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# LARGE-SCALE DEMONSTRATION OF BIOVENTING IN THE NORTHERN UNITED STATES; VOLUME 1: FINAL REPORT

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**14. ABSTRACT**

This study was conducted to examine the effectiveness of bioventing for remediating petroleum hydrocarbons under the colder climatic conditions that exist in the northern United States. The study was conducted in an abandoned fire training pit (FPTA#1) at F.E. Warren AFB, Wyoming. The study included a 26-month field effort that entailed examining pure oxygen, pulsed air injection and passive soil warming for the potential to enhance biodegradation performance.

The data demonstrated the effectiveness of bioventing for remediating hydrocarbon contamination commonly associated with fire training pits showing decreases in the mass of semi-volatile TPH, benzene, toluene, ethylbenzene, xylenes and naphthalene of 52.4, 76.4, 37.2, 19.0 and 18.0 percent, respectively. The masses of volatile TPH and xylene were shown to increase 36.5 and 57.1 percent, respectively. Biodegradation rates were calculated based on measured oxygen utilization rates and showed that there was no significant enhancement due to passive soil warming below the 3-foot depth. Neither pulsed air nor pure oxygen injection significantly affected the biodegradation rates compared to conventional continuous air injection.

It was concluded that bioventing was effective at remediating contamination resulting from fire training exercises in colder climates, that although there was a slight benefit at the shallow depths the passive soil warming method was not useful, and that pulsed air or pure oxygen was not useful for increasing biodegradation rates.

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## PREFACE

This report was prepared by Battelle, 505 King Avenue, Columbus, Ohio 43201, under Contract No. F08635-95-C-0064, for the Armstrong Laboratory Environics Directorate (AL/EQW), 139 Barnes Drive, Suite 2, Tyndall Air Force Base, Florida 32403-5323. The reported work was funded by the United States Air Force.

This report describes the Large-Scale Demonstration of Bioventing in the Northern United States Study conducted at F.E. Warren Air Force Base, Wyoming. The study was designed to examine bioventing performance under cold climate conditions and included evaluations of pulsed air injection, pure oxygen injection, and passive soil warming as enhancements to conventional bioventing methods. The report includes the design and operation of the bioventing system and system enhancements, the experimental methodologies used to monitor the technology performance, the data analysis techniques, a discussion of the experimental findings, and recommendations for future application of the technology and enhancements.

The work was performed between January 1993 and March 1995. The AL/EQW project manager was Ms. Catherine Vogel.

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# EXECUTIVE SUMMARY

## A. OBJECTIVE

The objectives of this research project were to evaluate the effectiveness of in situ air injection bioventing technology for the remediation of petroleum-contaminated soils under northern climatic conditions existing at the Fire Protection Training Area #1 (FPTA#1) at F.E. Warren Air Force Base in Cheyenne, Wyoming, and to assess the effect of bioventing system flow rates and operating conditions on the performance of this large-scale system under actual field conditions.

## B. BACKGROUND

Bioventing is an in situ bioremediation technology designed to take advantage of the metabolic activity of indigenous microorganisms in the vadose zone to destroy targeted contaminants. The basic operating principle of bioventing is to provide these microorganisms with the oxygen that they require for aerobic metabolism. Oxygen is provided through induced air flow in the contaminated soils using a system of blowers and vent wells.

FPTA#1 was used from 1950 to 1965 as a fire prevention training ground (Engineering-Science, 1985). Three to four times a month flammable liquids, including waste oils, solvents, gasoline, JP-4 jet fuel, and other combustible liquids, were dumped into one of two circular earthen berms and ignited, and the resultant fire was extinguished with water and protein foam. Other contamination at the site included the dumping of chlorobromomethane directly on the ground outside of the earthen berms, gasoline spilled in 1973 during in fire protection training exercises, and use of the area as a landfill. There was visible evidence of soil contamination at FPTA#1 in the late 1980s, with vegetation absent over a sizeable area within and near the berms as well as areas of soil that were darkly stained and had the odor of petroleum products.

Results from the 1987 to 1988 analyses of groundwater for volatile halogenated organic compounds detected trichloroethylene (TCE) most frequently, although 1,2-dichloroethene was detected at the highest concentration (Larson et al., 1991). The maximum TCE and 1,2-dichloroethene concentrations were 29 micrograms per liter ($\mu$g/L) and 54 $\mu$g/L, respectively, at that time. The source of the TCE in the groundwater has been determined to be upgradient, although some contamination from the site is possible. No analysis for chlorobromomethane was done at this

time. Later sampling found similar TCE levels in most wells, although TCE concentrations had increased significantly in three wells to a maximum of 57 μg/L (Peterson et al., 1993). Analyses for bromochloromethane all resulted in nondetectable levels.

Results from the 1987 to 1988 analyses of soil for volatile halogenated organic compounds also detected TCE most frequently, with maximum concentrations of 71 milligrams per kilogram (mg/kg) (Larson et al., 1991). TCE contamination of the soil at relatively shallow depths suggested that local spills were the probable source of this contamination. The total petroleum hydrocarbon (TPH) analyses of the soil indicated concentrations of up to 8,800 mg/kg, with an average TPH level at the site of 2,000 mg/kg. Later soil analyses showed that both the TCE and the TPH concentrations were lower (Peterson et al., 1993), with the maximum TCE concentration only 10 mg/kg, and maximum TPH concentration reaching 2,540 mg/kg with an average TPH of 382 mg/kg. All samples with detectable TCE levels occurred in or near the earthen berms, generally below 4 feet in depth. Bromochloromethane was detected in only one soil sample at a concentration of 6.6 mg/kg.

## C. SCOPE

This field research project involved the design and installation of a large-scale air injection bioventing system; laboratory analyses of soil and groundwater samples collected from the site during system installation and at the completion of the study; operation, maintenance, and monitoring of the large-scale bioventing demonstration system; conducting routine in situ respiration tests over the course of the study; and collecting and analyzing system operating data to evaluate the impact of temperature, injection flow rate, air injection pulsing, and pure oxygen injection on field-determined biological activity and contaminant volatilization rates throughout the field site. The methodology, results, and data interpretation from these field activities are summarized in this report.

## D. METHODOLOGY

The monitoring of the large-scale bioventing system operated at the FPTA#1 site consisted primarily of soil gas measurements for respiration gas (oxygen and carbon dioxide) constituents, hydrocarbon composition in soil gas, and changes in these characteristics in response to changes in site conditions or bioventing system operating characteristics.

Soil gas TPH was measured using a GasTech TraceTechtor™ analyzer. Two different sampling procedures were used over the course of the field study. The first method, used from 1/93 to 10/93, involved connecting the analyzer directly to the gas sampling probe, with the internal pump of the analyzer used to withdraw a sample. The second method, used from 11/93 to 3/95, involved the use of an external pump to withdraw a volume of gas into a 1-liter Tedlar™ bag. This volume was then flushed to ensure an unadulterated and undiluted sample. The Tedlar™ bag was then refilled with 1 liter of soil gas sample for TPH, $O_2$, and $CO_2$ analyses. The analyzers were used outdoors when the temperature was above 20°F, and indoors when the temperature was below 20°F. If $O_2$ concentrations were less than 12 percent, a 1:1 dilution fitting (GasTech) was used during TPH measurements. $O_2$ and $CO_2$ concentrations in soil gas were measured using a GasTech model 3252OX analyzer. Sampling methods were identical to those used for TPH when samples were at ambient levels of $O_2$ or less. Samples with greater than 21 percent $O_2$ due to pure $O_2$ injection were quantified after mixing appropriate ratios of sample and $O_2$-free calibration gas in a 1-L Tedlar bag.

Soil and air temperatures were measured using a Fluke model 51 K/J thermometer and Type K thermocouples. Air flow rates were measured in air delivery pipes between injection points using a Dwyer thermal anemometer. Vacuum was measured using a vacuum gauge with a range of 0 to 30 inches of Hg, connected to the inlet line of the soil gas sampling pump.

Laboratory analyses to support field-determined site parameters included soil sample volatile and semivolatile hydrocarbon compositions; water sample volatile and semivolatile hydrocarbon compositions; and soil gas composition via the stainless steel evacuated canister and Tenax™ sorbent tube sampling methods.

Soil and water samples were analyzed for volatile hydrocarbons through methanol extraction and purge-and-trap analysis of the extract with gas chromatography (GC) analysis using a flame ionization detector (FID). Initial samples were purged manually, whereas final samples were purged using an autopurging system. Semivolatile hydrocarbon analyses of site soils and groundwater were carried out through methylene chloride soxhlet extraction using GC analysis with a FID.

Methanol extracts of initial soil samples were sent to an outside laboratory for chlorinated solvent analysis using EPA Method 8240. Final soil samples were analyzed for chlorinated solvents using manual purge-and-trap of soil methanol extracts using GC/mass spectrometric (GC/MS) analysis. Soil samples were analyzed for polycyclic aromatic hydrocarbons (PAHs) through methylene chloride soxhlet extraction with GC/MS analysis.

Canister samples were analyzed for volatile hydrocarbons and respiration gases. $O_2$ and $CO_2$ analyses of canister gas samples were conducted using a GC with a thermal conductivity detector (TCD). Tenax samples were analyzed for volatile organic compounds (VOCs) by thermal desorption using a thermal desorber connected to a GC with a FID.

Data reduction for soil and water samples involved the conversion of specific constituent mass data from raw chromatographic data to representative concentration units appropriate for the given medium. In addition, contaminant degradation and oxygen respiration rate determinations were used to provide a quantitative description of system characteristics over the duration of the study.

TPH analyses were calibrated using a 25-compound external standard containing C-5 to C-15 *n*-alkanes along with benzene; toluene; *m*-xylene; ethylbenzene; 1,3,5-trimethylbenzene; 1,2,4-trimethylbenzene; 1,2,3-trimethylbenzene; naphthalene; and methylnaphthalene. Purge-and-trap extraction analysis was quantified from C-5 up to but not including C-12, and soxhlet extraction analysis was quantified from C-12 to C-15. A five-point calibration curve was established over a three-log concentration range for each standard compound to quantify the mass of each compound in a sample. PAH analyses were calibrated using a 16-compound standard, with a five-point calibration curve being established for each analyte and internal standards used to quantify the mass of each analyte in a sample. Chlorinated solvent analyses were calibrated using a 13-compound standard, with the calibration and quantitation methods used being identical to those for the PAH constituents. Quantitation of soil gas $O_2/CO_2$ during atmospheric $O_2$ injection was based on a four-point calibration curve generated from standards (Scott Specialty Gases, Longmont, CO) and air containing from 1 to 21 percent $O_2$ and from 0.04 to 15 percent $CO_2$. Samples containing $O_2$ concentrations greater than 21 percent due to pure $O_2$ injection were quantified with two additional standards: a pure $O_2$ standard and a 1:1 mix of pure $O_2$ and pure $N_2$. Concentration calculations were based on the mass of each contaminant divided by the dry weight of the soil, the volume of water extracted, or the volume of gas injected for analysis.

