbon was present (Dragun, 1988). However, the attention of the microbiologist has usually focused on agricultural surface soils because the relationship between the microflora and higher plants are most important in the A horizon where populations and nutrients are most abundant (Alexander, 1977). Because of the focus on the A horizon, it was generally accepted that microorganisms were not available for biodegradation of organic chemicals in deeper soils. Recent research has dispelled this theory. Microbial characterization of soil samples collected prior to venting at the Hill AFB project (Hinchee et al., 1989a) revealed large numbers of hydrocarbon degraders at depths up to 20 m (65 ft). Concentrations generally ranged from  $10^3$  to  $10^6$  colony forming units (CFU) per gram dry weight. Samples taken during construction of a background well in uncontaminated soil also revealed the presence of hydrocarbon degraders throughout a 15 m (50 ft) profile. Concentrations ranged from 3 to 6 orders of magnitude less in background samples than in contaminated samples however.

In addition to a source of carbon and energy, the biodegradation process is dependent on soil factors including pH, soil moisture, temperature, and presence of available inorganic nutrients (Dragun, 1988). Most microorganisms function best in a pH range of 6 to 8 with optimum being slightly above 7 (Dragun, 1988). A shift in pH generally results in a shift of microbial population because of the ability of certain species to survive a wider range in pH. For example, an acidic environment may contain a proportionately larger fungi

population, not because fungi prefer a low pH but because fewer bacteria and actinomycetes survive in that environment (Alexander, 1977).

Soil microorganisms require soil moisture for metabolic processes and for solubilization of energy and nutrient supplies. A study of polyaromatic hydrocarbon (PAH) biodegradation in the vadose-zone concluded that the solubility of PAHs was the growth limiting factor for microbial populations. A decline in number of PAH degrading organisms was shown to follow a decline in PAH concentration in the aqueous phase. Researchers increased the solubility of PAHs by addition of acetone and organism counts increased dramatically. The organisms were not inhibited by the acetone nor were they able to degrade it. It was concluded that the major objective in bioremediation of contaminated soil is to release organics bound to soil thereby increasing solubility and biodegradation (Werner, 1989). A review of 23 *in situ* bioremediation projects concluded that biodegradation depends entirely on contact between contaminants in the water phase and the microorganisms (Staps, 1989).

The effect of soil moisture as it relates to microbial activity and crop production has been addressed in the literature. However, (with the exception of pesticide biodegradation) there is little information on the relationship between the requisite amount of soil moisture and biodegradation of organic chemicals (Dragun, 1988). Column studies on soils from Hill AFB yielded insignificant increases in microbial activity with increasing soil moisture without nutrient addition. However, following nutrient addition, respiration increased significantly with increased soil moisture. After 48 days there was a 3, 3.5, and 4.5 fold increase in CO<sub>2</sub> evolution at 25, 50, and 75% of field capacity, respectively. These data suggest that microorganisms in the Hill AFB soil were

limited by either nutrients or moisture, or a combination of both (Hincbee et al., 1989a). The soil columns in this study were dosed with approximately 1000 mg/kg JP-4 and oxygen was supplied by a constant flow of air.

Since liquid water is required for microbial activity, the minimum temperature required for biodegradation is obviously above freezing. The upper temperature limit is thought to be approximately 50° C because essential microbial enzymes are denatured above this temperature (Dragun, 1988). As with pH, populations vary with changes in temperature. Optimum temperature for soil microbial reactions is in the range of 30 to 35°C.

Cell growth and maintenance requires a number of nutrients in addition to a source of available carbon. At a minimum the following nutrients must be available in the proper form and amount for microbial proliferation: nitrogen, phosphorus, potassium, sodium, sulfur, calcium, magnesium, iron, manganese, zinc, copper, cobalt, and molybdenum (Alexander, 1977). In general, nitrogen and phosphorus can be considered macronutrients because they are required in the largest quantities. The remaining compounds are considered micronutrients because they are required in minute quantities which are usually naturally available in excess in the soil (Dragun, 1988).

If nutrient addition is required it is usually limited to nitrogen and phosphorus. Microbial cells contain 5 to 15 parts of carbon to 1 part of nitrogen but 10:1 is a reasonable average for aerobic flora (Alexander, 1977). The generally accepted C:N ratio of aquatic flora in domestic wastewater is 4.3 to 1 based on the experimentally derived formula ( $C_5H_9O_{2.5}N$ ) for cell protoplasm (Metcalf and Eddy, 1979). The apparent difference in soil and wastewater flora may be due to differing species in soil and domestic wastewater or the higher availability of nitrogen in domestic wastewater. A carbon, nitrogen, phosphorus

(C:N:P) ratio of 250:10:3 is considered optimum for biodegradation in soil but 100:10:2 has been used in some applications (Staps, 1989). In general, one unit of nitrogen assimilated into cell material is accompanied by 10 units of carbon assimilated and 20 units of carbon volatilized as CO<sub>2</sub> (Alexander, 1977). The 100:10:2 ratio is conservative because it assumes all carbon is assimilated into cell mass. The 250:10:3 ratio is probably also conservative because although it is closer to the combined assimilation/volatilization ratio it does not consider recycling of the organic nitrogen or phosphorus. In determining the appropriate ratio one must also consider the delivery efficiency which explains why the most conservative value is often used.

Uncontaminated soils with low natural organic carbon content are frequently aerobic to substantial depths because diffusion of atmospheric oxygen exceeds microbial respiration (Richter, 1987; Hincbee et al., 1989a). However, microbial activity in soils heavily contaminated with petroleum hydrocarbons is usually limited by oxygen because respiration rates and evolution of CO<sub>2</sub> exceed diffusion rates of atmospheric oxygen. For this reason, biodegradation research has focused first on methods of supplying oxygen or some other terminal electron acceptor and second on supplying nutrients to indigenous populations.

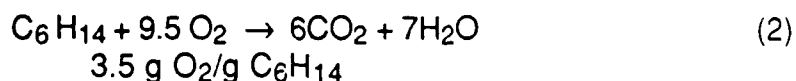
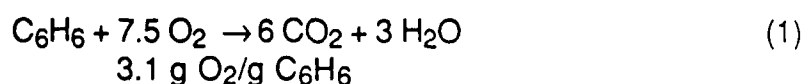
### **Conventional Enhanced Biodegradation**

Biodegradation of contaminants in aquifers has been studied for two decades (Lee et al., 1988). Original research focused on biologically treating groundwater rather than the source, usually located in the unsaturated-zone. Since ground water is typically the exposure route of most concern, it is only natural that it was the target of early research (Hincbee et al., 1987). This

research focused on methods of providing oxygen and nutrients to the indigenous microbial population to stimulate biodegradation of contaminants in ground water.

Many contaminants, including fuels, are highly insoluble and hydrophobic. These compounds tend to partition into the soil and are solubilized slowly by soil water, thus providing a source of ground water contamination for many years. Hinchee et al. (1987) provide a hypothetical case for fuels where a typical 3,800 L (1000 gallon) spill would be distributed with 50 L (13 gallons) in ground water, 3650 L (962 gallons) in soil, and 100 L (25 gallons) in soil vapor. Understanding the phenomenon of partitioning, combined with the high cost of pump and treat technology, has redirected research towards the source of contamination in the unsaturated-zone.

Although the focus is now on the source of contamination rather than the contaminated ground water, the objective of providing oxygen and nutrients remains. In conventional biodegradation, water is typically used to carry oxygen and nutrients to the organisms. Stoichiometry for typical aerobic biodegradation to mineralization of benzene and hexane follows:



Equations 1 and 2 represent maximum oxygen requirements to completely mineralize benzene and hexane, respectively, because they are based on the assumption that either there is no cell synthesis or endogenous respiration, or that cell synthesis and endogenous respiration are occurring at the same rate with no net accumulation of biomass. If cell synthesis occurs at a

faster rate than endogenous respiration, there is accumulation of biomass and the oxygen requirement for biodegradation is reduced. Assuming cell synthesis and no endogenous respiration, the theoretical oxygen requirement for the biodegradation of hexane, calculated in Appendix A, is reduced to 1.5 g O<sub>2</sub>/g C<sub>6</sub>H<sub>14</sub> based on half reactions for bacterial systems (Sawyer and McCarty, 1978). Based on complete mineralization of hexane (Equation 2), 1.58 moles of O<sub>2</sub> are required for each mole of CO<sub>2</sub> produced. Assuming cell synthesis without endogenous respiration the ratio of O<sub>2</sub> consumed to CO<sub>2</sub> produced, on a mole/mole basis, is increased to 2.78 (Appendix A). In this research, O<sub>2</sub>/CO<sub>2</sub> ratios average 2.2 mole/mole and ranged from 1.2 to 3.7 mole/mole (Appendix J) indicating that some endogenous respiration was occurring. Since biomass accumulation and endogenous respiration in soil is difficult to measure, the conservative approach (Equation 2) was used as the basis for predicting biodegradation of fuel hydrocarbons.

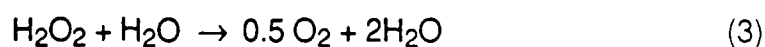
Oxygen saturation in water, following air sparging, is temperature dependent and ranges from 8 to 12 mg/L (Lee et al., 1988). Assuming an aqueous solubility of 9 mg/L, 111 L of water are required to deliver 1 g of O<sub>2</sub> to the subsurface. This equates to 389 L of water to provide enough O<sub>2</sub> to mineralize 1 g of hexane, or 388 kg of water per g of hexane.

A typical 1 m<sup>3</sup> (35.3 ft<sup>3</sup>) of dry sand (40% porosity and 1600 kg/m<sup>3</sup> (100 lb/ft<sup>3</sup>)) contaminated with 10,000 mg/kg of hexane contains 16 kg (35.3 lb) of hexane. Therefore, 6,200 m<sup>3</sup> (1.6 million gal) or 15,500 pore volumes of water are required to aerate each m<sup>3</sup> (35.3 ft<sup>3</sup>) of contaminated soil with saturated (9 mg O<sub>2</sub>/L) water. A pore volume is defined as the unit volume of voids per unit volume of soil (porosity). A relatively small 3,800 L (1000 gal) spill would require 1 million m<sup>3</sup> (280 million gal) of water to provide adequate oxygen for

complete mineralization. Wilson and Ward (1987) indicate that 32,000 pore volumes of air sparged water are required at hydrocarbon saturation levels, which are assumed to be about 2% (20,000 mg/kg) hydrocarbons by weight.

Researchers realized that providing extremely large volumes of water was not only expensive but may require decades in low permeability soils. Emphasis has moved toward increasing the O<sub>2</sub> concentration in water, thereby reducing required water volumes. Sources of O<sub>2</sub> investigated include pure oxygen, hydrogen peroxide, and ozone. Sparging with pure O<sub>2</sub> provides dissolved O<sub>2</sub> concentrations of 40 to 50 mg/L (Lee et al., 1988).

A number of studies have investigated hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a source of dissolved O<sub>2</sub> in water (Lee et al., 1988). Most conclude that 500 mg/L H<sub>2</sub>O<sub>2</sub> is the maximum allowable concentration based on toxicity to microbial populations and rapid breakdown that causes bubble formation and reduced permeability (Lee et al., 1988). One mol/L of H<sub>2</sub>O<sub>2</sub> provides approximately 0.5 mol/L (235 mg/L) of dissolved O<sub>2</sub> as illustrated by Equation 3.



Therefore, in a soil contaminated at 10,000 mg/kg hexane, 6,200 m<sup>3</sup> (1.6 million gallons) of air sparged water, 1,240 m<sup>3</sup> (328,000 gallons) of pure oxygen sparged water, or 237 m<sup>3</sup> (63,000 gallons) of water containing 500 mg/L H<sub>2</sub>O<sub>2</sub> are required for each m<sup>3</sup> (35.3 ft<sup>3</sup>) of soil. Under the best conditions (100% utilization), a 3,800 L (1000 gallon) spill would require 41,600 m<sup>3</sup> (11 million gallons) of water containing 500 mg/L H<sub>2</sub>O<sub>2</sub> to provide the necessary O<sub>2</sub> for aerobic biodegradation. This analysis assumes complete mineralization of hexane to CO<sub>2</sub> and water. Since a portion of available

hydrocarbon is converted to cell mass, oxygen requirements may be proportionately less. However, the analysis is valid for comparative purposes.

Lee et al. (1988) describe a number of projects using  $H_2O_2$  as a source of  $O_2$ , and various degrees of success are reported. In 1984, the Air Force Engineering and Services Center sponsored a research project at a jet fuel contaminated site at Kelly AFB, Texas which examined the use of  $H_2O_2$  as an oxygen source for enhancing biodegradation. Severe problems with soil permeability were encountered, reducing the delivery of  $O_2$  and nutrients. Permeability reductions were attributed to silt and clay soils together with precipitation of calcium phosphates formed by the reaction of injected phosphates with calcium in the soil. Little biodegradation was observed at the site due to the inability to deliver  $O_2$  and nutrients (Wetzel et al., 1987; Downey et al., 1988). A second site at Eglin AFB, Florida, was selected in an attempt to study hydrogen peroxide technology under ideal soil conditions. Bench scale microcosm studies conducted prior to field research confirmed that existing microbial populations could degrade soluble aromatic compounds in less than two weeks under enriched oxygen and nutrient conditions (Hinchee et al., 1989b; Downey and Elliot, 1990). Hydrogen peroxide was injected into approximately 60,000  $m^3$  (16 million gallons) of ground water which was delivered to the JP-4 contaminated field site both by spray irrigation and infiltration galleries. Rapid peroxide destabilization and oxygen loss at the point of injection severely limited the amount of oxygen delivered and resulted in low rates of hydrocarbon mineralization. The loss of oxygen resulted in a cost of \$3.30 to \$5.30 per kg (\$1.50 to \$2.40 per lb) of  $O_2$  delivered or \$11.60 to \$18.50 per kg (\$5.25 to \$8.40 per lb) of hydrocarbon mineralized (Downey et al., 1988). At a concentration of 16 kg hydrocarbon per  $m^3$  (1 lb hydrocarbon

per ft<sup>3</sup>) of soil the cost of oxygen alone would range from \$186.00 to \$296.00 per m<sup>3</sup> (\$142.00 to \$227.00 per yd<sup>3</sup>).

Researchers concluded that H<sub>2</sub>O<sub>2</sub> decomposition rates were higher than O<sub>2</sub> utilization rates and that most of the H<sub>2</sub>O<sub>2</sub> decomposed and was lost to the atmosphere. A review of the literature led researchers to believe that similar problems occurred at other bioremediation sites, and that unless H<sub>2</sub>O<sub>2</sub> decomposition rates were substantially lowered, H<sub>2</sub>O<sub>2</sub> was not an economical source of O<sub>2</sub> (Hinchee and Downey, 1988; Hinchee et al., 1989b). This research, coupled with the soil washing experiments described above, illustrate the need of field research to prove the efficacy of remediation technologies demonstrated in the laboratory (Downey and Elliot, 1990).

Laboratory and field studies utilizing H<sub>2</sub>O<sub>2</sub> as an oxygen source were conducted by the U.S. EPA on aviation gasoline contaminated aquifer material from Traverse City, Michigan (U.S. EPA, 1990). Fifty-four % of the initial mass of aviation gasoline in columns degraded. However, it was not possible to distinguish between abiotic and biotic degradation. Researchers concluded that at a hydrogen peroxide concentration of 100 mg/L, oxygen gas production far exceeded the oxygen demand and that 45% of the available oxygen was transferred to the gaseous phase. Additionally, the rate of oxygen consumption decreased indicating that inhibition of microbial populations may have occurred. The field study conducted at Traverse City supported observations from the laboratory study. Hydrogen peroxide decomposed rapidly even though precautions were taken to minimize iron driven decomposition reactions. It was concluded that decomposition resulted from enzymatic catalysis. Neither an oxygen nor hydrocarbon mass balance was possible at field scale. Researchers were only able to conclude that hydrogen peroxide

successfully increased the concentration of available oxygen in down-gradient ground water (U. S. EPA, 1990).

### Enhanced Biodegradation Through Soil Venting

Soil venting technology, discussed previously, provides large volumes of air to the vadose-zone. Table 2 provides a comparison of the O<sub>2</sub> carrying capacity of water and air for the theoretical biodegradation of hexane.

Table 2. Comparison of water and air as carriers of oxygen.

| Carrier                                           | g carrier/<br>g oxygen | g carrier/<br>g hexane | L carrier/<br>g oxygen | L carrier/<br>g hexane |
|---------------------------------------------------|------------------------|------------------------|------------------------|------------------------|
| Air saturated water (9 mg/L)                      | 110,000                | 385,000                | 110                    | 388                    |
| Pure oxygen saturated water (45 mg/L)             | 22,000                 | 77,000                 | 22                     | 78                     |
| Water containing 500 mg/L of<br>hydrogen peroxide |                        |                        |                        |                        |
| 235 mg/L oxygen-100 % Utilized                    | 4,200                  | 14,700                 | 4                      | 14                     |
| 235 mg/L oxygen-30% Utilized                      | 14,000                 | 49,000                 | 14                     | 49                     |
| Air containing 20.9% oxygen                       | 4                      | 15                     | 4                      | 13                     |

Table 2 illustrates that air has a much greater potential than water for delivering O<sub>2</sub> to the vadose-zone on a mass/mass basis. On a volume of carrier per unit mass of oxygen basis, air is also much more effective than water with the exception of 100% utilized hydrogen peroxide. In addition, O<sub>2</sub> provided by air is more easily delivered throughout a formation because air is less viscous than water and the higher O<sub>2</sub> concentration in air provides the necessary driving force for diffusion into less permeable zones within the formation.

A review of available literature on soil venting was accomplished to determine if other researchers had considered or documented biodegradation as a result of oxygen being supplied through the venting process. The first documented evidence of enhanced biodegradation through soil venting

resulted from a failed experiment. Texas Research Institute, Inc., (TRI) working for the American Petroleum Institute (API), conducted a large scale model experiment to test the effectiveness of a surfactant treatment to enhance recovery of spilled gasoline. The experiment accounted for only 30 of the 246 L (8 of the 65 gallons) originally spilled and raised questions about where the balance of the gasoline went. Microbial activity was ruled out at the time due to the low dissolved oxygen content of the water. Volatilization was the only remaining pathway for removal and it was for this reason that follow-on soil venting research (Texas Research Institute, 1984) was initiated. In order to conduct the large scale model experiment, a column study was required to determine a diffusion coefficient. This column study evolved into a biodegradation study where it was concluded that as much as 38% of spilled product was biologically mineralized. Researchers concluded that venting should not only remove gasoline by physical means but would also enhance microbial activity (Texas Research Institute, 1980).

These findings would likely have generated additional research into the concept of enhancing *in situ* biodegradation through soil venting, but the follow-on research by TRI may actually have discouraged such efforts. In the follow-on large-scale model aquifer study that investigated soil venting (Texas Research Institute, 1984), biodegradation was reported to be insignificant. Effluent air was monitored for CO<sub>2</sub> to document biological degradation. Average CO<sub>2</sub> concentrations, in two test reactors, were 570  $\mu\text{L/L}$  (ppm) (range 380 to 940  $\mu\text{L/L}$  (ppm)) and 670  $\mu\text{L/L}$  (ppm) (range 440 to 1130  $\mu\text{L/L}$  (ppm)), respectively. The ambient concentration of 350  $\mu\text{L/L}$  (ppm) was subtracted from average concentrations to determine hydrocarbons removed by degradation. Assuming a C<sub>6</sub> hydrocarbon molecule and that all CO<sub>2</sub> came from microbial

oxidation, calculations showed that less than 1 mole of gasoline was oxidized to CO<sub>2</sub> in each experiment. This equated to less than 0.2% of the original spill of 80 L (Texas Research Institute, 1984). Low CO<sub>2</sub> concentrations may have resulted from the pH of the water added to the model aquifer. Researchers used Austin City water which varied from pH 9.7 to 9.9 due to lime treatment. The pH of effluent water from the experimental tanks ranged from 8.3-9.2. This high pH likely inhibited or prevented significant microbial activity as the critical pH range is reported from 5.5 to 8.5 (U.S. EPA, 1989). Even if microbial activity had existed, the high pH of the soil/water system would have acted as a CO<sub>2</sub> sink converting much of the evolved CO<sub>2</sub> and existing CaCO<sub>3</sub> to bicarbonate and calcium ion.

Since publication of the 1984 TRI soil venting results, supporting research concerning the volatilization aspect has been conducted both in the laboratory and in the field. Most of this work was reviewed as part of the research project reported in this document to search for documented associations between soil venting and biodegradation. Based on a review of current and past research, enhanced biodegradation through soil venting has had only limited attention, most of which has occurred in the last two years.

Wilson and Ward (1987) suggested that using air as a carrier for oxygen could be 1000 times more efficient than transferring it to the water, especially in deep unsaturated-zones hard to flood. A fine sand or silt saturated with hydrocarbons would require 4,000 pore volumes of air to provide the stoichiometric O<sub>2</sub> required for aerobic degradation compared to 32,000 pore volumes of air saturated water. They made the connection between soil venting and biodegradation by observing that, "...soil venting uses the same principle (of moving air through soil) to remove volatile components of the hydrocarbon."

In a general overview of the soil venting process, Bennedsen et al. (1987) conclude that soil venting provides large quantities of oxygen to the vadose-zone possibly stimulating aerobic degradation. They state that water and nutrients would also be required for significant degradation and encouraged additional investigations into this area of study.

In describing sources of  $O_2$  for *in situ* biodegradation, Riser (1988) suggested that air should be particularly effective for contaminated soils in the unsaturated-zone. This conclusion was based on the fact that air is much less viscous than water and has a twenty-fold greater oxygen content on a mass per unit volume basis. However, a calculation using 21% oxygen in air and 9 mg/L in water indicates that air actually carries thirty times more oxygen than water on a mass per unit volume basis (Table 2). Air moves more easily through the soil and if air and water filled porosity are about equal, and pressure gradients are equal, then air should be about 1000 times more effective than water in transferring oxygen to the subsurface. The basis of this conclusion, although not specifically stated, must be a combination of the increased oxygen carrying capacity of air (mass/volume basis); lower viscosity of air compared to water; and increased diffusivity of oxygen from air as compared to oxygen from water. Riser (1988) makes the connection between soil venting and providing oxygen to the vadose-zone for biodegradation of contaminants. Table 2 indicates that on a mass of oxygen per mass of carrier basis, air is approximately 27,000 times more efficient than air saturated water. On a mass of oxygen per volume of carrier basis, air is approximately 30 times more efficient than air saturated water. Information in Table 2 does not consider relative oxygen diffusion rates in air versus water.

Biodegradation enhanced by soil venting has been observed at several field sites although documentation is limited. Investigators at a soil venting site for remediation of gasoline contaminated soil claim significant biodegradation as measured by a temperature rise when air was supplied. Investigators pulse pumped air through a pile of excavated soil and observed a consistent temperature rise that they attributed to biodegradation. They claim that the pile was cleaned up during the summer primarily by biodegradation (Conner, 1988). However, they did not control for natural volatilization from the above ground pile and there were not enough data provided to critically review the biodegradation claim.

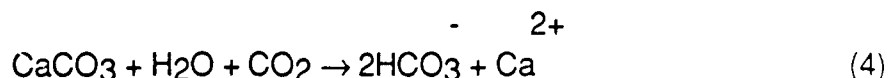
Researchers at Traverse City, Michigan, measured toluene concentration over time as an indicator of aviation gasoline contamination in the vadose-zone. They assumed the absence of advection and transience (diffusion), attributing all toluene decay to biodegradation. Investigators imply that because toluene decayed near the oxygenated ground surface that soil venting is an attractive remediation alternative for light, volatile hydrocarbon spills (Ostendorf and Kampbell, 1989). There is little question that toluene readily degrades under aerobic conditions. However, it is not clear from their paper that investigators were measuring biodegradation or volatilization or a combination of both. Also, the absence of advection and transience (diffusion) assumption may not be valid, especially near the ground surface.

Chevron Research Company is assignee of United States Patent No. 4,765,902, awarded August 23, 1988, for the *in situ* biodegradation of spilled hydrocarbons using soil venting as a source of oxygen (Ely and Heffner, 1988). Experimental design and data are not provided but findings are presented graphically. Recovery at a gasoline and diesel oil site revealed slightly higher

biodegradation removal than evaporation. Recovery at a gasoline-only site indicated that about two-thirds of the removal was by volatilization and one-third was by biodegradation. At a site containing only fuel oils, approximately 75 L/well/day (20 gal/well/day) of fuel oil were removed by biodegradation whereas vapor pressures were too low for any removal by volatilization. Inventors claim that the process has advantages over strict soil venting because removal is not dependent only on vapor pressure. In the examples stated in the patent, CO<sub>2</sub> was maintained between 6.8 and 11% and O<sub>2</sub> between 2.3 and 11% in vented air. The patent suggests that the addition of water and nutrients may not be acceptable because of flushing to the water table, but they also claim nutrient addition as part of their patent. The patent recommends flow rates between 850 and 7,000 L/min (30 and 250 ft<sup>3</sup>/min) per well and states that air flows higher than required for volatilization may be optimum for degradation. In addition to biodegradation, the patent claims removal of hydrocarbons by creation of aerosols.

An international evaluation of *in situ* bioremediation reviewed 23 relevant projects in The Netherlands, West Germany, and the United States. Of the 23 sites, only one described soil venting as a means of providing oxygen for biostimulation. The project (N5) was conducted by a Dutch firm, Delft Geotechnics, and describes a soil venting project used both as a physical and biological process. Ninety-six % of gasoline (petrol) and 33% of diesel were removed in 12 months (Staps, 1989). Test plots were constructed in sandy soil to which 125 kg of gasoline were added. Test plots were inoculated with effluent water ( the source of which was not stated) and nutrients were added using a C:N:P ratio of 100:10:2. Plots were vented and off-gas analyzed by gas chromatography. A mass balance for gasoline (petrol) indicated significant

biodegradation but CO<sub>2</sub> production indicated that biological mineralization was negligible (Eyk and Vreeken, 1988). Researchers concluded that CO<sub>2</sub> was lost to the ground water as bicarbonate by the reaction:



Using the CaCO<sub>3</sub> concentrations before and after the experiment, the fraction of petrol lost by biological degradation was computed. Adding this loss to other measured losses resulted in a 96% recovery of added gasoline (Eyk and Vreeken, 1988).

The full-scale soil venting project at Hill AFB, described above, provides documented evidence of enhanced biodegradation through soil venting both in the laboratory and in the field (Hinchee et al., 1989a). Column studies on nutrient amended soils from Hill AFB, dosed with approximately 1000 mg/kg JP-4 and using air as a source of oxygen, resulted in significant increases in microbial respiration. After 48 days there was a 3, 3.5, and 4.5-fold increase in CO<sub>2</sub> evolution at moisture contents of 25, 50, and 75% of field capacity, respectively.

During the initial 70 days of venting at Hill AFB, undiluted off-gases were monitored for CO<sub>2</sub>, O<sub>2</sub>, and hydrocarbon concentrations. The fraction of JP-4 that was biodegraded dropped rapidly from initial values of approximately 30% to steady-state values of approximately 15% within 30 days after venting began. Although volatilization was the primary mechanism of removal, from 15% to 30% of the jet fuel was biodegraded *in situ* during the first 70 days of venting (Hinchee et al., 1989a).

This literature review has demonstrated the efficacy of soil venting for the remediation of fuel contaminated soils. Soil venting is not only effective in the physical removal of volatile hydrocarbons by volatilization, but also as a source of oxygen for biological mineralization for both the volatile and non-volatile fractions of spilled fuels. Treatment of off-gas has been shown to constitute a minimum of 50% of soil venting remediation costs. This research will investigate methods for enhancing biological mineralization while minimizing volatilization, with the goal of eliminating or reducing the need for expensive off-gas treatment.

## MATERIALS AND METHODS

### Site Description

An *in situ* field demonstration of enhanced biodegradation through soil venting was conducted at the site of an abandoned tank farm located on Tyndall AFB, Florida. The site is contaminated with fuel, primarily JP-4, and free product has been observed floating on the shallow ground water table. Tyndall AFB is located on a peninsula that extends along the shoreline of the Gulf of Mexico in the central part of the Florida Panhandle. The highest ground on the peninsula is 7.6 to 9.1 m (25 to 30 ft) above mean sea level. The uppermost sediments, at Tyndall AFB, are sands and gravels of Pleistocene to Holocene age (Environmental Science and Engineering, 1988). Soils at the site are best described by the Mandarin series consisting of somewhat poorly drained, moderately permeable soils that formed in thick beds of sandy material (U.S. DA, 1984).

The climate at the site is sub-tropical with an annual average temperature of 20.5° C (69° F). Average daily maximum and minimum temperatures are 25° C and 16° C (77° F and 61° F), respectively. Temperatures of 32° C (90° F) or higher are frequently reached during summer months, but temperatures above 38° C (100° F) are reached only rarely. Average annual rainfall at Tyndall AFB is 140 cm (55.2 inches) with approximately 125 days of recordable precipitation during the year. The depth to ground water on Tyndall AFB varies from about 0.3 to 3.0 m (1 to 10 ft). The water-table elevation rises during periods of heavy rainfall and declines during periods of low rainfall. Yearly fluctuations in ground water elevations of approximately 1.5 m (5 ft) are typical (Environmental Science and Engineering,

1988). Prior to dewatering at the site, the water table was observed to be as shallow as 46 cm (1.5 ft).

### **Overall Project Research Plan**

The scope of work was comprised of three major tasks: site characterization, test plan preparation, and field testing.

#### ***Task 1-Site Characterization***

Site characterization activities included: determination of the location of test plots for treatment; determination of contaminant levels and distribution in ground water, soil, and soil gas; distribution of total and hydrocarbon degrading bacteria in the soils; determination of soil texture and soil organic matter content; installation of permanent soil gas sampling probes and monitoring wells; and determination of soil gas permeability. The results of the site characterization were used to design the field test and served to provide a baseline of information for the investigation.

#### ***Task 2-Test Plan Preparation***

Following site characterization, a Test Plan was prepared describing these results and outlining experiments to be performed in the field, along with instrumentation, and analytical methods to be used in further site activities.

#### ***Task 3-Field Test***

Following development of the Test Plan, treatment plots were constructed together with installation of air and water/nutrient delivery systems. Systems were tested and modified as necessary prior to the field test start-up on October 4, 1989.

### **Field Testing Objectives**

A seven month field study (October, 1989, to May, 1990) was designed to address the following basic questions:

1. Does soil venting enhance biodegradation of JP-4 at this site?
2. Does moisture addition coupled with soil venting enhance biodegradation at this site?
3. Does nutrient addition coupled with soil venting and moisture addition enhance biodegradation at this site?
4. Will the hydrocarbons in the off-gas biodegrade when passed through uncontaminated soil?

In addition, other factors were addressed, to a limited extent, including:

1. Evaluation of ventilation rate manipulation to maximize biodegradation and minimize volatilization.
2. Calculation of specific biodegradation rate constants from a series of respiration tests conducted during shutdown of the air extraction system.
3. Determination of the effects of biodegradation and volatilization on a subset of selected JP- 4 components.
4. Determination of the potential for nitrogen fixation under aerobic and anaerobic conditions.
5. Evaluation of alternative vent placement and vent configuration to maximize biodegradation and minimize volatilization.

## Test Plot Design and Operation

### *Test Plot Configuration*

In order to accomplish project objectives, two treatment plots (Figures 1 and 2) and two background plots (Figures 3 and 4) were constructed and operated in the following manner:

1. Contaminated Treatment Plot 1 (V1) - Venting only for approximately 8 weeks, followed by moisture addition for approximately 14 weeks, followed by moisture and nutrient addition for approximately 7 weeks.
2. Contaminated Treatment Plot 2 (V2) - Venting coupled with moisture and nutrient addition for 29 weeks.
3. Background Plot 3 (V3) - Venting with moisture and nutrient addition at rates similar to V2, with injection of hydrocarbon contaminated off-gas from V1.
4. Background Plot 4 (V4) - Venting with moisture and nutrient addition at rates similar to Vent 2.

### *Air Flow*

Air flow was maintained throughout the field test duration except during *in situ* respiration tests. Flow rates were adjusted to maintain aerobic conditions in treatment plots, and background plots were operated at similar air retention times. Off-gas treatment experiments in one background plot (V3) involved operation at a series of flow rates and retention times. A schematic of the air flow system is illustrated in Figure 5. Soil gas was withdrawn from the

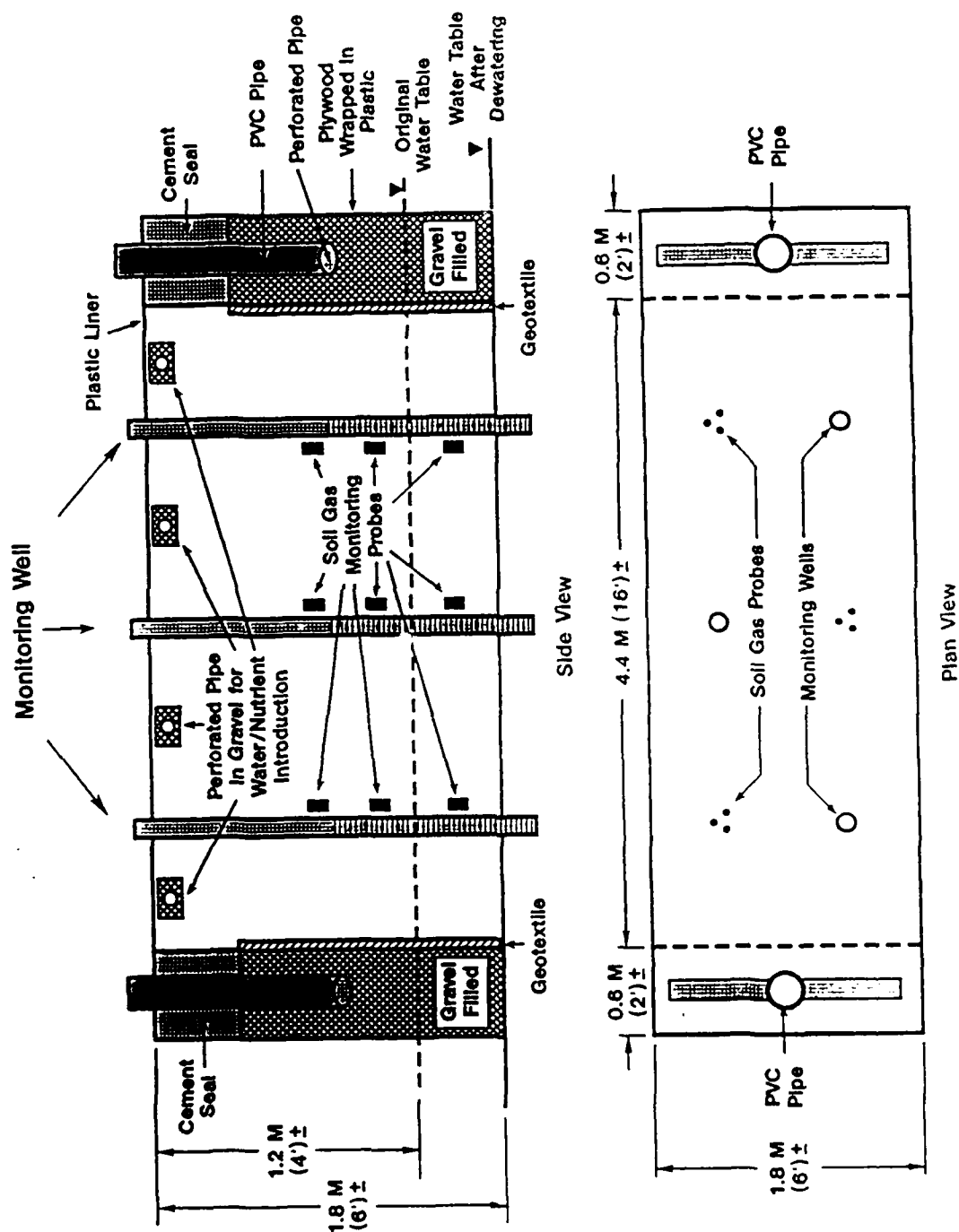


Figure 1. Design of two contaminated test cells installed at Tyndall AFB, Florida.



Figure 2. Photograph of two contaminated test cells installed at Tyndall AFB, Florida.

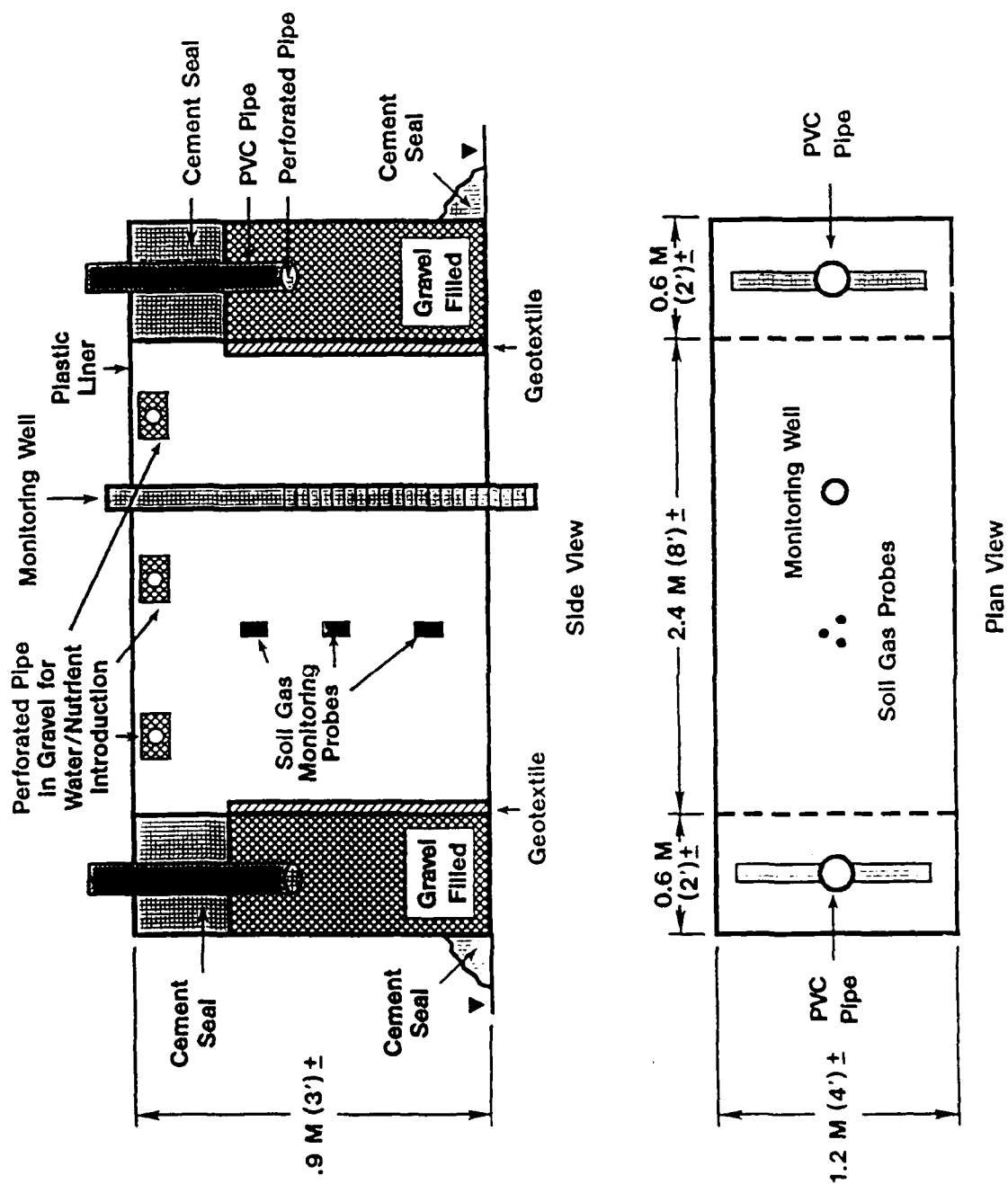


Figure 3. Design of two background test cells installed at Tyndall AFB, Florida.



Figure 4. Photograph of two background test cells installed at Tyndall AFB, Florida.