## E. TEST DESCRIPTION

Sampling trips to FPTA#1 were conducted on a nominal monthly basis to monitor the performance of the bioventing system. The main emphasis of these trips was to measure soil gas $O_2$, $CO_2$, and TPH, along with soil and injection air temperature, injection air flow rates, and vacuum readings in the 34 monitoring points installed throughout the field site. Injection flow rates were

adjusted according to the results of the soil gas sampling and air flow rate measurements to ensure adequate oxygen in the subsurface. Any broken air delivery pipes were repaired during these trips.

Respiration tests were conducted to monitor changes in respiration rates over the operational period of the bioventing system and were conducted approximately quarterly. These tests consisted of measuring initial soil gas concentrations with the injection system on, then shutting the system off and monitoring the soil gas concentrations over a 5-day period. The measurement frequency for each monitoring point depended on historical respiration rates and/or initial $O_2$ concentrations. Soil gas monitoring points were monitored until $O_2$ concentrations reached 2 percent. The soil temperature and vacuum also were measured during the respiration tests.

Surface emission tests were conducted to quantify hydrocarbon emission rates due to injection of air into the subsurface during bioventing system operation. These tests entailed the use of surface emission isolation flux chambers to quantify TPH, boiling point splits (C-6 to C-15 *n*-paraffins), and specific *n*-paraffin and aromatic compounds released from the site. Ambient air was introduced into the chamber at a known controlled rate to sweep volatile contaminants out of the chamber for collection and concentration. Test compounds of interest were collected from the effluent of flux chambers using Tenax solid sorbent media for low- to medium-boiling-point-range compounds (two tubes in tandem with breakthrough tubes on each), and evacuated stainless steel canisters for the collection of whole air samples (two canisters at each location before and during air injection) for the higher-molecular-weight fraction of the compound range of interest.

Soil samples were obtained during installation of the bioventing system and at the end of the project to determine changes in soil concentrations over the operational period of the system. Initial soil samples were collected from the actual boreholes drilled for monitoring point installation, whereas final samples were collected within a distance of 1 foot away from the monitoring points. Soil boreholes were drilled to a depth of 8 feet, with soil samples collected using 2-foot split spoons segmented into 6-inch brass sleeves. Random sleeves from initial sampling were collected for analysis, and the final samples matched the depths and locations of selected initial samples.

Groundwater samples were collected manually from the three monitoring wells in the vicinity of FPTA#1. Samples were collected using a Teflon bailer after purging three well volumes. Well volumes were determined after measuring the water surface and well bottom elevations, and the well diameters. Volatile samples were collected in 40-mL volatile organic analysis (VOA) vials, and semivolatile samples were collected in 500-mL glass bottles.

## F. RESULTS

Soil analytical results showed the existence of discrepancies between the initial and final soil samples at many sampling points. These discrepancies are believed to stem from the highly heterogeneous nature of the soil at the former landfill site. The soil results indicate that significant differences in TPH concentrations detected from adjacent sampling brass tubes are rather common. Average concentrations and mass calculations across the site do show a decline in mass over time, however.

The boiling point ranges of the soil samples were analyzed for trends in the shift in compound distribution over the course of the study. Average concentration values for each boiling point range were calculated using results from 30 sampling locations where both initial and final soil analytical results were available. These averaged initial and final boiling point range soil concentrations indicate that an approximately 50 percent decrease in concentration occurred for C-12 and heavier boiling point ranges; however, no significant changes in the lighter compounds were observed in the test soils. Concentration-normalized boiling point results suggest a general trend of increases in composition of heavier compounds (>C-13 to C-14) during the study. The TPH mass remaining at the test site at the end of the study was approximately 6,099 pounds, a reduction of 42.3 percent in the total TPH mass from the beginning of the study. Of the remaining contaminants 4,462 pounds were in the semivolatile fraction and 1,637 pounds were found in the volatile fraction of the soil extracts. The overall mass removal efficiency of benzene, toluene, ethylbenzene, and xylenes (BTEX) was 28 percent, with benzene mass removal of 76.4 percent observed during the course of the study.

Contaminant mass removal was estimated based on both the analytical soil results and field-observed respiration rates. The accuracy of mass removal based on soil analytical results is largely dependent on the representativeness of the soil samples collected from the site which, in turn, is affected by the site heterogeneity. The field-observed respiration rates are considered a more reliable indicator of mass removal because they are less affected by soil heterogeneity. The respiration results are averaged over the large soil volumes associated with each soil gas probe, whereas the soil analytical results are determined from a much smaller soil volume. The averaging of soil gas sampling would therefore tend to average over heterogeneous soil textural and concentration conditions, giving a more integrated, representative picture of respiration rates and contaminant distribution taking place throughout the site than is possible from discrete soil core samples. The soil

mass removal estimated from the respiration data suggested that nearly 15,000 pounds of TPH was degraded during the study, and the respiration data are considered to be a more realistic indicator of overall contaminant removal than the soil analytical results.

The initial and final soil samples analyzed for PAHs show little PAH contamination, with only one sample exceeding the detection limits for PAH analysis. The final soil analysis revealed no PAH concentrations above the detection limits ranging from 0.5 to 1.2 micrograms per gram ($\mu$g/g) of dry soil.

The principal chlorinated solvent contaminants identified in the initial and final soil samples were methylene chloride, TCE, and tetrachloroethylene (PCE). It is likely that the methylene chloride represented laboratory contamination during extraction and analysis, because prior soil investigations found low methylene chloride concentrations of $\leq$0.16 mg/kg (Peterson et al., 1993) and final soil methylene chloride results from Utah Water Research Laboratory (UWRL) analysis also were low ($\leq$0.57 $\mu$g/g). Initial TCE concentrations ranged from most samples being below detection limit to 14 $\mu$g/g of dry soil, whereas PCE was detected in only one sample at 4.2 $\mu$g/g of dry soil. The final soil analysis showed most TCE concentrations less than 0.1 $\mu$g/g of dry soil, with a maximum of 5.3 $\mu$g/g of dry soil, whereas PCE was detected in only one sample at 0.001 $\mu$g/g of dry soil.

A two-factor analysis of variance (ANOVA) indicated that neither soil contaminant level, nor injection flow rate, nor their interaction had a statistically significant impact on surface TPH emission rates at the 95 percent confidence level (CL). The mean of emission rates ($1.99 \times 10^{-7}$ to $2.52 \times 10^{-7}$ hexane-equivalent grams per square meter per second [g/m$^2$-s]) for the lower injection flow rates (0 to 2 actual cubic feet per minute [acfm]) was actually slightly higher than the mean of the emission rates ($1.77 \times 10^{-8}$ to $5.87 \times 10^{-8}$ hexane-equivalent g/m$^2$-s) for the higher injection flow rates (32 to 50 acfm); however, no significant difference existed between them. In addition, the comparison with soil contaminant levels indicated that there was no statistically significant difference among the surface TPH emission rates for background, low-, and high-TPH concentration areas based on the 95 percent CL; TPH emission rates ranged from $1.11 \times 10^{-7}$ to $2.76 \times 10^{-7}$ hexane-equivalent g/m$^2$-s.

The results of the groundwater sampling indicate that TPH concentrations decreased from the first to the second sampling event, although concentrations were below 1 mg/L for all samples. Examination of BTEX concentrations show that nearly all samples were below U.S. Environmental Protection Agency (U.S. EPA) drinking water maximum contaminant levels (MCLs). The only sample that exceeded BTEX MCLs was from monitoring well M-92, where benzene was found at

13.1 μg/L in January 1993. No benzene was detected in a duplicate sample from January 1993, nor was any found in the September 1993 sample.

Comparison of the two different soil gas sampling methods used showed no statistical difference in measurement of $O_2$, $CO_2$, and TPH. Comparison of field measurements and laboratory GC analysis of canister samples also showed no statistical difference in measurement of $O_2$ and $CO_2$.

Results from the nominal monthly soil gas monitoring events indicate that there was adequate oxygenation at most monitoring points (MPs) for the duration of the monitoring period, with many of the monitoring points remaining at approximately ambient $O_2$ concentrations, including some monitoring points experiencing no injection (MP-20 to -26, -30, and -31). Exceptions include MP-32, -33, -11, and monitoring points surrounding the plastic-covered area. Oxygen was depleted at MP-32 and -33 most likely because of the high $O_2$ demand due to high soil contaminant levels and inadequate $O_2$ delivery due to subsurface high-water-content conditions. Oxygen depletion at MP-11 was seen primarily during the summer months, when temperatures were elevated, resulting in an increase in $O_2$ utilization. The monitoring points in the plastic-covered area experienced fluctuating $O_2$ levels due to frequent breaks in the air supply pipe in the vicinity of injection point I20.

In general, more respiration rates determined from $O_2$ uptake data were significant at the 95 percent CL than those generated from $CO_2$ production data, and therefore $O_2$ uptake data were used in all data reduction efforts. In addition, the number of significant zero- and first-order rates determined during each respiration test were approximately equal, and zero-order rates were used to examine the effects of operational changes and time due to the inherent simplicity of zero-order rate expressions.

Oxygen uptake rates measured at the site typically were low, 0.1 percent/hour or less, with rates usually highest in the summer months and lower in the winter. To determine if respiration rates changed over time, the effect of temperature on respiration rates was quantified using the Arrhenius relationship. Results of this analysis predict a doubling of the respiration rate with an increase of approximately 10.3°C (over a temperature range from 5°C to 25°C), which is comparable to the van't Hoff rule of a doubling in rate for every 10°C.

There was a general trend toward nonsignificant rates at the end of the operational period indicating contaminant removal at these points over time. Comparison of respiration rates for all monitoring points revealed that there was a decrease in the percentage of significant rates over the operating period, with the percentage of significant rates decreasing from an average of 62.1 percent

for the first four respiration tests to only 15.7 percent for the March 1995 respiration test, again confirming the removal of mass from throughout the site over time.

To evaluate the effect of a plastic cover on the passive warming of the subsurface and stimulation of in situ respiration rates, the mean measured soil temperatures at each depth for monitoring points inside and outside the covered area were compared before and after cover removal. Regression analyses of temperatures inside versus outside the covered area for each of the three depths indicated that, for the shallow depth with the cover present, the temperature was higher inside the covered area than outside by 0.84 $\pm$ 0.63°C over the full range of temperatures. There was no difference in soil temperatures inside and outside the covered area after the cover was removed, indicating a beneficial effect of the cover on increasing soil temperatures at a depth of 3 feet. For the medium depth with the cover present, the temperatures of the monitoring points inside and outside the covered area were equal at 13.7°C. At temperatures below 13.7°C (generally November through May) monitoring points inside were warmer than those outside the covered area, but were cooler at temperatures above 13.7°C. This same pattern occurred when the cover was removed with the isothermal point at 13.3°C, suggesting that there was no effect at the medium depth due to the presence of the cover. The results for the deep monitoring points indicate that there was no statistical difference between points inside and outside the covered area when the cover was present, whereas insufficient data were available for regression analysis after the cover was removed.

Temperature data from both monitoring points and soil thermocouples were combined to allow additional analyses on the effectiveness of the plastic cover. Regression analyses of temperature versus depth were performed, with differences between inside and outside temperatures determined using 95 percent confidence intervals (CI) about the mean. Where regressions were determined to be nonsignificant, one-way ANOVAs were performed between statistically identical temperatures inside and statistically identical temperatures outside. Results indicate that the inside soil temperatures were significantly warmer than outside soil temperatures at comparable depths from September through March when the cover was present. This difference persisted after the cover was removed, indicating that the cover was not responsible for the observed temperature differences. This was likely due to the higher soil water content inside the covered area (12.6 percent) compared to that outside the covered area (5.8 percent).

The field evaluation of the effect of pure $O_2$ injection and elevated soil $O_2$ levels on temperature-corrected in situ respiration rates indicated that a total of 18 of 32 atmospheric $O_2$-influenced rates were statistically identical to rates measured during pure $O_2$ injection. Of the

rates that were statistically different, six atmospheric $O_2$-influenced rates were less than the pure $O_2$-influenced rates, whereas eight rates were greater than the pure $O_2$-influenced rates. The single respiration rate determined at an $O_2$ concentration significantly higher than ambient (MP13D, December 1994) was statistically higher than four of the atmospheric $O_2$-influenced rates at that monitoring point, while it was statistically identical to the remaining two rates. Laboratory results of oxygen uptake under ambient oxygen and pure $O_2$ atmospheres indicate that there was no difference in oxygen utilization under different oxygen atmospheric regimes.

Although neither pulsed nor continuous operation delivered adequate $O_2$ to MP-5 and -11 during summer months, the pulsed system was slightly less effective in maintaining $O_2$ levels. It would require either a higher flow rate or longer operating times in the pulse cycle during the summer months to meet apparent oxygen consumption rates at these monitoring points.

## G. CONCLUSIONS

Based on the results obtained from the large-scale bioventing system operated under a variety of flow rate and system configurations, the following conclusions can be reached:

1. There was a decrease of 4,468 pounds TPH observed at the site over the 26-month operating period. There was a total BTEX and naphthalene reduction of 28 percent and 18 percent, respectively. Benzene showed the most significant mass removal of the BTEX compounds, with 76 percent (49 pounds) mass removal during the study. There was no significant change in the soil contaminant boiling point distribution for low-boiling-point compounds (<C-6 to C-12), whereas higher-boiling-point compounds (C-12 to >C-15) showed average reductions of 52 percent by the end of the study. Soil TPH removal of 14,842 pounds was estimated based on oxygen uptake rates measured within the site during the study.

2. No significant increases in hydrocarbon surface emission rates were measured under a variety of flow conditions, nor were differences in emission rates significant between background and contaminated soil locations. Air injection during operation of the bioventing system had no measurable impact on air quality at the F.E. Warren site from uncontrolled soil emissions.

3. No significant hydrocarbon concentrations were measured in groundwater samples, with maximum TPH concentrations of less than 1 mg/L. Only one sample exceeded BTEX MCL concentrations.

4. Respiration rates typically were low (<0.1 percent/hour), with higher rates during summer months and lower rates during the winter. After correcting these rates to 12°C for selected monitoring points, rates were either statistically the same or showed a slight decrease over the period of operation. The percentage of nonsignificant rates increased for the last two respiration tests, confirming the removal of contaminant mass throughout the site by the end of the study.

5. Thermocouple data from monitoring points and soil thermocouples in the plastic-covered area indicated that there were seasonal variations in the effect of the plastic cover, but that the overall impact of the cover was not statistically significant.

6. Mechanical problems with the pure $O_2$ injection system limited the quantity of data obtained to evaluate the impact of pure $O_2$ injection on in situ soil respiration rates. Examination of respiration rates at monitoring points adjacent to the first pure $O_2$ injection point, I13, indicated that there were no significant differences in rates under either air injection or the elevated $O_2$ concentrations achieved at this site. The effectiveness of pure $O_2$ injection in increasing subsurface $O_2$ concentrations was limited due to mechanical problems and subsurface heterogeneity, although soil gas oxygen concentrations as high as 50 percent were measured at some points in the site.

7. Pulsed air injection occurred for a period of 9 months and achieved oxygenation of subsurface soil comparable to continuous air injection at the adjacent monitoring points. Oxygen depletion occurred at several monitoring points under both injection strategies, however, particularly during the warmer temperatures of summer.

## H. RECOMMENDATIONS

Based on these findings, the following recommendations can be made regarding the application of air injection bioventing systems at other Air Force sites.

1. Surface emission rates appear insignificant from even the shallow surface soil site represented by the F.E. Warren site investigated in this study. Concern for enhanced surface emission impacts to ambient air quality appears unwarranted, and continued monitoring of surface emissions appears unnecessary at most sites. The decision to carry out costly surface emission tests should be the exception, not the rule, at air injection bioventing sites, and site-specific characteristics, particularly close proximity to subsurface structures, should drive the decision to monitor gas migration away from the air injection system.

2. Contaminant removal using bioventing was successful at the F.E. Warren site, despite the generally low hydrocarbon concentrations observed there. No indication of inhibition or toxicity associated with chlorinated solvents was evident from the field respiration data, and it appears that bioventing should be pursued by the Air Force as a long-term approach for fire training pit site remediation.

3. Passive soil warming using the black plastic surface cover employed in this study was generally ineffective in significantly increasing overall contaminant removal rates over the course of the study. Effects were observed at shallow depths (3 feet), but any effects at greater depths appear to have been overwhelmed with variations in subsurface soil conditions. Alternative cover material should be considered or a more active approach should be applied in general to take advantage of the increasing respiration rates observed with increasing soil temperatures.

4. Application of pure oxygen to the F.E. Warren site was plagued by mechanical problems. Pure oxygen soil environments did not appear to affect soil respiration rates in either a positive or a negative way based on both laboratory and field respiration rate results. The cost and complexity of pure oxygen injection at bioventing sites must be a

major consideration in its adoption as, based on Recommendation 1 (above), the major advantage of pure oxygen injection, i.e., the reduction in required gas flow and corresponding reduction in potential contaminant emission rates, may be of minor importance at most sites. The general application of pure oxygen injection to increase biodegradation rates at bioventing sites cannot be recommended based on the results of this study.

5. Pulsed air injection appeared to be less than optimized at the F.E. Warren site based on depressed oxygen levels measured at some soil gas sampling points surrounding the pulsed air injection well. To take advantage of the pulsed air injection operating mode at a site, it appears that the sequencing of the air injection periods should be based on monitoring of soil gas oxygen response to air injection, rather than on a fixed on/off cycle. Feedback from an oxygen sensor at a location within the flow field, or routine adjustments of the cycle based on ongoing manual soil gas monitoring, should improve the overall efficiency of oxygen transfer of bioventing systems operated in a pulsed venting mode.

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# SECTION I
# INTRODUCTION

## A. OBJECTIVE

The objective of this project was to evaluate the effectiveness of bioventing for the remediation of petroleum-contaminated soils under northern climatic conditions. The site selected for this evaluation was Fire Protection Training Area 1 (FPTA#1) at F.E. Warren Air Force Base (AFB) in Cheyenne, Wyoming (Figure 1). The effects of bioventing system air flow rate and operating conditions on the performance of this large-scale system were assessed under actual field conditions. The range of operating conditions investigated in this field study included an area within the site that incorporated a plastic surface cover to attempt to provide passive warming of shallow contaminated surface soils; the use of pulsed atmospheric air injection in a portion of the site; the use of pure oxygen injection in a portion of the site; and the evaluation of the effect of air injection flow rate on soil surface air emissions.

A 26-month field sampling and site monitoring period also was used to evaluate large-scale system operating and contaminant removal performance over a wide range of soil temperature conditions that were known to occur at this site. Performance monitoring included monthly soil gas oxygen, carbon dioxide, and total petroleum hydrocarbon (TPH) concentrations, quarterly in situ respiration tests, semi-annual surface emission tests, and initial and final soil contaminant and limited groundwater sampling. In addition to the field sampling effort, a companion laboratory study was conducted to provide additional supporting information regarding the rate and extent of contaminant degradation under more controlled environmental conditions than are possible at the field scale. Some of the results of this laboratory study, particularly for soil respiration rates under pure oxygen conditions, are included in this report. Additional laboratory results are the subject of a companion project report.

## B. BACKGROUND

Bioventing is an in situ bioremediation technology designed to take advantage of the metabolic activity of indigenous microorganisms in the vadose zone to destroy targeted contaminants. The basic operating principle of bioventing is to provide these microorganisms with the oxygen that they require

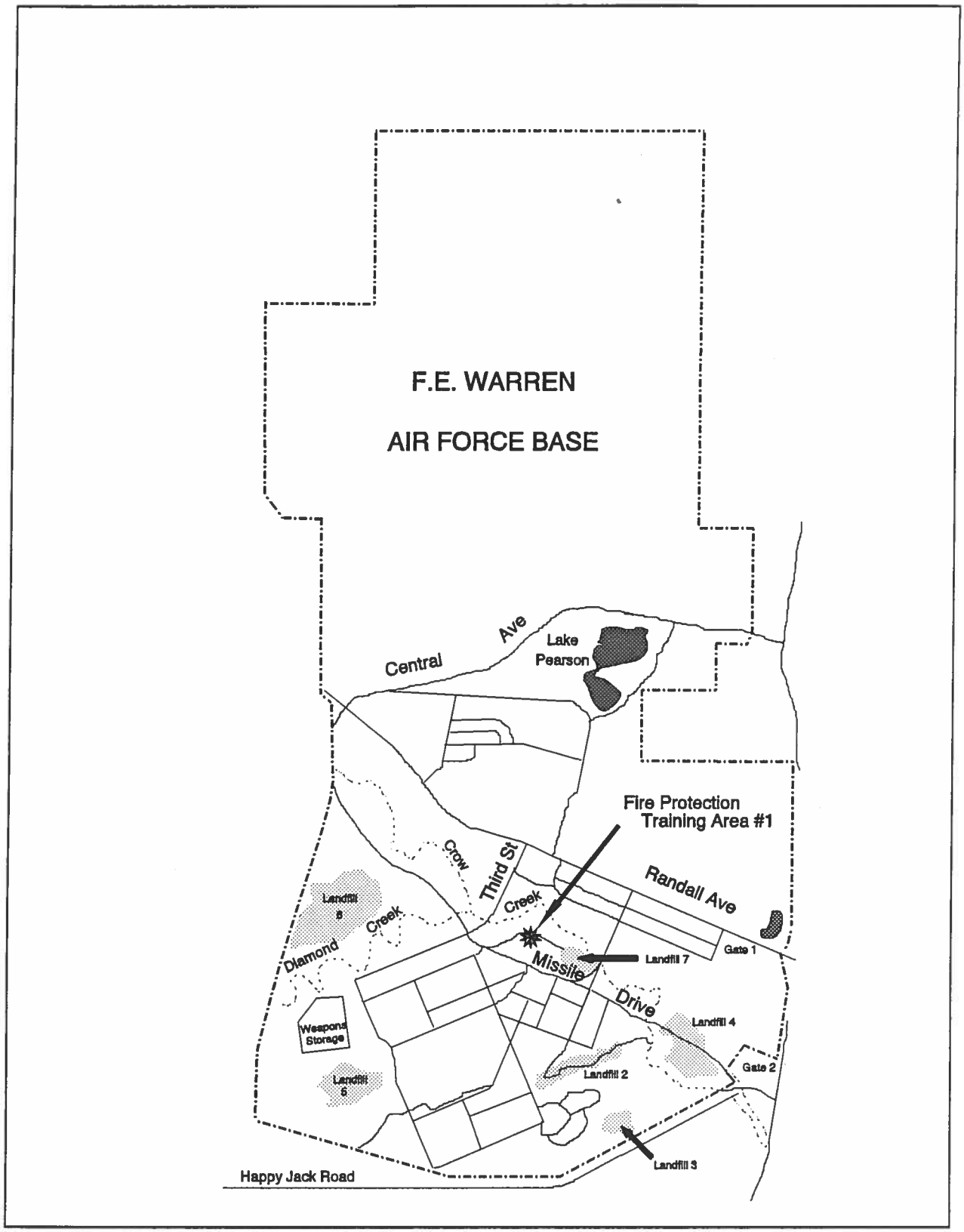


**Figure 1.** Map of F.E. Warren AFB Showing Location of FPTA#1.

for aerobic metabolism. Oxygen is provided through induced air flow in the contaminated soils using a system of blowers and vent wells.