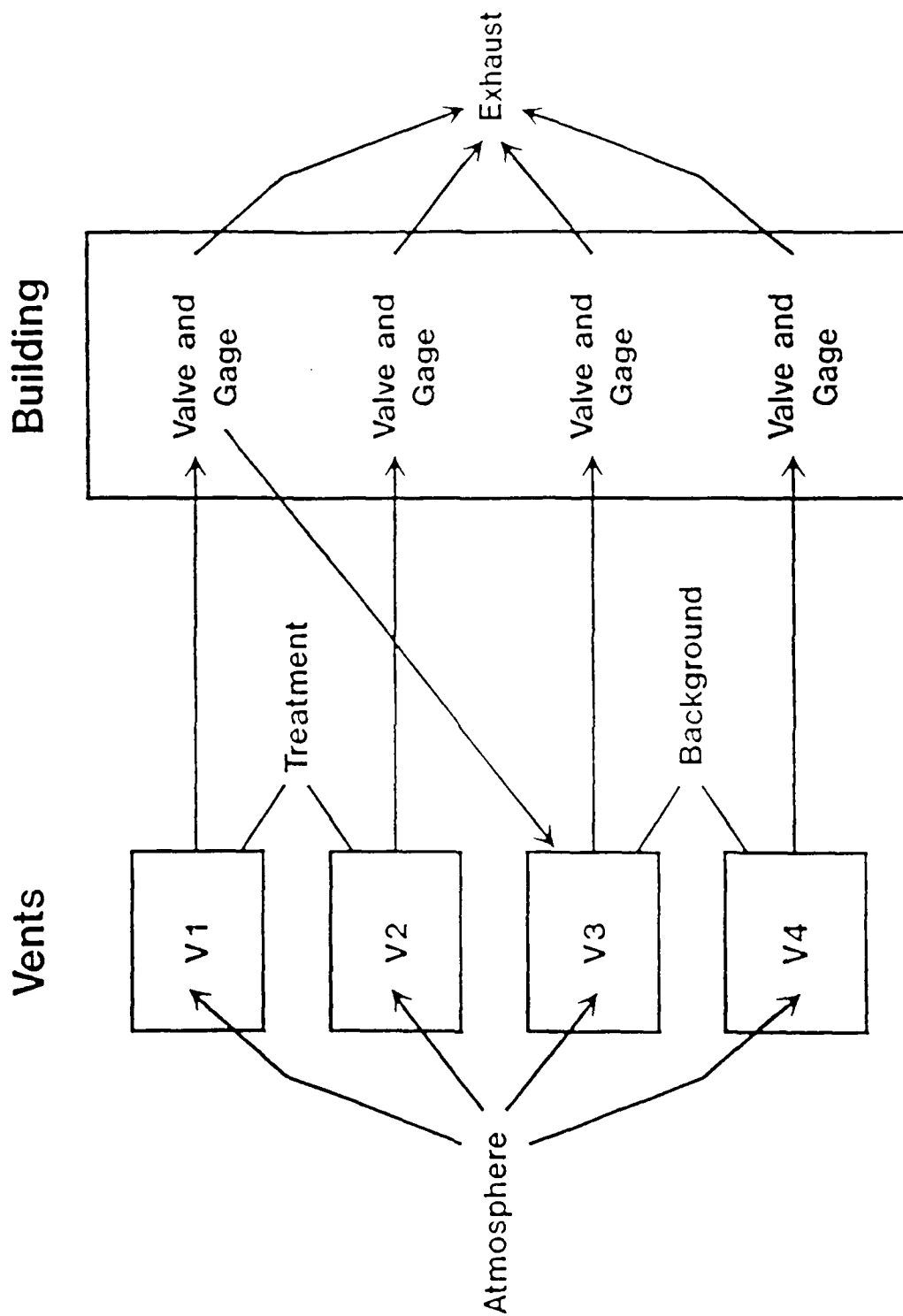


Figure 5. Air flow schematic for Tyndall AFB, Florida.

center monitoring well in V1 and V2 and from the only monitoring well in V3 and V4. This configuration was selected to minimize leakage of outside air observed when air was withdrawn from the ends of the plots. In all but one plot, V3, atmospheric air was allowed to passively enter at both ends. The atmospheric air entering V1, V2, and V4 was assumed to be hydrocarbon free. This assumption was shown to be valid because the highest background hydrocarbon concentration observed was only 6  $\mu\text{L/L}$  (ppm) and that level of contamination was observed only on rare occasions and for short durations. This concentration of atmospheric hydrocarbon contamination is insignificant considering the relatively short duration of low level atmospheric contamination and the high hydrocarbon concentration (1000 to 10,000  $\mu\text{L/L}$  (ppm)) observed in the treatment plots. The soil gas was drawn into the on-site building (Figure 6) where it was valved and gaged (Figure 7). Sample ports provided access to the gas streams. Sample ports were also located at the point of discharge from the plots. Most of the off-gas was discharged by means of an exterior stack. Off-gas from V1 was pumped back to the upstream ends of V3. The system was designed to provide variable air flow rates of 0.28 to 14 L/min in V1 and V2 and 0.044 to 2.2 L/min in V3 and V4. Experimental calculations supporting the design are located in Appendix A.

Flow rates through all test plots were measured with calibrated rotameters. Calibration corrections based on negative pressure in the rotameters were performed on December 12, 1989, and January 8, 1990. This was necessary because of deterioration of PVC lines on the flow control panel and removal of in-line valves on V1 and V2 that were initially set to minimize pressure drop through the rotameters. In addition, bubble tube calibrations

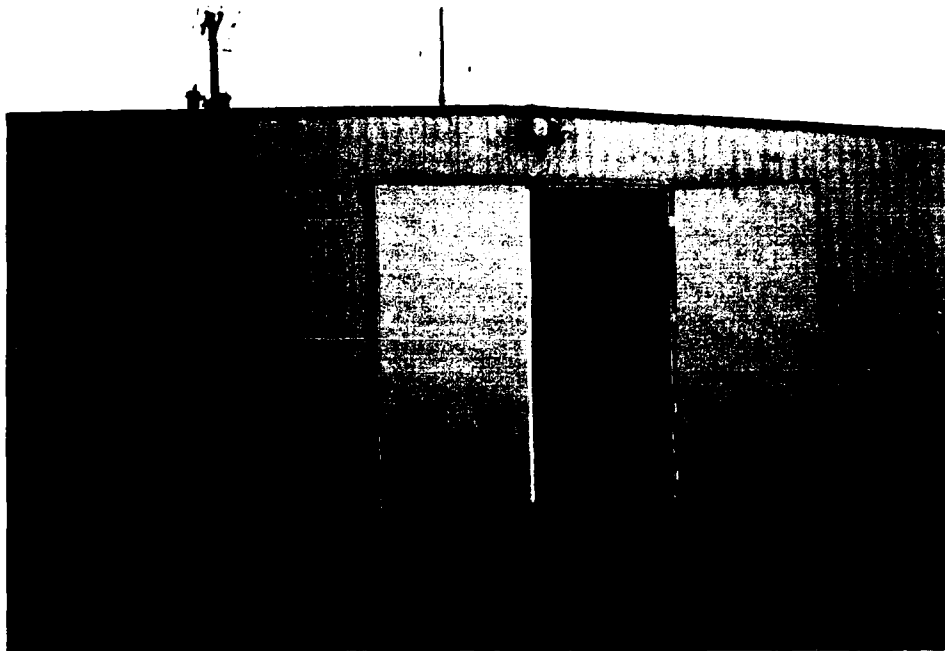


Figure 6. Photograph of site building at Tyndall AFB, Florida.



Figure 7. Photograph of air flow measurement devices installed at Tyndall AFB, Florida.

were performed January 8, 1990, to confirm the accuracy of the rotameter calibration corrections. Tables 3 and 4 summarize results of the two rotameter calibrations and Figures 8 through 11 compare calibration data results for plots V1, V2, V3, and V4. Figures 8 through 10 illustrate good agreement between pressure corrected rotameter readings and actual bubble tube measurements. Figure 10 illustrates the reproducibility of the calibration corrections since there was no change to the V3 piping between calibrations.

Based on valve removal dates, the December 12, 1989, calibration is valid from October 4 through December 29, 1989, and October 4, 1989, through January 8, 1990, for Treatment Plots V1 and V2, respectively. The January 8, 1990, calibration is valid for the remaining V1 and V2 measurements through the end of the project. The December 12, 1989, calibration is valid for all V3 measurements and the January 8, 1990, calibration is valid for all V4 measurements.

### *Water Flow*

To allow control of soil moisture, tap water was applied to the surface of the treatment plots. Figure 12 is a schematic of the water/nutrient delivery design. The design flow rates allowed variation from 10 to 100 mL/min in the contaminated treatment plots, and 2.5 to 25 mL/min in the background vents. This corresponds to average annual surface application rate of 43 to 430 cm (17 to 170 in). Based on vacuum and oxygen measurements in the soil gas monitoring probes, it was determined that a flow rate of 100 mL/min in the Treatment Plots inhibited air flow and oxygen transfer. Using the same technique, a flow rate of 50 mL/min (215 cm/yr surface application rate) was

Table 3. Rotameter calibration corrections measured December 12, 1989.

| Treatment Plot V1(#270216) |                 |                            |                                |
|----------------------------|-----------------|----------------------------|--------------------------------|
| Rotameter<br>Setting       | Vacuum<br>(kPa) | Chart Flow<br>Rate (L/min) | Corrected Flow<br>Rate (L/min) |
| 7                          | 81              | 7.75                       | 3.4                            |
| 7.75                       | 78              | 8.75                       | 4.2                            |
| 8                          | 76              | 9                          | 4.5                            |
| 9                          | 74              | 10.1                       | 5.2                            |
| 9.4                        | 69              | 10.6                       | 5.9                            |
| 10                         | 68              | 11.3                       | 6.5                            |
| 11                         | 64              | 12.4                       | 7.5                            |
| 12                         | 61              | 13.6                       | 8.6                            |
| 13                         | 54              | 14.7                       | 10.0                           |
| 13.25                      | 54              | 15                         | 10.2                           |

| Treatment Plot V2 (#270215) |                 |                            |                                |
|-----------------------------|-----------------|----------------------------|--------------------------------|
| Rotameter<br>Setting        | Vacuum<br>(kPa) | Chart Flow<br>Rate (L/min) | Corrected Flow<br>Rate (L/min) |
| 9                           | 74              | 10.2                       | 5.2                            |
| 10                          | 69              | 11.3                       | 6.3                            |
| 11                          | 68              | 12.4                       | 7.1                            |
| 12                          | 61              | 13.5                       | 8.5                            |
| 13                          | 57              | 14.5                       | 9.5                            |
| 13.4                        | 54              | 15                         | 10.2                           |

| Treatment Plot V3 (Rotameter #3) |                 |                            |                                |
|----------------------------------|-----------------|----------------------------|--------------------------------|
| Rotameter<br>Setting             | Vacuum<br>(kPa) | Chart Flow<br>Rate (L/min) | Corrected Flow<br>Rate (L/min) |
| 40                               | 81              | 7                          | 3.1                            |
| 50                               | 78              | 8.3                        | 4.0                            |
| 52                               | 76              | 8.7                        | 4.3                            |
| 55                               | 74              | 9.4                        | 4.8                            |
| 60                               | 74              | 10.4                       | 5.4                            |
| 70                               | 68              | 12.6                       | 7.3                            |
| 80                               | 66              | 14.8                       | 8.7                            |

| Treatment Plot V4    |                 |                            |                                |
|----------------------|-----------------|----------------------------|--------------------------------|
| Rotameter<br>Setting | Vacuum<br>(kPa) | Chart Flow<br>Rate (L/min) | Corrected Flow<br>Rate (L/min) |
| 112                  | 79              | 2.5                        | 1.2                            |

Table 4. Rotameter calibration corrections and bubble tube measurements taken January 8, 1990.

| Treatment Plot V1(#270216)  |              |                         |                             |                          |
|-----------------------------|--------------|-------------------------|-----------------------------|--------------------------|
| Rotameter Setting           | Vacuum (kPa) | Chart Flow Rate (L/min) | Corrected Flow Rate (L/min) | Bubble Tube Cal. (L/min) |
| 2                           | 84           | 1.75                    | 0.71                        |                          |
| 3                           | 84           | 3                       | 1.22                        |                          |
| 4                           | 84           | 4.2                     | 1.70                        |                          |
| 5                           | 83           | 5.3                     | 2.26                        |                          |
| 6                           | 82           | 6.5                     | 2.82                        |                          |
| 7                           | 82           | 7.8                     | 3.38                        |                          |
| 7.75                        | 82           | 8.75                    | 3.79                        |                          |
| 9                           | 81           | 10.1                    | 4.45                        |                          |
| 10                          | 80           | 11.3                    | 5.15                        |                          |
| 11                          | 75           | 12.5                    | 6.35                        |                          |
| 12                          | 74           | 13.5                    | 6.95                        |                          |
| 13.4                        | 73           | 15                      | 7.86                        |                          |
| 14                          | 73           | 15.7                    | 8.23                        |                          |
| 15                          | 67           | 16.8                    | 9.77                        |                          |
| 3.75                        |              |                         |                             | 1.14                     |
| 5                           |              |                         |                             | 1.71                     |
| 5.5                         |              |                         |                             | 1.94                     |
| 7.75                        |              |                         |                             | 3.05                     |
| 9                           |              |                         |                             | 4.22                     |
| 14.2                        |              |                         |                             | 8.06                     |
| Treatment Plot V2 (#270215) |              |                         |                             |                          |
| Rotameter Setting           | Vacuum (kPa) | Chart Flow Rate (L/min) | Corrected Flow Rate (L/min) | Bubble Tube Cal. (L/min) |
| 2                           | 84           | 2                       | 0.81                        |                          |
| 3                           | 84           | 3.2                     | 1.30                        |                          |
| 4                           | 84           | 4.4                     | 1.78                        |                          |
| 5                           | 84           | 5.5                     | 2.23                        |                          |
| 6                           | 83           | 6.6                     | 2.81                        |                          |
| 7                           | 83           | 7.8                     | 3.32                        |                          |
| 8                           | 83           | 9                       | 3.83                        |                          |
| 9                           | 83           | 10.2                    | 4.34                        |                          |
| 10                          | 82           | 11.3                    | 4.90                        |                          |
| 11                          | 82           | 12.4                    | 5.42                        |                          |
| 12                          | 81           | 13.5                    | 6.01                        |                          |
| 13.4                        | 80           | 15                      | 6.84                        |                          |
| 14                          | 78           | 15.5                    | 7.45                        |                          |
| 15                          | 74           | 16.6                    | 8.54                        |                          |
| 3.75                        |              |                         |                             | 1.08                     |
| 5.5                         |              |                         |                             | 2.03                     |
| 8                           |              |                         |                             | 3.65                     |
| 9                           |              |                         |                             | 4.32                     |
| 13.4                        |              |                         |                             | 7.68                     |
| 13.8                        |              |                         |                             | 8.02                     |
| 14.2                        |              |                         |                             | 8.48                     |
| 15                          |              |                         |                             | 9.04                     |

Table 4 cont. Rotameter calibration corrections and bubble tube measurements taken January 8, 1990.

| Treatment Plot V3 (Rotameter #3) |                 |                            |                                |                             |
|----------------------------------|-----------------|----------------------------|--------------------------------|-----------------------------|
| Rotameter<br>Setting             | Vacuum<br>(kPa) | Chart Flow<br>Rate (L/min) | Corrected Flow<br>Rate (L/min) | Bubble Tube<br>Cal. (L/min) |
| 20                               | 84              | 1.6                        | 0.65                           |                             |
| 30                               | 83              | 3.8                        | 1.62                           |                             |
| 40                               | 81              | 6                          | 2.67                           |                             |
| 50                               | 74              | 8.2                        | 4.22                           |                             |
| 60                               | 72              | 10.4                       | 5.61                           |                             |
| 70                               | 69              | 12.5                       | 7.09                           |                             |
| 80                               | 64              | 14.8                       | 8.94                           |                             |
| 17.5                             |                 |                            |                                | 0.67                        |
| 25                               |                 |                            |                                | 1.35                        |
| 30                               |                 |                            |                                | 1.85                        |
| 45                               |                 |                            |                                | 3.32                        |
| 70                               |                 |                            |                                | 6.58                        |

| Treatment Plot V4 (Rotameter set at 40) |                 |                            |                                |
|-----------------------------------------|-----------------|----------------------------|--------------------------------|
| Rotameter<br>Setting (V3)               | Vacuum<br>(kPa) | Chart Flow<br>Rate (L/min) | Corrected Flow<br>Rate (L/min) |
| 20                                      | 84              | 1.66                       | 0.67                           |
| 30                                      | 83              | 1.66                       | 0.71                           |
| 40                                      | 81              | 1.66                       | 0.74                           |
| 50                                      | 74              | 1.66                       | 0.85                           |
| 60                                      | 72              | 1.66                       | 0.90                           |
| 70                                      | 68              | 1.66                       | 0.94                           |
| 80                                      | 64              | 1.66                       | 1.00                           |

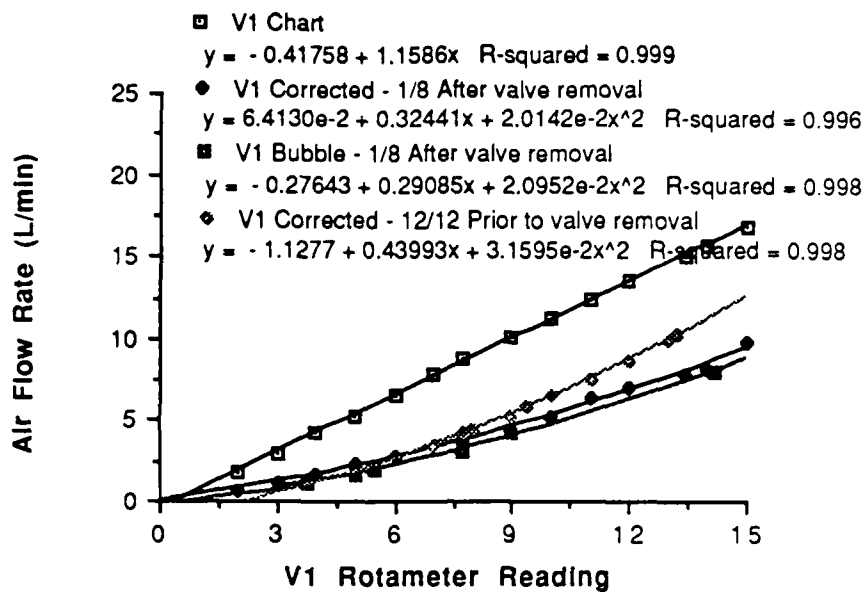


Figure 8. Calibration data for Treatment Plot V1.

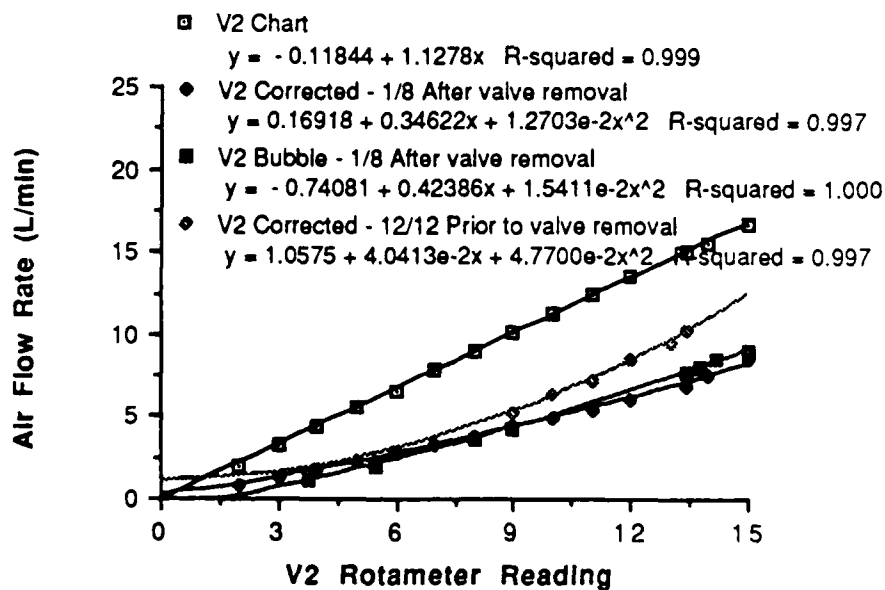


Figure 9. Calibration data for Treatment Plot V2.

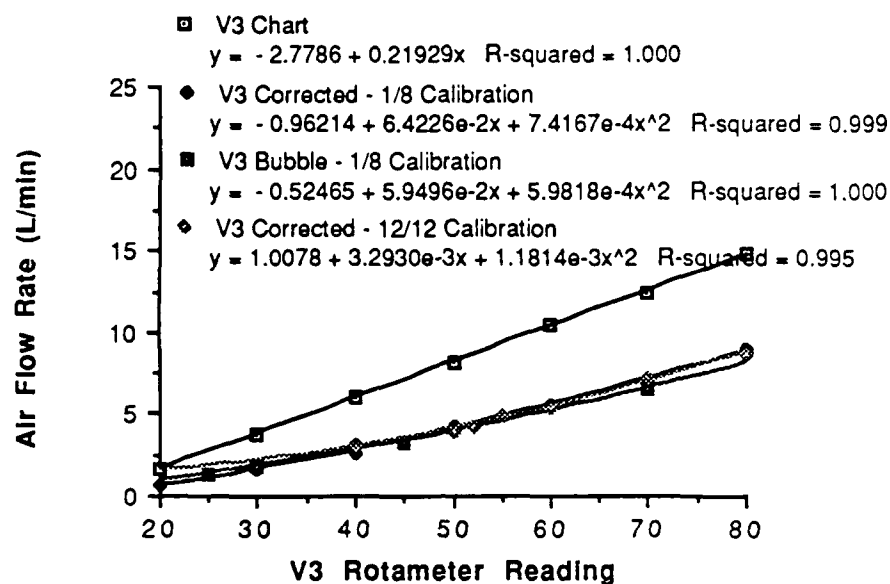


Figure 10. Calibration data for Off-Gas Treatment Plot V3.

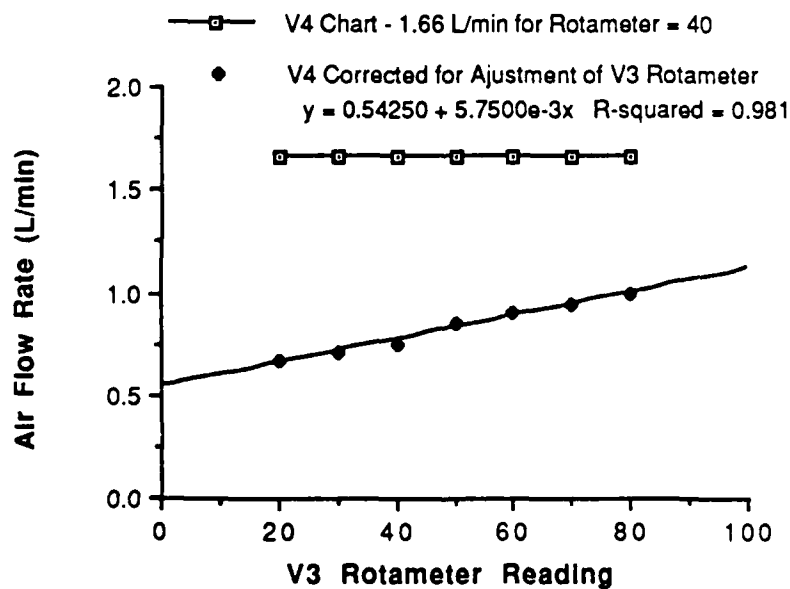


Figure 11. Calibration data for Background Plot V4 collected January 8, 1990.

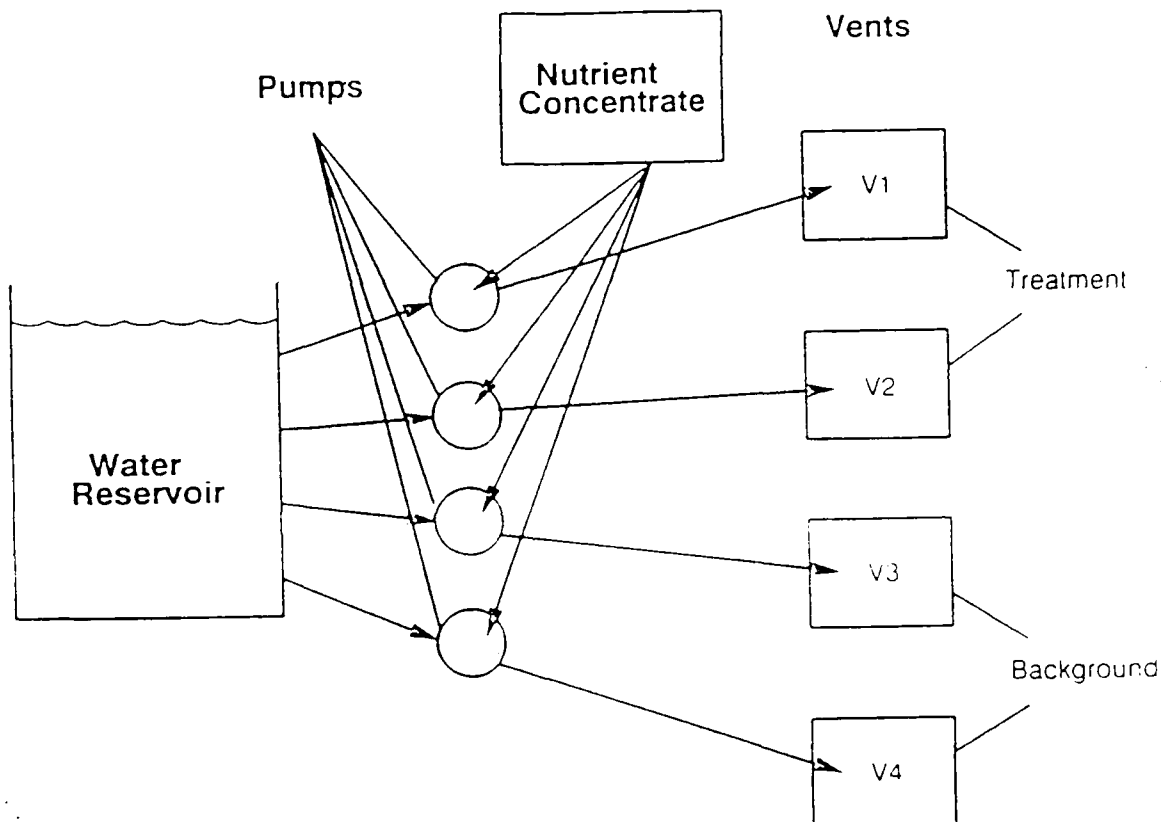


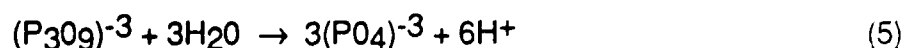
Figure 12. Schematic of water/nutrient flow design for Tyndall AFB, Florida.

selected as the final water application rate. This rate did not appear to inhibit oxygen transfer to the soil gas monitoring points. Experimental calculations supporting the design are located in Appendix A.

### *Nutrient Addition Rates*

The objective of nutrient addition was to apply sufficient inorganic nitrogen (N), phosphorus (P), and potassium (K) to ensure, as far as possible, that these nutrients would not become limiting during the biodegradation of fuel hydrocarbons in the test plots (Appendix A). Optimizing nutrient addition rates was not the primary objective of this phase of the study.

Sodium trimetaphosphate (Na-TMP), ammonium chloride (NH<sub>4</sub>Cl), and potassium nitrate (KNO<sub>3</sub>) were used as sources of P, N, and K, respectively. Existing nutrient formulations generally use Na- or K-orthophosphate as a phosphorus source. The relatively high concentration of orthophosphate in these formulations, together with the calcium and iron present in ground water results in the precipitation of insoluble phosphate salts. Excessive precipitation of the phosphate and other salts may lead to plugging of the aquifer and, therefore, is detrimental to the operation of conventional water-based bioremediation systems (Downey et al., 1988). Na-TMP is a polyphosphate (Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub>) with a ring structure; therefore, its phosphorous is not present in the nutrient form (orthophosphate). However, upon hydrolysis, the trimetaphosphate ion forms three orthophosphate ions through a series of intermediate steps illustrated by Equation 5.



The kinetics of the various hydrolysis steps are relatively slow. Preliminary laboratory studies at Battelle, Columbus indicate that TMP hydrolysis in sandy soils occurs at a rate of approximately 10%/hr (Aggarwal et al., 1990). Thus, using TMP in the formulations should provide nutrient phosphorus while minimizing orthophosphate concentrations and aquifer plugging that is observed when orthophosphate itself is used as a source of phosphorus.

Nutrient requirements were to have been based on results of the July 15, 1989, sampling of Treatment Plots 1 and 2. These samples were collected from the middle of the Treatment Plots at depths of 1, 2, and 3 ft. However, deeper samples were not possible in July because of a high water table, limiting the overall usefulness of this sampling event for design purposes.

*The July, 1989, sampling was not used for initial design purposes* because of the incomplete sampling and because sample results were not available in time for design of the nutrient delivery/measuring system. For this reason an estimate of 2,000 mg/kg total hydrocarbons was used to size rotameters and the nutrient tank. Preliminary results of the July sampling, received after design and purchase of the delivery system, indicated average concentrations in the range of 20,000 mg/kg total hydrocarbons. It was decided that the disparity was best managed by maximizing existing equipment to maintain project schedules. Concentrations of nutrients were maximized in the nutrient tank and the delivery rate was increased to the maximum of 20 mL/min. Table 5 summarizes the nutrient delivery rates obtained by the nutrient delivery equipment.

Table 5. Summary of maximized nutrient addition rates for Treatment Plots.

|                                        | NH <sub>4</sub> CL   | Na-TMP   | KNO <sub>3</sub>    |
|----------------------------------------|----------------------|----------|---------------------|
| Chemical concentration in tank (g/L)   | 29                   | 2.40     | 0.18                |
|                                        | NH <sub>4</sub> CL-N | Na-TMP-P | KNO <sub>3</sub> -K |
| Nutrient concentration in tank (g/L)   | 8                    | 0.73     | 0.07                |
| Nutrient deliv. @ 20 mL/min (g/day)    | 219                  | 21       | 2                   |
| Nutrient deliv. @ 20 mL/min (g/29 wks) | 44,500               | 4,263    | 398                 |

Using pretreatment soil samples collected to a depth of 1.5 m (5 ft), during September, 1989, the average total hydrocarbon concentration (methylene chloride extraction) was 5135 (SD  $\pm$  5032) and 7690 (SD  $\pm$  7681) mg/kg, hexane equivalent, in Treatment Plots V1 and V2, respectively. Assuming a dry soil weight of 1440 kg/m<sup>3</sup> (90 lb/ft<sup>3</sup>); a treatment plot soil volume of 20 m<sup>3</sup>; a C:N:P ratio of 100:10:1; and that two-thirds of the total hydrocarbon is mineralized and one-third is assimilated into cell mass; the required mass of nitrogen and phosphorus for biodegradation of all hydrocarbon in the treatment plots should be 4,931 and 493 g, respectively, for V1, and 7,381 and 738 g, respectively, for V2. Table 6 summarizes operation of the test plots including the periods of nutrient addition. Assuming that maximized nutrient delivery rates (Table 5) were maintained during nutrient addition periods (Table 6), 252 kg of NH<sub>4</sub>Cl (65,960 g NH<sub>4</sub>Cl-N) should have been delivered. An inventory of chemicals at the completion of the project indicated that 170 kg of NH<sub>4</sub>Cl (44,580 g NH<sub>4</sub>Cl-N) had been delivered. The lower delivery rate resulted from a tendency for the flow rates to drift downward throughout the project requiring daily flow rate adjustments. However, this analysis indicates that Treatment Plot V2, which received nutrients throughout the project, received approximately six times the theoretical nutrient requirement.

Table 6. Operating conditions prior to respiration tests in each plot.

| Test No. | V 1                                                                     | V 2                                                     | V 3                                                                                                         | V 4                                                     |
|----------|-------------------------------------------------------------------------|---------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|
| 1        | 3 weeks venting<br>no added moisture<br>no added nutrients              | 3 weeks venting,<br>moisture, and<br>nutrient addition  | 3 weeks diluted<br>off-gas from V1,<br>moisture, and<br>nutrient addition<br>Note: PVC problems             | 3 weeks venting,<br>moisture, and<br>nutrient addition  |
| 2        | 8 weeks venting<br>no added moisture<br>no added nutrients              | 8 weeks venting,<br>moisture, and<br>nutrient addition  | 8 weeks diluted<br>off-gas from V1,<br>moisture, and<br>nutrient addition<br>Note: Inlet PVC pipe<br>broken | 8 weeks venting,<br>moisture, and<br>nutrient addition  |
| 3        | 13 weeks venting,<br>5 weeks of moisture,<br>no nutrient addition       | 13 weeks venting,<br>moisture, and<br>nutrient addition | 5 weeks of direct<br>flow from V1<br>13 weeks of moisture<br>and nutrient addition                          | 13 weeks venting,<br>moisture, and<br>nutrient addition |
| 3 A      | 16 weeks venting,<br>8 weeks moisture,<br>no nutrient addition          | 16 weeks venting,<br>moisture, and<br>nutrient addition | 8 weeks of direct<br>flow from V1<br>16 weeks of moisture<br>addition, no nutrients<br>since Test 3         | 16 weeks venting,<br>moisture, and<br>nutrient addition |
| 4        | 22 weeks venting,<br>14 weeks moisture,<br>no nutrient addition         | 22 weeks venting,<br>moisture, and<br>nutrient addition | 19 weeks of direct<br>flow from V1<br>22 weeks of moisture<br>addition, no nutrients<br>since Test 3        | 22 weeks venting,<br>moisture, and<br>nutrient addition |
| 4 a      | N/A                                                                     | N/A                                                     | 3 days direct<br>injection of high<br>concentration JP-4                                                    | N/A                                                     |
| 5        | 29 weeks venting,<br>21 weeks moisture,<br>7 weeks nutrient<br>addition | 29 weeks venting,<br>moisture, and<br>nutrient addition | 7 weeks of venting<br>atmospheric air<br>29 weeks of moisture<br>addition, no nutrients<br>since Test 3     | 29 weeks venting,<br>moisture, and<br>nutrient addition |

Treatment Plot V1 received nutrients for the final seven weeks of the project for a nitrogen/phosphorus loading of approximately 7,190 and 700 g, respectively. Since approximately half of the hydrocarbon had been removed from V1 prior to nutrient addition, the theoretical nitrogen and phosphorus requirement would be approximately 2,464 and 246 g, respectively. Therefore, although V1 received nutrients for only seven weeks, approximately three times the theoretical requirement was delivered. Also, increasing nutrient concentrations in ground water samples collected from V2 at 1- 2- 3- and 5-month intervals, after initiation of nutrient addition, indicated that significant amounts of nutrients were passing unused through the Treatment Plot.

This excess nutrient addition resulted from an abnormally high estimate of soil hydrocarbon concentration based on preliminary results of the limited July, 1989, samples and the four month extension to the project. Also, nutrient additions were calculated on the basis of total hydrocarbons without considering the fraction removed by volatilization and the fact that only approximately one-third of the biodegraded fuel would be converted to cell mass and two-thirds mineralized to CO<sub>2</sub> and water. The intent was to ensure that nutrients, if being delivered, were not limiting. This analysis indicated that the objective was achieved. Soil samples collected at the termination of experiments were compared to initial soil samples to confirm uniform nutrient delivery throughout the test plots.

## Evaluation of Control Variables

### *Demonstrating Enhanced Biodegradation and Effects of Moisture and Nutrient Addition*

The vented gas was monitored throughout the seven month project to assess the overall effect of moisture, nutrient addition, and venting rate on the utilization of oxygen, the production of carbon dioxide, and the mass of volatilized hydrocarbon in the vented gas. In addition, five respiration tests were conducted following periods of operation under varying conditions of moisture and nutrient addition. The respiration (shutdown) tests consisted of measuring oxygen consumption and carbon dioxide production with time following shutdown of the air venting system. Results (Appendix B) of operational and shutdown data were used to calculate the percentages of total hydrocarbons removed by biodegradation and volatilization, and oxygen consumption rate constants ( $k$ ) under varying conditions of flow rate, moisture, and nutrient addition. Table 6 summarizes operating conditions throughout the project and prior to the respective respiration tests for both treatment and background plots. Air samples were collected in stainless steel canisters and analyzed by gas chromatography to confirm field measurements of total hydrocarbons, oxygen, and carbon dioxide.

Gravimetric soil moisture analyses of both treatment and background plots were completed prior to start-up and during the final characterization effort. In addition, a limited number of samples were collected from the Treatment plots after two months of operation to determine the extent to which venting caused drying of the soil. This information is only an indicator of the range of soil moisture under which the field test was operated. Additional Air Force

Engineering and Services Center (AFESC) supported research for optimizing soil moisture for biodegradation is ongoing at this site.

*Demonstrating Hydrocarbon  
Removal with Soil Sample Data*

In addition to the operational and respiration (shutdown) data, comparison of the pre- and post-treatment soil samples may be a significant indicator of the success of the technology. The problem associated with conclusions based on comparison of pretreatment and post-treatment soil sampling is the inherent high variability of field measured soil hydrocarbon concentrations. A pilot test for *in situ* air stripping of trichloroethylene (TCE) contaminated soil found that some post-test soil concentrations were three orders-of-magnitude higher than pre-test concentrations (Anastos et al., 1985). Although some of the increase may have been attributed to migration of TCE toward the extraction points, the authors attribute the results to high variability (over five orders-of-magnitude) in soil concentrations in both sets of samples.

Initial site characterization confirmed similar heterogeneity at the field site selected for this project. Soil gas analyses revealed variability throughout the treatment area of up to three orders-of-magnitude. Soil gas concentrations in the A probes (30 to 45 cm; 1-1.5 ft) were over four times higher in V1 than in V2. Based on the September, 1989, soil samples, hydrocarbon concentrations varied over two orders-of magnitude in V1 and V2 and average hydrocarbon concentrations were 50% higher in V2 than in V1. The disparity between soil gas phase and soil solid phase results for samples occurred because the hydrocarbon concentrations in V1 were highest at the 30 cm level whereas in V2 the 30 cm level had the lowest hydrocarbon concentration. The high water table in July, 1989, prior to the dewatering effort, prevented a soil gas survey

using the deeper soil gas probes; the result was an erroneous interpretation of relative contamination levels. The disparity between soil gas phase and soil solid phase results illustrates the danger of drawing firm conclusions from limited soil gas surveys.

Statistically significant conclusions, concerning cleanup effectiveness, based on soil sample results are difficult unless the soil is cleaned to the extent that order-of-magnitude variability is no longer a factor. The high variability in soil hydrocarbon concentrations at the field site poses two questions. First, does the variability in soil concentrations allow for conclusions based on results of pretreatment and post-treatment soil samples? Second, is it possible to compare treatment plots statistically? Considering the first problem, a primary objective was to clean the soil within the time frame allowed for the project. Since minimizing volatilization was also an objective, there was some concern that time limitations would not allow both objectives to be met. In an attempt to satisfy both objectives, Treatment Plot 2 was operated with moisture and nutrient addition from the beginning in an attempt to maximize cleanup rate and extent. In addition, a four month extension to the project was requested and granted. Considering the second problem, total hydrocarbon concentrations, based on methylene chloride extractions of the September, 1989, samples, averaged 5135 (SD  $\pm$  5032) and 7690 (SD  $\pm$  7681) mg/kg for V1 and V2, respectively. A paired students t-test of these data indicates that hydrocarbon concentrations in V1 and V2 are not statistically different and technically could be compared to each other. Although this strategy may be statistically sound, it was used with caution because of the high variability in soil hydrocarbon concentrations.

Background plots were located within 30 m (100 feet) of the treatment plots during the initial characterization effort in July, 1989. Hydrocarbon concentrations were below detectable levels throughout the background area. Both background plots were vented and received amendments provided to treatment plots. One background plot was used to quantify background *in situ* respiration while the other was used to evaluate the capacity of the soil to degrade hydrocarbons in the off-gas from Treatment Plot 1.

#### *Hydrocarbon Vapor Off-Gas Biodegradation*

The soil venting project at Hill AFB, Utah demonstrated that venting is an efficient method for delivering oxygen for microbial degradation (Hinchee et al., 1989a). Unfortunately, soil venting produces an effluent which may require expensive treatment prior to discharge. Re-injection of the off-gas or an alternate extraction configuration for maximizing microbial degradation is an attractive and potentially cost effective alternative to conventional vent system design. To assess the feasibility of alternate venting designs, hydrocarbon off-gas from V1 was pumped to the upstream ends of V3. Hydrocarbon, oxygen, and carbon dioxide were monitored at the inlet and discharge points of V3 with the intent of observing a loss of oxygen and stoichiometric equivalent amount of hydrocarbon (Equation 2).

Initially, and for a period of approximately two months, off-gas from V1 was diluted prior to injection to V3 to ensure adequate oxygen/hydrocarbon ratios. Operation during this period was hindered by deterioration of PVC fittings associated with piping between V1 and V3 and the fact that the water table had fallen 30 to 60 cm (1 to 2 ft) below the walls of the V3 plot. PVC piping was removed from the system; the water table was artificially raised; and off-gas from

V1 was injected directly into V3 for approximately three months. This was possible because by that time, oxygen/hydrocarbon ratios in V1 off-gas were adequate for complete mineralization. Hydrocarbon concentrations in the discharge air stream of V3 were consistently lower than the inlet concentrations. Unfortunately, oxygen concentrations were consistently higher in the discharge than in the inlet gas streams. It was obvious that the plot was leaking significantly and masking any oxygen consumption resulting from the observed loss of hydrocarbons. Although leakage was obvious, the magnitude of the hydrocarbon loss could not be totally explained by the leakage calculated from increased oxygen concentrations.