The equipment utilized by the technology is similar to that used for soil vapor extraction (SVE); however, the two technologies have significantly different operating principles. SVE is a contaminant removal process and, thus, SVE systems are designed to exploit the volatile nature of the contaminant. Systems operate in an extraction mode at relatively high air extraction rates and, in many cases, the system off-gas requires some form of ex situ treatment prior to discharge to the atmosphere. Bioventing systems are operated in either an injection or an extraction mode, depending on site-specific requirements. Because the objective of bioventing is to support in situ biodegradation of contaminants, system air flow rates are maintained high enough to provide the required oxygen to the soils, yet low enough to minimize volatile discharges to the atmosphere.

The development of bioventing began in the 1980s when it was observed that the hydrocarbon vapors recovered from SVE could not account for all of the mass of hydrocarbon removed from unsaturated soils (van Eyk and Vreeken, 1988). Since then, both government and industry have put significant effort into the development of the technology. The U.S. Air Force initiated its research and development program in bioventing in 1988 with a study at Hill AFB, Site 914, in Utah. The system at this site initially was operated as an SVE unit, but was modified to a bioventing system after 9 months of operation. Moisture and nutrient addition were studied at this site; however, while moisture addition appeared to improve biodegradation, nutrient addition did not. Final soil sampling demonstrated that benzene, toluene, ethylbenzene, and xylenes (BTEX) and TPH levels were reduced to below regulatory levels, and this site became the first Air Force site that was closed through in situ bioremediation. During this study, it became apparent that bioventing had great potential for remediating JP-4 fuel-contaminated soils. It was apparent also that additional research would be needed before the technology could be applied routinely in the field.

Following the Hill AFB Site 914 study, a more controlled bioventing study was conducted at Tyndall AFB in Florida. This study was designed to monitor specific process variables and their subsequent effects on biodegradation of hydrocarbons. Several important findings resulted from this work, including the effect of air flow rates on removal by biodegradation and volatilization, the effect of temperature on biodegradation rates, the lack of microbial stimulation from the addition of moisture and nutrients, and the importance of natural nitrogen supply through nitrogen fixation. In addition, initial and final contaminant measurements showed greater than 90 percent removal of BTEX. Although this study was short-term, it illustrated the effectiveness of bioventing.

The studies conducted at Hill AFB and Tyndall AFB provided valuable information on bioventing. However, it was apparent that long-term, controlled bioventing studies were necessary to fully evaluate and optimize the technology. In 1991, long-term bioventing studies were initiated at Hill AFB Site 280 and Eielson AFB Site 20 in Alaska. These studies were joint efforts between the United States Environmental Protection Agency (U.S. EPA) and the U.S. Air Force Environics Directorate of the Armstrong Laboratory. These studies involved intensive monitoring of several process variables, including the effect of soil temperature on biodegradation rates, surface emissions analyses, and optimization of flow rate.

Based on the success of these previous studies, in 1992, the U.S. Air Force Center for Environmental Excellence (AFCEE) initiated the Bioventing Initiative, which involved installing pilot-scale bioventing systems at approximately 120 contaminated sites located throughout the continental United States and in Hawaii, Alaska, and Johnston Atoll. These sites varied dramatically in climatic and geologic conditions. Contaminants typically were petroleum hydrocarbons from JP-4 jet fuel, heating oils, waste oils, gasoline, and diesel; however, some fire training areas also were studied where significant concentrations of solvents were present.

This report contains the results of a large-scale bioventing study that was conducted at F.E. Warren AFB in Cheyenne, Wyoming. The study took place at the site of an abandoned fire protection training area (FPTA#1). The study included a 26-month field effort consisting of 1 year of conventional operation followed by incorporation of several enhancements to the system. To isolate the impact of these enhancements, the system was designed so that the area being vented could be segregated into four discrete sections and the blowers to each of these sections could be operated independently. The enhancements in the study included passive soil warming, pulsed air injection, and pure oxygen injection. The focus of the study was to see if incorporating one or more of these enhancements would provide increased microbial activity as measured by increased respiration activity.

FPTA#1 was used from 1950 to 1965 as a fire prevention training ground (Engineering-Science, 1985). Three to four times a month flammable liquids, including waste oils, solvents, gasoline, JP-4 jet fuel, and other combustible liquids, were dumped into one of two circular earthen berms and ignited, and the resultant fire was extinguished with water and protein foam. Other contamination at the site included the dumping of chlorobromomethane directly on the ground outside of the earthen berms, gasoline spilled in 1973 during fire protection training exercises, and use of the area as a landfill. There was visible evidence of soil contamination at FPTA#1 in the late 1980s, with

vegetation absent over a sizeable area within and near the berms as well as areas of soil that were darkly stained and had the odor of petroleum products.

Results from the 1987 to 1988 analyses of groundwater for volatile halogenated organic compounds detected trichloroethylene (TCE) most frequently, although 1,2-dichloroethene was detected at the highest concentration (Larson et al., 1991). The maximum TCE and 1,2-dichloroethene concentrations were 29 micrograms per liter ($\mu$g/L) and 54 $\mu$g/L, respectively, at that time. The source of the TCE in the groundwater has been determined to be upgradient, although some contamination from the site is possible. No analysis for chlorobromomethane was done at this time. Later sampling found similar TCE levels in most wells, although TCE concentrations had increased significantly in three wells to a maximum of 57 $\mu$g/L (Peterson et al., 1993). Analyses for bromochloromethane were all nondetectable.

Results from the 1987 to 1988 analyses of soil for volatile halogenated organic compounds also detected TCE most frequently, with maximum concentrations of 71 milligrams per kilogram (mg/kg) (Larson et al., 1991). TCE contamination of the soil at relatively shallow depths suggested that local spills were the probable source of this contamination. The TPH analysis of the soil indicated concentrations of up to 8,800 mg/kg, with an average TPH level at the site of 2,000 mg/kg. Later soil analyses showed that both the TCE and the TPH concentrations were lower (Peterson et al., 1993), with the maximum TCE concentrations only 10 mg/kg, and maximum TPH concentration reaching 2,540 mg/kg with an average TPH of 382 mg/kg. All samples with detectable TCE levels occurred in or near the earthen berms, generally below 4 feet in depth. Bromochloromethane was detected in only one soil sample at a concentration of 6.6 mg/kg.

## C. SCOPE/APPROACH

The 26-month field research project involved the design and installation of a large-scale air injection bioventing system; laboratory analysis of soil and groundwater samples collected from the site during system installation and at the completion of the study; operation, maintenance, and monitoring of the field-scale bioventing demonstration system; conducting routine in situ respiration tests over the course of the study; and collecting and analyzing system operating data to evaluate the impact of temperature, injection flow rate, air injection pulsing, and pure oxygen injection on field-determined biological activity and contaminant volatilization rates throughout the field site. The methodology, results, and data interpretation from these field activities are summarized in this report.

The monitoring of the field-scale bioventing system operated at the FPTA#1 site consisted primarily of soil gas measurements for respiration gas (oxygen [$O_2$] and carbon dioxide [$CO_2$]) constituents, hydrocarbon composition in soil gas, and changes in these characteristics in response to changes in site conditions or bioventing system operating characteristics.

Soil gas TPH was measured using a GasTech TraceTechtor™ analyzer. Two different sampling procedures were used over the course of the field study. The first method, used from 1/93 to 10/93, involved connecting the analyzer directly to the gas sampling probe, with the internal pump of the analyzer used to withdraw a sample. The second method, used from 11/93 to 3/95, involved the use of an external pump to withdraw a volume of gas into a 1-liter Tedlar™ bag. This volume was then flushed to ensure an unadulterated and undiluted sample. The Tedlar® bag was then refilled with 1 liter of soil gas sample for TPH, $O_2$, and $CO_2$ analysis. The analyzers were used outdoors when the temperature was above 20°F, and indoors when the temperature was less than 20°F. If $O_2$ concentrations were less than 12 percent, a 1:1 dilution fitting (GasTech) was used during TPH measurements. $O_2$ and $CO_2$ concentrations in soil gas were measured using a GasTech model 3252OX analyzer. Sampling methods were identical to those used for TPH when samples were at ambient levels of $O_2$ or less. Samples with greater than 21 percent $O_2$ due to pure $O_2$ injection were quantified after mixing appropriate ratios of sample and $O_2$-free calibration gas in a 1-L Tedlar™ bag.

Soil and air temperatures were measured using a Fluke model 51 K/J thermometer and Type K thermocouples. Air flow rates from the bioventing blowers and pure $O_2$ injection system were measured using calibrated flowmeters and air flow velocities in air delivery pipes between injection points were measured using a Dwyer thermal anemometer. Vacuum was measured using a vacuum gauge with a range of 0 to 30 inches of mercury (Hg), connected to the inlet line of the soil gas sampling pump.

Laboratory analyses to support field-determined site parameters included soil sample volatile and semivolatile hydrocarbon compositions; water sample volatile and semivolatile hydrocarbon compositions; and soil gas composition via the stainless steel evacuated canister and Tenax™ sorbent tube sampling methods.

Soil samples were analyzed for volatile hydrocarbons through methanol extraction and purge-and-trap analysis of the extract with gas chromatography (GC) analysis using a flame ionization detector (FID). Water samples were purged directly with GC analysis using a FID. Initial samples were purged manually, whereas final samples were purged using an autopurging system. Nonvolatile

hydrocarbon analyses of site soils and groundwater were carried out through methylene chloride soxhlet and liquid-liquid extraction, respectively, using GC analysis with a FID.

Methanol extracts of initial soil samples were sent to an outside laboratory for chlorinated solvent analysis using EPA Method 8240. Final soil samples were analyzed for chlorinated solvents using manual purge and trap of soil methanol extracts using GC/mass spectrometric (GC/MS) analysis. Soil samples were analyzed for polycyclic aromatic hydrocarbons (PAHs) through methylene chloride soxhlet extraction with GC/MS analysis.

Canister samples were analyzed for volatile hydrocarbons and respiration gases. $O_2$ and $CO_2$ analyses of canister gas samples were conducted using a GC with a thermal conductivity detector (TCD). Tenax™ samples were analyzed for volatile organic compounds (VOCs) by thermal desorption using a thermal desorber connected to a GC with a FID.

Data reduction for soil and water samples involved the conversion of specific constituent mass data from raw chromatographic data to representative concentration units appropriate for the given medium. In addition, contaminant degradation and oxygen respiration rate determinations were used to provide a quantitative description of system characteristics over the duration of the study.

TPH analyses were calibrated using a 25-compound external standard containing C-5 to C-15 *n*-alkanes along with benzene, toluene, *m*-xylene, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, naphthalene, and methylnaphthalene. Purge-and-trap extraction analysis was quantified from C-5 up to but not including C-12, and soxhlet extraction analysis was quantified from C-12 through C-15. A five-point calibration curve was established over a three-log concentration range for each standard compound to quantify the mass of each compound in a sample. PAH analyses were calibrated using a 16-compound standard, with a five-point calibration curve being established for each analyte and internal standards used to quantify the mass of each analyte in a sample. Chlorinated solvent analyses were calibrated using a 13-compound standard, with calibration and quantitation methods used being identical to those for the PAH constituents. Quantitation of soil gas $O_2/CO_2$ during atmospheric $O_2$ injection was based on a four-point calibration curve generated from standards (Scott Specialty Gases, Longmont, CO) and air containing from 1 to 21 percent $O_2$ and from 0.04 to 15 percent $CO_2$. Samples containing $O_2$ concentrations greater than 21 percent due to pure $O_2$ injection were quantified with two additional standards: a pure $O_2$ standard and a 1:1 mix of pure $O_2$ and pure $N_2$. Concentration calculations were based on the mass of each contaminant divided by the dry weight of the soil, the volume of water extracted, or the volume of gas injected for analysis.

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## SECTION II

## SITE CHARACTERIZATION, SYSTEM DESIGN, LAYOUT, AND INSTALLATION

### A. SITE CHARACTERIZATION

The results from the United States Geological Survey's (USGS's) draft remedial investigation report (USGS, 1993) were used as the basis for the preliminary site characterization. During remedial investigation activities, numerous soil samples were taken from soil borings in the area of FPTA#1. The analytical results of these samples showed the existence of two well-defined "hot spots" of TPH concentration. The bioventing system was located to encompass these hot spots.

One of the hot spots was located to the northwest adjacent to the concrete slab. It was believed that this area was used to store combustible materials prior to their being burned. Although it was not known how the materials got into the soil, it was believed that they had been spilled both during storage and during subsequent movement to the burn area. The USGS reported soil concentrations of TPH as high as 8,800 parts per million (ppm) in this area. Chlorinated solvents, such as TCE, were found at concentrations as high as 71 ppm.

The second hot spot is in the southeastern section of the site and is associated with the bermed area where actual burning took place. The TPH concentrations in this area were as high as 7,400 ppm. Chlorinated solvents were reported in this area at concentrations as high as 49 ppm.

Previous site tests were conducted by Engineering-Science, Inc. as part of the U.S. Air Force's Bioventing Field Initiative. These tests included a soil gas permeability test and an initial in situ respiration test. The results from the soil gas permeability test showed that the soil was permeable enough to allow for a minimum radius of influence (RI) of 30 feet. The 30-foot RI was used in the design of the bioventing system used for this study. The in situ respiration test indicated biological activity was occurring in the soils at FPTA#1 and that the soil microorganisms probably were oxygen limited. These results confirmed the site as amenable to bioventing.

An initial site characterization was conducted in coordination with the installation of the bioventing system. Discrete soil intervals were sampled during the drilling of the boreholes for each of 34 soil gas monitoring points located around the 22 vent wells shown in Figure 2. The samples were collected by split spoon using brass sleeves. The samples were placed on ice and shipped to the Utah Water Research Laboratory (UWRL) for contaminant analyses.

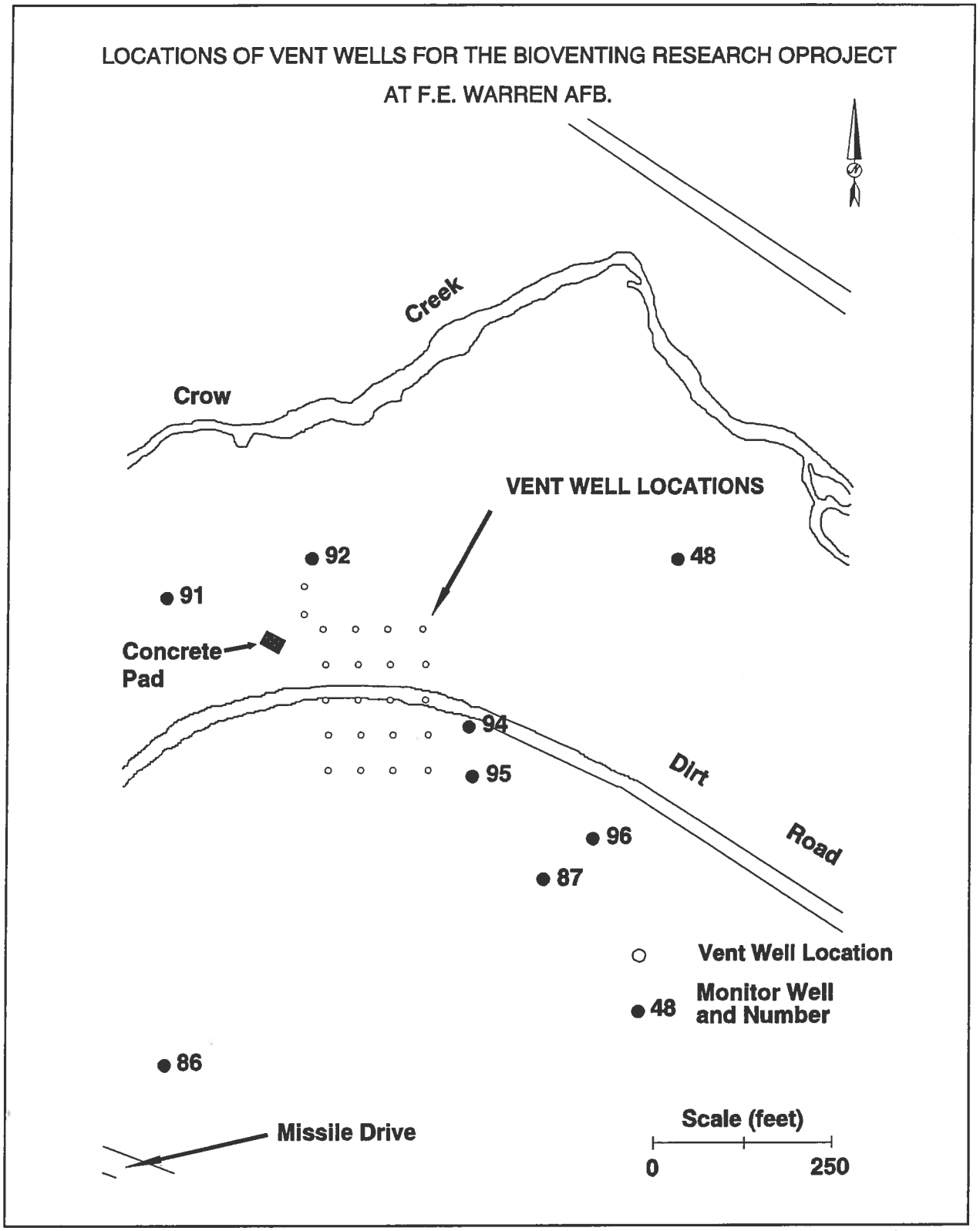


**Figure 2.** Locations of the 22 Vent Wells Around which the 34 Boreholes Were Advanced for Collecting Soil Samples and Installation of the Soil Gas Monitoring Points.

The results from soxhlet extraction and soil purge-and-trap analysis of the soil samples are presented in Appendix 1. The data confirmed the presence of the two hot spots and intermittent contamination throughout the site. The TPH concentrations ranged from less than 1 ppm to as high as 5,200 ppm in the hot spot located in the southeastern section of the bioventing system. Analyses for chlorinated solvents showed concentrations from below detectable levels to 170 ppm in the soils at FPTA#1. These results were also in good agreement with those reported in the draft remedial investigation report.

Following the installation of the bioventing vents and soil gas sampling points, an initial set of soil gas samples were collected and analyzed to determine the oxygen and carbon dioxide concentration profile prior to venting activities. The oxygen data from 3, 5.5, and 8 feet below ground surface (bgs) are plotted in Figures 3 through 5, respectively. It can be seen from these profiles that the areas around the hot spots are characterized by lower oxygen concentrations than other areas of FPTA#1 where the contaminant concentrations are not as high. The $O_2$ concentrations in more contaminated areas around MP-29 were as low as 1 percent, lower than the typical limiting concentration of 5 percent seen at the majority of other bioventing sites.

The $CO_2$ profiles shown in Figures 6 through 8 show that the $CO_2$ concentrations in the areas of depleted $O_2$ were elevated. These profiles give a strong indication that biological activity was responsible for the oxygen depletion and that microbial activity in these areas would benefit from bioventing. Other areas that were characterized by depleted $O_2$ and elevated $CO_2$ also would benefit from bioventing; however, the extent was dependent on the concentration of biodegradable contaminants and the development of a microbial population capable of degrading these compounds.

## B. SYSTEM DESIGN, LAYOUT, AND INSTALLATION

The bioventing system for FPTA#1 at F.E. Warren AFB was designed using the data from the USGS draft remedial investigation report (USGS, 1993) and the results from the site tests conducted by Engineering-Science, Inc. The system layout is shown in Figure 9. The system consisted of 22 air injection vent wells (I1 through I22) equipped with flow monitoring points and thermocouples, 34 trilevel soil gas monitoring points (MP-1 through MP-34), four 2-inch schedule 80 polyvinyl chloride (PVC) air distribution manifolds, thermocouples, pressure gauges, and flow monitoring ports. The system was connected to four 2-horsepower (hp) regenerative air blowers equipped with temperature