It was determined that a higher concentration of hydrocarbon, injected at a lower flow rate, would be needed to observe oxygen consumption resulting from mineralization of the hydrocarbon. Eighteen L (5 gallons) of JP-4 were sparged with air for 24 hours to strip the lighter compounds so that a relatively constant concentration of JP-4 vapor could be maintained. The JP-4 vapor was diluted with atmospheric air to achieve the necessary oxygen/hydrocarbon ratio required for mineralization prior to injection into V3. This test lasted three days and was successful to the extent that an oxygen loss of approximately 3% was observed even though the discharge was diluted by leakage of near atmospheric concentrations of oxygen. A mass balance approach was used to quantify both the rate of leakage and the rate of oxygen consumption ( $k$ ) in V3. The mass balance problem is illustrated and equations for the calculated leakage rate and  $k$  values are presented in Appendix A.

## Analytical Methods

### *Field Methodology*

A Summit Interests (Denver, Colorado) Portable GC, Model 1000, with an FID detector was used to determine total hydrocarbons in soil gas. Carbon dioxide and oxygen concentrations in soil gas were measured using a Gastechtor, Model 32520X, manufactured by Gastech Inc. (Newark, California), which includes an IR detector for CO<sub>2</sub> and an electrochemical cell for O<sub>2</sub> analyses. A Scott flow blender was used with both instruments to dilute samples. Dilution was necessary to remain within the linear range of the FID and to ensure adequate O<sub>2</sub> for FID operation since combustion air is taken from the airstream sampled. Dilution of CO<sub>2</sub> samples was necessary for measurements above the 5% upper scale range of the Gastechtor instrument. Carbon dioxide samples collected after January 2, 1990, did not require dilution because a full-scale model of the Gastechtor was obtained. Figure 13 illustrates the sampling train used to obtain field samples and Figure 14 is a photograph of the actual equipment. The sampling train was designed not only to allow dilution but to ensure that samples were collected at the same pressure (atmospheric) under which the instruments were calibrated.

*Total Hydrocarbon Measurements.* Total hydrocarbon concentrations were measured in both the treatment and background plots during a soil gas survey conducted at the site during the period of July 14 to 19, 1989. Hydrocarbon concentrations in the treatment plots were found to be much too high to allow measurement within the linear response range of the GC/FID. It was for this reason that the Scott air flow blender was obtained. The air flow

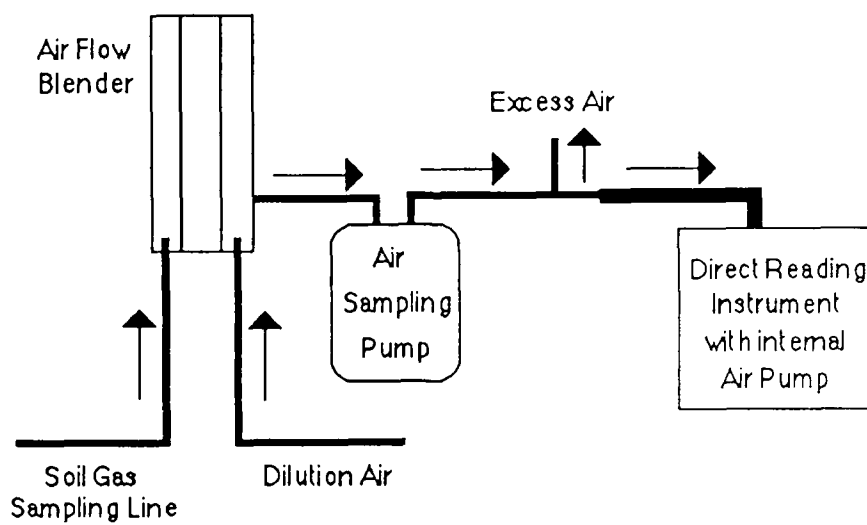


Figure 13. Illustration of sampling train used to obtain field samples.



Figure 14. Photograph of sampling train used to obtain field samples.

blender was calibrated with a bubble tube meter to obtain accurate air flow rates.

Figures 15 and 16 are the calibration curves for the flow blender. In all cases the left rotameter was used for the sample flow and the right rotameter for dilution flow. The hydrocarbon concentration of the dilution air was assumed to be zero in all cases. Specific rotameter settings measured for the calibration were used when possible and actual calibrated flow rates were used. If additional rotameter settings were required, flow rates were obtained from the calibration equation. This procedure for field soil gas hydrocarbon samples was used throughout the project.

The portable GC purchased for this project was shipped directly to Tyndall AFB for use during the July, 1989, visit. This was necessary because of the short time frame between contract award and the initial site visit. Standard gases ordered for GC calibration did not arrive on time necessitating the formulation of standards on site. Because of time restraints during the July, 1989, visit it was not possible to critically evaluate the GC until a later date. A series of calibration curves were subsequently run to evaluate linearity and reproducibility. Figure 17 is a summary of calibration curves. Trials 1 through 7 were run at the Utah Water Research Laboratory (UWRL), Utah State University. With the exception of Data Sets 7 and 8, bulk standards were diluted with the Scott flow blender to obtain the calibration curves shown. Data Set 7 represents three separate formulations in tedlar bags with no dilution. The instrument was calibrated under various conditions of power supply (battery only and charger connected) to evaluate possible differences.

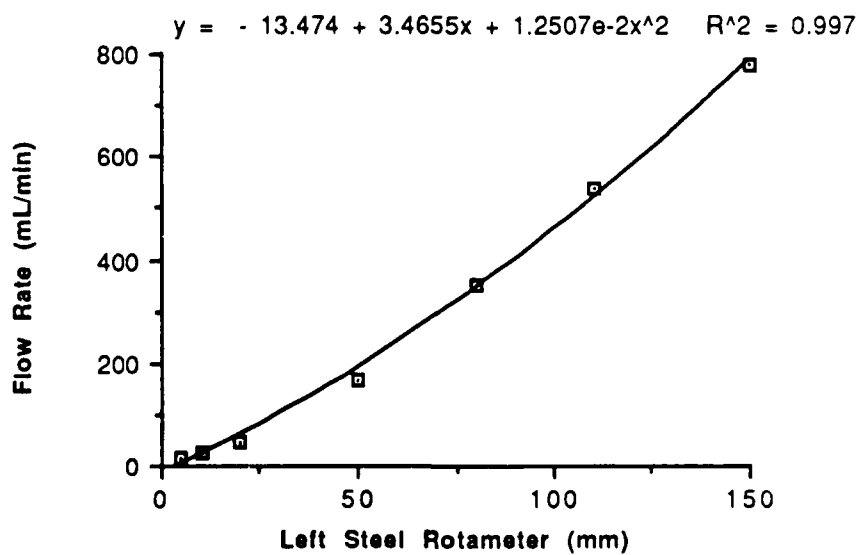
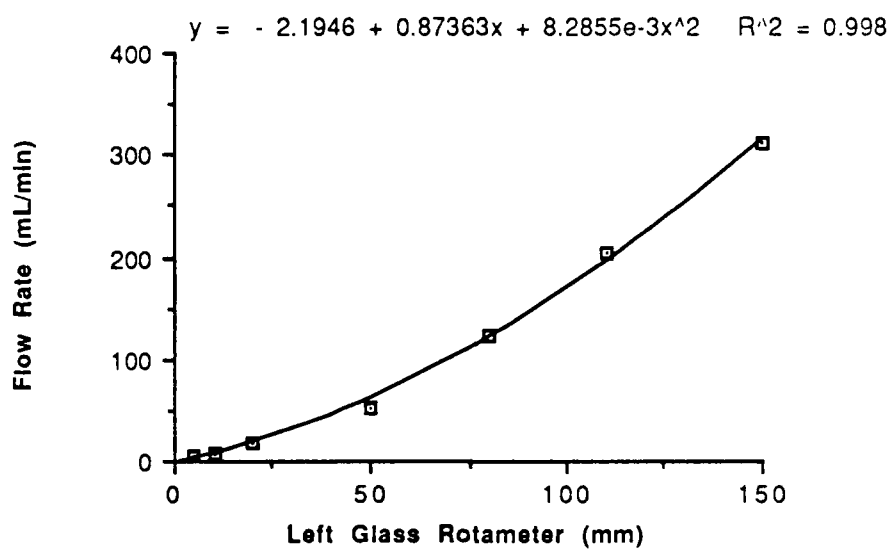


Figure 15. Calibration curves for the left (sample) rotameter.

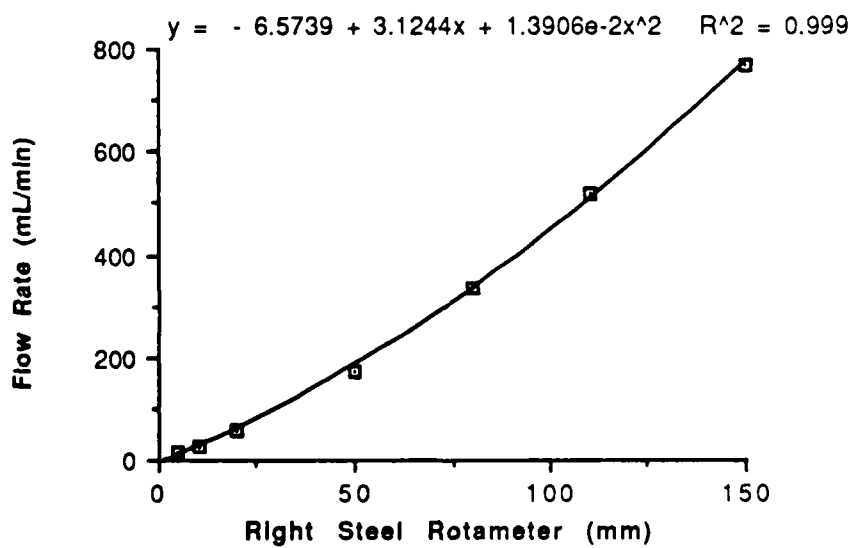
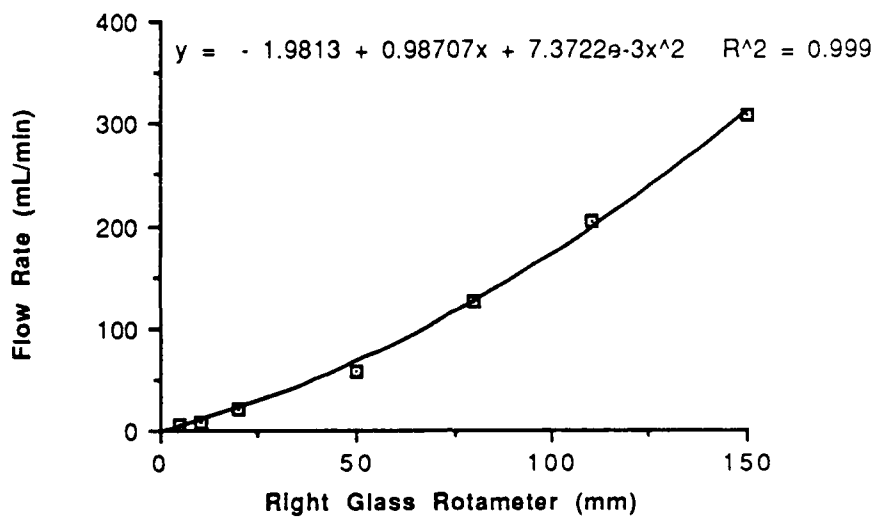


Figure 16. Calibration curves for the right (dilution) rotameter.

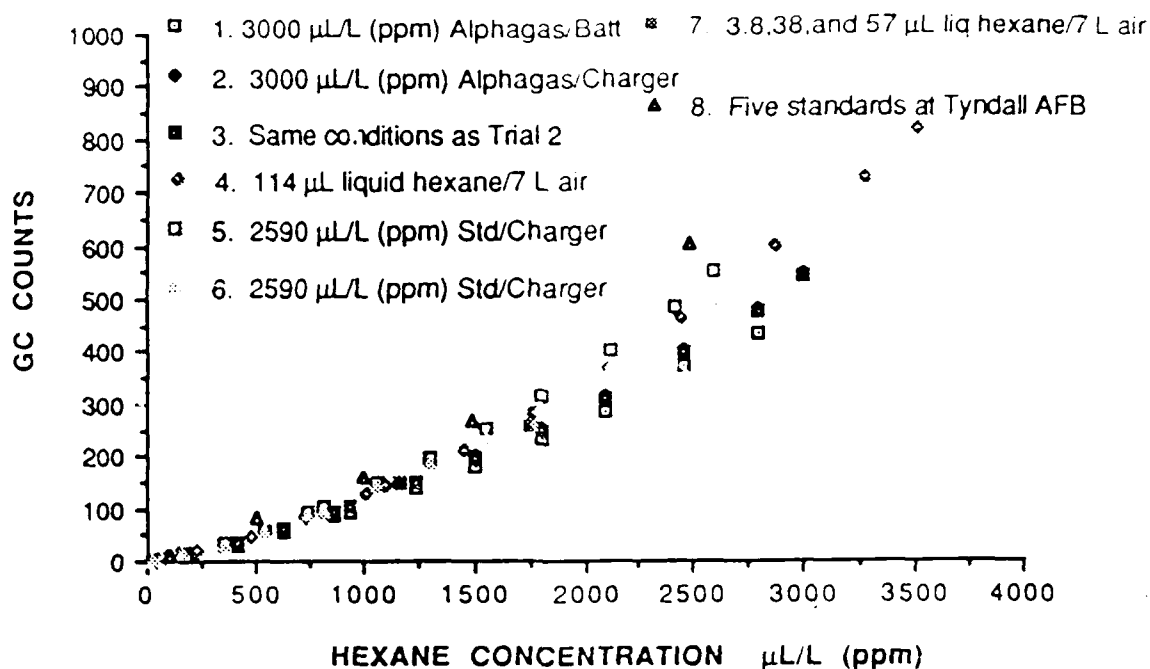


Figure 17. Summary of calibration curves for the SIP 1000 GC showing nonlinearity at higher concentration ranges.

The calibration curves show excellent agreement between the formulated bulk standards and the commercial 2590  $\mu\text{L/L}$  (ppm) standard. Interestingly, agreement between commercial standards was not as good. All standards were in agreement and linear up to 1000  $\mu\text{L/L}$  (ppm).

Trial 8 was run at Tyndall AFB on 29 September, 1989, after receiving standards ordered for the project. The slightly higher GC counts probably result from the difference in atmospheric pressure between Utah and Florida. A pressure correction reduces the GC counts to the range of GC counts measured at the UWRL in Utah. In the linear response range of the instrument (0-1000  $\mu\text{L/L}$  (ppm)), a GC count is equivalent to approximately 6.3  $\mu\text{L/L}$  (ppm) hexane.

Figure 18 illustrates the 29 September, 1989, calibration at Tyndall AFB and the regression for the 101, 505, and 1005  $\mu\text{L/L}$  (ppm) hexane standards obtained from Air Products Inc. (Panama City, Florida).

Figures 17 and 18 show that the instrument has a linear response from 0 to 1000 ppm but is not linear at higher concentrations. However, regressions of data in discrete ranges between 0 to 1000, 1000 to 2000, and 2000 to 3000  $\mu\text{L/L}$  (ppm) were linear with high regression coefficients (coefficient of determination). Recommended laboratory practice suggests however, that if possible, the instrument should be used in the 0 to 1000  $\mu\text{L/L}$  (ppm) range.

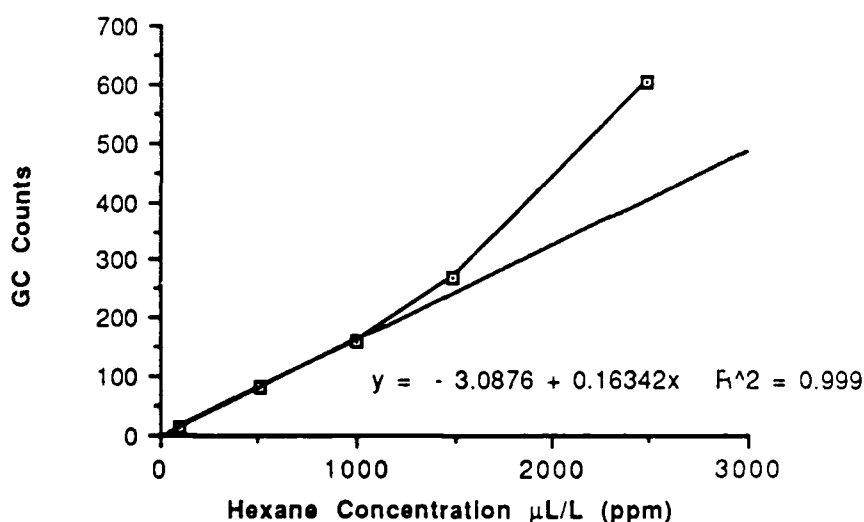


Figure 18. Five standard calibration at Tyndall AFB on September 29, 1989.

The Scott air flow blender has a dilution capacity of 100 to 1 but is more accurately read at ratios less than 50 to 1. The combination of a 50 to 1 dilution ratio and a maximum GC concentration of 1000  $\mu\text{L/L}$  (ppm) proved to be adequate as maximum concentrations, following initiation of venting, did not

exceed 33,000  $\mu\text{L/L}$  (ppm). Single point calibrations, with commercial standards, were run daily both before and after sample collection.

*Carbon Dioxide and Oxygen Analyses.* As described above, instrumentation was a Gastechtor, Model 32520X, manufactured by Gastech Inc. (Newark, California). Ranges for  $\text{O}_2$  and  $\text{CO}_2$  were 0 to 25 % and 0 to 5%, respectively (A replacement Gastechtor with a 0 to 25%  $\text{CO}_2$  scale was used after January 2, 1990). This instrument was also delivered directly to Tyndall AFB for the July, 1989, visit because of the time constraints described above. The  $\text{CO}_2$  range was not high enough for the expected maximum concentrations. However, because dilution was necessary for hydrocarbon analyses, it was decided to keep the instrument as delivered and dilute the sample when necessary. This strategy allowed the use of the hydrocarbon sampling train while providing a more accurate  $\text{CO}_2$  measurement at low concentrations.

Calibration of the  $\text{O}_2$  scale was accomplished by zeroing the instrument to nitrogen gas and spanning to 20.9% with atmospheric air. Carbon dioxide calibration was accomplished by zeroing (0.03%) with atmospheric air and spanning to either a 3.5, 5.1, or 20.1% commercial standard. Calibrations were accomplished daily both before and after sample collection.

#### *Laboratory Methods*

*Total Organic Carbon (TOC) in Water Samples.* Water samples were collected in the field and stored in amber glass bottles with teflon-lined caps at 4°C with minimal exposure to light until analysis. Total organic carbon was determined using Method 415.1 (U.S. EPA, 1986). In this method, organic carbon is converted to carbon dioxide by catalytic combustion. The amount of

carbon dioxide formed is measured directly by an infrared detector. An Oceanography International Model 0524B Carbon Analyzer was used for all TOC determinations.

*Specific Organic Compounds and Total Hydrocarbons in Water*

*Samples.* A purge and trap method, Method 5030 (U.S. EPA, 1986), was used to extract and concentrate volatile compounds from water samples. A 100  $\mu$ L aliquot of sample was injected into 5 mL of organic-free DDW contained within a purging chamber, where it was purged at 40 mL/min with organic-free nitrogen for 12 min. Volatile organic compounds purged from the chamber were collected on Tenax sorbent tubes. The Tenax sorbent tubes were then analyzed for specific volatile organics listed in Table 7 using a Supelco thermal desorption unit interfaced to a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector and Baseline 810 Chromatography Data acquisition system.

Table 7. Specific organic compounds determined by gas chromatographic analysis.

| Aromatics       | Aliphatics          |               |
|-----------------|---------------------|---------------|
| benzene         | 2-methylbutane      | n-octane      |
| toluene         | n-pentane           | n-decane      |
| p-xylene        | 2-methylpentane     | n-dodecane    |
| n-propylbenzene | n-hexane            | n-tridecane   |
| n-butylbenzene  | 2,4-dimethylpentane | n-tetradecane |
|                 | n-heptane           | n-pentadecane |

Semi-volatile compounds were determined using a liquid-liquid extraction method, Method 3510 (U.S. EPA, 1986), followed by gas chromatograph analysis using a flame ionization detector. A 500 mL aliquot of the sample was extracted three times with 30 mL volumes of dichloromethane.

The dichloromethane extracts were combined and concentrated to 5 mL using a Kuderna-Danish apparatus. The concentrated extracts were dried over anhydrous sodium sulfate and then analyzed for specific non-volatile organics listed in Table 7 using a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector and a Baseline 810 Chromatography Data acquisition system. Total petroleum hydrocarbons were determined using a hexane standard and a mixed aliphatic standard containing C-5 to C-15 hydrocarbons.

*Specific Volatile Organic Compounds and Total Hydrocarbons in Soil Samples.* Volatile organic compounds in the soil cores were determined using a modification of EPA Methods 5030 and 8020 (U.S. EPA, 1986). A subsample of soil, approximately 80 g, was extruded from the core and placed directly into a tared, wide mouth glass vial containing a known volume of methanol. The vial was quickly sealed with a screw-top teflon-lined septa cap and reweighed to determine the exact amount of soil added (soil moisture content was determined and hydrocarbon concentrations are reported in mg/kg dry weight). Methanol was then added to fill the vial and eliminate head space above the liquid before completing a final weight for the soil/methanol mixture. The soil/methanol mixture was tumbled for approximately 1 hour, then was centrifuged at 2000 rpm for 20 minutes to separate the phases. An aliquot of the methanol layer was injected into 5 mL of organic-free DDW contained within a purge chamber located on a Tekmar LSC-1 Liquid Sample Concentrator, where it was purged with 40 mL/min of nitrogen for 12 minutes. The volatile organics purged from the methanol extract were collected on Tenax sorbent tubes. Prior to use, the Tenax sorbent tubes were stored in muffled glass culture tubes, placed within air tight metal containers, at 4°C. The Tenax sorbent tubes were then analyzed for specific volatile organics listed in Table 7

using a Supelco thermal desorption unit interfaced to a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector and Baseline 810 Chromatography Data acquisition system. Total petroleum hydrocarbons were determined using a hexane standard and a mixed aliphatic standard containing C-5 to C-15 hydrocarbons.

*Specific Non-Volatile Organic Compounds and Total Hydrocarbons in Soil Samples.* A modification of a gas chromatographic method reported by Vandegrift and Kampbell (1988) was used for the analysis of the specific non-volatile compounds in the soil core samples. A subsample of soil, approximately 100 g, was extruded from the core and placed directly into a tared wide mouth glass jar (soil moisture content was determined and hydrocarbon concentrations are reported in mg/kg dry weight). The jar was then reweighed to determine the exact amount of soil added. A known volume (80 to 100 mL) of dichloromethane was added and the jar was sealed with a screw-top teflon-lined septa cap. The soil/dichloromethane mixture was tumbled for approximately 1 hour, then centrifuged at 2000 rpm for 20 minutes to separate the phases. A 50 mL aliquot of the dichloromethane was removed and concentrated to 5 mL using a Kuderna-Danish apparatus. The concentrated extract was then analyzed for specific non-volatile organics listed in Table 7 using a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector and a Baseline 810 Chromatography Data acquisition system. Total petroleum hydrocarbons were determined using a hexane standard and a mixed aliphatic standard containing C-5 to C-15 hydrocarbons.

*Specific Organic Compounds and Total Hydrocarbons in Soil Gas (Canister) Samples.* Soil gas samples were collected in evacuated stainless steel canisters. Prior to use, the canisters were muffled and evacuated to

establish a vacuum for sampling. Samples were analyzed for the specific constituents listed in Table 7 by direct injection of the vapor into a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector and a Baseline 810 Chromatography Data acquisition system. Total petroleum hydrocarbons were determined using a hexane standard and a mixed aliphatic standard containing C-5 to C-15 hydrocarbons.

*Total Nitrogen.* The determination of total nitrogen in air-dried soil samples was first attempted using the Dumas method with a Coleman (Coleman Instruments Division, Perkin-Elmer Corp., Oak Brook, Illinois) nitrogen analyzer (Bremner and Mulvaney, 1982). However, it was determined that this method was not sensitive enough to determine total nitrogen prior to nutrient addition. Total Kjeldahl Nitrogen (TKN) was determined on all samples to allow calculation of available organic nitrogen. The Semi-Micro-Kjeldahl Method (APHA, 1989) was used. Approximately 0.5 g of soil was digested using a Technicon Model BD-40 Block Digester prior to distillation and determination of ammonia nitrogen in the distillate by Nesslerization. Dissolved TKN in water samples was analyzed using the same method.

*Ammonium-Nitrogen.* Ammonium-nitrogen ( $\text{NH}_4^+\text{-N}$ ) was extracted from air-dried soil with 2 M KCl solution in a 1:10 (w:v) slurry. The slurry was shaken for 1 hour at 150 rpm on an orbital shaker. After centrifugation, the supernatant was analyzed by distillation with Nesslerization (APHA, 1989). Dissolved  $\text{NH}_4^+\text{-N}$  in water samples was analyzed using the same distillation with Nesslerization method.

*Nitrate and Nitrite-Nitrogen.* Soil nitrate and nitrite-nitrogen were determined in 1:10 (w:v) deionized water extracts. The concentrations of  $\text{NO}_3^-$  and  $\text{NO}_2^-\text{-N}$  in the extracts were determined using ion chromatography

(U.S. EPA, 1984). Ten grams of air-dried soil were suspended in 100 mL of laboratory grade deionized water in a 250-mL Erlenmeyer flask. The flask was covered with aluminum foil and shaken on an orbital shaker at 150 rpm for 1 hour. A 50-mL aliquot of the slurry was centrifuged at  $10,000 \times g$  for 15 minutes. The supernatant was then filtered through a  $0.45 \mu\text{m}$  pore size membrane filter that had been pre-rinsed with 100 mL of deionized water. The filtrate was analyzed for  $\text{NO}_3^-$ - and  $\text{NO}_2^-$ -N. Because  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are anions, they are highly mobile in soil. Nitrate and nitrite-nitrogen that is readily available to soil microbes should, therefore, be easily extracted with water. Using a simple water extract also helps avoid ion chromatography interference, which may arise from high concentrations of chloride in the KCl extract recommended by Keeney and Nelson (1982). Dissolved  $\text{NO}_3^-$ - and  $\text{NO}_2^-$ -N in water samples were analyzed using the same method.

*Water-Soluble Phosphate.* Available orthophosphate-phosphorus ( $\text{PO}_4$  -P) in the soil samples was estimated as water extractable  $\text{PO}_4$ -P (Olsen and Sommers, 1982). The same 1:10 (w:v) soil extract prepared for  $\text{NO}_3^-$ - and  $\text{NO}_2^-$ -N determinations was analyzed for  $\text{PO}_4$ -P by ion chromatography (U.S. EPA, 1984). Dissolved  $\text{PO}_4$  -P in water samples was determined using the same method.

*Total Phosphorus.* Total phosphorus was determined from a perchloric acid digestion of a 2 g portion of the air dried soil sample followed by vanadomolybdomate colorimetry as described by Olsen and Sommers (1982).

*Nitrogen Fixation (Acetylene Reduction) Potential.* Soil nitrogenase (nitrogen fixation) activity was assayed using the acetylene reduction assay (Knowles, 1982). Ten g of soil, at field moisture content, was weighed into 70 mL glass serum bottles. Each bottle was stoppered with a rubber septum and

flushed with nitrogen for 5 minutes using hypodermic needles to introduce and vent the nitrogen. Six mL of nitrogen were withdrawn from the bottle with a hypodermic syringe and 6 mL of acetylene were added to provide approximately 10 kPa (0.1 atm) of acetylene. The samples were incubated for 42 to 50 hours in the dark at 25°C. Ethylene production was monitored using gas chromatography and flame ionization detection (Knowles, 1982; Sorensen et al., 1981). Soil nitrogenase (nitrogen fixation) activity under aerobic conditions was assayed in an identical manner except that the samples were exposed to an air, rather than a nitrogen, atmosphere.

## RESULTS AND DISCUSSION

### Initial Site Characterization

The initial characterization effort was begun July 10 to 19, 1989. Many of the Task 1 (Site Characterization) samples were not collected during the initial visit because of a shallow water table. The remaining samples were collected during the September, 1989, visit following the dewatering effort. Activities during July, 1989, included equipment and materials acquisition; general selection of treatment and background test plots; initial soil gas survey of treatment and background areas; and collection of a portion of initial characterization samples from both treatment and background plots.

The general treatment and background areas were selected by digging a number of auger holes to check both for contamination and the presence of rubble which could prevent construction of the cells. A Bacharach TLV Sniffer, calibrated to hexane, was used to measure hydrocarbon vapor concentrations emitted from auger holes soil cores as well as the holes themselves. A soil gas survey, using a stainless steel soil gas probe and TLV Sniffer, was conducted to select a suitable site. The primary consideration during site selection was the presence/absence of contamination and the absence of rubble and utilities. Upon selecting the treatment and background plots, a detailed soil gas survey, using the previously described GC/FID and sampling train, was conducted to estimate contamination in the treatment area and confirm the absence of contamination in the background area. Permanent vapor monitoring probes were installed in the two treatment plots at three locations and three depths. The shallow "A" probes were measured as they were the only ones above the water table during the first sampling event.

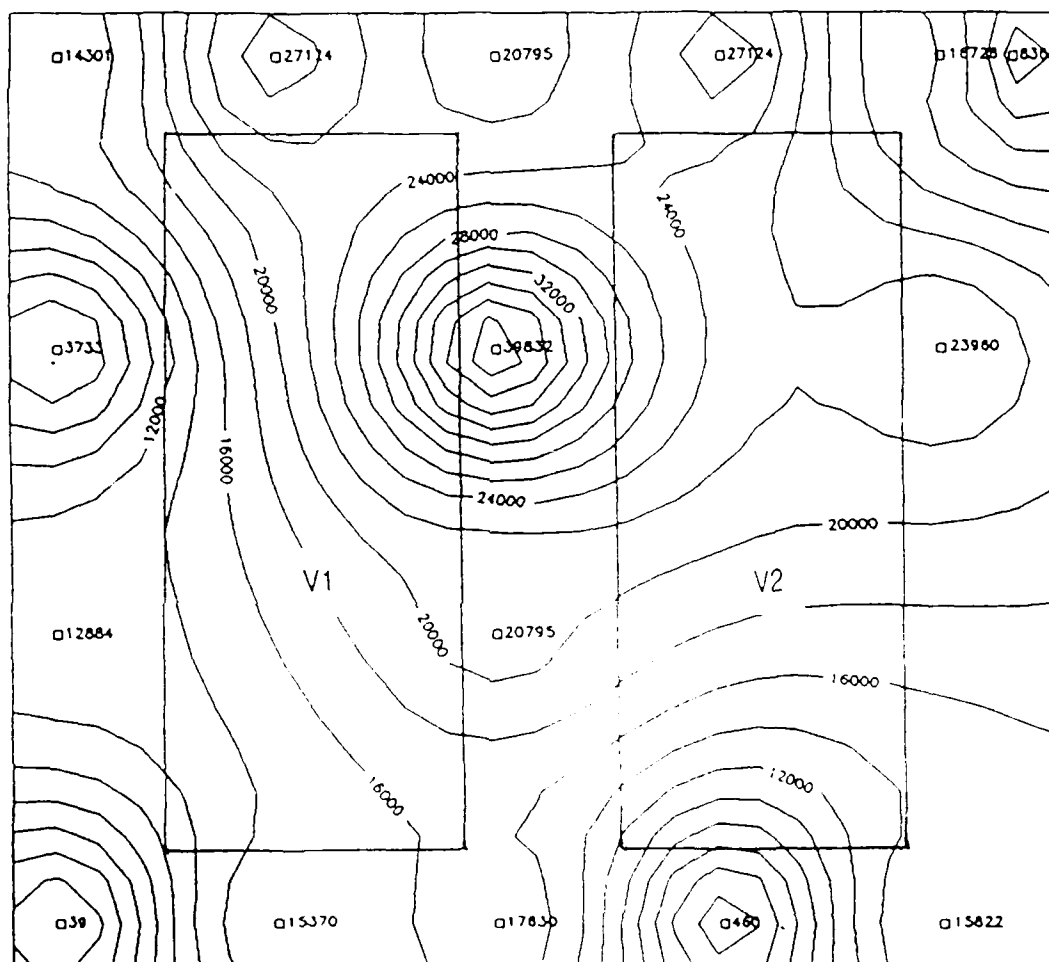
Table 8 summarizes all soil gas data collected from July 14 to 19, 1989, indicating both the location and depth of the soil gas survey. Raw data are in Appendix B. Figures 19, 20, and 21 are graphical representations of hydrocarbon, CO<sub>2</sub>, and O<sub>2</sub> soil gas data for the treatment area, respectively. Figures 22 and 23 illustrate CO<sub>2</sub> and O<sub>2</sub> data, respectively, for the background area. All hydrocarbon measurements were below detectable levels in the background area. Figures 24, 25, and 26 are hydrocarbon, CO<sub>2</sub>, and O<sub>2</sub> contours, respectively, for the "A" probes within the two treatment plots. Site characterization results revealed soil gas total hydrocarbon concentration variability throughout the treatment area up to three orders-of-magnitude. Soil gas concentrations in the "A" probes (30 to 45 cm; 1 to 1.5 ft) are over four times higher in Treatment Plot 1 than in Treatment Plot 2. Hydrocarbons were not detected in soil gas in the background area and the high O<sub>2</sub> and low CO<sub>2</sub> concentrations measured indicated little microbial activity in this area.

### **Operational Monitoring of Treatment Plots V1 and V2**

Treatment plots were operated for 188 days between October 4, 1989 and April 24, 1990. Operation was interrupted only for scheduled respiration tests. Discharge gases were monitored for oxygen (Figure 27), carbon dioxide (Figure 28), and total hydrocarbons (Figure 29) throughout the operational period. Raw data are tabulated chronologically in Appendix B, and summarized data together with engineering calculations are presented in Appendix C. Air flow rates in Treatment Plot V1 are compared with hydrocarbon removal rates (hexane equivalent) attributed to volatilization and biodegradation in Figures 30 and 31, respectively. The biodegradation component was calculated using the stoichiometric oxidation of hexane (Equation 2).

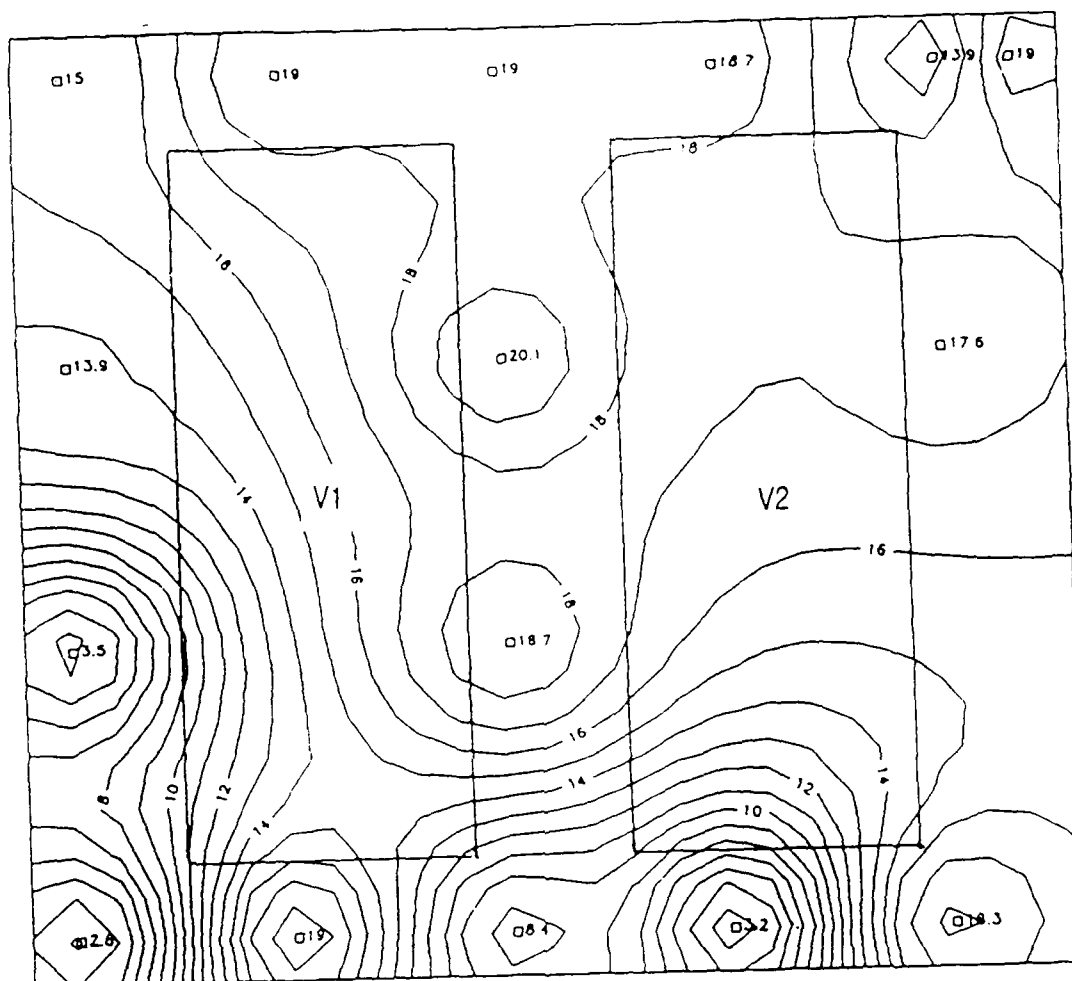
Table 8. Summary of soil gas data collected during initial site characterization.

| Date<br>mo/d/yr | Sample<br>Location | Coordinate<br>x (m) y (m) |    | Depth<br>cm | THC Conc.<br>μL/L (ppm) | CO2<br>% | O2<br>% |
|-----------------|--------------------|---------------------------|----|-------------|-------------------------|----------|---------|
| 7/14/89         | Treatment Area     | 30                        | 91 | 60          | 14,301                  | 15       | 7       |
| 7/14/89         | Treatment Area     | 32                        | 91 | 60          | 27,124                  | 19       | 2.6     |
| 7/15/89         | Clean Area         | 61                        | 91 | 60          | <1                      | 0.45     | 20.5    |
| 7/15/89         | Clean Area         | 67                        | 91 | 60          | <1                      | 0.4      | 20.9    |
| 7/15/89         | Clean Area         | 67                        | 85 | 60          | <1                      | 0.55     | 20.5    |
| 7/15/89         | Clean Area         | 67                        | 79 | 60          | <1                      | 0.18     | 20.9    |
| 7/15/89         | Clean Area         | 61                        | 79 | 60          | <1                      | 0.7      | 20.6    |
| 7/15/89         | Clean Area         | 61                        | 85 | 60          | <1                      | 0.5      | 20.9    |
| 7/15/89         | Positive Control   |                           |    |             | 13                      |          |         |
| 7/15/89         | Clean Area         | 64                        | 82 | 60          | <1                      | 0.48     | 20.8    |
| 7/15/89         | Clean Area         | 64                        | 88 | 60          | <1                      | 0.45     | 20.9    |
| 7/15/89         | Positive Control   |                           |    |             | 13                      |          |         |
| 7/15/89         | Treatment Area     | 34                        | 91 | 60          | 20,795                  | 19       | 2.6     |
| 7/15/89         | Treatment Area     | 36                        | 91 | 60          | 27,124                  | 18.7     | 2.8     |
| 7/15/89         | Treatment Area     | 38                        | 91 | 60          | 16,726                  | 13.9     | 10      |
| 7/15/89         | Treatment Area     | 38                        | 91 | 60          | 8,363                   | 19       | 6.5     |
| 7/15/89         | Treatment Area     | 38                        | 84 | 60          | 15,822                  | 18.3     | 2.7     |
| 7/15/89         | Treatment Area     | 36                        | 84 | 45          | 460                     | 3.2      | 18      |
| 7/15/89         | Treatment Area     | 34                        | 84 | 60          | 17,630                  | 8.4      | 7       |
| 7/15/89         | Treatment Area     | 32                        | 84 | 60          | 15,370                  | 19       | 2.8     |
| 7/15/89         | Treatment Area     | 30                        | 84 | 45          | 39                      | 2.8      | 18.3    |
| 7/15/89         | Treatment Area     | 34                        | 86 | 45          | 14,014                  | 19       | 3.8     |
| 7/15/89         | Treatment Area     | 34                        | 86 | 60          | 20,795                  | 18.7     | 3.2     |
| 7/15/89         | Treatment Area     | 34                        | 88 | 15          | 1,022                   | 3.4      | 18.5    |
| 7/15/89         | Treatment Area     | 34                        | 88 | 30          | 7,767                   | 16.1     | 10      |
| 7/15/89         | Treatment Area     | 34                        | 88 | 45          | 19,439                  | 20.9     | 5.3     |
| 7/15/89         | Treatment Area     | 34                        | 88 | 60          | 39,832                  | 20.1     | 4.3     |
| 7/15/89         | Standard Check     |                           |    |             | 1,000                   |          |         |
| 7/16/89         | Standard Check     |                           |    |             | 1,000                   | 3.5      | 20.9    |
| 7/16/89         | Treatment Area     | 38                        | 88 | 60          | 23,950                  | 17.6     | 2.5     |
| 7/16/89         | Treatment Area     | 30                        | 88 | 45          | 3,733                   | 13.9     | 5.9     |
| 7/16/89         | Treatment Area     | 30                        | 86 | 45          | 12,884                  | 3.5      | 16      |
| 7/16/89         | Surrounding Area   | 0                         | 91 | 60          | 22,603                  | 21.2     | 2.8     |
| 7/16/89         | Surrounding Area   | 0                         | 61 | 60          | 40                      | 3.8      | 17.9    |
| 7/16/89         | Surrounding Area   | 30                        | 61 | 60          | 13                      | 1.9      | 19      |
| 7/16/89         | Standard Check     |                           |    |             | 1,000                   |          |         |
| 7/17/89         | Treatment Area     | 30                        | 55 | 45          | Flame quench            | 5.8      | 14.2    |
| 7/17/89         | V1-2A              | 32                        | 87 | 30-45       | 12,206                  | 11.7     | 3       |
| 7/17/89         | V2-2A              | 37                        | 87 | 30-45       | 6,831                   | 2        | 17.5    |
| 7/18/89         | Standard Check     |                           |    |             | 1,000                   |          | 20.9    |
| 7/18/89         | V1-3A              | 32                        | 86 | 30-45       | 10,850                  | 2.8      | 11      |
| 7/18/89         | V1-3A              | 32                        | 86 | 30-45       | 9,235                   |          |         |
| 7/18/89         | V1-2A              | 32                        | 87 | 30-45       | 15,370                  | 22.7     | 4.5     |
| 7/19/89         | Standard Check     |                           |    | 30-45       | 1,000                   |          | 20.9    |
| 7/19/89         | V1-2A              | 32                        | 87 | 30-45       | 22,603                  | 13.2     | 2.8     |
| 7/19/89         | V1-1A              | 32                        | 88 | 30-45       | 26,672                  | 15       | 2.6     |
| 7/19/89         | V2-1A              | 36                        | 88 | 30-45       | 5,732                   | 3.6      | 15      |
| 7/19/89         | Standard Check     |                           |    | 30-45       | 1,010                   |          |         |
| 7/19/89         | V2-2A              | 37                        | 87 | 30-45       | 6,687                   | 2.95     | 17      |
| 7/19/89         | V2-3A              | 36                        | 86 | 30-45       | 4,299                   | 2.7      | 15      |