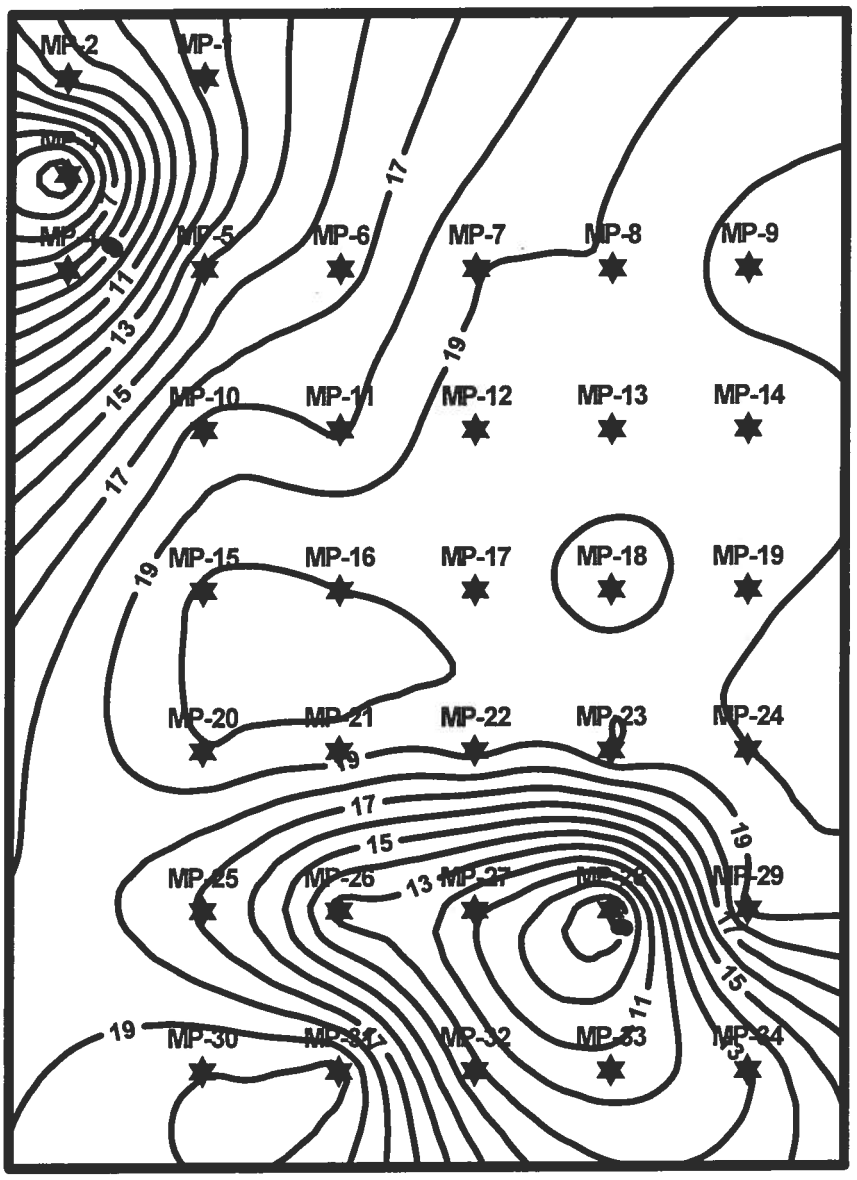


**Figure 3**. Initial Oxygen Profile at 3 Feet bgs at FPTA#1 at F.E. Warren AFB.

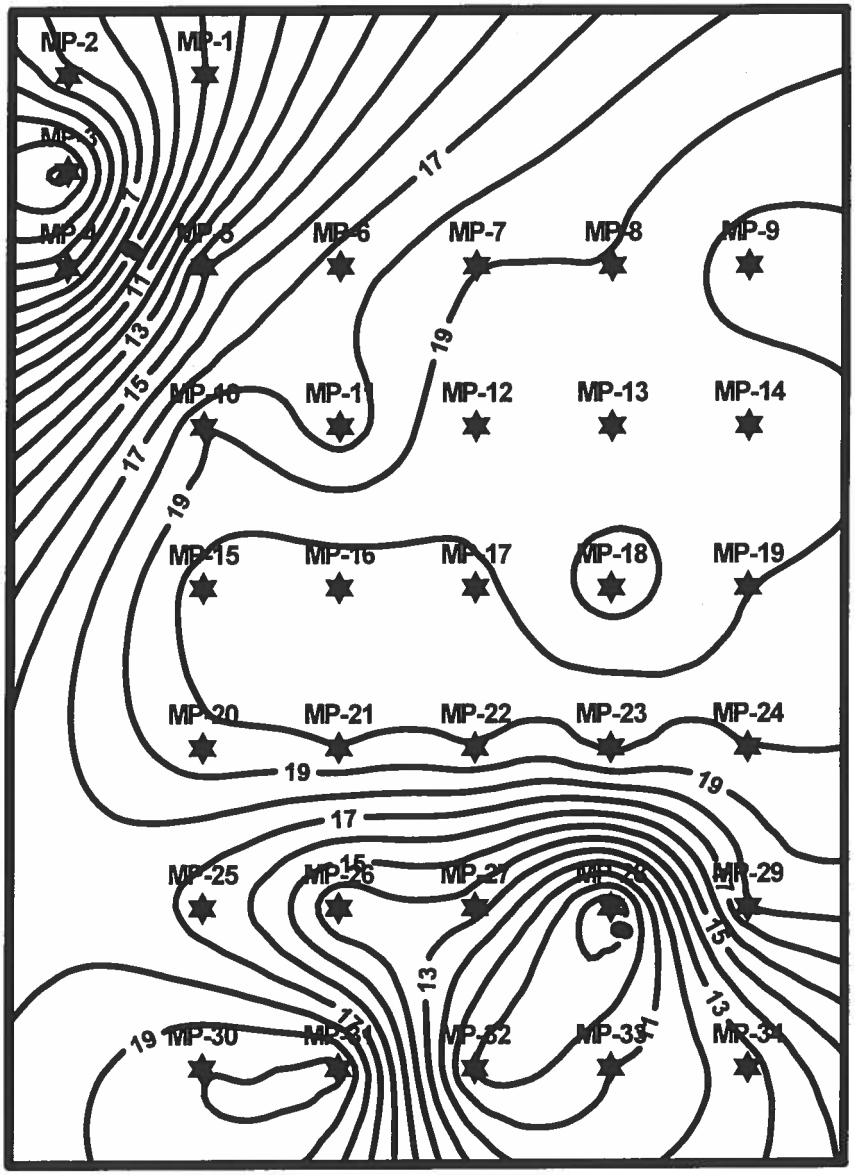


**Figure 4.** Initial Oxygen Profile at 5.5 Feet bgs at FPTA#1 at F.E. Warren AFB.

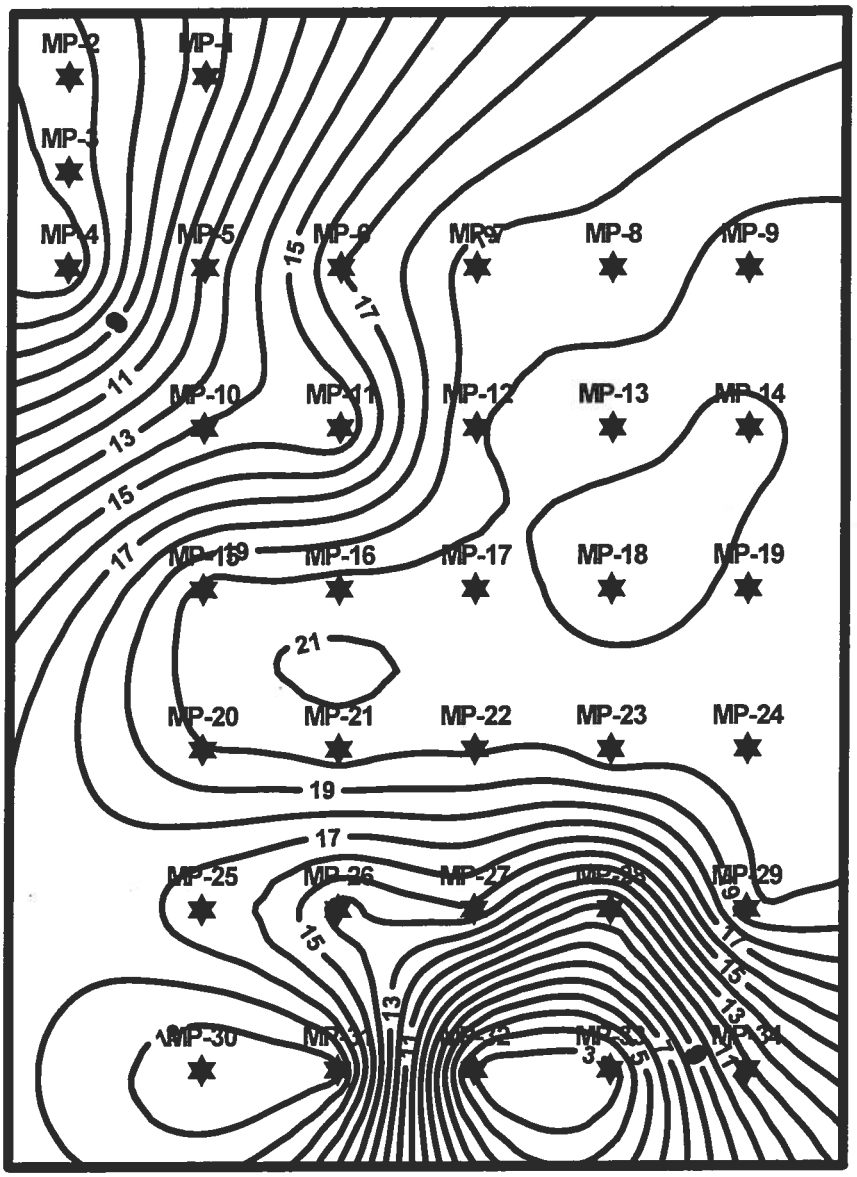


**Figure 5.** Initial Oxygen Profile at 8.0 Feet bgs at FPTA#1 at F.E. Warren AFB.

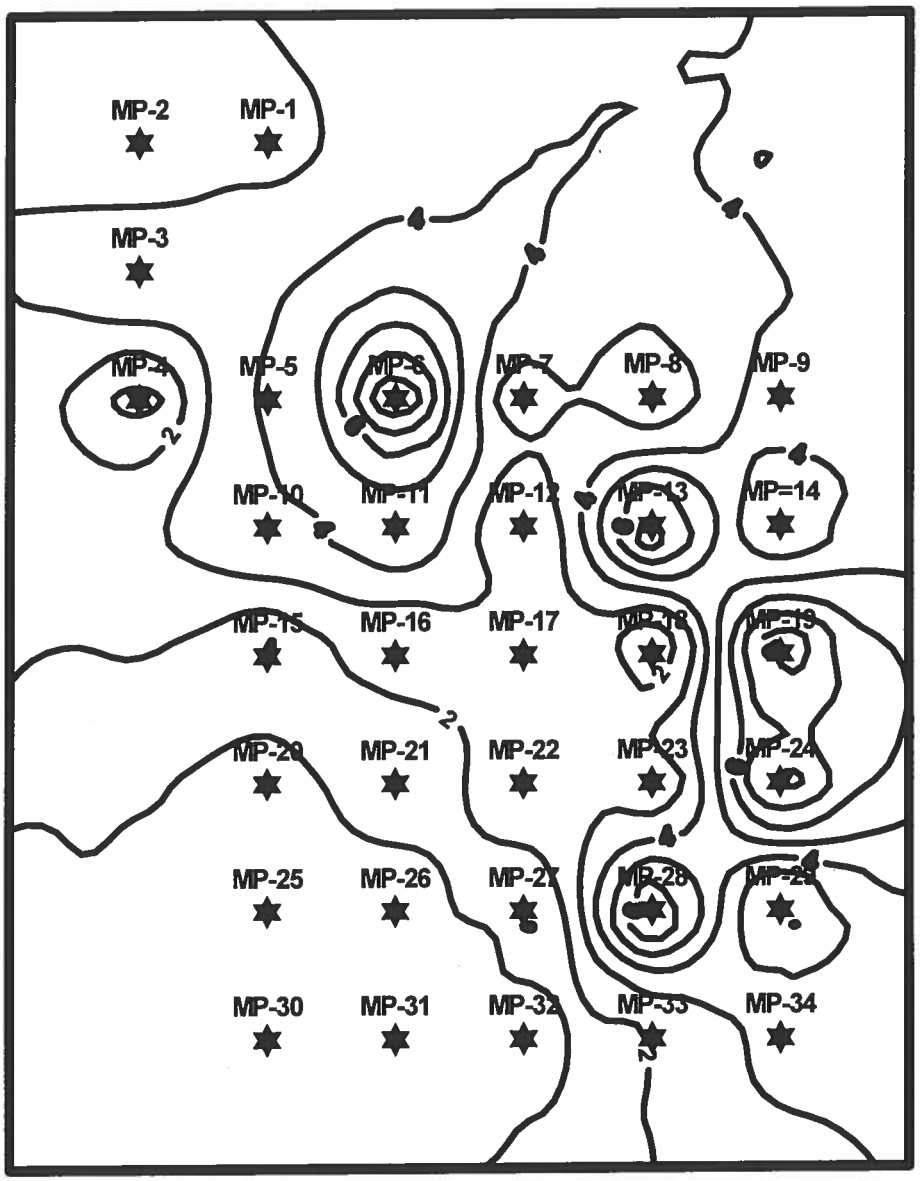


**Figure 6**. Initial Carbon Dioxide Profile at 3.0 Feet bgs at FPTA#1 at F.E. Warren AFB.

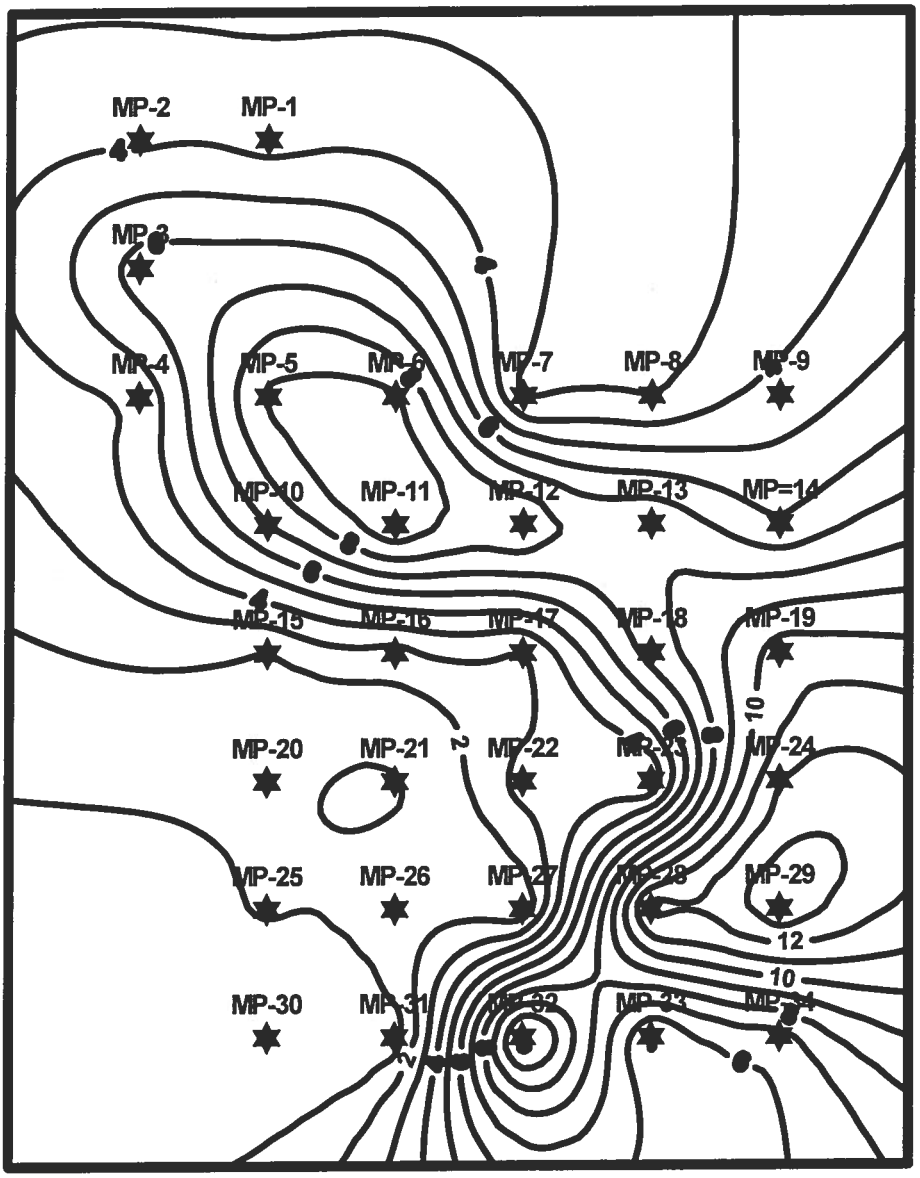


**Figure 7.** Initial Carbon Dioxide Profile for 5.5 Feet bgs at FPTA#1 at F.E. Warren AFB.

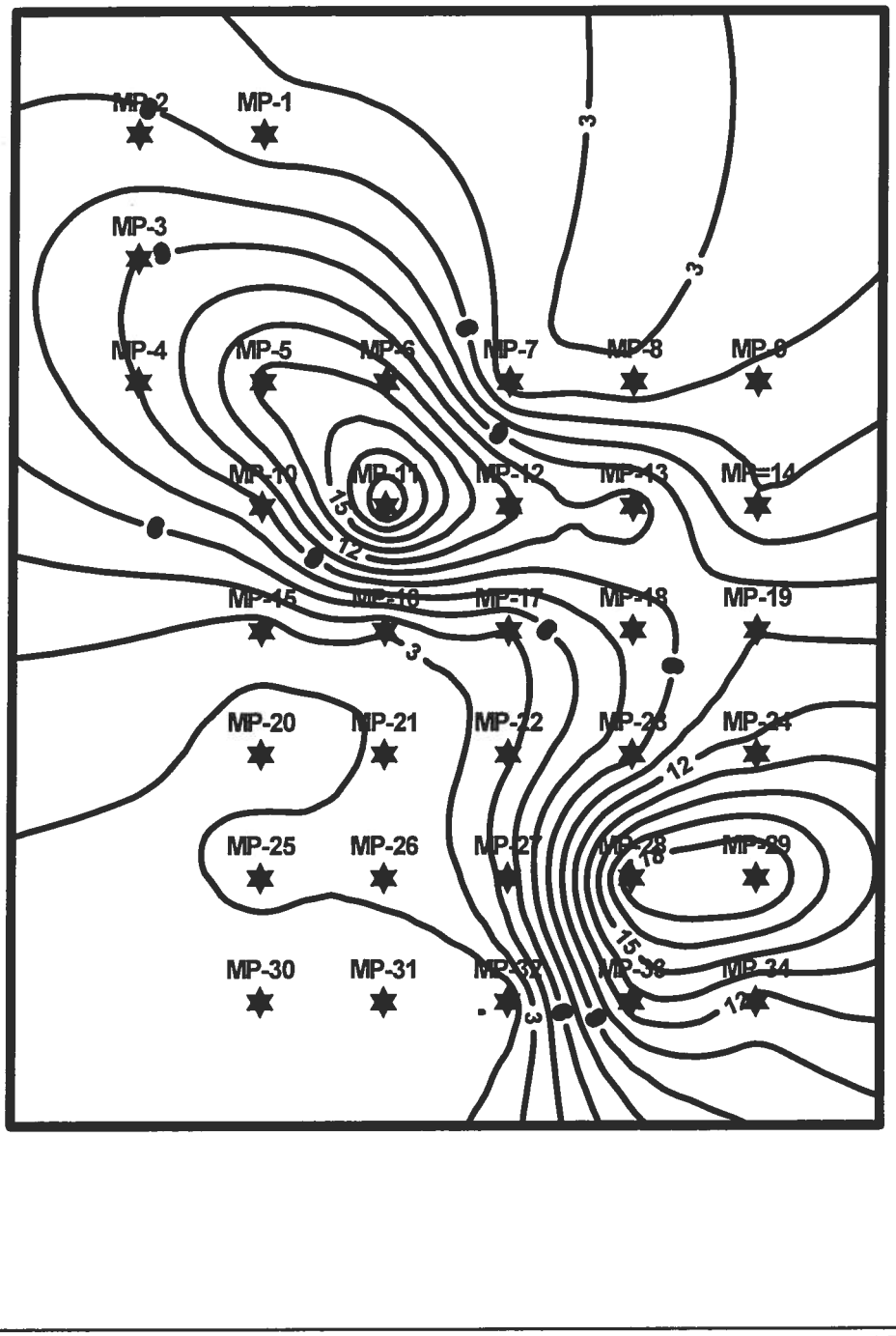


**Figure 8.** Initial Carbon Dioxide Profile at 8.0 Feet bgs at FPTA#1 at F.E. Warren AFB.

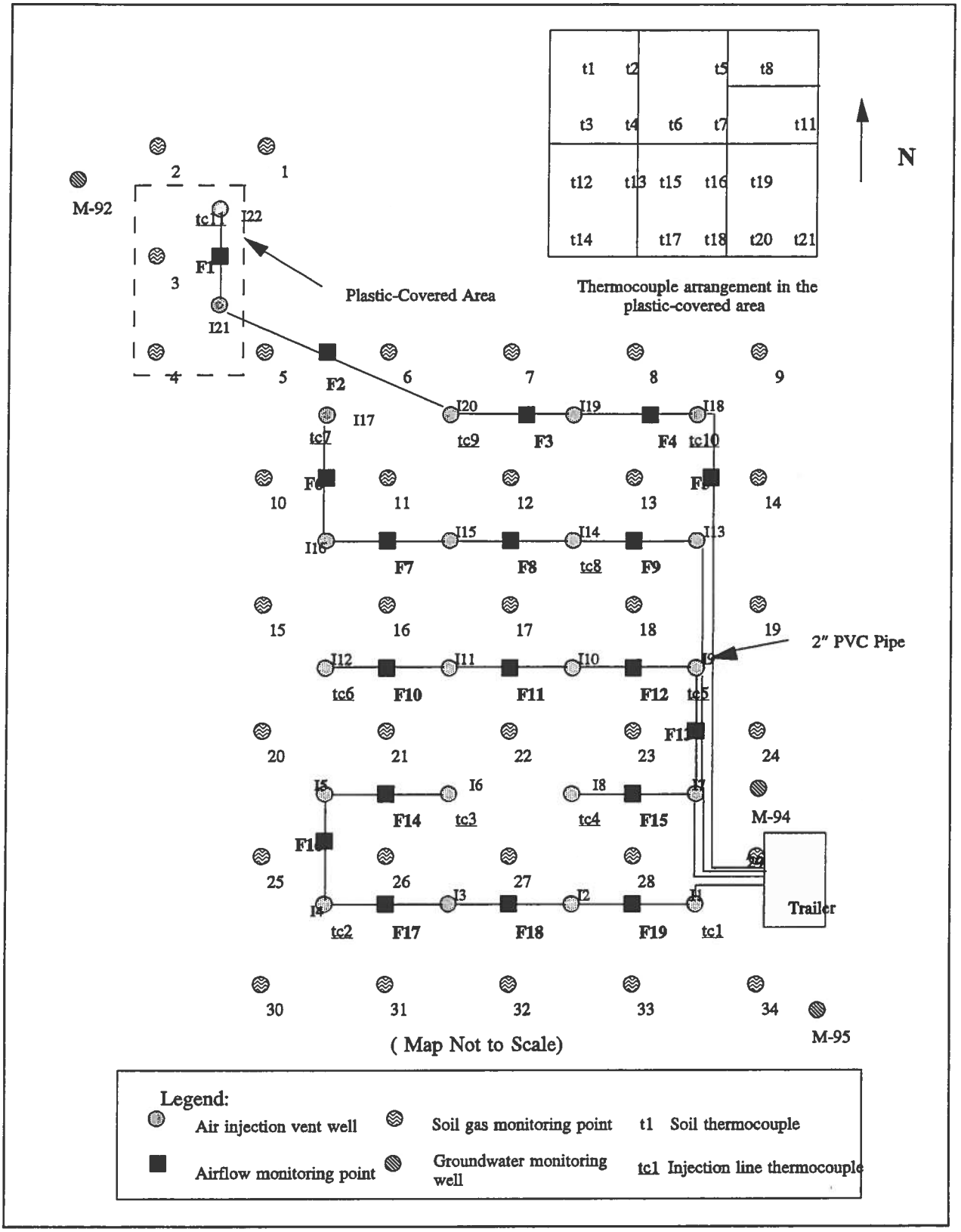


**Figure 9.** Layout of the Bioventing System Installed in FPTA#1 at F.E. Warren AFB.

sensors, flowmeters, and pressure gauges. The system covered approximately 40,000 $ft^2$ and was designed to treat soils between the ground surface and water table at approximately 10 feet deep.