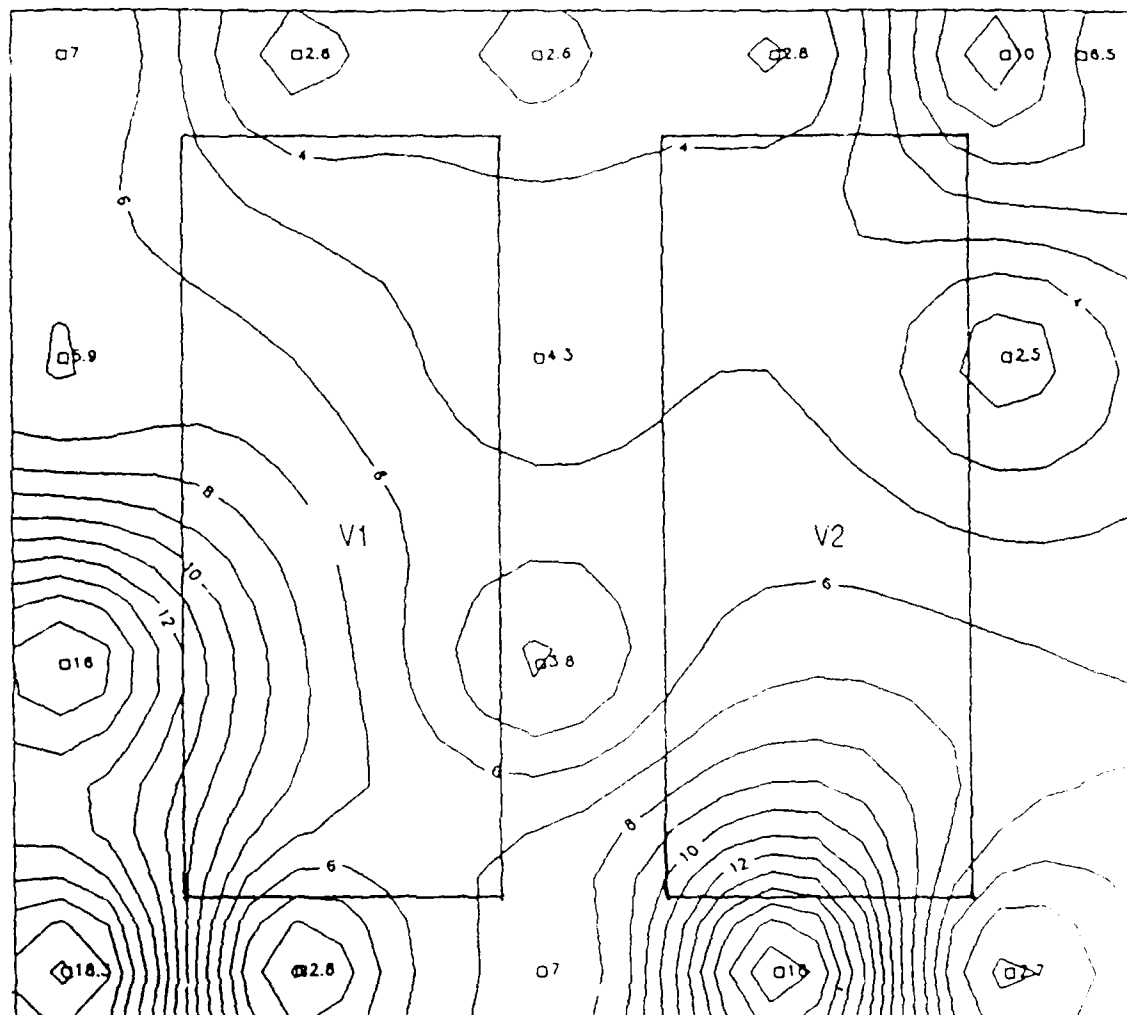
Scale: 1 cm = 64.4 cm ( 1 in = 5.37 ft )

Figure 19. Soil gas characterization of treatment area (8.7 x 8 m plot), hydrocarbon concentrations ( $\mu\text{L/L}$  (ppm) hexane equivalent). Sampled July 15 and 16, 1989.



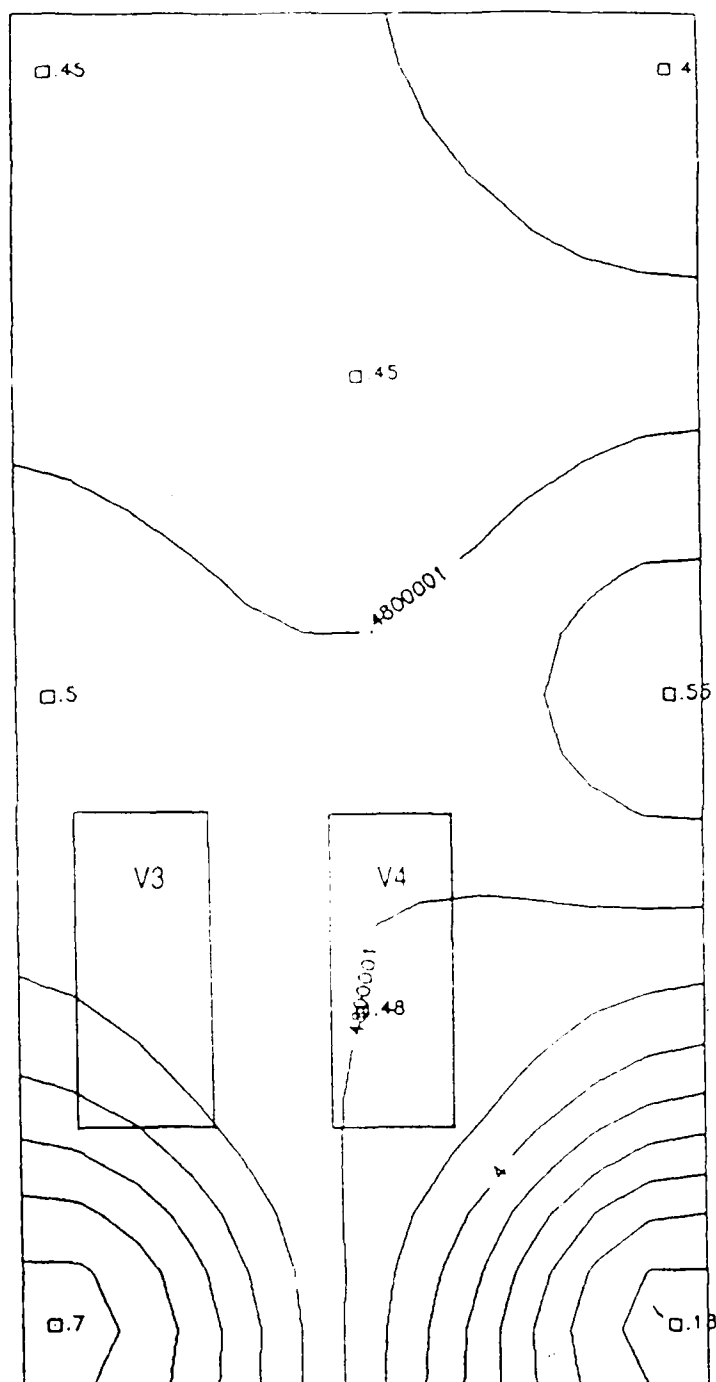
Scale: 1 cm = 64.4 cm ( 1 in = 5.37 ft.)

Figure 20. Soil gas characterization of treatment area (8.7 x 8 m plot), carbon dioxide concentrations (%). Sampled July 15 and 16, 1989.



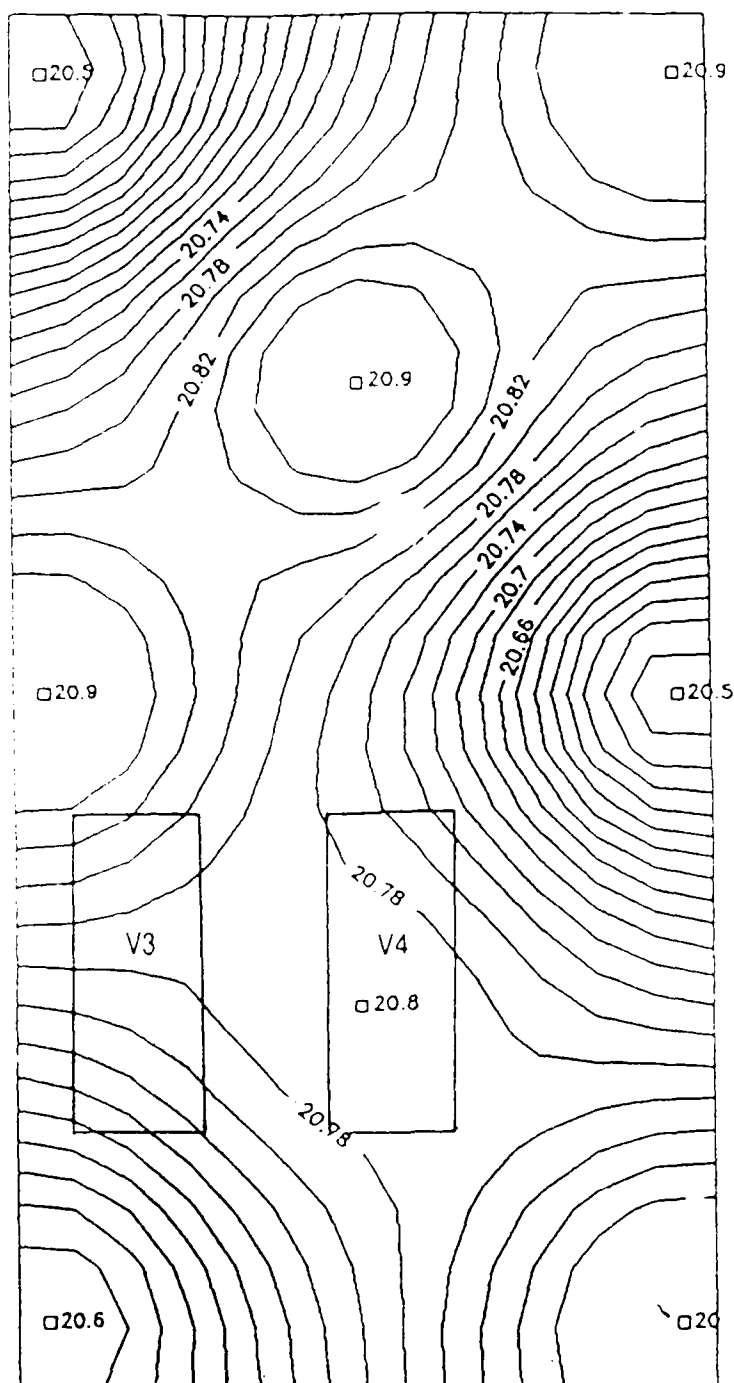
Scale: 1 cm = 60 cm ( 1 in = 5 ft )

Figure 21. Soil gas characterization of treatment area (8.7 x 8 m plot), oxygen concentrations (%). Sampled July 15 and 16, 1989.



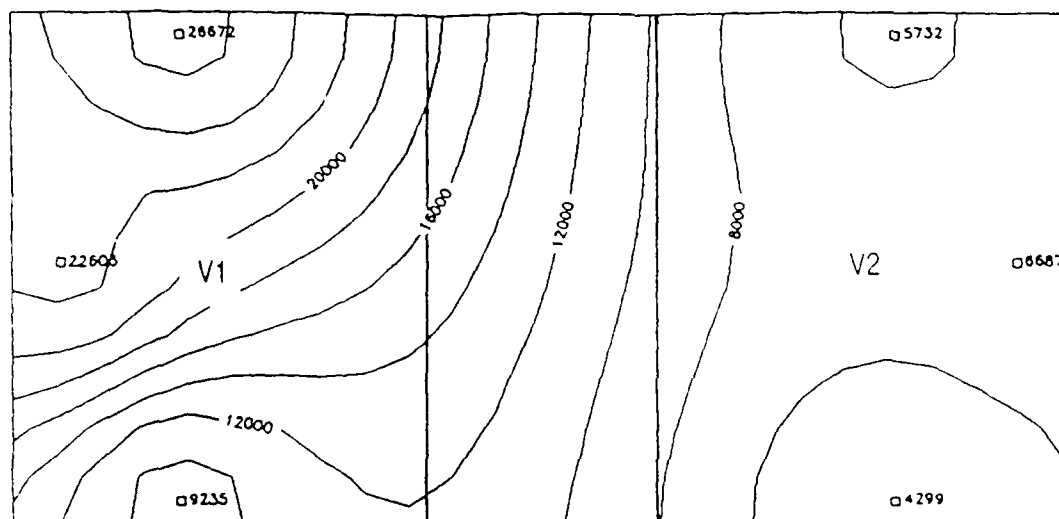
Scale: 1 cm = 74 cm ( 1 in = 6.2 ft )

Figure 22. Soil gas characterization of background area (5.4 x 2.7 m plot), carbon dioxide concentration (%). Sampled July 15 and 16, 1989.



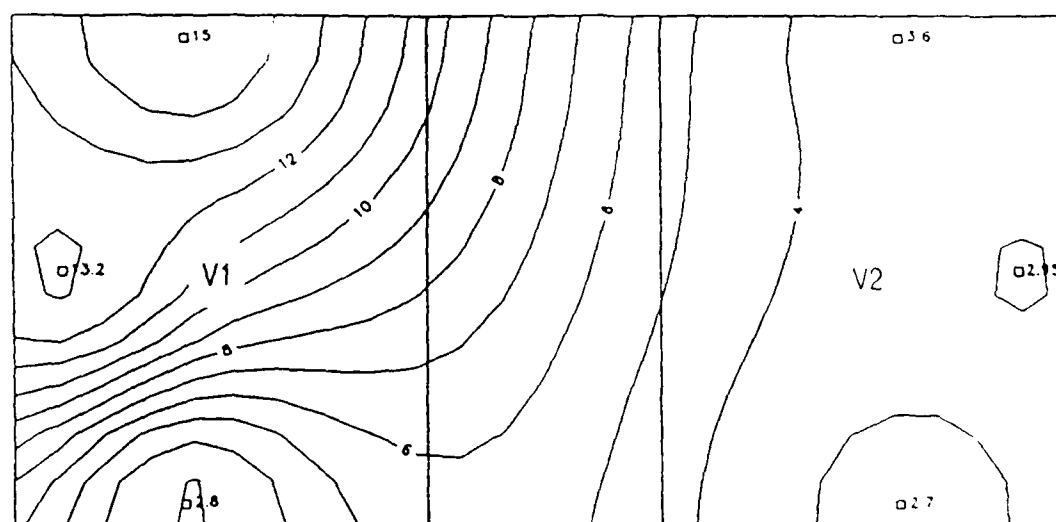
Scale: 1 cm = 74 cm ( 1 in = 6.2 ft )

Figure 23. Soil gas characterization of background area (5.4 x 2.7 m plot), oxygen concentration (%). Sampled July 15 and 16, 1989.



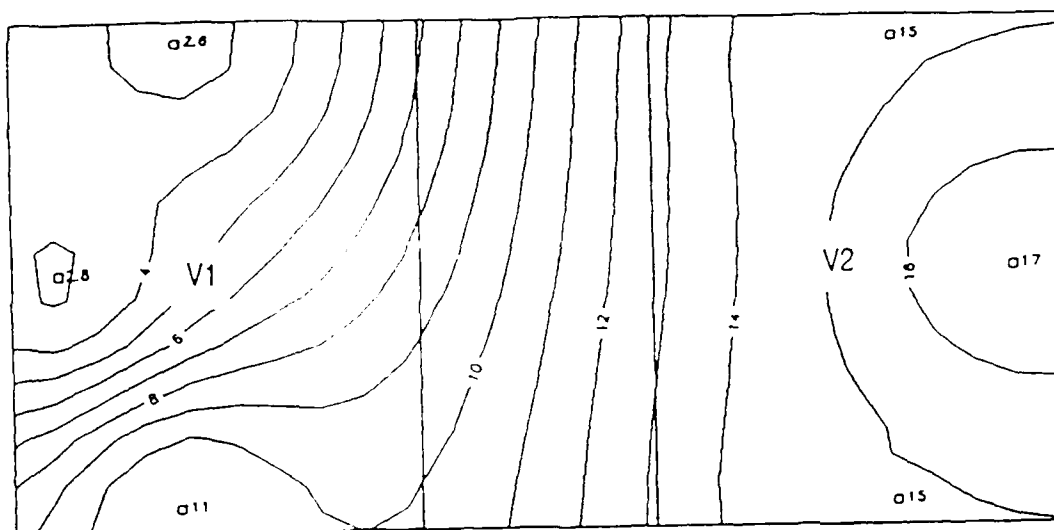
Scale: 1 cm = 40 cm ( 1 in = 3.3 ft )

Figure 24. Hydrocarbon concentrations ( $\mu\text{L/L}$  (ppm) hexane equivalent) in "A" (30 cm to 45 cm; 1 to 1.5 ft) vapor monitoring probes. Sampled July 17 through 19, 1989.



Scale: 1 cm = 40 cm ( 1 in = 3.3 ft )

Figure 25. Carbon dioxide concentrations (%) in "A" (30 cm to 45 cm; 1 to 1.5 ft) vapor monitoring probes. Sampled July 17 through 19, 1989.



Scale: 1 cm = 40 cm ( 1 in = 3.3 ft )

Figure 26. Oxygen concentrations (%) in "A" (30 cm to 45 cm; 1 to 1.5 ft) vapor monitoring probes. Sampled July 17 through 19, 1989.

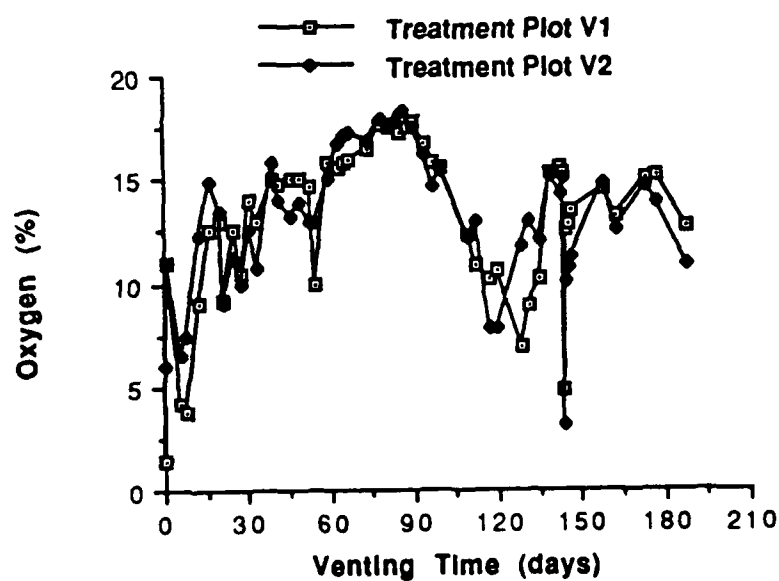


Figure 27. Oxygen measured in discharge gas from Treatment Plots V1 and V2 during the field study.

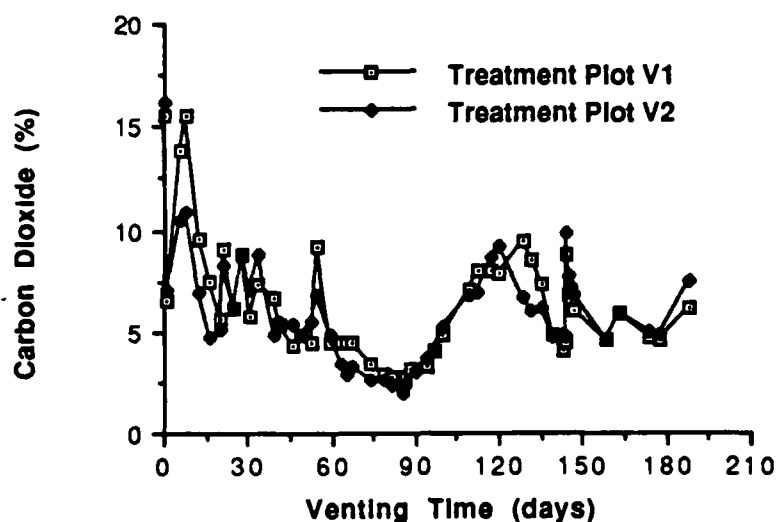


Figure 28. Carbon dioxide measured in discharge gas from Treatment Plots V1 and V2 during the field study.

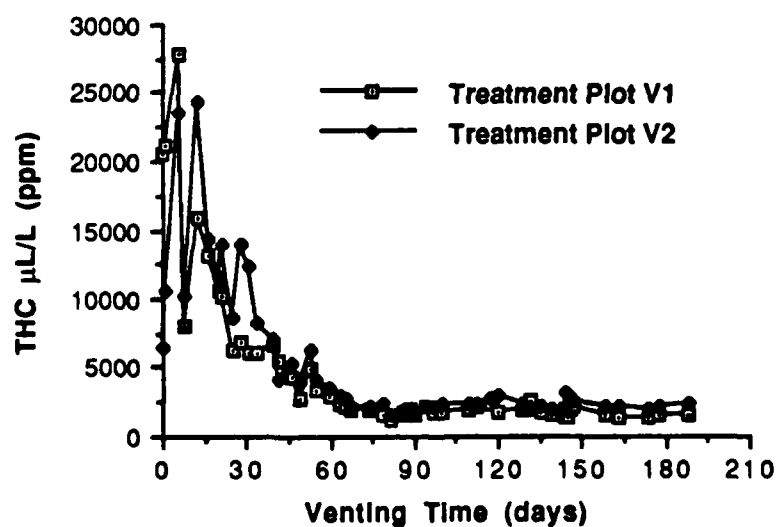


Figure 29. Total hydrocarbons (THC) measured in discharge gas from Treatment Plots V1 and V2 during the field study.

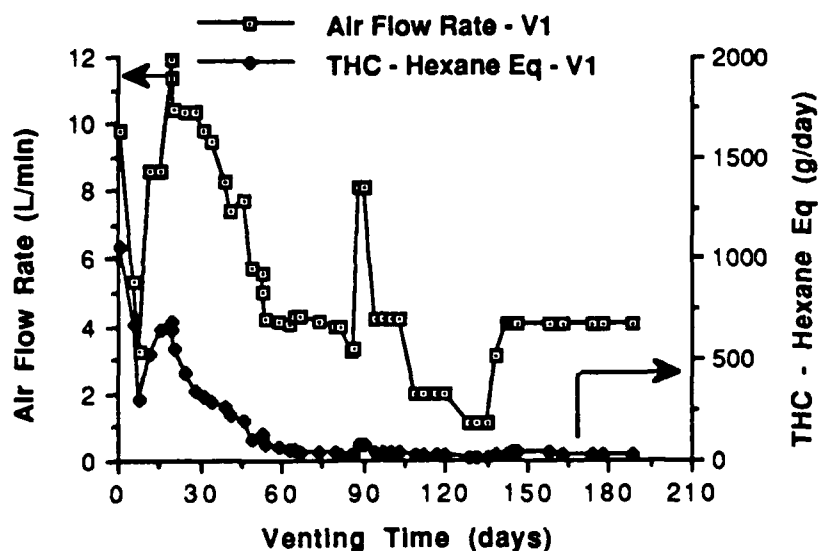


Figure 30. Comparison of air flow and hydrocarbon removal rates attributed to volatilization in Treatment Plot V1 during the field study.

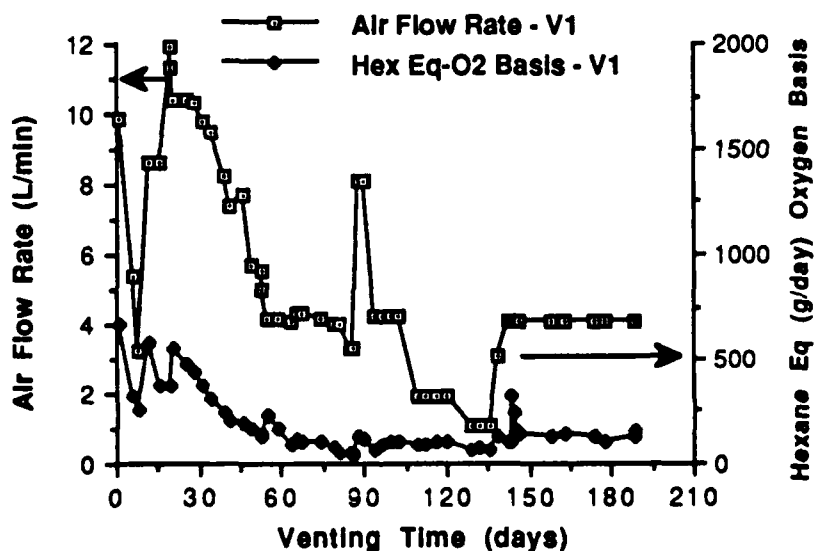


Figure 31. Comparison of air flow and hydrocarbon removal rates attributed to biodegradation (oxygen basis) in Treatment Plot V1 during the field study.

Oxygen consumption was calculated as the difference between oxygen in Background Plot V4 and oxygen in the treatment plots. Using the oxygen concentration in the background plot, rather than atmospheric oxygen concentration, the natural biodegradation of organic carbon in uncontaminated soil was accounted for. This method ensures that the biodegradation of fuel hydrocarbons was not overestimated. Biodegradation based on carbon dioxide production was similarly calculated. Air flow rates in Treatment Plot V1 are compared with the combined hydrocarbon removal rate due to volatilization and biodegradation in Figure 32. Air flow rates in Treatment Plot V2 are compared with hydrocarbon removal rates (hexane equivalent) attributed to volatilization and biodegradation in Figures 33 and 34, respectively. Air flow rates in Treatment Plot V2 are compared with the combined hydrocarbon removal rate due to volatilization and biodegradation in Figure 35. Hydrocarbon removal rates attributed to volatilization and biodegradation are presented in Figures 36 and 37, respectively, for Treatment Plots V1 and V2. Hydrocarbon removal rates comparing hydrocarbon removal attributed to volatilization and biodegradation in Treatment Plots V1 and V2 are presented in Figures 38 and 39, respectively. Removal rates in Figures 38 and 39 are expressed in mg/(kg day) and are based on an estimated soil bulk density of 1440 kg/m<sup>3</sup> (90 lb/ft<sup>3</sup>) and a treatment volume of 20 m<sup>3</sup> (704 ft<sup>3</sup>).

Biodegradation becomes increasingly important over time as a hydrocarbon removal mechanism as illustrated in Figures 40 and 41 for Treatment Plots V1 and V2, respectively. Percentages of combined volatilization and biodegradation removal rates attributable to biodegradation are compared in Figure 42 for Treatment Plots V1 and V2.

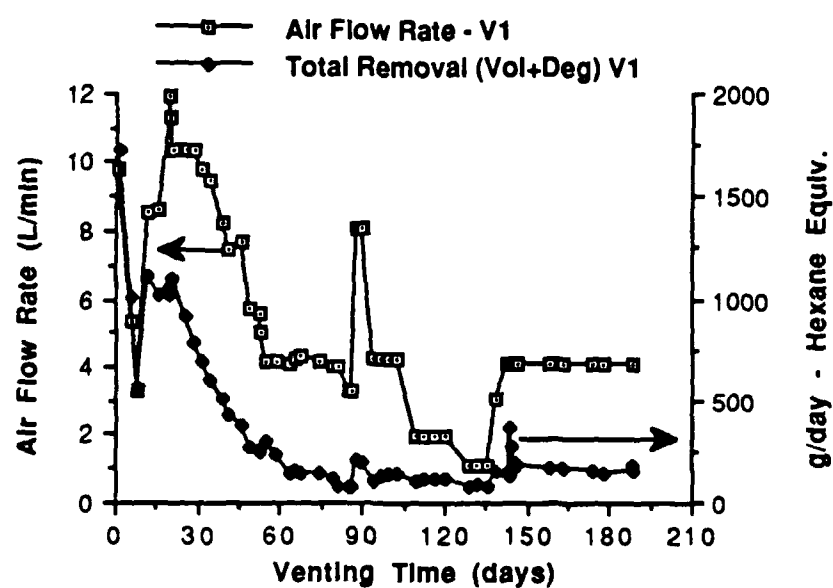


Figure 32. Comparison of air flow and combined hydrocarbon removal rates attributed to volatilization and biodegradation (oxygen basis) in Treatment Plot V1 during the field study.

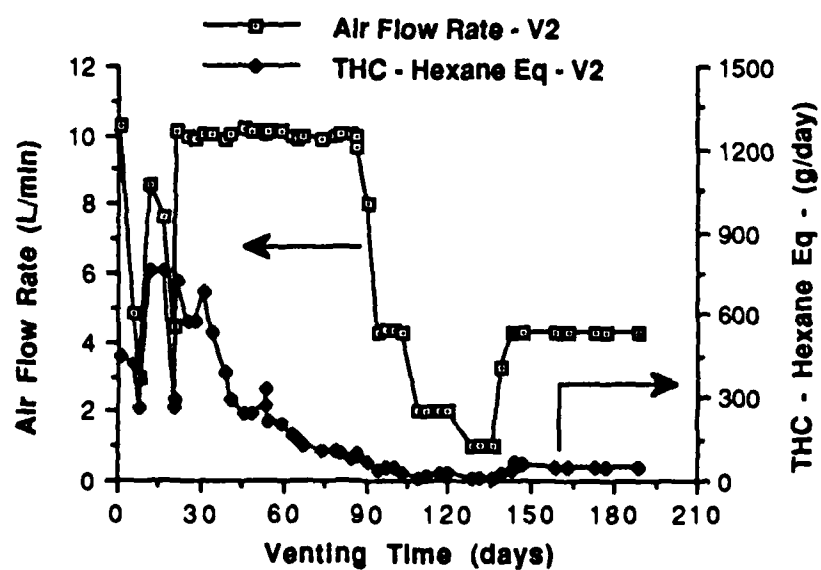


Figure 33. Comparison of air flow and hydrocarbon removal rates attributed to volatilization in Treatment Plot V2 during the field study.

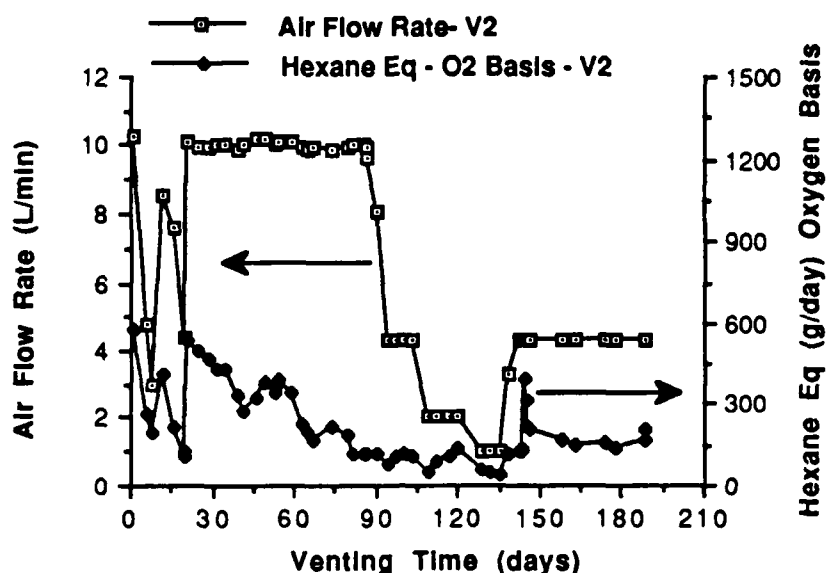


Figure 34. Comparison of air flow and hydrocarbon removal rates attributed to biodegradation (oxygen basis) in Treatment Plot V2 during the field study.

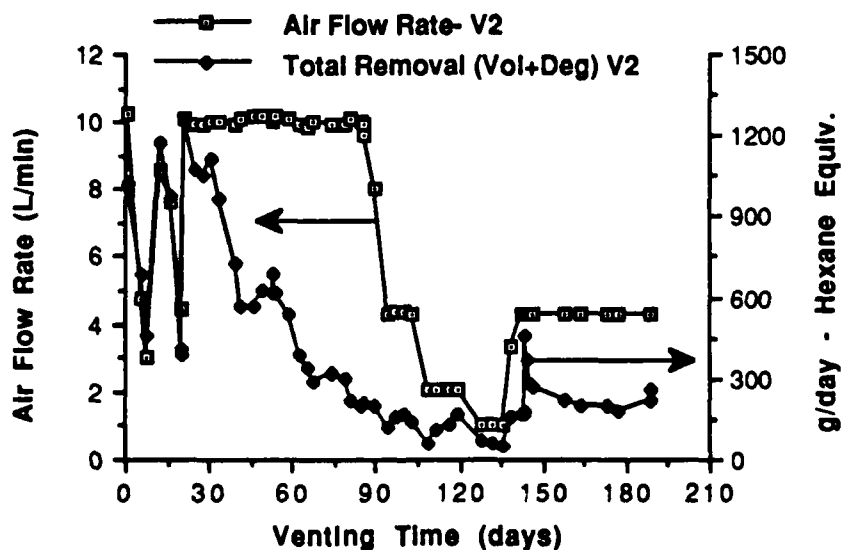


Figure 35. Comparison of air flow and combined hydrocarbon removal rates attributed to volatilization and biodegradation (oxygen basis) in Treatment Plot V2 during the field study.

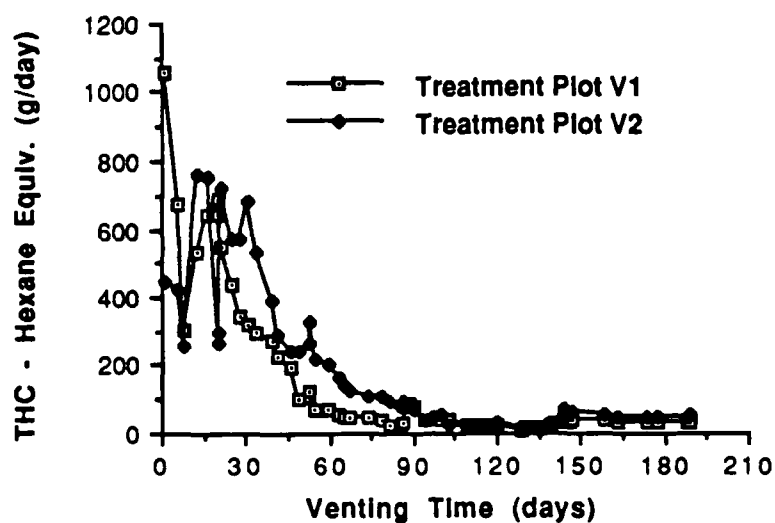


Figure 36. Hydrocarbon removal rates attributed to volatilization in Treatment Plots V1 and V2 during the field study.

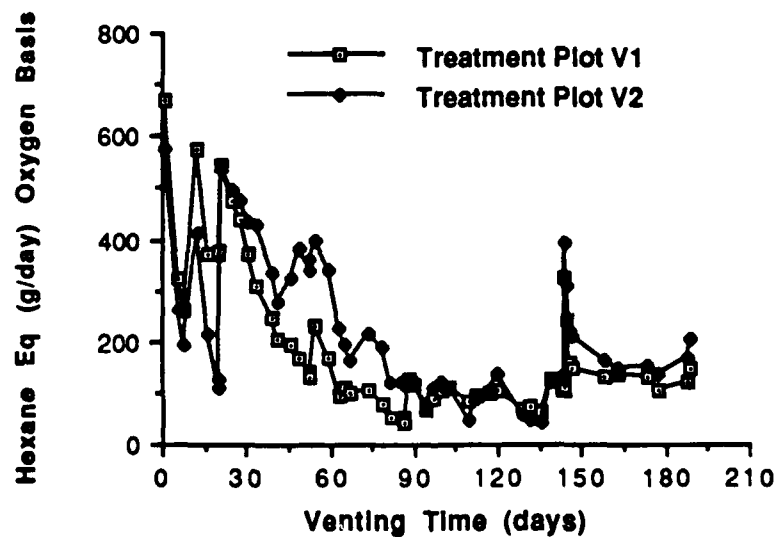


Figure 37. Hydrocarbon removal rates attributed to biodegradation (oxygen basis) in Treatment Plots V1 and V2 during the field study.

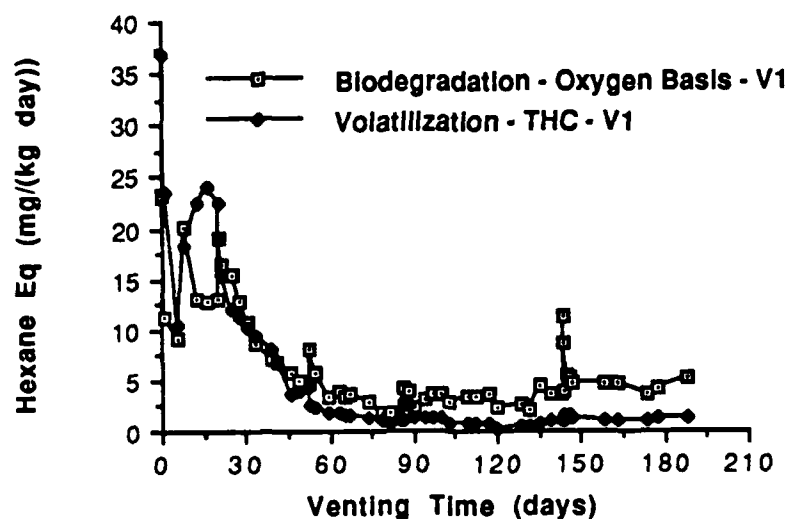


Figure 38. Hydrocarbon removal rate attributed to volatilization and biodegradation (oxygen basis) in Treatment Plot V1 during the field study.

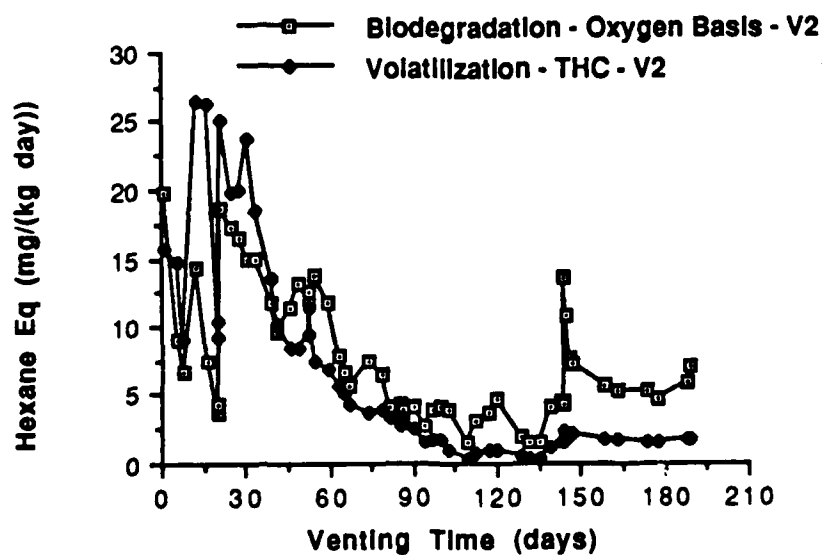


Figure 39. Hydrocarbon removal rate attributed to volatilization and biodegradation (oxygen basis) in Treatment Plot V2 during the field study.

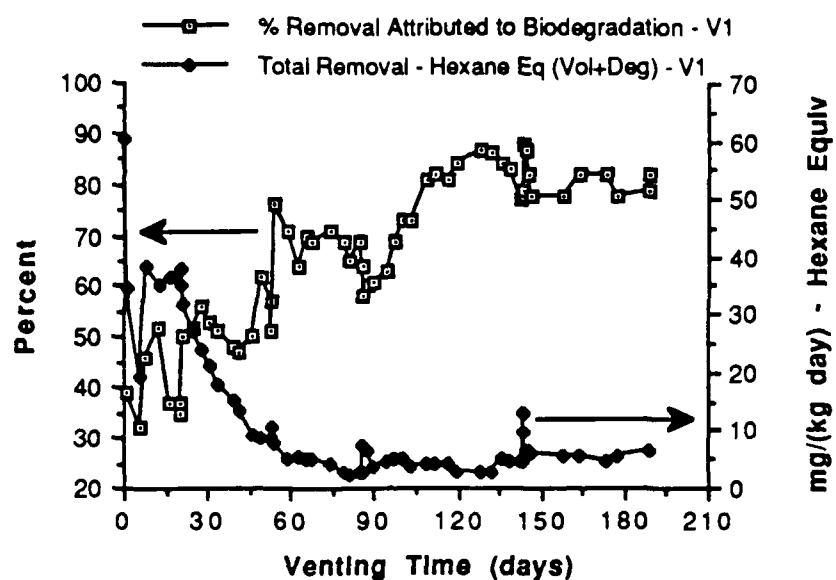


Figure 40. Comparison of the combined volatilization and biodegradation removal rates and the percent of removal rate attributed to biodegradation (oxygen basis) in Treatment Plot V1 during the field study.

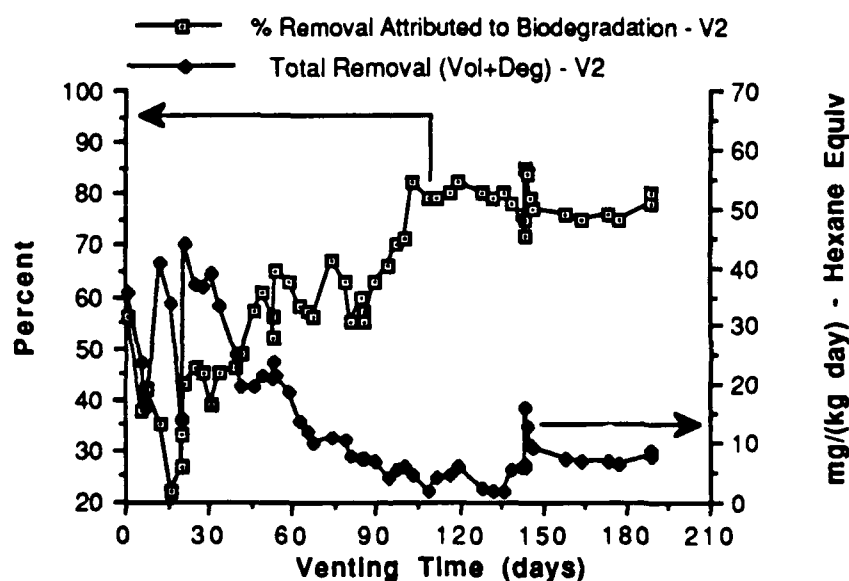


Figure 41. Comparison of the combined volatilization and biodegradation removal rates and the percent of removal rate attributed to biodegradation (oxygen basis) in Treatment Plot V2 during the field study.

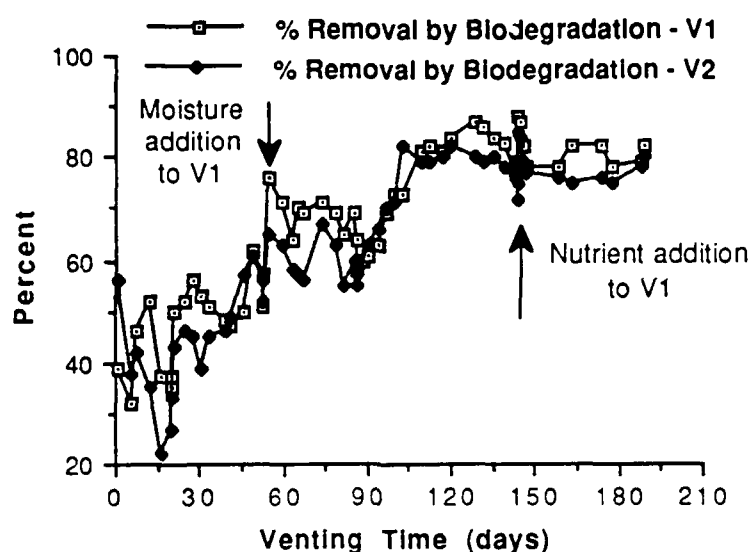


Figure 42. Comparison of the percent of combined volatilization and biodegradation hydrocarbon removal rates attributed to biodegradation (oxygen basis) in Treatment Plots V1 and V2 during the field study.

As illustrated in Figure 42, biodegradation rates were similar in Treatment Plots V1 and V2 throughout the experimental period, and neither moisture nor nutrient addition appear to have increased biodegradation rates. Cumulative hydrocarbon removal by volatilization and biodegradation is compared in Figures 43 and 44, respectively for Treatment Plots 1 and 2. The higher hydrocarbon removal rates, from both volatilization and biodegradation, in Treatment Plot V2 over Treatment Plot V1, as illustrated in Figures 43 and 44, are consistent with the initial soil samples (Appendix D) in each plot. Using soil samples collected to a depth of 1.5 m (5 ft), the average total hydrocarbon concentration (methylene chloride extracts) was 5135 (SD  $\pm$  5032) and 7690 (SD  $\pm$  7681) mg/kg, hexane equivalent, in Treatment Plots V1 and V2, respectively. Cumulative hydrocarbon removal data for volatilization, biodegradation, and total removal for Treatment Plots V1 and V2, are summarized in Figures 45 and 46, respectively. Biodegradation of

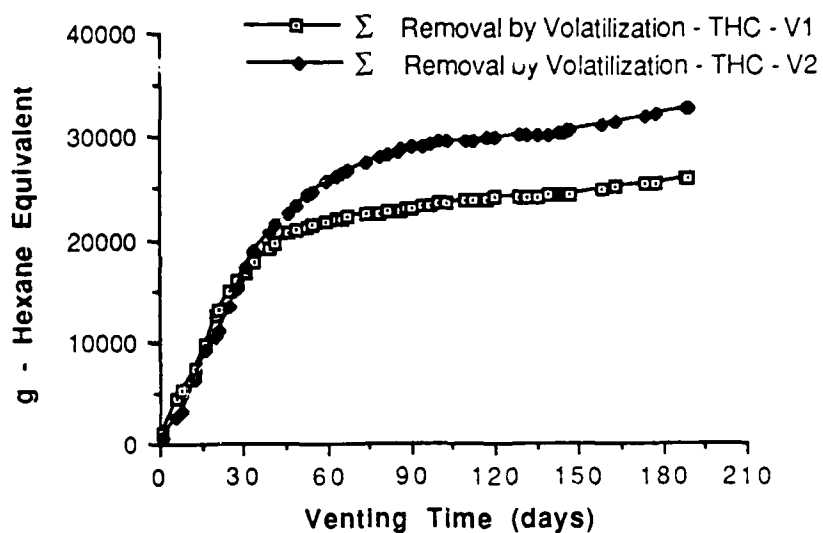


Figure 43. Comparison of cumulative hydrocarbon removal attributed to volatilization in Treatment Plots V1 and V2 during the field study.

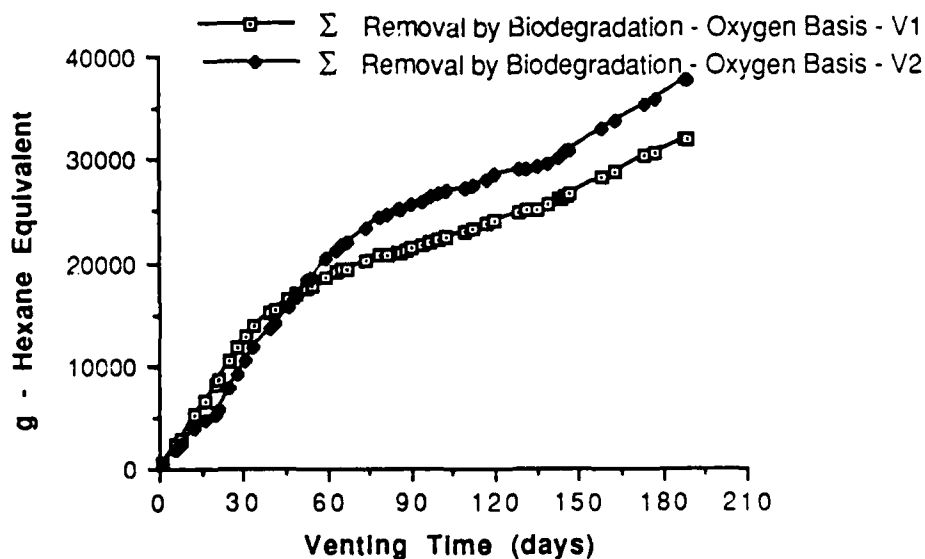


Figure 44. Comparison of cumulative hydrocarbon removal attributed to biodegradation (oxygen basis) in Treatment Plots V1 and V2 during the field study.

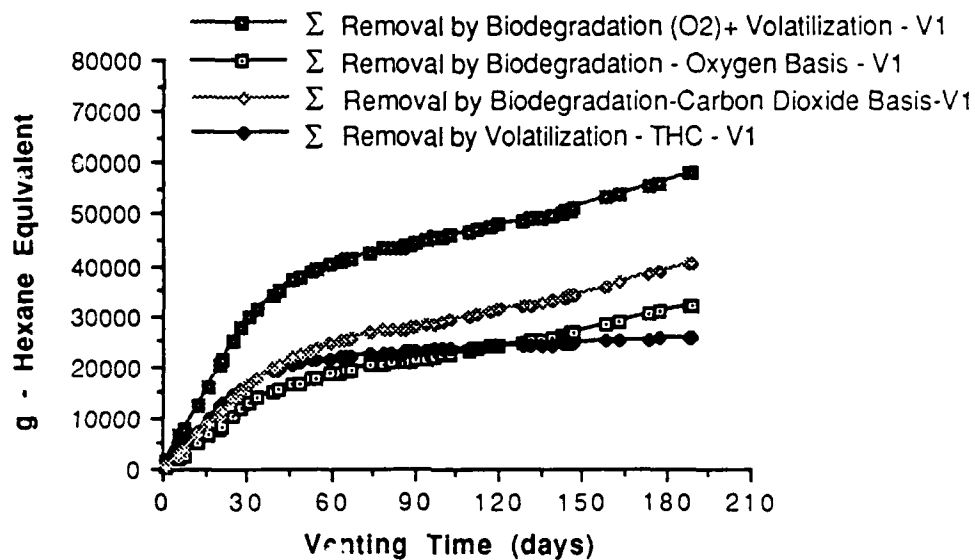


Figure 45. Cumulative hydrocarbon removal in Treatment Plot V1 during the field study.

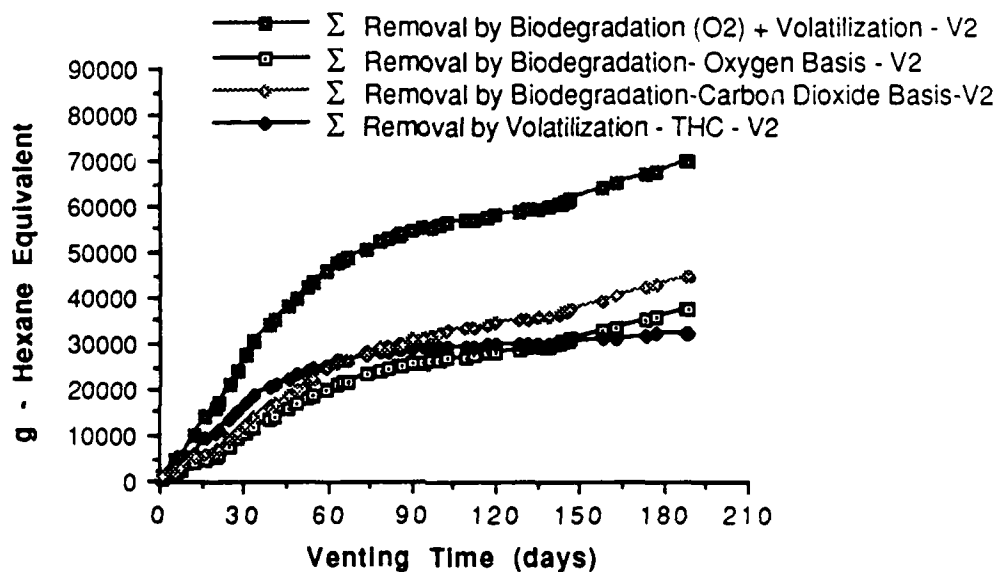


Figure 46. Cumulative hydrocarbon removal in Treatment Plot V2 during the field study.

hydrocarbon, calculated from the production of carbon dioxide, is included on Figures 45 and 46 for comparison with biodegradation based on the consumption of oxygen. Carbon dioxide concentrations in uncontaminated soil (Background Plot V4), rather than atmospheric carbon dioxide concentrations, were used as the basis for calculating the stoichiometric amount of hydrocarbon (hexane equivalent) biodegraded. At this site, biodegradation of fuel hydrocarbons calculated on the basis of carbon dioxide measurements indicated more biodegradation than calculations based on oxygen measurements. It is not known whether the difference in biodegradation is the result of an abiotic oxygen source, an abiotic carbon dioxide source, other unidentified mechanisms, or simply a systematic sampling error. Comparisons between biodegradation and volatilization have been presented using the oxygen basis because there are more potential sources and sinks for carbon dioxide than for oxygen in the subsurface (Hinchee, 1989b. Personal conversation on September 29, 1989). Since the data have been presented using an oxygen basis for fuel hydrocarbon biodegradation, biodegradation estimates are conservative.

Total hydrocarbon removal from combined volatilization and biodegradation, based on oxygen and carbon dioxide, for Treatment Plots V1 and V2, is summarized in Figure 47. Total hydrocarbon removal through the experimental period was 2,010 and 2,440 mg/kg (hexane equivalent) for Treatment Plot V1 and V2, respectively. Initial average soil hydrocarbon contamination was 5,100 and 7,700 mg/kg (hexane equivalent) in Treatment Plot V1 and V2, respectively.

Operational data for the treatment plots are remarkably similar considering that Treatment Plot V2 received moisture and nutrients throughout

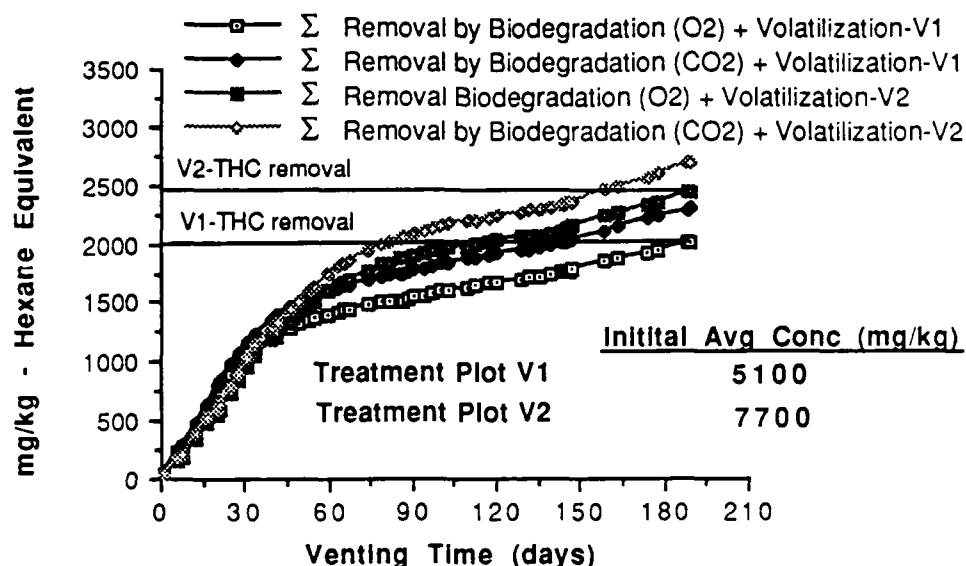


Figure 47. Cumulative removal of hydrocarbon from combined volatilization and biodegradation (oxygen and carbon dioxide basis) in Treatment Plots V1 and V2 during the field study.

the experimental period and Treatment Plot V1 received moisture after eight weeks of operation and nutrients after 22 weeks of operation (Table 6). The relationships demonstrated above indicate that moisture and nutrients were not a limiting factor in hydrocarbon biodegradation removal rate.

#### *Effect of Respiration Test Shutdowns on Operational Data*

In the hydrocarbon biodegradation rate data presented, a noticeable spike occurs at Day 146. The spike is a result of data collected immediately and at relatively short time intervals following a respiration test, when oxygen concentrations were depleted, and prior to completely purging the treatment vents. Respiration test shutdowns were initiated at 20, 53, 86, 144, and 188 days of venting and similar spikes occur but are not as noticeable due to the longer measurement interval following these other respiration tests.

A decrease in oxygen and increases in carbon dioxide and total hydrocarbons is expected following shutdown of venting systems in

contaminated soil. Biological activity consumes available oxygen more rapidly than it can naturally diffuse into the soil from the atmosphere. Because venting systems rapidly become diffusion limited, shutdown allows the system to equilibrate and hydrocarbon concentrations increase. In fact, this hydrocarbon spike has been described as a method (pulsed pumping) to volatilize compounds from the vadose-zone while minimizing venting operation time (Johnson, 1988). However, this research indicates that although the spike occurs, it is insignificant as far as cumulative removal is concerned. The spike in hydrocarbon removal rate at Day 146 is unnoticeable in the cumulative removal graphs because the duration of the spike following initiation of venting is extremely short compared to overall venting time.

#### **Flow Rate vs Total Hydrocarbon Removal Rate and Percent Biodegradation in Treatment Plots**

Ely and Heffner (1988) suggested that air flow rates higher than required for volatilization of hydrocarbons may be optimum for biodegradation. However, rate constants ( $k$ ) for oxygen consumption and carbon dioxide production have been shown, through respiration tests in this research, to follow zero order kinetics for oxygen concentrations above 1%. Therefore, lower flow rates, resulting in longer retention times should result in higher percentages of hydrocarbon removal by biodegradation.

Figures 40 and 41 illustrate an overall increase throughout the experimental period in the percentage of hydrocarbon removal attributable to biodegradation. Figures 30, 31, 33, and 34 illustrate that after the more volatile compounds are physically removed, biodegradation becomes increasingly important as the primary removal mechanism.

A comparison of air flow rate with percent of hydrocarbon removal attributed to biodegradation is presented in Figures 48 and 49 for Treatment Plots V1 and V2, respectively. Percent biodegradation appears to be inversely proportional to flow rate in Treatment Plot V1 throughout the experimental period. However, in Treatment Plot V2, percent biodegradation increases through 60 days of venting even though the air flow rate remained constant. This supports the observation above that after the more volatile compounds are physically removed (Figure 29), biodegradation becomes increasingly important as the primary removal mechanism. After initial stripping of the more volatile compounds (Figure 29), percent removal by biodegradation begins to plateau at a constant air flow rate. At this point, reducing air flow rate may be the only way to significantly increase the percent of removal attributed to biodegradation.

An experiment was conducted to evaluate the relationship between air flow rate, total hydrocarbon removal rate, and percent of total removal attributed to biodegradation following the period of high volatilization removal (after approximately 75 days of venting). The period of high volatilization removal is shown on Figures 29, 30, and 33. Beginning at Day 89, air flow rates in Treatment Plots V1 and V2 were varied over a seven week period from January 8, 1990, to February 28, 1990. Flow rates were approximately 8, 4, 2, and 1 L/min which equate to approximately 2, 1, 0.5, and 0.25 air filled void volumes per day, respectively.

Oxygen, carbon dioxide, and hydrocarbon concentrations were allowed to stabilize at each air flow rate. Raw data are chronologically presented in

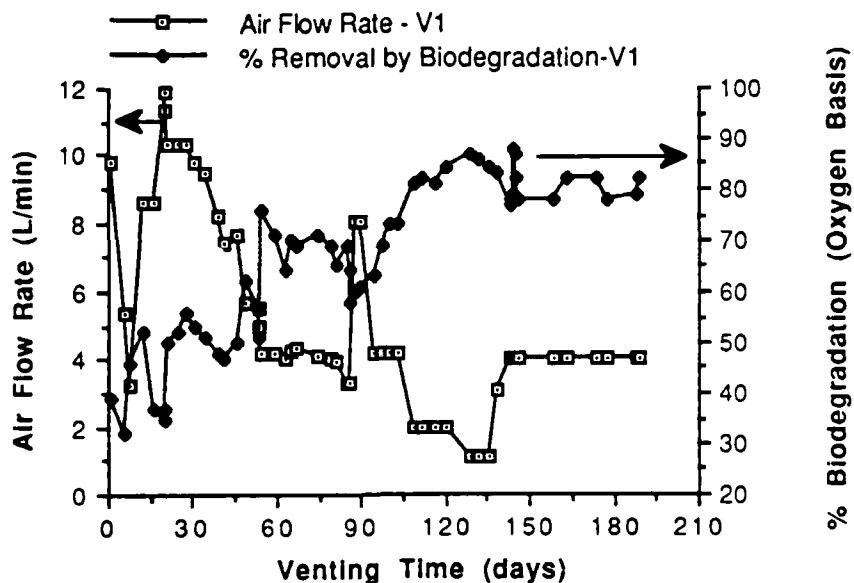


Figure 48. Comparison of air flow and percent hydrocarbon removal attributed to biodegradation in Treatment Plot V1 observed during the field study.

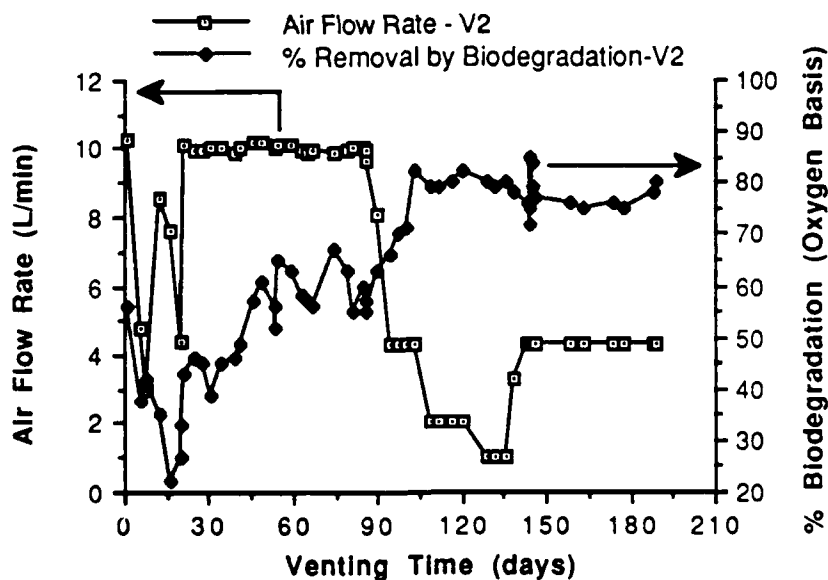


Figure 49. Comparison of air flow and percent hydrocarbon removal attributed to biodegradation in Treatment Plot V2 observed during the field study.

Appendix B and the stabilized data at each flow rate are summarized in Table 9. Figures 50 and 51 illustrate the data in Table 9 for Treatment Plot V1 using oxygen and carbon dioxide measurements, respectively, along with total hydrocarbons as the basis for calculating percent removal by biodegradation. Similarly, Figures 52 and 53 illustrate the data in Table 9 for Treatment Plot V2 using oxygen and carbon dioxide measurements, respectively.

Table 9 and Figures 50 through 53 reveal a trade-off between maximizing the percent of hydrocarbon removed by biodegradation and maximizing the overall hydrocarbon removal rate, thereby minimizing the operational time required to remediate a contaminated site. Using the data in Table 9 for Treatment Plot V1 and assuming that 100,000 g (3500 mg/kg) of hydrocarbons must be removed, a hypothetical case can be evaluated. If 62% biodegradation is desired, then 8 L/min (two air void volumes per day) would be selected with an expected operational time of 571 days. However, if 85% biodegradation were desired, then 1 L/min (0.25 air void volumes per day) would be selected with an expected operational time of 1370 days. Although operational time is increased by a factor of 2.4, total air requirement actually decreases from 6.6 to 2.2 million L. Optimal air flow conditions in V1 appear to be 2 L/min (0.5 air void volumes per day) where 82% biodegradation is achieved. Although 85% biodegradation is achieved at 1 L/min in V1, hydrocarbon removal rate is greatly reduced. Operating at 2 L/min in V1, expected operation time is 820 days (1.4 times that required at 8 L/min) and the total air requirement is only 2.3 million L. It is emphasized that operational times in this case are merely hypothetical as relationships between air flow and removal rate are applicable only over the seven week field test period.

Table 9. Summary of flow rate versus total hydrocarbon removal and percent biodegradation for Treatment Plots V1 and V2 observed during the field study.

| Treatment Plot V1 Discharge |         |        |            |                      |                        |                       |                        |                            |                           |                     |                     |                     |                     |
|-----------------------------|---------|--------|------------|----------------------|------------------------|-----------------------|------------------------|----------------------------|---------------------------|---------------------|---------------------|---------------------|---------------------|
| Date/Time                   | CO2 (%) | O2 (%) | THC (µL/L) | Avg Air Flow (L/min) | Hexane Eq. CO2 (g/day) | Hexane Eq. O2 (g/day) | Hexane Eq. THC (g/day) | Hexane Eq. THC+CO2 (g/day) | Hexane Eq. THC+O2 (g/day) | % Biol Deg O2 Basis | % Biol Deg O2 Basis | % Biol Deg O2 Basis | % Biol Deg O2 Basis |
| 1/12/90 8:56                | 3.0     | 17.8   | 1,582.6    | 8.06                 | 180                    | 109                   | 66                     | 246                        | 175                       | 73                  | 62                  | 73                  | 62                  |
| 1/22/90 10:30               | 4.8     | 15.5   | 1,822.4    | 4.22                 | 149                    | 108                   | 40                     | 188                        | 147                       | 79                  | 73                  | 79                  | 73                  |
| 2/12/90 15:00               | 7.8     | 10.6   | 2,227.7    | 1.94                 | 117                    | 100                   | 22                     | 139                        | 122                       | 84                  | 82                  | 84                  | 82                  |
| 2/28/90 10:00               | 7.3     | 10.2   | 1,852.4    | 1.14                 | 68                     | 62                    | 11                     | 78                         | 73                        | 86                  | 85                  | 86                  | 85                  |

| Treatment Plot V2 Discharge |         |        |            |                      |                        |                       |                        |                            |                           |                     |                     |                     |                     |
|-----------------------------|---------|--------|------------|----------------------|------------------------|-----------------------|------------------------|----------------------------|---------------------------|---------------------|---------------------|---------------------|---------------------|
| Date/time                   | CO2 (%) | O2 (%) | THC (µL/L) | Avg Air Flow (L/min) | Hexane Eq. CO2 (g/day) | Hexane Eq. O2 (g/day) | Hexane Eq. THC (g/day) | Hexane Eq. THC+CO2 (g/day) | Hexane Eq. THC+O2 (g/day) | % Biol Deg O2 Basis | % Biol Deg O2 Basis | % Biol Deg O2 Basis | % Biol Deg O2 Basis |
| 1/12/90 9:40                | 3.0     | 17.5   | 1,758.4    | 8.02                 | 179                    | 122                   | 73                     | 252                        | 194                       | 71                  | 63                  | 71                  | 63                  |
| 1/22/90 10:30               | 5.2     | 15.4   | 2,270.0    | 4.32                 | 167                    | 112                   | 51                     | 217                        | 163                       | 77                  | 69                  | 77                  | 69                  |
| 2/12/90 15:00               | 9.1     | 7.9    | 2,877.4    | 2.03                 | 145                    | 134                   | 30                     | 175                        | 164                       | 83                  | 82                  | 83                  | 82                  |
| 2/28/90 10:00               | 6.1     | 12.0   | 2,106.7    | 1.08                 | 53                     | 49                    | 12                     | 65                         | 60                        | 82                  | 81                  | 82                  | 81                  |

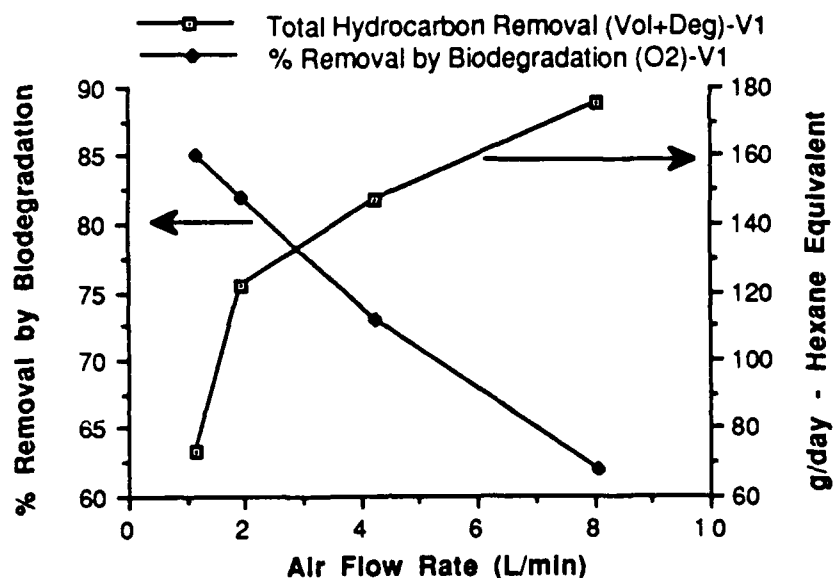


Figure 50. Comparison of air flow rate versus total hydrocarbon removal and percent of total removal attributed to biodegradation in Treatment Plot V1 ( $O_2$  basis) during the variable air flow rate study.

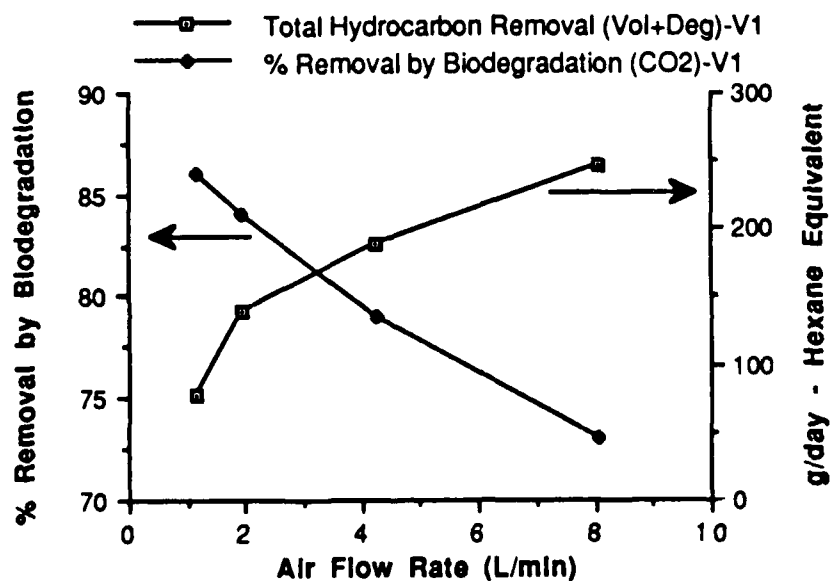


Figure 51. Comparison of air flow rate versus total hydrocarbon removal and percent of total removal attributed to biodegradation in Treatment Plot V1 ( $CO_2$  basis) during the variable air flow rate study.

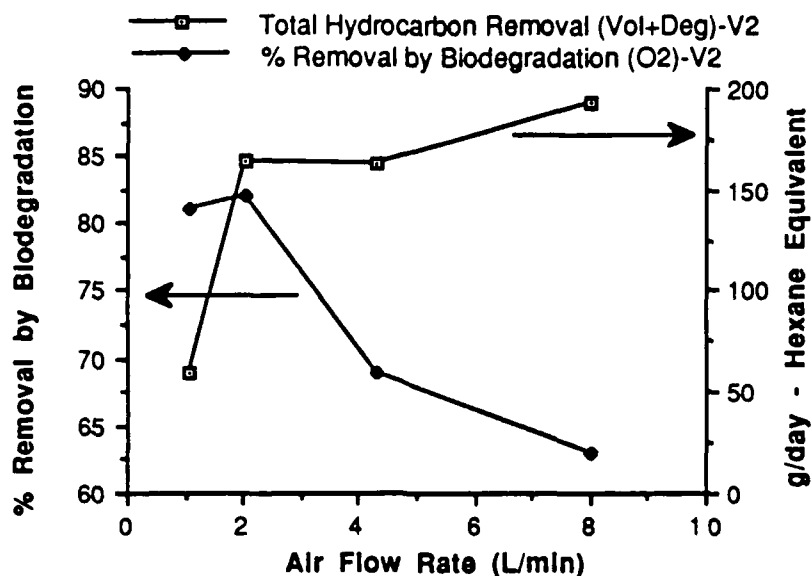


Figure 52. Comparison of air flow rate versus total hydrocarbon removal and percent of total removal attributed to biodegradation in Treatment Plot V2 ( $O_2$  basis) during the variable air flow rate study.

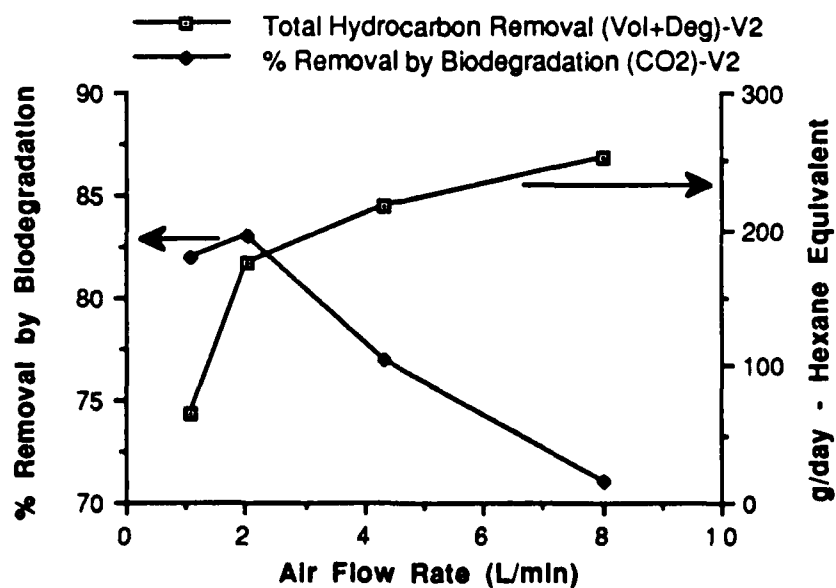


Figure 53. Comparison of air flow rate versus total hydrocarbon removal and percent of total removal attributed to biodegradation in Treatment Plot V2 ( $CO_2$  basis) during the variable air flow rate study.

However, it is likely that similar relationships would exist throughout the remediation period although the magnitude of removal rates vary widely throughout the remediation period (Figures 32 and 35).

The observed relationship between air flow rate, hydrocarbon removal rate, and percent of removal attributed to biodegradation are consistent with other experimental observations. First, the data suggest that the system is diffusion limited (at least at flow rates greater than 1 L/min) resulting in higher hydrocarbon concentrations per unit volume of air extracted with decreasing air flow rates (Table 9). A diffusion limited system is one in which diffusion of hydrocarbons into the air stream is the limiting factor in removal rate. This is illustrated in Figures 30 through 35 where higher air flow rates in Treatment Plot V2 over those in Treatment Plot V1 had little effect on the rate of hydrocarbon removal after about 15 days of venting. During the first 15 to 20 days of venting the system was advection limited, meaning that hydrocarbon removal rate was limited by air flow rate. An unexplained drop in hydrocarbon concentration occurred at an air flow rate of 1 L/min (Table 9). This could have been a measurement error or simply resulted from the fact that this was the last measurement in the test, and seven weeks of venting simply reduced concentrations. Also, the higher hydrocarbon concentration in air at lower flow rates likely provides microbes with a carbon source that may not have been available at lower hydrocarbon concentrations. Second, lower air flow rates result in longer retention times, and since mineralization rates are relatively constant over time, as determined by respiration tests in this research, this increased retention time results in increased hydrocarbon mineralization.

Ely and Heffner (1988) suggested that air flow rates higher than required for volatilization of hydrocarbons may be optimum for biodegradation. However, this research has documented that if the object is to minimize

volatilization, the reverse is true, and that decreasing flow rates will increase the percent of hydrocarbon removal by biodegradation and decrease the percent of hydrocarbon removal by volatilization.

*Eliminating Off-Gas Treatment by  
Increased Biodegradation and  
Decreased Volatilization of  
Spilled Jet Fuel*

One of the goals of this research was to demonstrate that a fuel contaminated site can be remediated without the need for expensive off-gas treatment. If off-gas treatment can be eliminated, operational costs for site remediation using enhanced biodegradation through soil venting are primarily associated with the costs of providing air, moisture, nutrients, and monitoring. As shown by this research, moisture and nutrient addition may not be necessary and monitoring costs can be minimized for long term remedial actions. If moisture and nutrients are not required, and monitoring is minimized, then operational costs are primarily controlled by the cost of providing air. As demonstrated above, the air requirement for achieving total remediation at 82% biodegradation is one-third that required to remediate the site at 62% biodegradation even though the operational time is extended only 1.4-fold. The result is smaller quantities of contaminated gas and hydrocarbon mass generated, reducing the need for off-gas treatment. Therefore, even though operational time is extended for a system designed to maximize biodegradation and minimize volatilization of hydrocarbons, the overall operational costs for total remediation may be significantly lower.

### Potential Temperature Effects in Treatment Plots V1 and V2

As described above, hydrocarbon removal rates appear to have been unaffected by moisture and nutrient addition. This conclusion, supported by the respiration tests, is based on the similarities in hydrocarbon removal rates in Treatment Plots V1 and V2 throughout the experimental period. Although hydrocarbon removal rates in the treatment plots were similar, there was a general decline in hydrocarbon removal rates from initiation of the field study; reaching minimum values near the middle of the experimental period; followed by a general increase in hydrocarbon removal rates through the completion of the field study. This depression in total hydrocarbon removal rate, observed during the experimental period, was primarily a result of a similar depression in the fraction of total removal attributed to biodegradation (Figures 38 and 39). Since the treatment plots appeared unaffected by moisture and nutrient addition, soil temperature may be the cause of the depression in biodegradation rates. Soil temperature at this field site was related to ambient air temperature because air was continually drawn through the soil. More importantly, the moisture provided to the treatment plots affected soil temperature as the applied water temperature was a function of air temperature because this water was temporarily stored in the site building prior to delivery to the treatment plots.

Local ambient temperature data were obtained from a weather station located near the field site. Since soil temperature at a given time is a function of earlier ambient air temperature, mean ambient temperature was calculated for

5, 10, 15, and 20 days prior to the time when limited soil temperatures were collected.

The moving 5, 10, 15, and 20 day average ambient above ground air temperature data are presented in Figure 54, and the 10 day moving average above ground air temperature data are compared with measured soil temperature in Figure 55. Soil temperature data before January 5, 1990, were not collected at the field site. Therefore, the relationship between ambient temperature and soil temperature (Figure 56) was used to estimate soil temperatures prior to this date (Figure 57). Figures 58 and 59 illustrate that the observed depression in hydrocarbon removal rate follows the depression in soil temperature in Treatment Plots V1 and V2. The data collected in this study indicate that soil temperature was important in controlling hydrocarbon removal rate in the treatment plots.

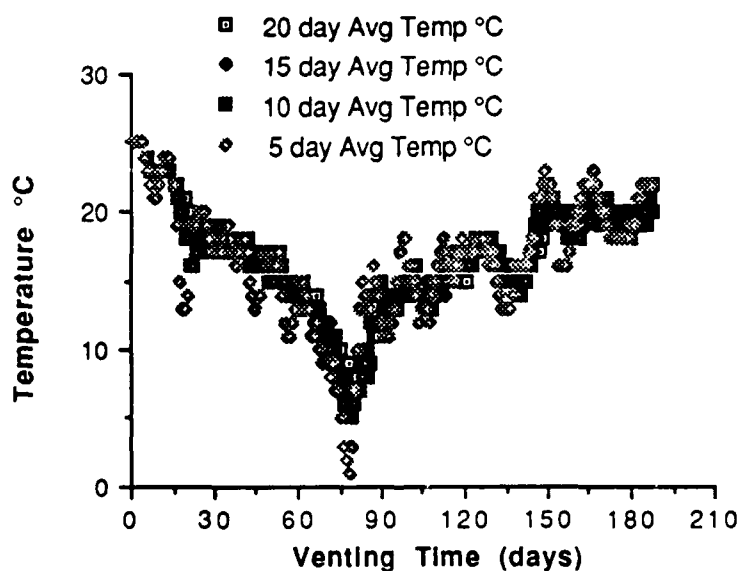


Figure 54. Moving average of the daily mean ambient above ground air temperature for 5, 10, 15, and 20 days averaging period prior to the venting time shown.

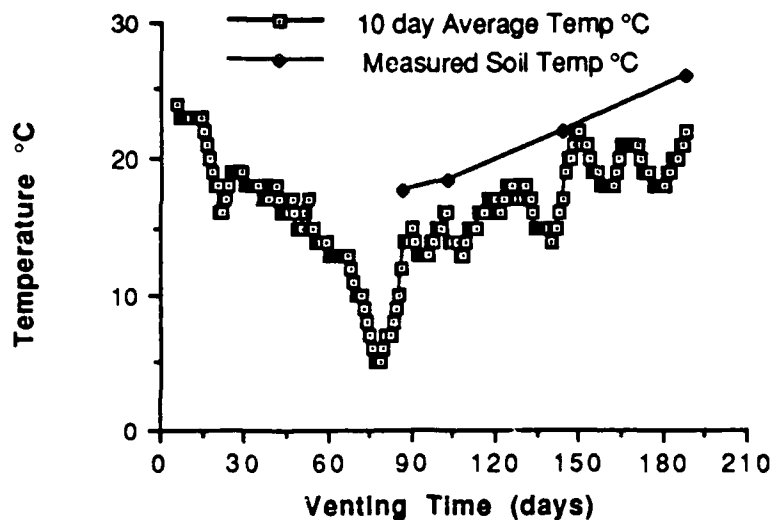


Figure 55. Comparison of the 10 day moving average of the mean ambient above ground air temperature and corresponding measured soil temperature.

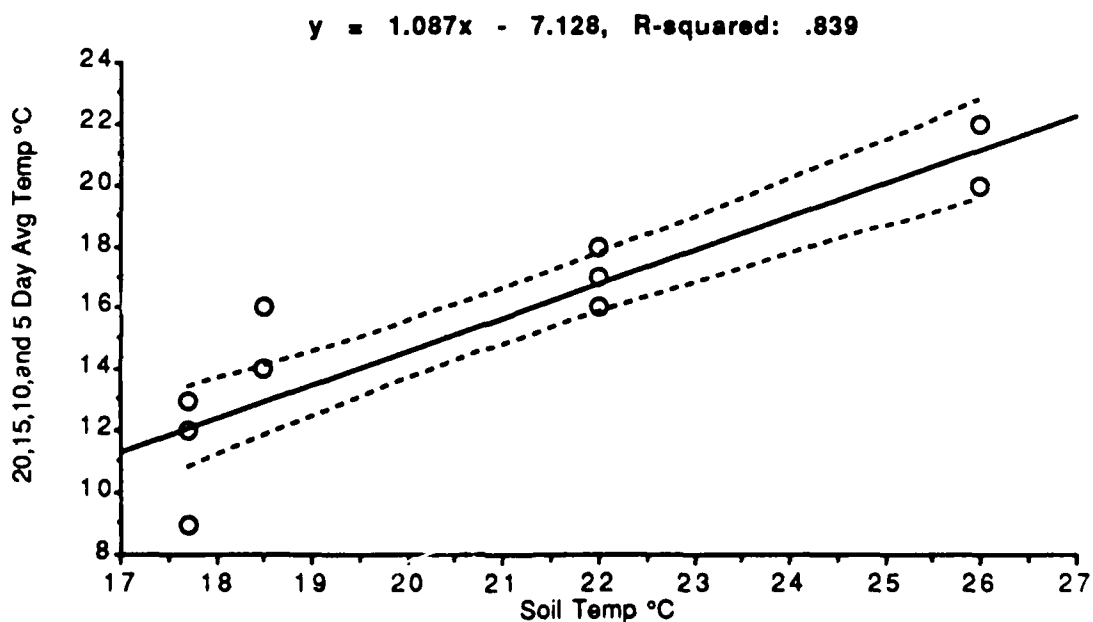


Figure 56. Regression results and 95% confidence interval bands for comparison between 5, 10, 15, and 20 day moving average of the daily mean ambient above ground air temperature and measured soil temperature collected during days 86 to 188 of the field venting study.

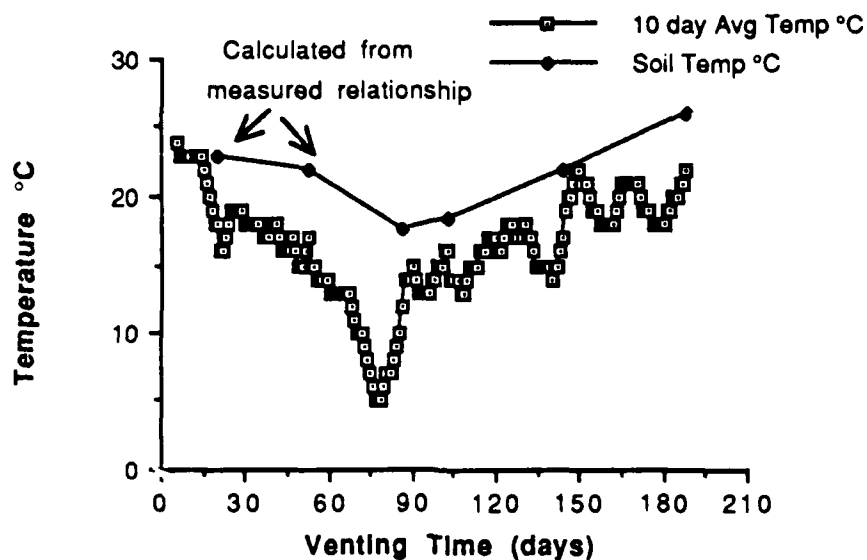


Figure 57. Comparison of the 10 day moving average of the mean ambient above ground air temperature and corresponding measured and estimated soil temperature.

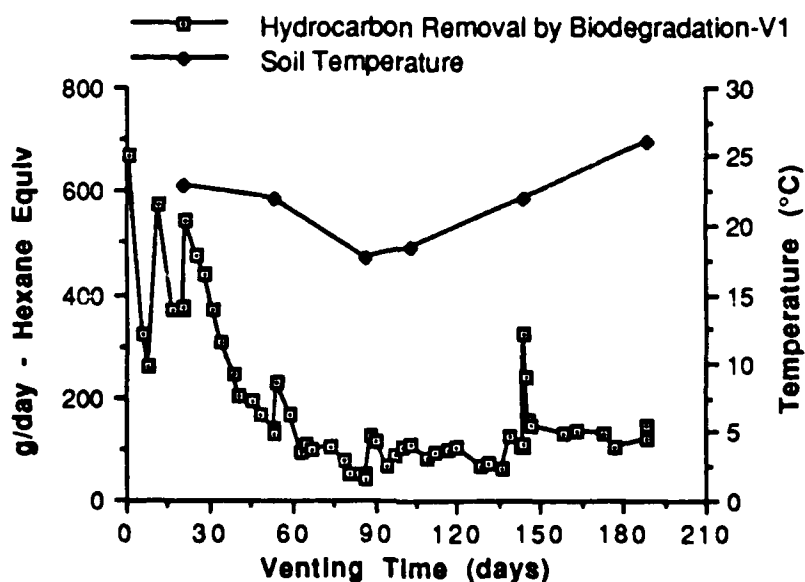


Figure 58. Comparison of measured and estimated soil temperature and hydrocarbon removal rate attributed to biodegradation (oxygen basis) in Treatment Plot V1.

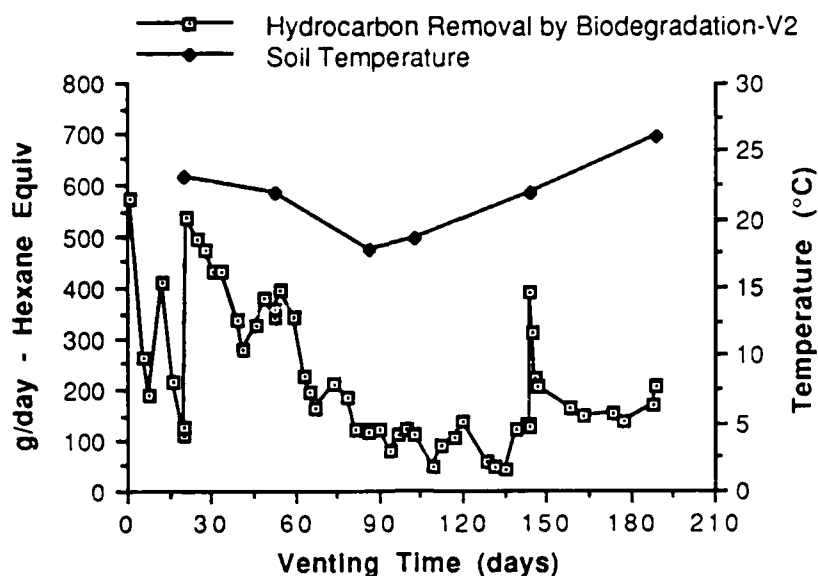


Figure 59. Comparison of measured and estimated soil temperature and hydrocarbon removal rate attributed to biodegradation (oxygen basis) in Treatment Plot V2.

### Operational Monitoring of Off-Gas Treatment Plot V3

Hydrocarbon vapors from Treatment Plot V1 were introduced into the uncontaminated soil of Off-Gas Treatment Plot V3 to assess the potential for biological mineralization. For a period of 53 days, a side-stream of the off-gas from Treatment Plot V1 was diluted prior to introduction into Off-Gas Treatment Plot V3. This was necessary to ensure adequate oxygen (9.5 moles oxygen/mole hexane) for biological mineralization. From venting Days 54 to 138, Off-Gas Treatment Plot V3 received the entire undiluted gas stream from Treatment Plot V1 because oxygen/hydrocarbon ratios were adequate for mineralization. As described in the Methods and Materials Section, leakage in Off-Gas Treatment Plot V3 resulted in higher oxygen concentrations in the discharge gas than was observed in the inlet gas stream coming from Treatment Plot V1. However, the reductions in hydrocarbon concentrations between the inlet and discharge were proportionately larger than the observed

oxygen increases. This indicated that biodegradation was occurring but was being masked by leakage of near atmospheric concentrations of oxygen. The leakage, and actual biodegradation rates were calculated by means of a mass balance equation presented in Appendix A. A high hydrocarbon/low flow rate test was conducted for three days (venting Days 139 to 142) to determine if biodegradation could not only be calculated from the mass balance, but observed as a loss in oxygen between the inlet and discharge gas streams. If biodegradation was occurring, higher hydrocarbon concentrations should result in more oxygen consumption, and lower flow rates should both minimize leakage rates and increase oxygen consumption.

Air sparged JP-4 and dilution air were used to produce an inlet hydrocarbon concentration of approximately 7900  $\mu\text{L/L}$  (ppm) at an oxygen concentration of 20.4%. The system stabilized after approximately 24 hours and discharge gas contained approximately 900  $\mu\text{L/L}$  (ppm) hydrocarbons and 17.5% oxygen. Stoichiometrically, the observed decrease in hydrocarbon concentrations should have resulted in a decrease of 6.6 % oxygen if no leakage had occurred. Although the observed oxygen consumption was only 2.9%, this brief test was successful in verifying that predicted biodegradation of off-gas was measurable. Following the high hydrocarbon concentration test, Off-Gas Treatment Plot V3 was operated by drawing atmospheric air through the plot until the end of the field test (venting Days 143 through 184). Upon introduction of atmospheric air, total hydrocarbons in the discharge air stream dropped to 2.2  $\mu\text{L/L}$  (ppm) within 24 hours. Carbon dioxide concentration in V3 remained elevated, by approximately 1%, above Background Plot V4 for a period of approximately 20 days. By the end of the field study, total hydrocarbons and carbon dioxide in V3 and V4 discharge gases were essential identical.

Cumulative hydrocarbons injected into and discharged from Off-Gas Treatment Plot V3 are compared in Figure 60. Summarized data and calculations based on the mass balance presented in Appendix A are located in Appendix C. Of the total hydrocarbons passing through Treatment Plot V3, 41% were biodegraded and 59% passed through untreated. However, the percentages of injected hydrocarbon vapors degraded in V3 varied widely and were dependent on air flow rate, hydrocarbon loading rate, and acclimation of the soil microbes, over time, to the hydrocarbon vapors.

Figure 61 illustrates that oxygen consumption rate constants ( $k$ ) (Appendix C), calculated from the mass balance (Appendix A), are relatively consistent (Mean = 1.56 %  $O_2$ /day, SD  $\pm$  0.91 %  $O_2$ /day) in Off-Gas Treatment Plot V3, and that there was a statistically significant (95% confidence) increase in oxygen consumption over the field test period. The increase in oxygen consumption rate constants ( $k$ ) over time may indicate an acclimation of soil microbes to the hydrocarbon vapor. However, the values of  $k$  presented in Figure 61 represent an integration over the field test period because calculated values (Appendix C) were not corrected for temperature, hydrocarbon loading rate, moisture content, or other possible site variables. Calculated rate constants in Off-Gas Treatment Plot V3 were significantly greater than those observed in the Background Plot and approached the rate constants observed in the treatment plots during respiration (shutdown) tests. The relative consistency of rate constants observed in Off-Gas Treatment Plot V3 indicate that the percent of hydrocarbon vapor biodegraded in clean soil is, at least partially, a function of retention time/flow rate. A statistically significant relationship (95% confidence level) between flow rate and the percent of injected hydrocarbon vapor biodegraded is illustrated Figure 62. Although the

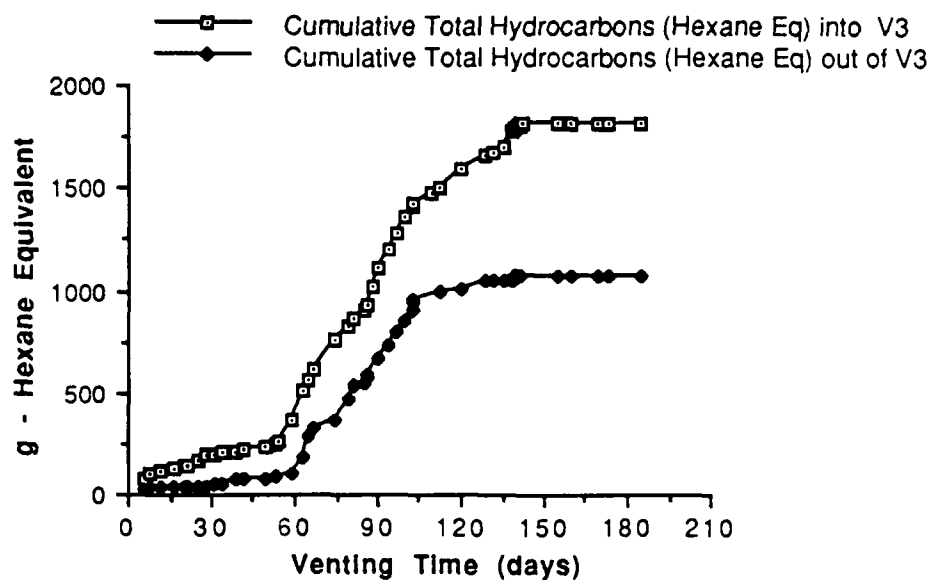


Figure 60. Cumulative hydrocarbons injected into, and discharged from Off-Gas Treatment Plot V3 during the field study.

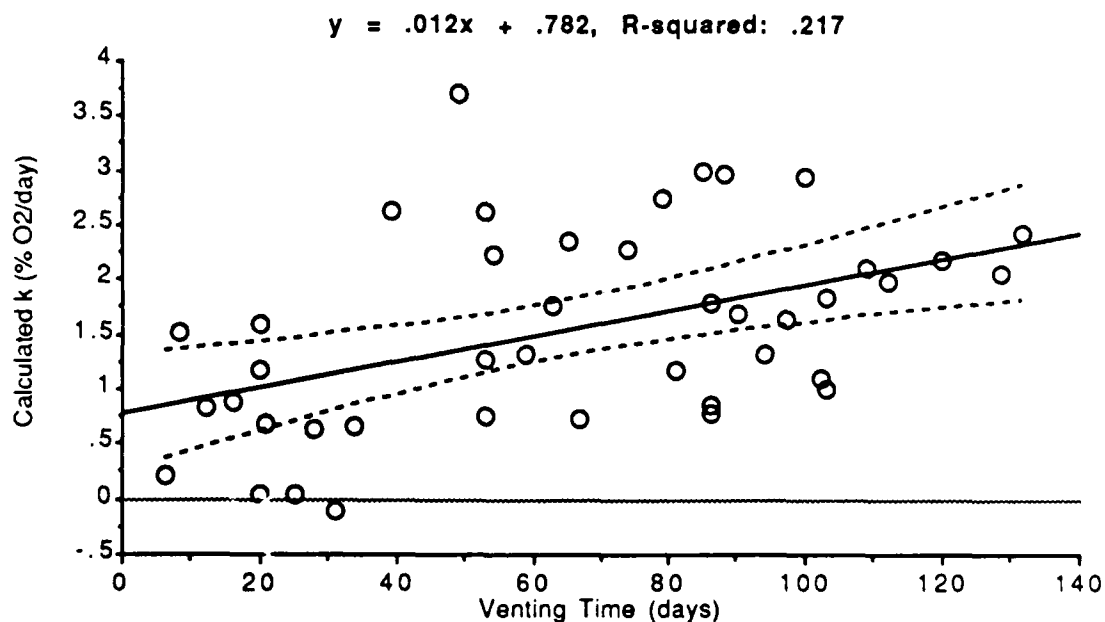


Figure 61. Oxygen consumption rate constants calculated from a mass balance in Off-Gas Treatment Plot V3 determined throughout the field study.

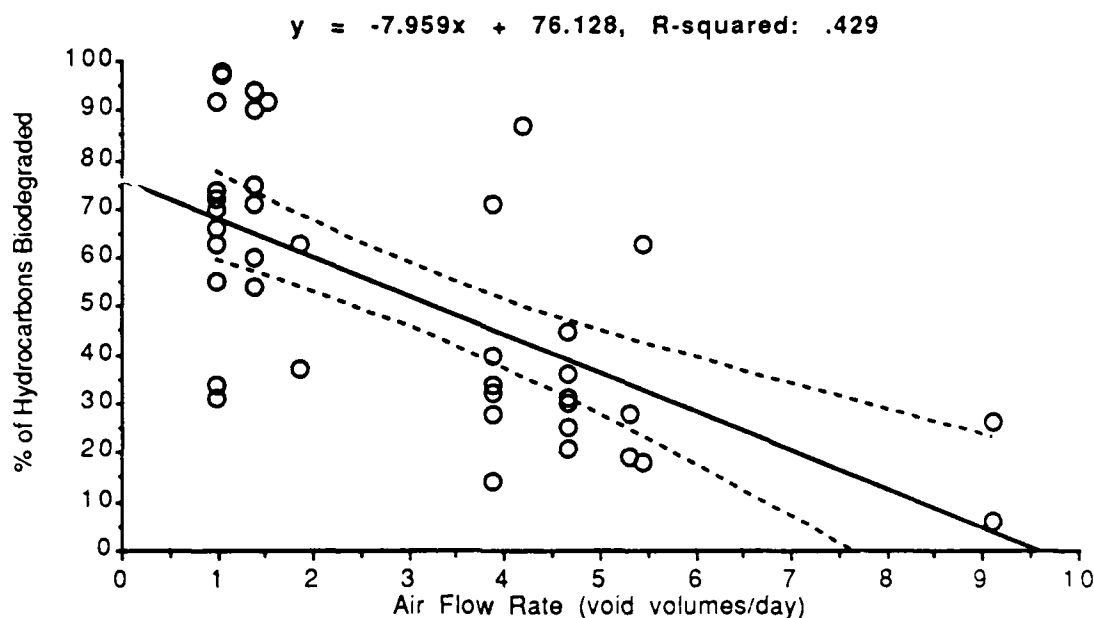


Figure 62. Correlation and 95% confidence band for relationship between air flow rate and the percent of hydrocarbon vapor degraded in the uncontaminated soil of Off-Gas Treatment Plot V3.

relationship between air flow rate and percent biodegradation is significant (Figure 62), a relatively wide spread in percent biodegradation for given flow rates exists. This occurred because of the wide range of hydrocarbon concentrations injected into Off-Gas Treatment Plot V3 throughout the field test.

Therefore, percent biodegradation was not only associated with air flow rate (retention time), but also with hydrocarbon loading rate, at the 95% confidence level, (Figure 63).

The average off-gas biodegradation rate (Appendix C) was  $1.34$  ( $SD \pm 0.83$ )  $\text{mg}/(\text{kg day})$ , or  $1.93$  ( $SD \pm 1.2$ )  $\text{g}/(\text{m}^3 \text{ day})$ . Hydrocarbon biodegradation rates in units of  $\text{mg}/(\text{kg day})$  and  $\text{g}/(\text{m}^3 \text{ day})$ , respectively, were positively correlated (95% confidence level) to total hydrocarbon loading as illustrated in Figures 64 and 65.

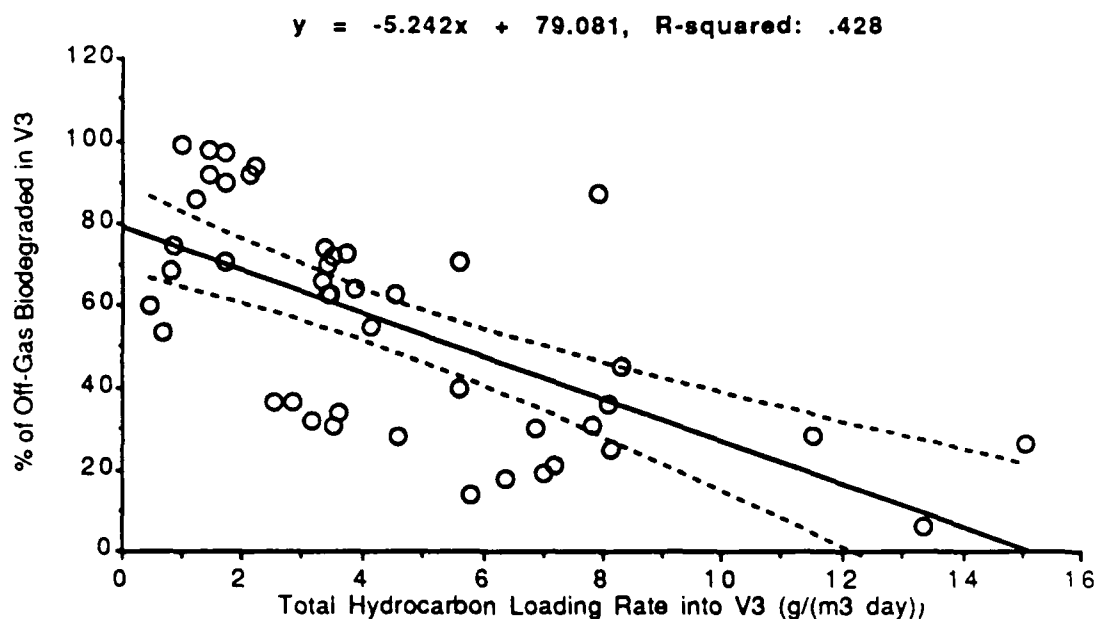


Figure 63. Correlation and 95% confidence band for relationship between hydrocarbon loading rate and the percent of hydrocarbon vapor degraded in the uncontaminated soil of Off-Gas Treatment Plot V3.

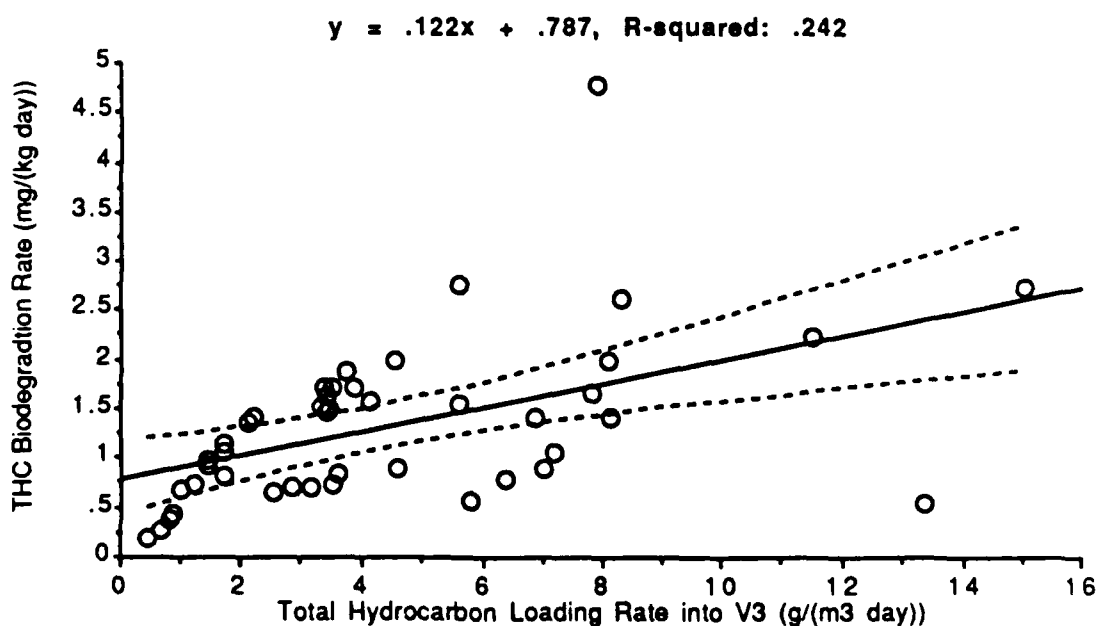


Figure 64. Correlation and 95% confidence band for relationship between hydrocarbon loading rate and hydrocarbon biodegradation rate mg/(kg day) in the uncontaminated soil of Off-Gas Treatment Plot V3.

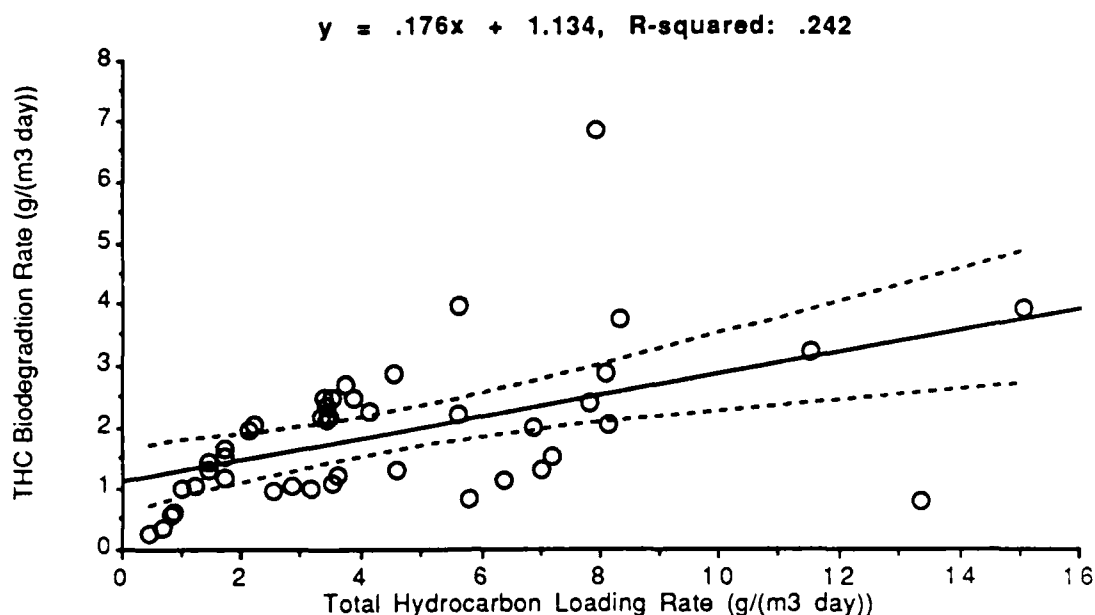


Figure 65. Correlation and 95% confidence band for relationship between hydrocarbon loading rate and hydrocarbon biodegradation rate g/(m<sup>3</sup> day) in the uncontaminated soil of Off-Gas Treatment Plot V3.

During 188 days of venting at Treatment Plot V1, 25,800 g were removed through volatilization. Assuming an average off-gas biodegradation rate of 1.93 g/(m<sup>3</sup> day), 71 m<sup>3</sup> of uncontaminated soil would be required to completely biodegrade the off-gas from the 20 m<sup>3</sup> of contaminated soil in Treatment Plot V1. Therefore, a soil volume ratio of approximately 3.6 to 1, uncontaminated to contaminated soil, would be required to completely biodegrade the off-gas from a bioventing system operated similar to this field project. However, if air flow rates in contaminated soil were designed to maximize biodegradation, the ratio of uncontaminated to contaminated soil required would be proportionally less.

The data presented indicate that uncontaminated soil at this test site can be successfully used as a biological reactor for the mineralization of hydrocarbon vapors (off-gas) generated during remediation of fuel contaminated soil using the Enhanced Biodegradation Through Soil Venting Technology investigated in this field study.

## Respiration Tests

Respiration Tests, 1 through 5, were conducted October 24 through 26; November 28 through December 1, 1989; January 3 through 8; March 3 through 11; and April 24 through 26, 1990, respectively. In addition, two limited respiration tests, 3A and 4A, were conducted from January 25 through 26, and March 9 through 12, 1990. The respiration tests were designed to determine the order and rate of hydrocarbon biodegradation kinetics under varying conditions of moisture and nutrient addition described in Table 6. Treatment Plot V2 received moisture and nutrients throughout the experimental period and therefore serves as a control for kinetic changes due to soil temperature and other factors not related to moisture and nutrients. The respiration tests were conducted by first shutting down the air delivery system to both the treatment and background plots, followed by measurement of oxygen consumption and carbon dioxide production over time. One percent oxygen concentration was the minimum that could be accurately measured. Raw data are presented chronologically in Appendix B, while summarized respiration data for individual respiration tests are presented in Appendices E through I. Appendix J contains graphs of the raw data including zero order plots of O<sub>2</sub> consumption and CO<sub>2</sub> production, and first order plots of O<sub>2</sub> consumption, for all vapor monitoring points in the treatment and background plots. Figures 66, 67, and 68 are plots of respiration data for vapor monitoring well V1-1B and are typical of the plots for other vapor monitoring wells contained in Appendix J.

Figures 66 and 67 illustrate that oxygen consumption follows a zero order kinetic model better than a first order kinetic model for all tests at vapor monitoring well V1-1B.

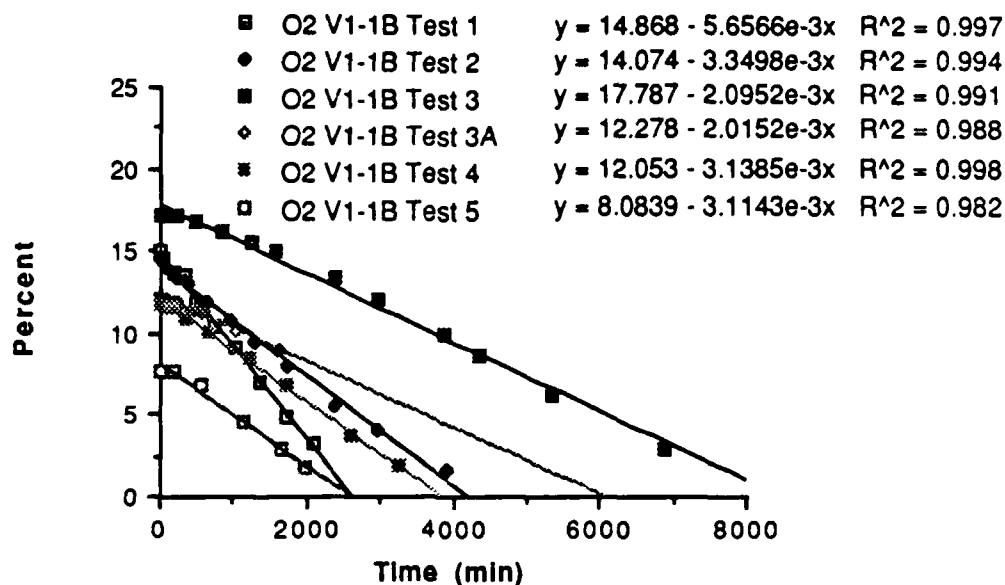


Figure 66. Zero order plot of oxygen consumption in Vapor Monitoring Well V1-1B for Respiration Tests 1 through 5.

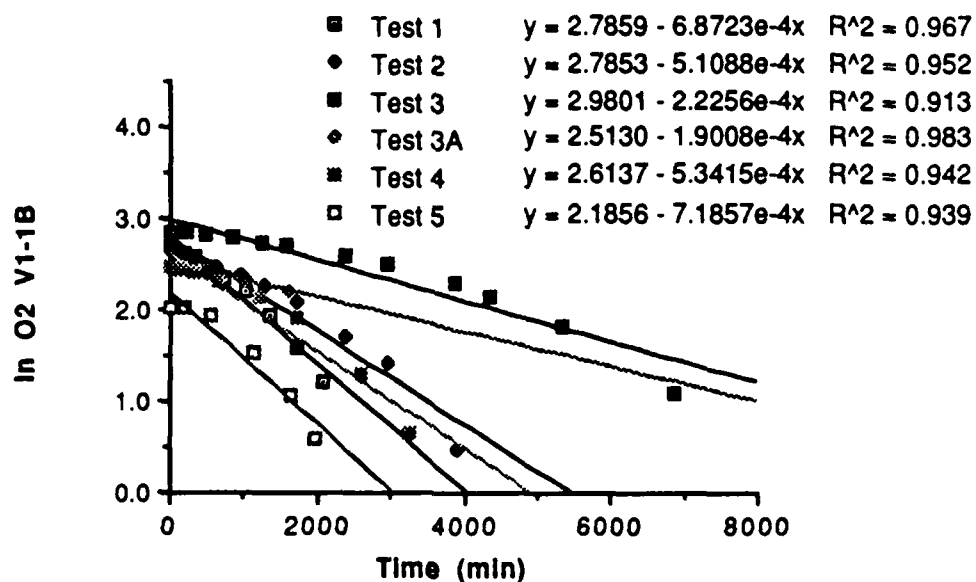


Figure 67. First order plot of oxygen consumption in Vapor Monitoring Well V1-1B for Respiration Tests 1 through 5.

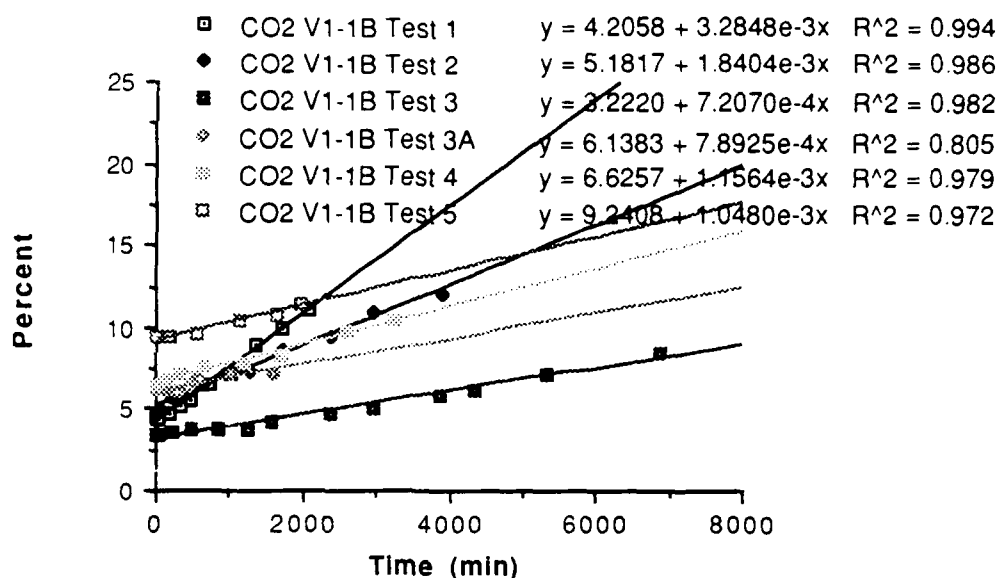


Figure 68. Zero order plot of carbon dioxide production in Vapor Monitoring Well V1-1B for Respiration Tests 1 through 5.

From inspection of the plots in Appendix J and the summary statistics in Table 10, it appears that respiration in Treatment Plot V1 was best modeled by zero order kinetics at all locations except V1-1A and V1-2A. At these locations, first order plots achieved higher coefficients of determination on the majority of tests. Respiration in V2 was also most consistently modeled by zero order kinetics at most locations and during most tests. However, in seven of the nine locations, first order kinetics better described the data during at least 1 test (Table 10). Only location V2-1B was consistently better described by first order kinetics. From observation of the figures in Appendix J and the summary provided in Table 10, it was concluded that overall respiration for Treatment Plots V1 and V2 were most consistently modeled by zero order kinetics during all respiration tests. In a system not limited by substrate, such as fuel contaminated soil, biodegradation is likely to be best modeled by zero-order kinetics (Riser, 1988).

Table 10. Summary of coefficients of determination (R-squared) and rate constants (k) for treatment, off-gas, and background plots.

| Vapor Well Location | Test No. | Zero Order R-squared | Zero Order k |         | First Order R-squared | First Order k |         |
|---------------------|----------|----------------------|--------------|---------|-----------------------|---------------|---------|
|                     |          |                      | (%/min)      | (%/day) |                       | (1/min)       | (1/day) |
| V1-1A               | 1        | 0.975                | 0.00874      | 12.59   | <b>0.991</b>          | 0.00127       | 1.83    |
|                     | 2        | 0.925                | 0.00329      | 4.74    | <b>0.991</b>          | 0.000489      | 0.70    |
|                     | 3        | <b>0.996</b>         | 0.00256      | 3.69    | <b>0.947</b>          | 0.000279      | 0.40    |
|                     | 4        | 0.986                | 0.00558      | 8.04    | <b>0.997</b>          | 0.000698      | 1.01    |
|                     | 5        | <b>0.992</b>         | 0.00568      | 8.18    | 0.973                 | 0.00153       | 2.20    |
| V1-1B               | 1        | <b>0.997</b>         | 0.00566      | 8.15    | 0.967                 | 0.000687      | 0.99    |
|                     | 2        | <b>0.994</b>         | 0.00335      | 4.82    | 0.952                 | 0.000511      | 0.74    |
|                     | 3        | <b>0.991</b>         | 0.0021       | 3.02    | 0.913                 | 0.000223      | 0.32    |
|                     | 3A       | <b>0.998</b>         | 0.00202      | 2.91    | <b>0.983</b>          | 0.00019       | 0.27    |
|                     | 4        | <b>0.998</b>         | 0.00314      | 4.52    | 0.942                 | 0.000534      | 0.77    |
| V1-1C               | 5        | <b>0.982</b>         | 0.00311      | 4.48    | 0.939                 | 0.000719      | 1.04    |
|                     | 1        | <b>0.994</b>         | 0.0048       | 6.91    | 0.89                  | 0.000765      | 1.10    |
|                     | 2        | <b>0.994</b>         | 0.00304      | 4.38    | 0.959                 | 0.00043       | 0.62    |
|                     | 3        | <b>0.99</b>          | 0.00203      | 2.92    | 0.917                 | 0.000204      | 0.29    |
|                     | 4        | <b>0.987</b>         | 0.00273      | 3.93    | 0.922                 | 0.000463      | 0.67    |
| V1-2A               | 5        | <b>0.968</b>         | 0.00283      | 4.08    | 0.924                 | 0.000612      | 0.88    |
|                     | 1        | 0.934                | 0.0115       | 16.56   | <b>0.993</b>          | 0.00149       | 2.15    |
|                     | 2        | 0.878                | 0.0037       | 5.33    | <b>0.984</b>          | 0.000529      | 0.76    |
|                     | 3        | <b>0.99</b>          | 0.00249      | 3.59    | 0.927                 | 0.000327      | 0.47    |
|                     | 4        | <b>0.976</b>         | 0.00514      | 7.40    | 0.971                 | 0.00072       | 1.04    |
| V1-2B               | 5        | 0.975                | 0.00961      | 13.84   | <b>0.994</b>          | 0.00159       | 2.29    |
|                     | 1        | <b>0.996</b>         | 0.00618      | 8.90    | 0.935                 | 0.00086       | 1.24    |
|                     | 2        | <b>0.99</b>          | 0.00367      | 5.28    | 0.964                 | 0.000512      | 0.74    |
|                     | 3        | <b>0.998</b>         | 0.00219      | 3.15    | 0.918                 | 0.000233      | 0.34    |
|                     | 3A       | 0.963                | 0.00306      | 4.41    | <b>0.975</b>          | 0.00023       | 0.33    |
| V1-2C               | 4        | 1                    | 0.00392      | 5.64    | 0.953                 | 0.000533      | 0.77    |
|                     | 5        | <b>0.999</b>         | 0.00542      | 7.80    | 0.942                 | 0.00102       | 1.47    |
|                     | 1        | <b>0.964</b>         | 0.00411      | 5.92    | 0.906                 | 0.000555      | 0.80    |
|                     | 2        | <b>0.973</b>         | 0.00304      | 4.38    | 0.919                 | 0.000469      | 0.68    |
|                     | 3        | <b>0.983</b>         | 0.00201      | 2.89    | 0.889                 | 0.000218      | 0.31    |
| V1-3A               | 4        | <b>0.993</b>         | 0.00343      | 4.94    | 0.948                 | 0.000449      | 0.65    |
|                     | 5        | <b>0.99</b>          | 0.00402      | 5.79    | 0.928                 | 0.00071       | 1.02    |
|                     | 1        | <b>0.989</b>         | 0.000805     | 1.16    | 0.911                 | 0.00111       | 1.60    |
|                     | 2        | <b>0.97</b>          | 0.00305      | 4.39    | 0.954                 | 0.000289      | 0.42    |
|                     | 3        | <b>0.984</b>         | 0.00231      | 3.33    | 0.976                 | 0.000223      | 0.32    |
| V1-3B               | 4        | 0.963                | 0.00456      | 6.57    | <b>0.991</b>          | 0.000557      | 0.80    |
|                     | 5        | <b>0.972</b>         | 0.00616      | 8.87    | 0.955                 | 0.00113       | 1.63    |
|                     | 1        | <b>0.995</b>         | 0.0073       | 10.51   | 0.935                 | 0.001         | 1.44    |
|                     | 2        | 0.983                | 0.00372      | 5.36    | <b>0.985</b>          | 0.00046       | 0.66    |
|                     | 3        | 1                    | 0.00198      | 2.85    | 0.963                 | 0.000183      | 0.26    |
|                     | 3A       | 0.976                | 0.00266      | 3.83    | <b>0.98</b>           | 0.000203      | 0.29    |
|                     | 4        | 1                    | 0.00333      | 4.80    | 0.966                 | 0.00042       | 0.60    |
|                     | 5        | <b>0.993</b>         | 0.00405      | 5.83    | 0.96                  | 0.000657      | 0.95    |

Table 10 continued. Summary of coefficients of determination (R-squared) and rate constants (k) for treatment, off-gas, and background plots.

| Vapor Well Location           | Test No. | Zero Order R-squared | Zero Order k |         | First Order R-squared | First Order k |         |
|-------------------------------|----------|----------------------|--------------|---------|-----------------------|---------------|---------|
|                               |          |                      | (%/min)      | (%/day) |                       | (1/min)       | (1/day) |
| V1-3C                         | 1        | 0.989                | 0.00603      | 8.68    | 0.937                 | 0.000896      | 1.29    |
|                               | 2        | 0.984                | 0.00368      | 5.30    | 0.959                 | 0.000583      | 0.84    |
|                               | 3        | 0.998                | 0.00192      | 2.76    | 0.948                 | 0.000188      | 0.27    |
|                               | 4        | 0.987                | 0.00287      | 4.13    | 0.939                 | 0.000391      | 0.56    |
|                               | 5        | 0.979                | 0.00356      | 5.13    | 0.937                 | 0.000565      | 0.81    |
| V1-average of all regressions | 1        |                      | 0.00613      | 8.82    |                       | 0.000959      | 1.38    |
|                               | 2        |                      | 0.00339      | 4.89    |                       | 0.000475      | 0.68    |
|                               | 3        |                      | 0.00218      | 3.13    |                       | 0.000231      | 0.33    |
|                               | 4        |                      | 0.00386      | 5.55    |                       | 0.000529      | 0.76    |
|                               | 5        |                      | 0.00494      | 7.11    |                       | 0.000948      | 1.37    |
| V2-1A                         | 1        | 0.897                | 0.00612      | 8.81    | 0.841                 | 0.000641      | 0.92    |
|                               | 2        | 0.791                | 0.00341      | 4.91    | 0.871                 | 0.000303      | 0.44    |
|                               | 3        | 0.987                | 0.00269      | 3.87    | 0.971                 | 0.000153      | 0.22    |
|                               | 4        | 0.98                 | 0.00378      | 5.44    | 0.997                 | 0.000292      | 0.42    |
|                               | 5        | 0.975                | 0.00519      | 7.47    | 0.983                 | 0.000517      | 0.74    |
| V2-1B                         | 1        | 0.952                | 0.00546      | 7.86    | 0.991                 | 0.000754      | 1.09    |
|                               | 2        | 0.944                | 0.00592      | 8.52    | 0.991                 | 0.00101       | 1.45    |
|                               | 3        | 0.99                 | 0.00498      | 7.17    | 0.997                 | 0.00039       | 0.56    |
|                               | 3A       | 0.971                | 0.00473      | 6.81    | 0.995                 | 0.000623      | 0.90    |
|                               | 4        | 0.956                | 0.00397      | 5.72    | 0.995                 | 0.000711      | 1.02    |
| V2-1C                         | 5        | 0.952                | 0.00609      | 8.77    | 1                     | 0.00136       | 1.96    |
|                               | 1        | 0.983                | 0.00418      | 6.02    | 0.987                 | 0.000541      | 0.78    |
|                               | 2        | 0.985                | 0.00493      | 7.10    | 0.943                 | 0.000979      | 1.41    |
|                               | 3        | 0.998                | 0.00339      | 4.88    | 0.993                 | 0.000224      | 0.32    |
|                               | 4        | 0.996                | 0.00337      | 4.85    | 0.955                 | 0.000514      | 0.74    |
| V2-2A                         | 5        | 0.985                | 0.00327      | 4.71    | 0.938                 | 0.00105       | 1.51    |
|                               | 1        | 0.837                | 0.00491      | 7.07    | 0.766                 | 0.000405      | 0.58    |
|                               | 2        | 0.961                | 0.0039       | 5.62    | 0.996                 | 0.000339      | 0.49    |
|                               | 3        | 0.99                 | 0.00254      | 3.66    | 0.979                 | 0.000141      | 0.20    |
|                               | 4        | 0.999                | 0.00444      | 6.39    | 0.975                 | 0.000347      | 0.50    |
| V2-2B                         | 5        | 0.989                | 0.00572      | 8.24    | 0.992                 | 0.0005        | 0.72    |
|                               | 1        | 0.988                | 0.00637      | 9.17    | 0.978                 | 0.00078       | 1.12    |
|                               | 2        | 0.976                | 0.00394      | 5.67    | 0.932                 | 0.0008        | 1.15    |
|                               | 3        | 0.998                | 0.00358      | 5.16    | 0.986                 | 0.000232      | 0.33    |
|                               | 3A       | 0.975                | 0.00318      | 4.58    | 0.953                 | 0.000476      | 0.69    |
| V2-2C                         | 4        | 0.999                | 0.0052       | 7.49    | 0.942                 | 0.000674      | 0.97    |
|                               | 5        | 0.933                | 0.00459      | 6.61    | 0.912                 | 0.000995      | 1.43    |
|                               | 1        | 0.973                | 0.00584      | 8.41    | 0.97                  | 0.000932      | 1.34    |
|                               | 2        | 0.53                 | 0.0016       | 2.30    | 0.653                 | 0.000723      | 1.04    |
|                               | 3        | 0.994                | 0.00346      | 4.98    | 0.98                  | 0.000234      | 0.34    |
|                               | 4        | 0.998                | 0.00479      | 6.90    | 0.886                 | 0.000915      | 1.32    |
|                               | 5        | 0.645                | 0.00227      | 3.27    | 0.716                 | 0.00104       | 1.50    |

Table 10 continued. Summary of coefficients of determination (R-squared) squared and rate constants (k) for treatment, off-gas, and background plots.

| Vapor Well Location             | Test No. | Zero Order R-squared | Zero Order k |         | First Order R-squared | First Order k |         |
|---------------------------------|----------|----------------------|--------------|---------|-----------------------|---------------|---------|
|                                 |          |                      | (%/min)      | (%/day) |                       | (1/min)       | (1/day) |
| V2-3A                           | 1        | <b>0.941</b>         | 0.00645      | 9.29    | 0.875                 | 0.000586      | 0.84    |
|                                 | 2        | <b>0.905</b>         | 0.00387      | 5.57    | 0.971                 | 0.000394      | 0.57    |
|                                 | 3        | <b>0.995</b>         | 0.00322      | 4.64    | 0.992                 | 0.00019       | 0.27    |
|                                 | 4        | 0.976                | 0.00475      | 6.84    | <b>0.991</b>          | 0.000459      | 0.66    |
|                                 | 5        | 0.961                | 0.00538      | 7.75    | <b>0.996</b>          | 0.000507      | 0.73    |
| V2-3B                           | 1        | 0.978                | 0.00614      | 8.84    | <b>0.979</b>          | 0.000844      | 1.22    |
|                                 | 2        | 0.947                | 0.00536      | 7.72    | <b>0.987</b>          | 0.00107       | 1.54    |
|                                 | 3        | <b>0.996</b>         | 0.00328      | 4.72    | 0.995                 | 0.000208      | 0.30    |
|                                 | 3A       | <b>0.991</b>         | 0.00386      | 5.56    | 0.995                 | 0.000431      | 0.62    |
|                                 | 4        | <b>0.995</b>         | 0.00386      | 5.56    | 0.972                 | 0.000538      | 0.77    |
| V2-3C                           | 5        | <b>0.984</b>         | 0.00436      | 6.28    | 0.979                 | 0.000726      | 1.05    |
|                                 | 1        | <b>0.997</b>         | 0.00604      | 8.70    | 0.937                 | 0.00123       | 1.77    |
|                                 | 2        | <b>0.968</b>         | 0.00611      | 8.80    | 0.858                 | 0.0014        | 2.02    |
|                                 | 3        | <b>0.999</b>         | 0.00344      | 4.95    | 0.995                 | 0.000241      | 0.35    |
|                                 | 4        | <b>0.997</b>         | 0.00392      | 5.64    | 0.945                 | 0.00063       | 0.91    |
| V2 - average of all regressions | 5        | <b>0.903</b>         | 0.00362      | 5.21    | 0.877                 | 0.000826      | 1.19    |
|                                 | 1        |                      | 0.00572      | 8.24    |                       | 0.000746      | 1.07    |
|                                 | 2        |                      | 0.00434      | 6.25    |                       | 0.000780      | 1.12    |
|                                 | 3        |                      | 0.00340      | 4.89    |                       | 0.000224      | 0.32    |
|                                 | 4        |                      | 0.00423      | 6.09    |                       | 0.000564      | 0.81    |
| *V3-average of A,B,C locations  | 5        |                      | 0.00450      | 6.48    |                       | 0.000836      | 1.20    |
|                                 | 1        | 0.825                | 0.000289     | 0.416   | <b>0.83</b>           | 1.63E-05      | 0.023   |
|                                 | 3        | 0.982                | 0.000466     | 0.671   | <b>0.985</b>          | 0.000029      | 0.042   |
|                                 | 4        | <b>0.743</b>         | 0.000225     | 0.324   | 0.722                 | 1.52E-05      | 0.022   |
|                                 | 4A       | <b>0.99</b>          | 0.000715     | 1.030   | 0.989                 | 4.59E-05      | 0.066   |
| *V4-average of A,B,C locations  | 5        | 0.958                | 0.000389     | 0.560   | <b>0.961</b>          | 0.000021      | 0.030   |
|                                 | 1        | 0.787                | 0.000225     | 0.324   | <b>0.79</b>           | 1.19E-05      | 0.017   |
|                                 | 3        | 0.982                | 0.000207     | 0.298   | <b>0.985</b>          | 1.01E-05      | 0.015   |
|                                 | 4        | 0.962                | 0.000279     | 0.402   | <b>0.968</b>          | 1.43E-05      | 0.021   |
|                                 | 5        | 0.003                | 7.8E-06      | 0.011   | <b>0.011</b>          | 7.8E-07       | 0.001   |

\* Measurements at the A, B, and C locations were nearly identical.

Therefore, averages are representative of all locations.

Both zero and first order kinetic models were statistically significant and either could have been used to model and compare kinetics under varying moisture and nutrient conditions. Since biodegradation was shown to be best modeled by zero-order kinetics, and for simplicity, zero-order kinetics were selected as the basis for comparison.

Oxygen and carbon dioxide concentrations, measured in the vapor monitoring wells prior to initiating the respiration tests, were highly variable. Regardless of initial concentration, however, oxygen consumption and carbon dioxide production rates were relatively consistent. For this reason, the data were normalized by dividing oxygen concentration data measured in each vapor monitoring well by the initial oxygen concentration at each location. A regression of the normalized data versus time for each plot and each respiration test yielded a normalized zero order rate constant, that when multiplied by the initial average oxygen concentration in the plot, yielded the actual zero order rate constant ( $k = \%/min$ ).

The normalized regressions and 95% confidence interval bands for Treatment Plots V1 and V2 are illustrated in Figures 69 and 70, respectively, for Respiration Test 4. Regressions and 95% confidence interval bands for normalized data at all locations and from all tests are located in Appendix K, and both normalized and actual rate constant data are summarized in Table 11. Figures 71 and 72 graphically illustrate the rate constant data in Table 11.

In Treatment Plot V1, the rate constant showed a significant drop between Test 1 and Test 2, and between Test 2 and Test 3. The rate constant significantly increased between Test 3 and Test 4 in Treatment Plot V1, but did not significantly increase between Tests 4 and 5.

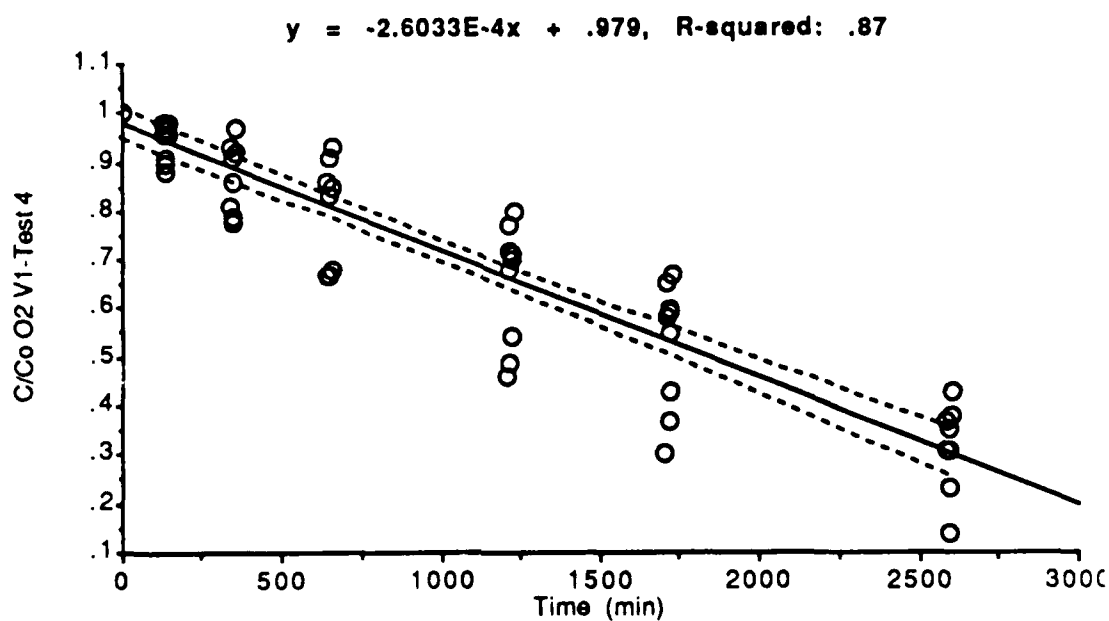


Figure 69. Regression of normalized data and 95% confidence band for Treatment Plot V1 and Respiration Test 4.

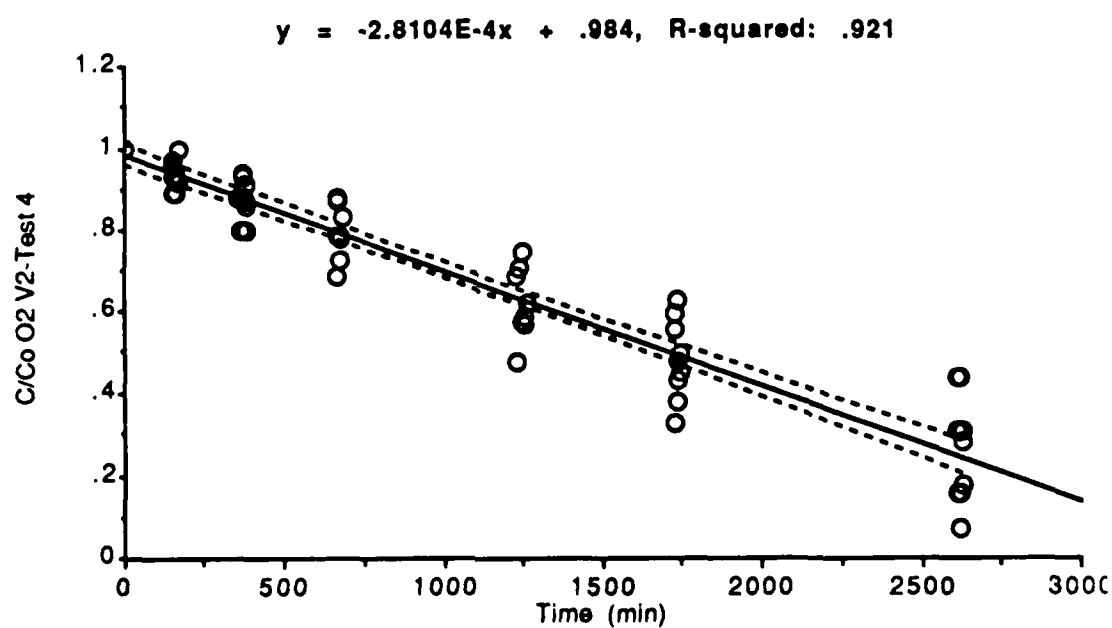


Figure 70. Regression of normalized data and 95% confidence band for Treatment Plot V2 and Respiration Test 4.

Table 11. Summary of normalized and actual zero order oxygen consumption rates and 95% confidence intervals.

| Location      | Initial<br>Avg O <sub>2</sub> (%) | Min 95% Norm<br>K (%O <sub>2</sub> /min) | Avg Norm<br>K (%O <sub>2</sub> /min) | Max 95% Norm<br>K (%O <sub>2</sub> /min) | Minimum 95%<br>K (%O <sub>2</sub> /min) | Average<br>K (%O <sub>2</sub> /min) | Maximum 95%<br>K (%O <sub>2</sub> /min) |
|---------------|-----------------------------------|------------------------------------------|--------------------------------------|------------------------------------------|-----------------------------------------|-------------------------------------|-----------------------------------------|
| <b>Test 1</b> |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| V1            | 15.4                              | .000356                                  | .000396                              | .000435                                  | .005487                                 | .006095                             | .006702                                 |
| V2            | 15.8                              | .000304                                  | .000343                              | .000382                                  | .004797                                 | .005413                             | .006031                                 |
| V3            | 18.2                              | .000010                                  | .000015                              | .000020                                  | .000187                                 | .000277                             | .000367                                 |
| V4            | 19.2                              | .000009                                  | .000013                              | .000017                                  | .000180                                 | .000251                             | .000322                                 |
| <b>Test 2</b> |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| V1            | 15.3                              | .000208                                  | .000223                              | .000238                                  | .003185                                 | .003416                             | .003648                                 |
| V2            | 13.7                              | .000312                                  | .000363                              | .000413                                  | .004280                                 | .004969                             | .005659                                 |
| V3            |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| V4            |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| <b>Test 3</b> |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| V1            | 17.6                              | .000116                                  | .000122                              | .000127                                  | .002049                                 | .002142                             | .002235                                 |
| V2            | 19.7                              | .000158                                  | .000173                              | .000189                                  | .003103                                 | .003416                             | .003729                                 |
| V3            | 17.4                              | .000028                                  | .000029                              | .000031                                  | .000480                                 | .000510                             | .000541                                 |
| V4            | 20.6                              | .000009                                  | .000010                              | .000011                                  | .000186                                 | .000205                             | .000225                                 |
| <b>Test 4</b> |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| V1            | 14.2                              | .000234                                  | .000260                              | .000286                                  | .003327                                 | .003696                             | .004065                                 |
| V2            | 16.2                              | .000260                                  | .000281                              | .000302                                  | .004212                                 | .004552                             | .004894                                 |
| V3            | 14.3                              | .000007                                  | .000015                              | .000023                                  | .000106                                 | .000214                             | .000322                                 |
| V4            | 20.3                              | .000012                                  | .000014                              | .000015                                  | .000240                                 | .000276                             | .000313                                 |
| V3 (4A)       | 17.2                              | .000040                                  | .000042                              | .000045                                  | .000685                                 | .000727                             | .000769                                 |
| <b>Test 5</b> |                                   |                                          |                                      |                                          |                                         |                                     |                                         |
| V1            | 10.3                              | .000347                                  | .000397                              | .000448                                  | .003576                                 | .004093                             | .004611                                 |
| V2            | 11.6                              | .000363                                  | .000439                              | .000515                                  | .004215                                 | .005096                             | .005979                                 |
| V3            | 19.2                              | .000017                                  | .000020                              | .000023                                  | .000331                                 | .000389                             | .000446                                 |
| V4            | 19.4                              | .000006                                  | .000004                              | .000007                                  | .000111                                 | .000008                             | .000126                                 |

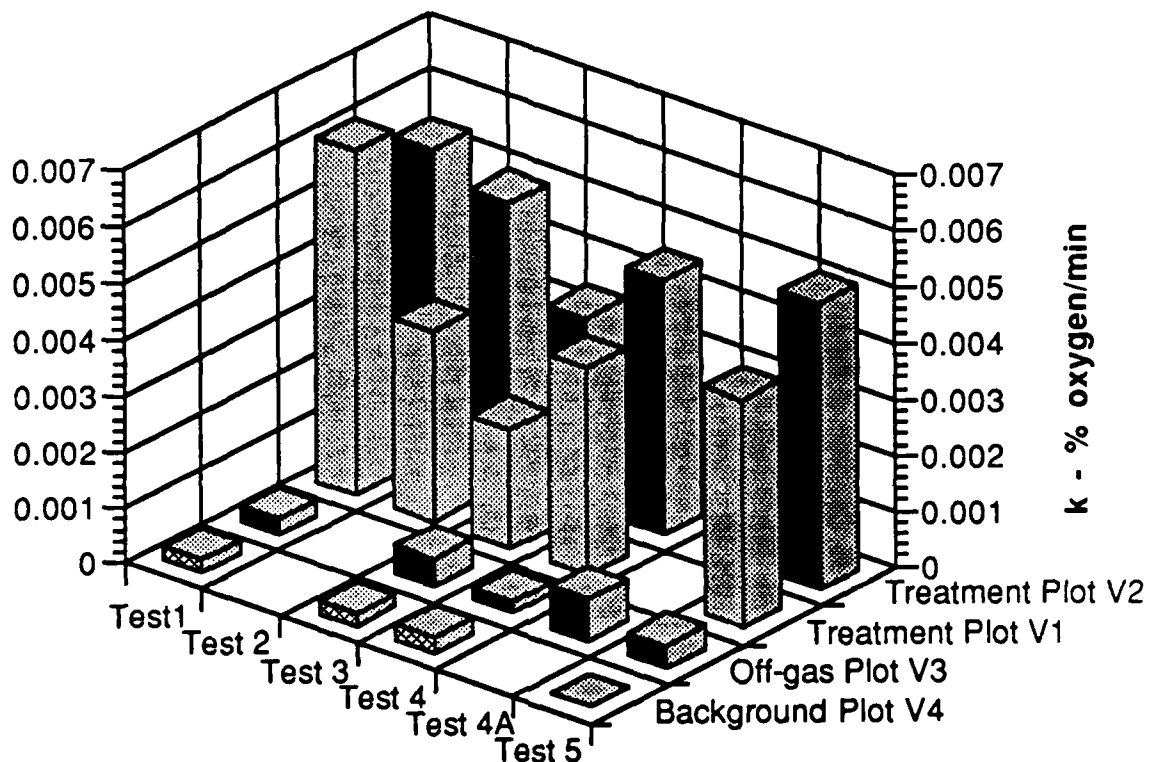


Figure 71. Average zero order rate constants determined by respiration tests.

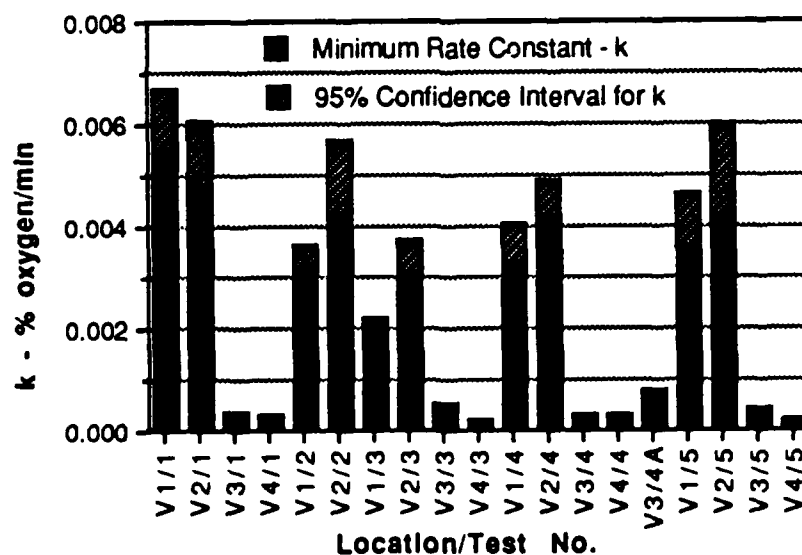


Figure 72. Zero-order rate constants ( $k$ ) and range of 95% confidence intervals determined by respiration tests. Mean  $k$  is at the center of the 95% confidence interval.

Since moisture was added to Treatment Plot V1 after Test 2 and nutrients after Test 4, their addition would seem, without further analysis, to be of no benefit and even detrimental, in the case of moisture addition. In Treatment Plot V2, there was a statistically significant drop in the rate constant from Test 2 to Test 3 and a statistically significant increase in the rate constant between Test 3 and Test 4. Although a depression appears in the rate constant data (Figures 71 and 72), there were no other statistically significant differences in Treatment Plot V2 rate constants.

Statistically significant differences in respiration rate between Treatment Plots V1 and V2, and the Background Plot V4, on all tests, and between Off-Gas Treatment Plot V3 and Background Plot V4, on Tests 3, 4A, and 5 are illustrated in Figures 71 and 72. From the data presented, it is concluded that biodegradation of jet fuel in contaminated soil, and biodegradation of hydrocarbon off-gas, resulted in statistically significant increases in respiration over that observed in uncontaminated soil.

### Static vs Dynamic Rate Constants In Treatment Plots V1 and V2

Static rate constants were determined during shutdown of the air delivery system. Theoretically, these rate constants should accurately model the operating system as well. Dynamic rate constants (Equation 6) require air retention time (Equation 7) data that are directly proportional to air filled porosity within the test plots. Air filled porosity was estimated by assuming a

$$\text{dynamic } k \text{ (\% O}_2\text{/min)} = \frac{\text{atmospheric O}_2 \text{ (\%)} - \text{treatment plot O}_2 \text{ (\%)}}{\text{air retention time (min)}} \quad (6)$$

$$\text{air retention time (min)} = \frac{\text{air filled porosity} \times \text{treatment volume (L)}}{\text{air flow rate (L/min)}} \quad (7)$$

bulk density, calculating total porosity, and applying moisture content data to determine air filled porosity.

Physical analysis of the soil texture (Appendix D) classified all samples as sand and a dry bulk density of 1440 kg/m<sup>3</sup> (90 lbs/ft<sup>3</sup>) was assumed based on a loose sand classification described by Terzaghi and Peck (1967). Moisture content data (Appendix L) was determined prior to operation, prior to moisture addition at Treatment Plot V1, and at the conclusion of the project after seven months of operation. Respiration Tests 1 and 2 were conducted prior to moisture addition at Treatment Plot V1 whereas Treatment Plot V2 had received moisture from the beginning of the project (Table 6). Therefore, soil moisture data collected December 1, 1989, prior to moisture addition to Treatment Plot V1, provided the best estimate of moisture content both before and after moisture addition. It was assumed that moisture content in Treatment Plots V1 and V2 were equal following moisture addition to Treatment Plot 1.

Moisture content on December 1, 1989, was determined from samples collected at 30, 60, 90, and 120 cm (1,2,3, and 4 ft) intervals. Average moisture content, by dry weight, was 6.48% (SD = 2.14%) and 9.78% (SD = 4.11%) in Treatment Plots V1 and V2, respectively. The samples collected at 150 cm (5 ft) were disregarded because they appeared to be saturated and the accuracy of these analyses was questionable. In addition, it was felt that the 120 cm (4 ft) sample better represented the moisture content in the 120 to 150 cm (4 to 5 ft) interval.

Air flow rates through all test plots were measured with calibrated rotameters. Calibration methods were described in the Materials and Methods Section. Flow rates were not totally stable prior to the first three respiration tests and this variability alone could lead to false comparisons of static and dynamic rates. A sensitivity analysis comparing dynamic and static rate constants considering possible variability in air flow rate, water level, and moisture content ( $\pm 2$  SD) is summarized in Tables 12 and 13 for Treatment Plots V1 and V2, respectively. The ranges of possible dynamic k values (Tables 12 and 13) were compared with the 95% confidence intervals for static k values (Table 11) and summarized in Tables 12 and 13 for Treatment Plots V1 and V2, respectively. The summaries in Tables 12 and 13 indicate that over the range of possible dynamic k values, there was no significant difference in static and dynamic rate constants in either Treatment Plots V1 or V2 for Tests 1, 3, 4, and 5. Dynamic k values for Test 2 were only slightly out of the 95% confidence range for V1 but there was a rather large difference in V2. The observed disparity between static and dynamic k values, assuming accurate air flow and soil moisture data, is likely related to the difference between initial average oxygen concentrations, measured in the vapor monitoring probes during respiration tests, and the discharge oxygen concentration, measured just prior to the respiration tests, used to calculate the dynamic rate constants.

Differences between the average oxygen concentration in vapor monitoring probes and the oxygen concentration in the discharge air streams are an indication of nonuniform flow through the treatment plots. Since static k values were determined by equally weighting data from each monitoring well (Figures 69 and 70, Appendix K), it follows that nonuniform flow through the

Table 12. Comparison of static and dynamic k (% oxygen/min) for Treatment Plot V1.

| Test No.                               | Water Depth<br>cm (ft) | Treatment<br>Volume m3 (ft3) | Moisture<br>(%) | Air Filled<br>Porosity | Rotameter<br>Reading (Cal) | Air Flow<br>(L/min)                   | Retention<br>Time (min) | Discharge<br>O2 (%) | Dynamic k<br>(% O2/min) | Static k<br>(% O2/min) | Difference<br>(%) | Initial<br>Average<br>O2 (%) |
|----------------------------------------|------------------------|------------------------------|-----------------|------------------------|----------------------------|---------------------------------------|-------------------------|---------------------|-------------------------|------------------------|-------------------|------------------------------|
| 1                                      | 268 (8.78)             | 23.5 (829)                   | 6.5             | 0.36                   | 14.5(12/1)                 | 11.89                                 | 704                     | 13                  | 0.01123                 | 0.00610                | 46                | 15.4                         |
|                                        | 268 (8.78)             | 23.5 (829)                   | 6.5             | 0.36                   | 11(12/1)                   | 7.53                                  | 1,111                   | 13                  | 0.00711                 | 0.00610                | 14                |                              |
|                                        | 268 (8.78)             | 23.5 (829)                   | 2.2             | 0.42                   | 14.5(12/1)                 | 11.89                                 | 826                     | 13                  | 0.00856                 | 0.00610                | 36                |                              |
|                                        | 268 (8.78)             | 23.5 (829)                   | 2.2             | 0.42                   | 11(12/1)                   | 7.53                                  | 1,304                   | 13                  | 0.00606                 | 0.00610                | -1                |                              |
|                                        | 268 (8.78)             | 23.5 (829)                   | 10.8            | 0.29                   | 14.5(12/1)                 | 11.89                                 | 581                     | 13                  | 0.01359                 | 0.00610                | 55                |                              |
| 2                                      | 268 (8.78)             | 23.5 (829)                   | 10.8            | 0.29                   | 11(12/1)                   | 7.53                                  | 918                     | 13                  | 0.00861                 | 0.00610                | 29                |                              |
|                                        | 230 (7.53)             | 19 (669)                     | 6.5             | 0.36                   | 8.6(12/1)                  | 4.99                                  | 1,353                   | 14.7                | 0.00458                 | 0.00342                | 25                | 15.3                         |
|                                        | 230 (7.53)             | 19 (669)                     | 6.5             | 0.36                   | 9.3(12/1)                  | 5.7                                   | 1,185                   | 14.7                | 0.00523                 | 0.00342                | 35                |                              |
|                                        | 230 (7.53)             | 19 (669)                     | 2.2             | 0.42                   | 8.6(12/1)                  | 4.99                                  | 1,589                   | 14.7                | 0.00390                 | 0.00342                | 12                |                              |
|                                        | 230 (7.53)             | 19 (669)                     | 2.2             | 0.42                   | 9.3(12/1)                  | 5.7                                   | 1,391                   | 14.7                | 0.00446                 | 0.00342                | 23                |                              |
| 3                                      | 230 (7.53)             | 19 (669)                     | 10.8            | 0.29                   | 8.6(12/1)                  | 4.99                                  | 1,118                   | 14.7                | 0.00555                 | 0.00342                | 38                |                              |
|                                        | 230 (7.53)             | 19 (669)                     | 10.8            | 0.29                   | 9.3(12/1)                  | 5.7                                   | 978                     | 14.7                | 0.00634                 | 0.00342                | 46                |                              |
|                                        | 232 (7.6)              | 19.2 (678)                   | 9.8             | 0.31                   | 8.2(12/1)                  | 4.6                                   | 1,289                   | 17.8                | 0.00241                 | 0.00214                | 11                | 17.6                         |
|                                        | 232 (7.6)              | 19.2 (678)                   | 9.8             | 0.31                   | 8.2(1/8)                   | 3.62                                  | 1,638                   | 17.8                | 0.00189                 | 0.00214                | -13               |                              |
|                                        | 232 (7.6)              | 19.2 (678)                   | 1.7             | 0.43                   | 8.2(12/1)                  | 4.6                                   | 1,777                   | 17.8                | 0.00174                 | 0.00214                | -23               |                              |
| 4                                      | 232 (7.6)              | 19.2 (678)                   | 1.7             | 0.43                   | 8.2(1/8)                   | 3.62                                  | 2,257                   | 17.8                | 0.00137                 | 0.00214                | -56               |                              |
|                                        | 232 (7.6)              | 19.2 (678)                   | 18.00           | 0.19                   | 8.2(12/1)                  | 4.6                                   | 795                     | 17.8                | 0.00390                 | 0.00214                | 45                |                              |
|                                        | 232 (7.6)              | 19.2 (678)                   | 18.00           | 0.19                   | 8.2(1/8)                   | 3.62                                  | 1,010                   | 17.8                | 0.00307                 | 0.00214                | 30                |                              |
|                                        | 233 (7.65)             | 19.4 (685)                   | 9.8             | 0.31                   | 9(1/8)                     | 4.22                                  | 1,418                   | 15.3                | 0.00395                 | 0.00370                | 6                 | 14.2                         |
|                                        | 233 (7.65)             | 19.4 (685)                   | 1.7             | 0.43                   | 9(1/8)                     | 4.22                                  | 1,955                   | 15.3                | 0.00286                 | 0.00370                | -29               |                              |
| 5                                      | 233 (7.65)             | 19.4 (685)                   | 18.0            | 0.19                   | 9(1/8)                     | 4.22                                  | 875                     | 15.3                | 0.00640                 | 0.00370                | 42                |                              |
|                                        | 226 (7.42)             | 19.6 (655)                   | 9.8             | 0.31                   | 9(1/8)                     | 4.22                                  | 1,357                   | 12.7                | 0.00604                 | 0.00409                | 32                | 10.3                         |
|                                        | 226 (7.42)             | 19.6 (655)                   | 1.7             | 0.43                   | 9(1/8)                     | 4.22                                  | 1,871                   | 12.7                | 0.00438                 | 0.00409                | 7                 |                              |
|                                        | 226 (7.42)             | 19.6 (655)                   | 18.0            | 0.19                   | 9(1/8)                     | 4.22                                  | 837                     | 12.7                | 0.00980                 | 0.00409                | 58                |                              |
| Dynamic k Range (95% confidence level) |                        |                              |                 |                        |                            |                                       |                         |                     |                         |                        |                   |                              |
| Dynamic k Range (95% confidence level) |                        |                              |                 |                        |                            | Static k Range (95% confidence level) |                         |                     | Significantly Different |                        |                   |                              |
| % O2/min                               |                        |                              |                 |                        |                            | % O2/min                              |                         |                     |                         |                        |                   |                              |
| 1                                      | .0061 to .0136         |                              |                 |                        |                            | .0055 to .0067                        |                         |                     | No                      |                        |                   |                              |
| 2                                      | .0039 to .0063         |                              |                 |                        |                            | .0032 to .0036                        |                         |                     | Yes                     |                        |                   |                              |
| 3                                      | .0014 to .0039         |                              |                 |                        |                            | .0020 to .0022                        |                         |                     | No                      |                        |                   |                              |
| 4                                      | .0029 to .0064         |                              |                 |                        |                            | .0033 to .0041                        |                         |                     | No                      |                        |                   |                              |
| 5                                      | .0044 to .0098         |                              |                 |                        |                            | .0036 to .0046                        |                         |                     | No                      |                        |                   |                              |



treatment plots would result in a difference between calculated static and dynamic rate constants.

### **Static vs Dynamic Rate Constants in Off-Gas Treatment Plot V3**

The rate constant for Off-Gas Treatment Plot V3 increased significantly, at the 89% confidence level, between Tests 1 and 3 indicating a likely increase in microbial activity due to degradation of off-gas from Treatment Plot V1. The dynamic rate constants in Off-Gas Treatment Plot V3 have been shown (Figure 61) to average 1.56 (SD  $\pm$  0.91) %/day ( .0011 (SD  $\pm$  .00063) %/min). The static rate constants (Table 11) determined from respiration tests are significantly less than the dynamic rates with the exception of Test 4A. This occurred because Off-Gas Treatment Plot V3 became substrate (hydrocarbon) starved rapidly after shutdown of the hydrocarbon injection system. Only in Test 4A were measurements taken immediately following shutdown, and at short enough time intervals, to observe the true early time rate constant which compares favorably with dynamic rate constants.

### **Potential Temperature Effects on Respiration Tests**

The potential effect of temperature on hydrocarbon removal due to biodegradation was previously discussed and hydrocarbon removal rates were shown to follow the pattern of both average ambient air temperature and soil temperature. A comparison of average soil temperature to oxygen consumption rate during respiration tests in Treatment Plots V1 and V2 is presented in

Figures 73 and 74, and a relationship between soil temperature and biological activity, as measured by the rate of oxygen consumption, is implied. It appears from the respiration data presented, that soil temperature had a much more significant effect on the rate of biodegradation than moisture and nutrient addition.

Treatment Plot V2 received moisture and nutrients throughout the experimental period and should be a control on temperature and other unmeasured variables. Figures 75 and 76 illustrate the results of two methods for correcting rate constants in Treatment Plot V1 using observed differences in rate constants, attributed to temperature, in Treatment Plot V2. Method 1 (Figure 75) was accomplished by using the rate constant determined in Treatment Plot V2 during Respiration Test 1 as a baseline. The rate constants in Tests 2 through 5 in Treatment Plot V2 were then subtracted from the baseline (Test 1) value to establish a difference due to temperature or other unmeasured variables. The differences in rate constants between tests determined in Treatment Plot V2 were then added to the measured rate constants in Tests 2 through 5 in Treatment Plot V1, thereby correcting all rate constants in V1 to the soil temperature during Test 1. Method 2 (Figure 76) also used the rate constant determined in Treatment Plot V2 during Respiration Test 1 as a baseline. The percent decrease in rate constants between Test 1 and Tests 2 through 5 in Treatment Plot V2 were calculated. The measured rate constants in Tests 2 through 5 in Treatment Plot V1 were then increased by the same percentages, thereby correcting all rate constants in Treatment Plot V1 by the percent of decrease in observed rate constants in Treatment Plot V2.

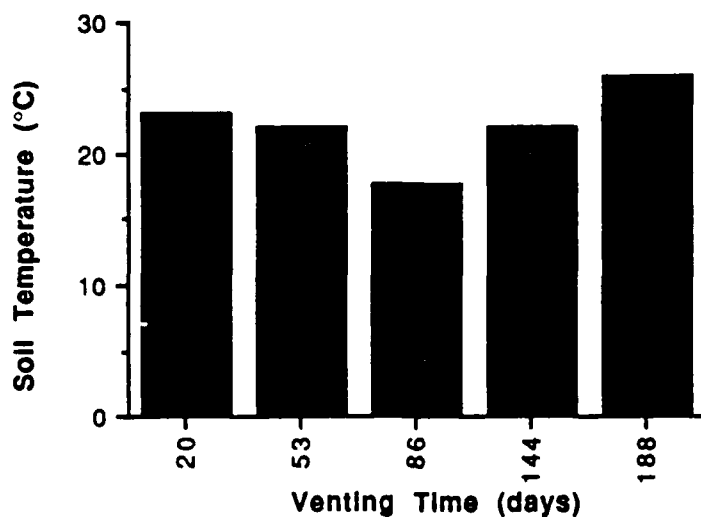


Figure 73. Average soil temperature measured or calculated to correspond with respiration tests.

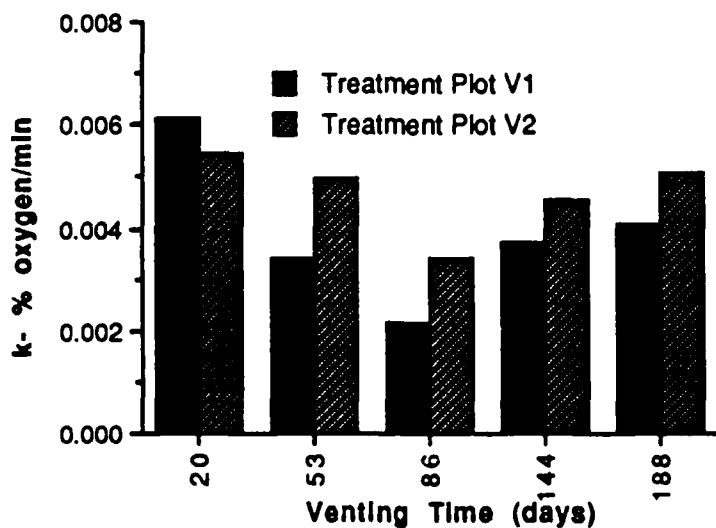


Figure 74. Oxygen consumption rate constants determined by respiration tests for Treatment Plots V1 and V2.

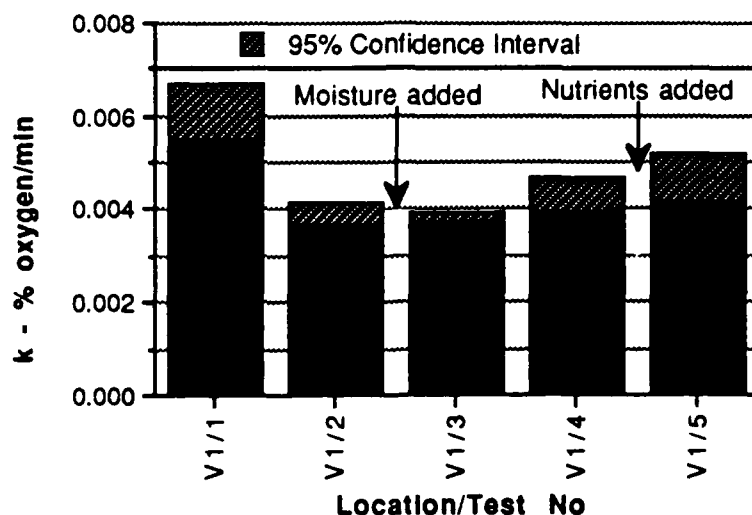


Figure 75. Temperature corrected (based on total change in V2) oxygen consumption rate constants ( $k$ ) determined by respiration tests for Treatment Plot V1. Mean  $k$  is at the center of the 95% confidence interval.

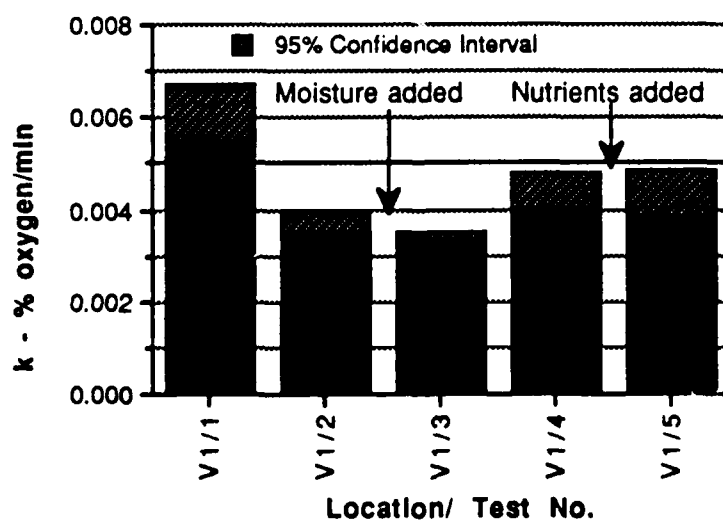


Figure 76. Temperature corrected (based on percent change in V2) oxygen consumption rate constants ( $k$ ) determined by respiration tests for Treatment Plot V1. Mean  $k$  is at the center of the 95% confidence interval.

In aquatic systems, the van't Hoff -Arrhenius equation predicts a doubling of the rate constant with each temperature increase of 10°C, assuming typical activation energy values (Benefield and Randall, 1980). Figure 77 is the Arrhenius Plot for determining activation energy using measured soil temperature and rate constant relationships from Tests 3, 4, and 5 for Treatment Plots V1 and V2.

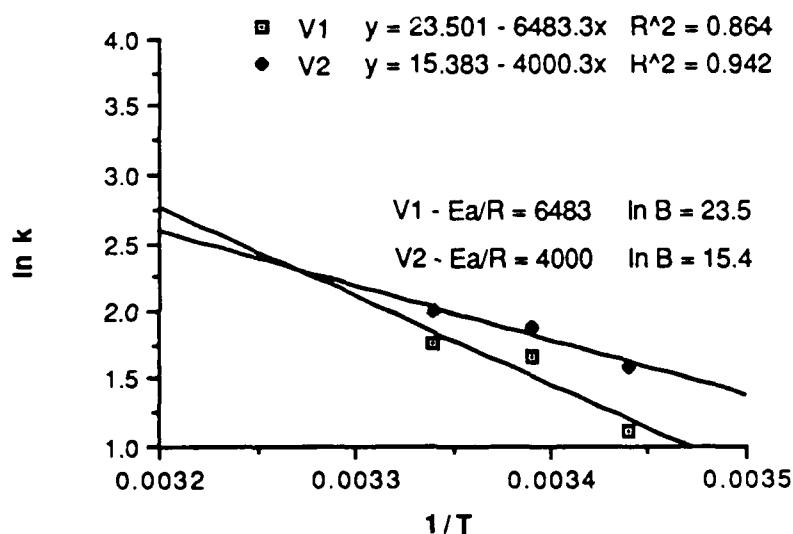


Figure 77. Arrhenius Plot for determining activation energy using measured soil temperature and rate constant relationships from Tests 3, 4, and 5 for Treatment Plots V1 and V2.

Using the Arrhenius constants determined from the plots in Figure 77, the rate constants for Treatment Plots V1 and V2 were corrected to 23 °C, the soil temperature of Test 1 (Figures 78 and 79, respectively). The Arrhenius correction for temperature resulted in insignificant rate constant differences between Tests 2, 3, 4, and 5 in Treatment Plot V2. Although a statistically significant difference in rate constants remained between Test 3 and Tests 2

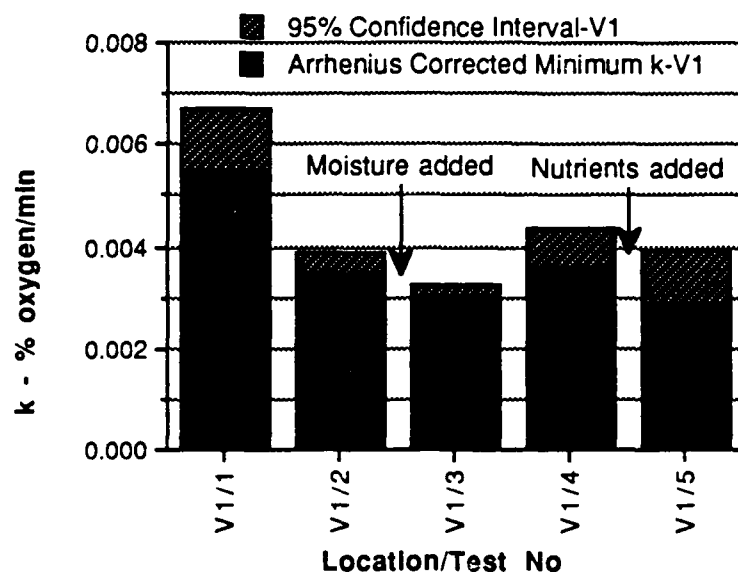


Figure 78. Temperature corrected (23 °C based on Arrhenius Plot) oxygen consumption rate constants (k) determined by respiration tests for Treatment Plot V1. Mean k is at the center of the 95% confidence interval.

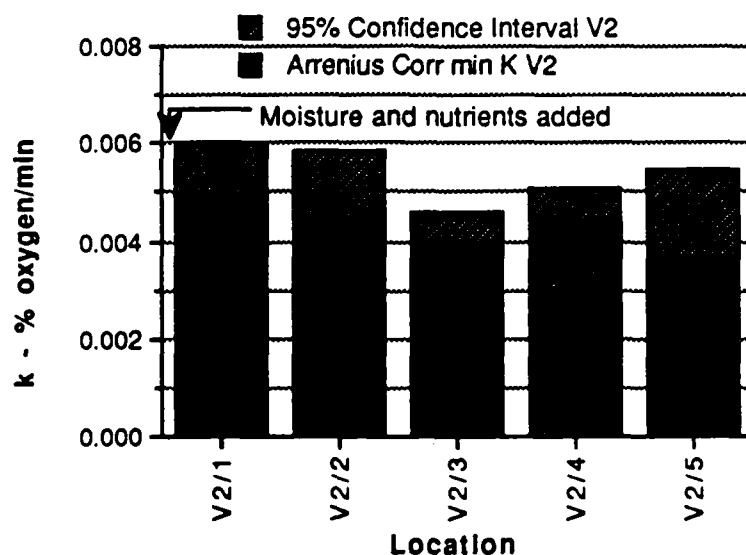


Figure 79. Temperature corrected (23 °C based on Arrhenius Plot) oxygen consumption rate constants determined by respiration tests for Treatment Plot V2.

and 4 in Treatment Plot V1, the magnitude of the difference is not important from a practical application standpoint. Test 1 in both treatment plots was not considered because it was conducted when hydrocarbon concentrations in the soil gas were still very high. Therefore, the Arrhenius equation modeled the effects of temperature on hydrocarbon biodegradation rate in Treatment Plot V2 and slightly underestimated temperature effects in Treatment Plot V1. Regardless of the method used (Figures 75, 76, and 78), observed rate constant differences during the field test likely resulted from changes in soil temperature.

Moisture was added to Treatment Plot V1 following Respiration Test 2 and nutrients were added following Respiration Test 4. Regardless of the temperature correction approach (Figures 75, 76, or 78), rate constants were not significantly increased between Tests 2 and 3, and between Tests 4 and 5. Therefore, it can be concluded that moisture and nutrient addition were of insignificant benefit to the rate of hydrocarbon biodegradation in Treatment Plot V1. The methods illustrated in Figures 76 and 78 show a significant decrease in the rate constant between Test 2 and 3, but Method 1 (Figure 75) does not.

Although moisture and nutrient addition did not effect biodegradation rates, data presented in Figures 73 through 79 indicate that soil temperature likely did. Figures 80 and 81 are correlations between measured soil temperature and oxygen consumption rate ( $k$ ) (including the 95% confidence interval range for  $k$ ) for Respiration Tests 3 through 5 for Treatment Plots V1 and V2, respectively. Figures 80 and 81 support the conclusion, with 95% confidence, that respiration rate as measured by oxygen consumption was related to soil temperature.

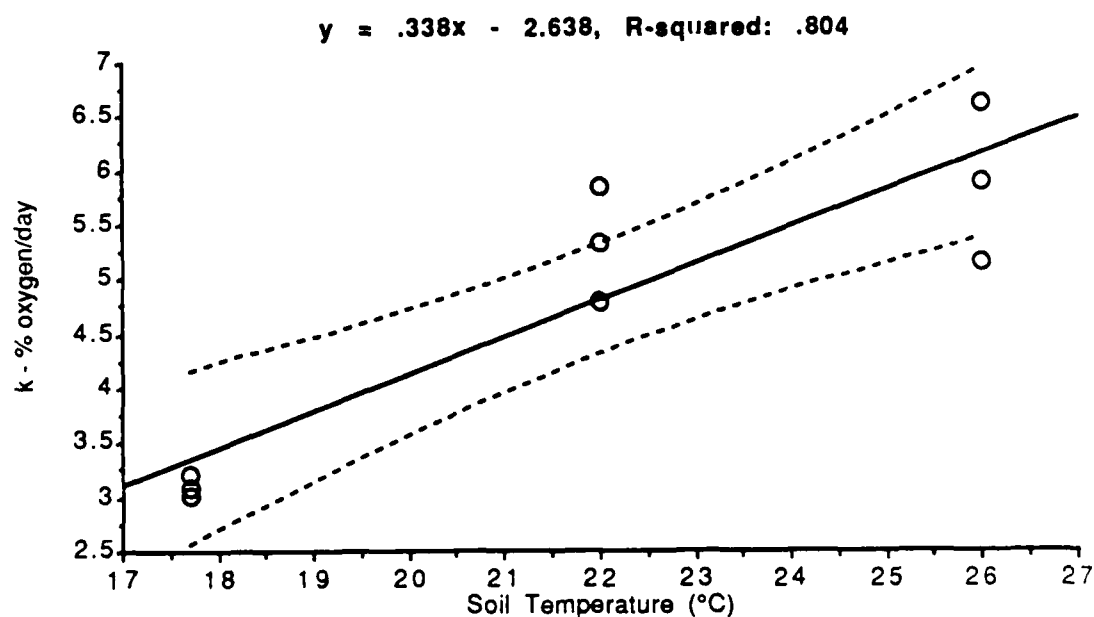


Figure 80. Correlation and 95% confidence band for relationship between measured soil temperature and oxygen consumption in Treatment Plot V1 during Respiration Tests 3 through 5.

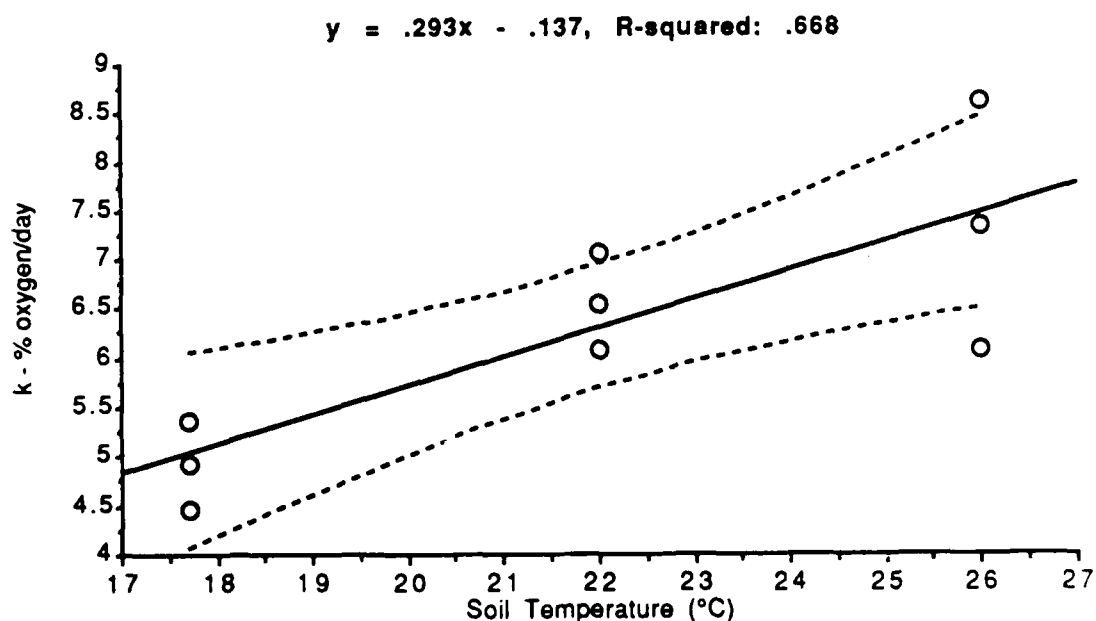


Figure 81. Correlation and 95% confidence band for relationship between measured soil temperature and oxygen consumption in Treatment Plot V2 during Respiration Tests 3 through 5.

### Nutrient Balance

The data previously presented indicate that either nutrients were not a limiting factor in the biodegradation of jet fuel at the field site, or that nutrients were not adequately delivered to the subsurface. Inorganic nutrient levels in initial soil samples, collected in July and September, 1989, were low in concentration, being generally  $< 3$  mg/kg of  $\text{NO}_3 + \text{NO}_2\text{-N}$  and  $\text{NH}_4\text{-N}$  (Appendix D). Initial concentrations of  $\text{PO}_4\text{-P}$  were below detectable levels ( $< 0.7$  mg P/kg) except for one sample containing 4.45 mg P/kg. Soil samples collected in December, 1989, indicated that  $\text{NH}_4\text{-N}$  concentrations in Treatment Plot V2, which had been receiving nutrients for two months, had significantly increased from an average of 2 mg N/kg to 25 mg N/kg. However, there was not a significant increase in  $\text{PO}_4\text{-P}$  concentrations in Treatment Plot V2 between the initial and December, 1989, soil samples, with concentrations still below detectable ( $< 0.7$  mg P/kg) levels. Nutrient concentrations in the December, 1989, soil samples from Treatment Plot V1, which had received no nutrients at that time, were essentially unchanged from the initial samples.

Final soil samples, collected in May, 1990, indicated that  $\text{NH}_4\text{-N}$  concentrations in Treatment Plot V2, which had received nutrients throughout the field test, had significantly ( $p < 0.06$ ) increased from an average of 2 mg N/kg to 22 mg N/kg, but there was no significant difference in  $\text{NH}_4\text{-N}$  concentrations between samples collected in December, 1989, and final samples collected in April, 1990. Treatment Plot V1 received nutrients for the final seven weeks of the field test. Final soil  $\text{NH}_4\text{-N}$  concentrations averaged 12 mg N/kg, but were not significantly different ( $p = 0.2$ ) than initial concentrations (Appendix D). Most of the final soil concentrations of  $\text{PO}_4\text{-P}$  remained below detectable levels

(< 0.7 mg P/kg) (Appendix D). Many of the soil samples had Total-P concentrations that were below the detection limit. Therefore, comparison by t-test was difficult because of the low number of comparable data points in each test plot. A t-test combining all comparable initial and final Total-P concentrations in all test plots indicated a significant ( $p < 0.08$ ) average increase from 26 to 43 mg P/kg. Ground water concentrations of  $\text{NH}_4\text{-N}$  increased throughout the field test in Treatment Plot V2. Initial concentrations averaged 2.4 mg N/L whereas final concentrations averaged 8560 mg N/L (Appendix D). In Treatment Plot V1, ground water  $\text{NH}_4\text{-N}$  concentrations increased from an average of 0.22 to 4319 mg N/L between initial and final samples. Ground water concentrations of  $\text{PO}_4\text{-P}$  increased by three orders-of-magnitude during the field test.

Evaluation of soil and water samples indicated that nutrients were delivered to the test plots, but that most of the nutrients passed through the vadose-zone to the ground water. If all of the nutrients delivered had remained in the vadose-zone,  $\text{NH}_4\text{-N}$  and Total-P concentrations should have increased by approximately 1000 mg N/kg, and 100 mg P/kg, respectively.

Total nitrogen (TKN) and total phosphorus concentrations in initial soil samples averaged 81 and approximately 22 mg/kg, respectively, in Treatment Plot V1. Average total phosphorus concentrations are only approximate because three of ten samples were below the detection limit of 15 mg/kg. During 188 days of venting in Treatment Plot V2, 32,000 g (1110 mg/kg) of hydrocarbons (hexane equivalent), or 26,800 g (930 mg/kg) of carbon (hexane equivalent) were removed as carbon dioxide. Alexander (1977) indicates that typical soil microbes volatilize 2 g of carbon, as carbon dioxide, for each gram of carbon assimilated into cell protoplasm. Assuming this ratio to be accurate,

approximately 13,400 g (465 mg/kg) of carbon were converted to cell mass. Using Alexander's (1977) C:N:P ratio of 100:10:1, approximately 46 and 5 mg/kg of nitrogen and phosphorus, respectively, should have been required to account for the observed fuel biodegradation. Since 81 and 22 mg/kg of nitrogen and phosphorus, respectively, were available naturally, it is not surprising that nutrient addition had no observable effect on fuel biodegradation rates. Using the same calculation method, the naturally available nutrients should be adequate for the biodegradation of fuel at concentrations at least up to 2000 mg/kg. Additional recycling of available nutrients should allow biodegradation of fuel at even higher initial soil hydrocarbon concentrations.

Significant biodegradation of jet fuel was observed at both Hill AFB, Utah, (Hinchee et al., 1989) and Tyndall AFB, Florida, without addition of nutrients. The source of available nutrients is extremely important if results of these two field studies are to be applied at other sites. A possible source of available organic nitrogen is non-symbiotic nitrogen fixation by indigenous microorganisms.

### **Nitrogen Fixation Potential**

Soil nitrogenase (nitrogen fixation) potential was assayed using the acetylene reduction assay described by Knowles (1982). The acetylene reduction assay is, as stated by Alexander (1977a), "...based on the finding that microorganisms that reduce  $N_2$ , which has a triple bond in the molecule, also can reduce acetylene, also a molecule with a triple bond." Alexander (1977a) also states, "It seems likely that many soils may support the (nitrogen) fixation when nitrate or available ammonium is present at low levels."

Anaerobic acetylene reduction (ethylene production) rates measured in initial soil samples, collected at 30, 60, and 90 cm (1, 2, and 3 ft) from Treatment Plots V1 and V2, averaged 200 nmole/(kg hr)(Appendix D). Soil samples collected in December, 1989, from Treatment Plot V1 at 30, 60, 90, 120, and 150 cm (1, 2, 3, 4, and 5 ft), had an average ethylene production rate of 125 nmole/(kg hr)(Appendix D).

Alexander (1977a) describes a method for estimating the rate of nitrogen fixation based on the rate of acetylene reduction (ethylene production). He concluded that a ratio of  $3\text{C}_2\text{H}_2 : 1\text{N}_2$  "...is frequently approached in pure culture or soil and is sometimes attained." He also warns that this ratio should be used with caution because it has been observed to range from 0.75 to 4.5 or greater. Assuming a 3:1 ratio, the nitrogen fixation potential, based on initial and December, 1989, soil samples was approximately 0.0448 and 0.028 mg N/(kg day), respectively. At this rate, fixing the observed 81 mg/kg (2,330 g) of organic nitrogen in Treatment Plot V1 would take from five to ten years. Fuel contamination has existed at this site for at least 20 years, therefore, it is conceivable that the observed organic nitrogen was fixed by soil microbes.

The presence of large quantities of carbon in soil (i.e., a fuel spill) stimulates nitrogen fixation because nitrogen fixing microbes are primarily heterotrophs dependent on carbon for energy and cell synthesis. Also, as observed at this field site, soil that is contaminated with petroleum hydrocarbons is usually anaerobic and nitrogen fixation is maximized under anaerobic conditions (Alexander, 1977a). It can be safely assumed that a source of carbon and an anaerobic condition in soil are provided following a fuel spill. Therefore, the spill itself may provide the optimum conditions for providing a source of nitrogen through non-symbiotic nitrogen fixation.

The average anaerobic acetylene reduction (ethylene production) rate, measured in final soil samples, was 24 nmole/(kg hr) (Appendix D), and was significantly ( $p=0.1$ ) less than the initial average rate of 200 nmole/(kg hr). Since  $\text{NH}_4\text{-N}$  was provided in large quantities, the reduced nitrogen fixation potential in final soil samples is consistent with the quote (Alexander, 1977a) above that, "It seems likely that many soils may support the (nitrogen) fixation when nitrate or available ammonium is present at low levels".

### **Initial and Final Hydrocarbon Concentrations in Soil Samples**

Soil hydrocarbon concentrations (initial and final) were estimated from methylene chloride extracts of soil samples. Methanol extracts of initial soil samples resulted in total hydrocarbon concentrations that were at least an order-of-magnitude lower than concentrations determined from methylene chloride extracts. Because of the large differences in hydrocarbon concentrations resulting from the two methods, final soil samples were extracted with methylene chloride only. Soil hydrocarbon concentrations were calculated by; multiplying total integrated area by the response factor for the hexane standard (hexane equivalent); multiplying the integrated area for each boiling point fraction by the average response factor of the standards bracketing that boiling point, and summing these boiling point fractions (weighted average); and by multiplying total integrated area in the chromatogram by the average response factor of all standards (combined average) (Appendix D).

Table 14 summarizes average results for the three methods described using five samples collected in the vadose-zone at 30, 60, 90, 120, and 150 cm (1, 2, 3, 4, and 5 ft) for Treatment Plots V1 and V2, and three vadose-zone

Table 14. Summary of average soil hydrocarbon concentrations in initial and final samples.

| Treatment Plot V1                                  |                         |                      |                       |                      |                                              |      |
|----------------------------------------------------|-------------------------|----------------------|-----------------------|----------------------|----------------------------------------------|------|
| Calculation Method and Location of Soil Samples    | Average Conc.           |                      | Average Conc.         |                      | Paired t-test (p) Comparing Initial to Final |      |
|                                                    | Initial Samples (mg/kg) | SD ( $\pm$ ) (mg/kg) | Final Samples (mg/kg) | SD ( $\pm$ ) (mg/kg) |                                              |      |
| Hexane Equivalent Average 30 to 150 cm (1 to 5 ft) | 5,135                   | 5,032                | 2,193                 | 1,926                | 2,942                                        | 0.02 |
| Weighted Average 30 to 150 cm (1 to 5 ft)          | 3,872                   | 3,775                | 2,198                 | 1,925                | 1,674                                        | 0.07 |
| Combined Average 30 to 150 cm (1 to 5 ft)          | 4,736                   | 4,634                | 2,194                 | 1,926                | 2,542                                        | 0.03 |
| Treatment Plot V2                                  |                         |                      |                       |                      |                                              |      |
| Hexane Equivalent Average 30 to 150 cm (1 to 5 ft) | 7,690                   | 7,681                | 4,835                 | 5,998                | 2,856                                        | 0.09 |
| Weighted Average 30 to 150 cm (1 to 5 ft)          | 5,799                   | 5,687                | 4,860                 | 6,044                | 940                                          | 0.48 |
| Combined Average 30 to 150 cm (1 to 5 ft)          | 6,733                   | 7,000                | 4,839                 | 6,007                | 1,895                                        | 0.19 |
| Treatment Plot V3                                  |                         |                      |                       |                      |                                              |      |
| Hexane Equivalent Average 30 to 90 cm (1 to 3 ft)  | 150                     | 202                  | 33                    | 28                   | 117                                          | 0.37 |
| Weighted Average 30 to 90 cm (1 to 3 ft)           | 212                     | 125                  | 34                    | 29                   | 178                                          | 0.11 |
| Treatment Plot V4                                  |                         |                      |                       |                      |                                              |      |
| Hexane Equivalent Average 30 to 90 cm (1 to 3 ft)  | 129                     | 102                  | 32                    | 10                   | 97                                           | 0.21 |
| Weighted Average 30 to 90 cm (1 to 3 ft)           | 110                     | 89                   | 34                    | 12                   | 76                                           | 0.24 |

samples collected at 30, 60, and 90 cm (1, 2, and 3 ft) for Off-Gas Treatment Plot V3 and Background Plot V4. Depending on the method used, total hydrocarbon removal, based on measured soil concentrations, ranged from 1,674 to 2,942 mg/kg and 940 to 2,856 mg/kg in Treatment Plots V1 and V2, respectively (Table 14).

Statistical comparisons between initial and final soil samples collected from 30 to 150 cm, using the Students t-Test for paired samples and the hexane equivalent method, confirmed a significant ( $p=0.02$  and  $p=0.09$ ) reduction in soil hydrocarbon concentrations between initial and final soil samples in Treatment Plots V1 and V2, respectively, (Table 14).

Average soil hydrocarbon concentrations in Off-Gas Treatment Plot V3 and Background Plot V4 did not significantly change between initial and final samples (Table 14).

### **Mass Balance of Soil Hydrocarbon**

During the field test period, 25,820 g (900 mg/kg) and 31,990 g (1,110 mg/kg), hexane equivalent, of total hydrocarbons were removed from Treatment Plot V1 by volatilization and biodegradation, respectively, for a total measured hydrocarbon removal of 2,010 mg/kg, hexane equivalent. In Treatment Plot V2, 32,600 g (1,130 mg/kg) and 37,640 g (1,310 mg/kg), hexane equivalent, were volatilized and biodegraded, respectively, for a total measured hydrocarbon removal of 2,440 mg/kg, (Figure 47; Appendix C). These measured hydrocarbon removal quantities are conservative because they do not account for accumulation of biomass. Biomass accumulation was not measured and it is unknown how much of the measured  $\text{CO}_2$  was the result of endogenous respiration.

Based on initial and final soil samples (Table 14) collected from 30 to 150 cm ( 1 to 5 ft), average soil hydrocarbon concentrations (hexane equivalent) were reduced by 2,940 and 2,860 mg/kg, respectively, in Treatment Plots V1 and V2 during the field test. Considering the wide range of soil hydrocarbon concentrations and the unknown amount of biomass accumulation, the extent of soil remediation predicted by measurement of the discharge gas streams from Treatment Plots V1 and V2, agree surprisingly well with the actual level of soil remediation determined from soil samples (Table 14). This mass balance indicates that added water did not flush significant amounts of fuel from the site. Flushing was not considered to be a significant removal mechanism due to the low aqueous solubility of jet fuel, and the field test design did not allow measurement of the quantity of hydrocarbons removed by flushing.

## CONCLUSIONS

This field scale investigation has demonstrated that soil venting is an effective source of oxygen for enhanced aerobic biodegradation of petroleum hydrocarbons (jet fuel) in the vadose-zone. Specific conclusions are:

1. Operational data and respiration tests indicated that moisture (6.5 to 9.8% by weight) and nutrients were not a limiting factor in hydrocarbon biodegradation in the sandy soil. Soil and water sample results indicated that nutrients were delivered to the treatment plots and passed through the vadose-zone to the ground water.
2. Air flow tests documented that decreasing flow rates increased the percent of hydrocarbon removal by biodegradation and decreased the percent of hydrocarbon removal by volatilization. Under optimal air flow conditions (0.5 air void volumes per day) 82% of hydrocarbon removal was biodegraded and 18% volatilized. Biodegradation removal rates ranged from approximately 2 to 20 mg/(kg day), but stabilized values averaged about 5 mg/(kg day). The effect of soil temperature on biodegradation rates was shown to approximate effects predicted by the van't Hoff-Arrhenius equation.
3. Off-gas treatment studies documented that uncontaminated soil at this test site could be successfully used as a biological reactor for the mineralization of hydrocarbon vapors (off-gas) generated during remediation of fuel contaminated soil using the enhanced biodegradation through soil venting technology investigated in this field study. The average off-gas biodegradation rate was 1.34 (SD  $\pm$  0.83) mg/(kg day), or 1.93 (SD  $\pm$  1.2) g/(m<sup>3</sup> day). The percent of off-gas biodegradation was inversely related to air flow rate

(retention time), and was directly related to hydrocarbon loading rate, at the 95% confidence level. Based on data collected at the field site, a soil volume ratio of approximately 4 to 1, uncontaminated to contaminated soil, would be required to completely biodegrade the off-gas from a bioventing system operated similar to this field project. However, if air flow rates in contaminated soil were designed to maximize biodegradation, the ratio of uncontaminated to contaminated soil required would be proportionally less.

4. Respiration Tests documented that oxygen consumption rates followed zero-order kinetics, and that rates were linear down to about 2 to 4 % oxygen. Therefore, air flow rates can be minimized to maintain oxygen levels between 2 and 4% without inhibiting biodegradation of fuel, with the added benefit that lower air flow rates will increase the percent of removal by biodegradation and decrease the percent of removal by volatilization.
5. Initial soil samples indicated that naturally available nitrogen and phosphorus were adequate for the amount of biodegradation measured, explaining the observation that nutrient addition had an insignificant effect on the rate of biodegradation. Acetylene reduction studies revealed an organic nitrogen fixation potential that could fix the observed organic nitrogen, under anaerobic conditions, in five to eight years.
6. Soil moisture levels did not significantly change during the field study. Soil moisture levels ranged from 6.5 to 7.4%, and 8.5 to 9.8%, by weight, respectively, in the sandy soils of Treatment Plots V1 and V2.

Neither venting nor moisture addition had a statistically significant effect on soil moisture at this site.

## ENGINEERING SIGNIFICANCE

This research has provided design parameters that may be used for a full-scale remediation project, at a similar JP-4 contaminated site, using enhanced biodegradation through soil venting. A full-scale project should attempt to biodegrade all contamination including any generated off-gas.

Figure 82 illustrates a configuration that may successfully remediate a similar JP-4 contaminated site and any off-gas that was generated. An air extraction well is drilled in uncontaminated soil at a distance from the contaminated site that will provide adequate uncontaminated soil volume (4:1) to treat generated off-gas. Air injection wells are drilled, as needed, into and on the opposite side of the contaminated area in a manner that will provide a relatively even distribution of air to the contaminated soil. It may be possible to design a system that will provide more air to more contaminated areas. Soil gas monitoring wells are installed in the contaminated area, and in the uncontaminated area, used as an off-gas treatment reactor, to monitor total hydrocarbons, carbon dioxide, and oxygen. Air flows are adjusted to assure aerobic conditions in the contaminated and off-gas treatment areas while ensuring that only carbon dioxide, not hydrocarbons, are emitted from the blower. A strategy for design should include as a minimum:

1. A gas permeability test where air is injected into the contaminated site, followed by measurement of oxygen consumption and carbon dioxide production, at the air injection point, to estimate fuel biodegradation rates.

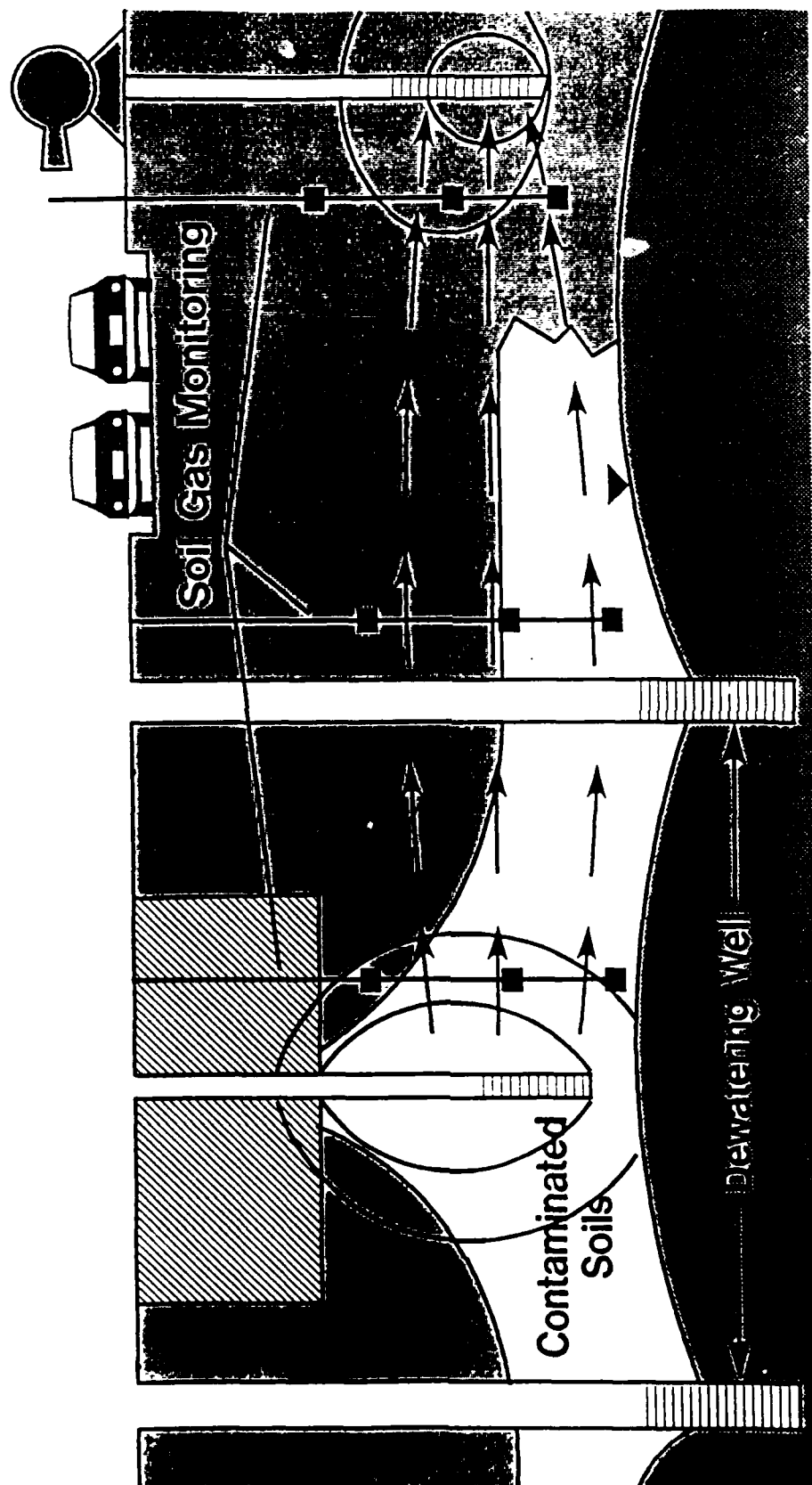


Figure 82. Potential configuration for enhanced bioreclamation through soil venting (air withdrawn from clean soil).

2. Initial soil samples to determine the texture and volume of contaminated soil, and the total hydrocarbon, total organic nitrogen (TKN), and total phosphorus concentrations in the contaminated and off-gas treatment areas.
3. Determination of C:N:P ratios and moisture content. Assuming no nutrient recycle, a C:N:P ratio of 300:10:1 should be adequate because approximately one-third of the hydrocarbons are converted to cell mass and two-thirds to carbon dioxide. Wider C:N:P ratios should not eliminate the site as a potential candidate for this technology because nutrient recycling may allow much wider C:N:P ratios. Nutrient addition should be considered only if C:N:P ratios are not satisfied and biodegradation rates are significantly less than *reported in this research*. In sandy soils, similar to the research site, moisture addition is probably not necessary unless moisture content is significantly less than the 6.5 to 9.8%, by weight, observed in the sandy soils during this research.
4. An air delivery system designed to provide 0.25 to 2 air void volumes per day through the contaminated area. If air will be pulled from directions other than the contaminated soil, appropriate design increases will be necessary.
5. Monitoring soil gas and adjusting air flow rate to assure aerobic conditions (2 to 4% O<sub>2</sub>) in the contaminated and off-gas treatment areas, and the absence, or acceptable concentrations of hydrocarbons in the blower discharge.

6. Depending on seasonal temperature fluctuations, operation during periods of maximum soil temperature may be optimum.
7. Manipulating the water table as required to create a deeper unsaturated zone for air/contaminant contact.

## RECOMMENDATIONS FOR FUTURE STUDY

To further pursue the development of an enhanced biodegradation of petroleum hydrocarbons through soil venting technology, the following studies are recommended:

1. Further investigate the relationship between soil temperature and hydrocarbon biodegradation rate.
2. Investigate methods to increase hydrocarbon biodegradation rate by increasing soil temperature with heated air, heated water, or low level radio frequency radiation.
3. Investigate the effect of soil moisture content on biodegradation rate in different soils with and without nutrient addition.
4. Investigate nutrient recycling to determine maximum C:N:P ratios that do not limit biodegradation rates.
5. Investigate different types of uncontaminated soil for use as a reactor for biodegradation of generated hydrocarbon off-gas and determine off-gas biodegradation rates.
6. Investigate gas transport in the vadose-zone to allow adequate *design of air delivery systems.*

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