The 22 vent wells were all of the same design (Figure 10). The vents were constructed from schedule 40 PVC well casing and were completed to a depth of 15 feet. The lower 10 feet of each vent consisted of a PVC well screen (0.02-inch slot) and was packed in sand. A section of PVC riser was connected to the screen and brought to approximately 1.5 feet above the ground surface. The top 5 feet of the annulus between the top of the screen and the ground surface was sealed with bentonite. The risers were connected to an air flow distribution manifold in the configuration shown in Figure 11.

Four air flow distribution manifolds were used to feed air to the 22 air injection vents. The manifold was constructed from 2-inch schedule 80 PVC pipe. Cement supports were used to prop the manifold at approximately 1.5 feet above the ground surface. Flow monitoring ports (F1 through F19 on Figure 9) were drilled into the manifold between each vent well to measure air velocities to determine the air flow for each vent. A type K thermocouple was inserted into each vent for measuring the temperature of the air injected at each point.

The trilevel soil gas monitoring points were all of the same design (Figures 12 and 13). They were designed so that soil gas could be extracted from 3.0, 5.5, and 8.0 feet BGS. Each point contained three 6-inch-long soil gas probes, filled with 0.25-inch-diameter pea gravel and connected to 0.25-inch-diameter nylon tubing (Figure 13). The tubing was fed along a PVC support rod and connected to the female end of a pneumatic couple. A 12-inch-diameter well cover was placed at the top of each soil gas monitoring point to house the pneumatic couples and protect them from the weather.

Type K thermocouples were installed along with each of the monitoring probes at 5.5 feet bgs for temperature monitoring at the medium depth. Additional monitoring point thermocouples were installed at the deep and shallow depths at MP-1 through -6 to obtain data to evaluate the effectiveness of a plastic cover in increasing subsurface temperatures. At approximate depths of 4 and 7 feet bgs within the plastic-covered area, 19 soil thermocouples also were installed. Injection line thermocouples (tc1 through tc11) were located at selected injection vent wells to measure the injection air temperature (Figure 9).

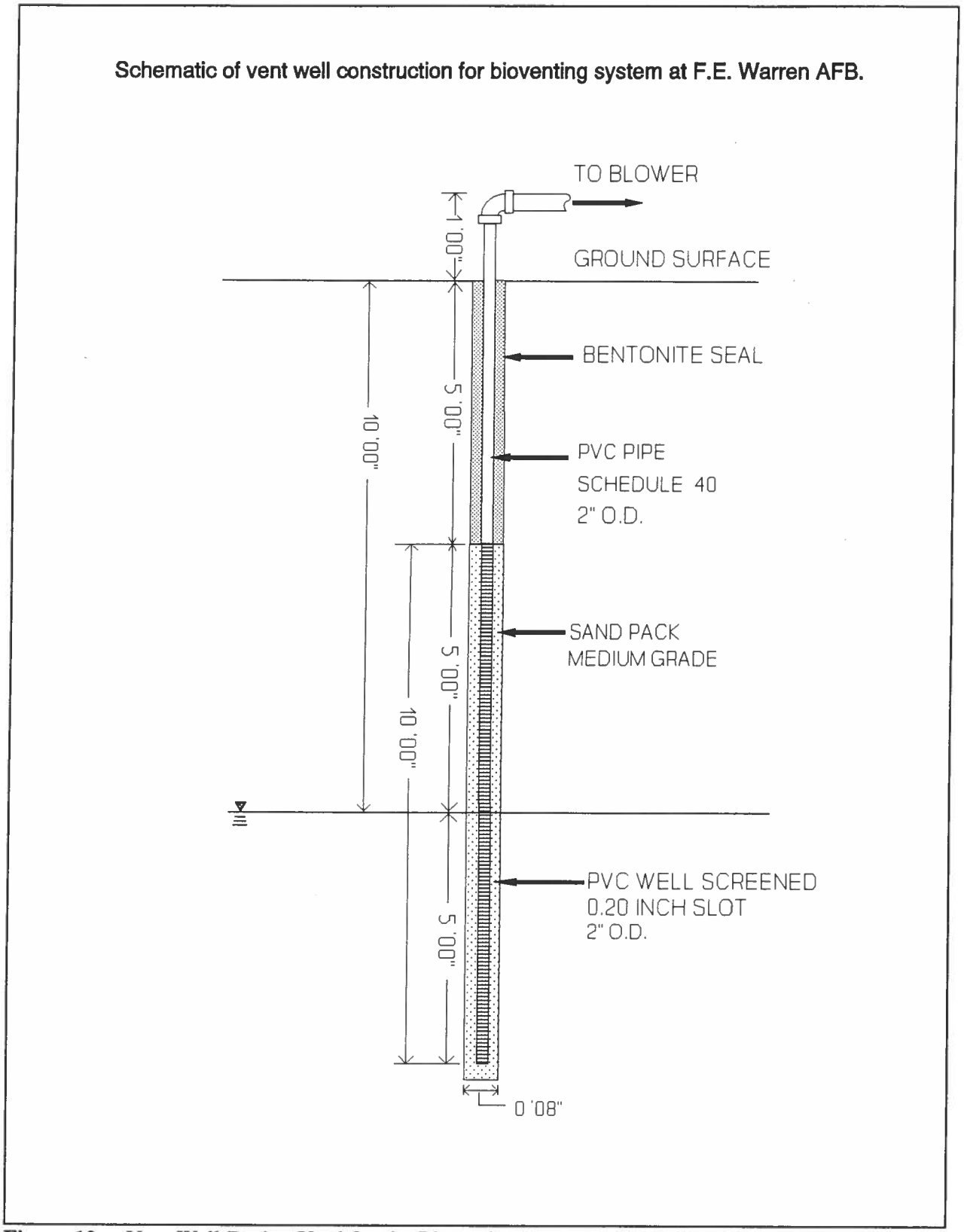


**Figure 10.** Vent Well Design Used for the Bioventing System at FPTA#1 at F.E. Warren AFB.

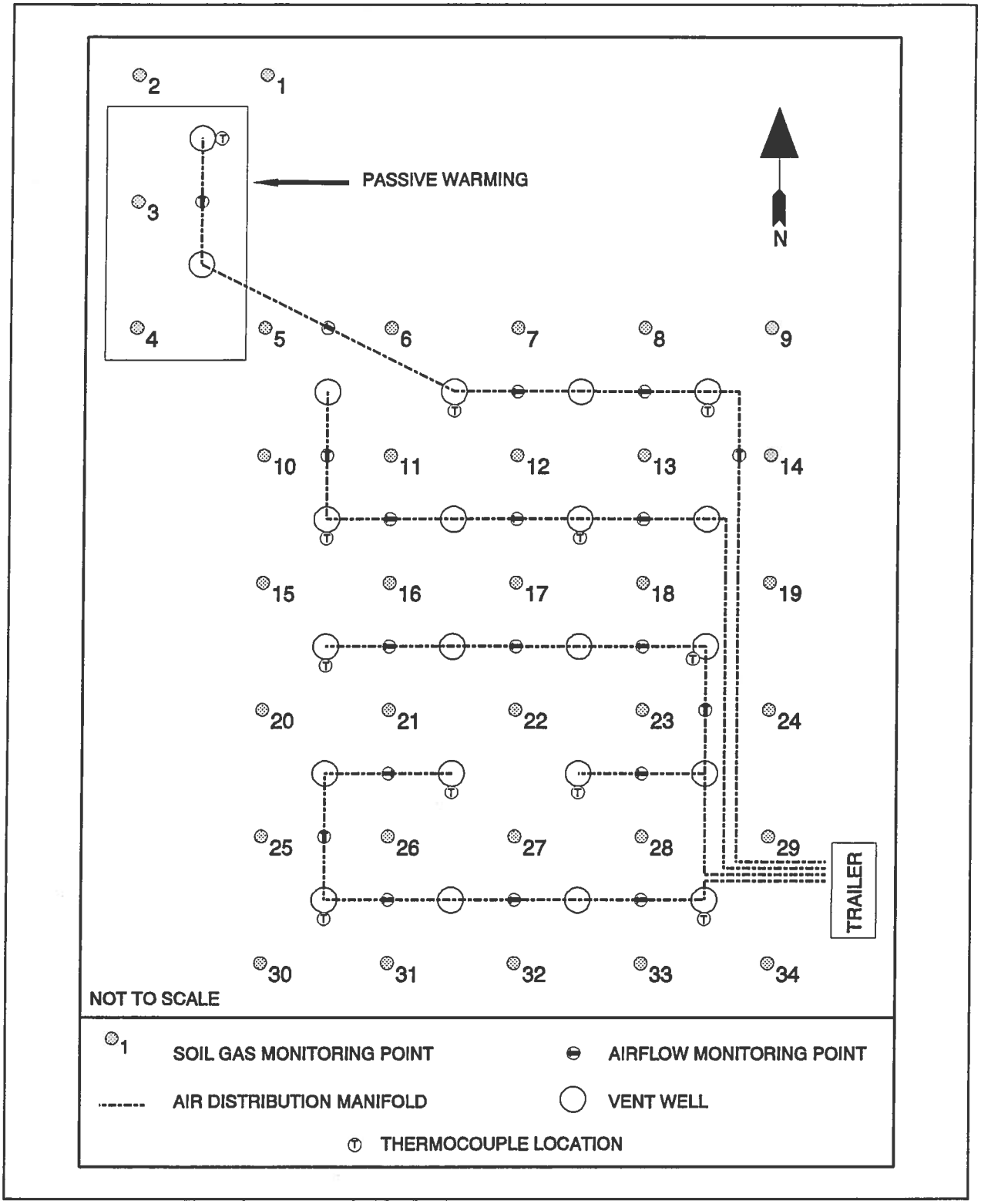


**Figure 11.** Layout of the Bioventing System at FPTA#1 at F.E. Warren AFB Showing the Relative Locations of the Vent Wells, Soil Gas Monitoring Points, and Air Distribution Manifold System.

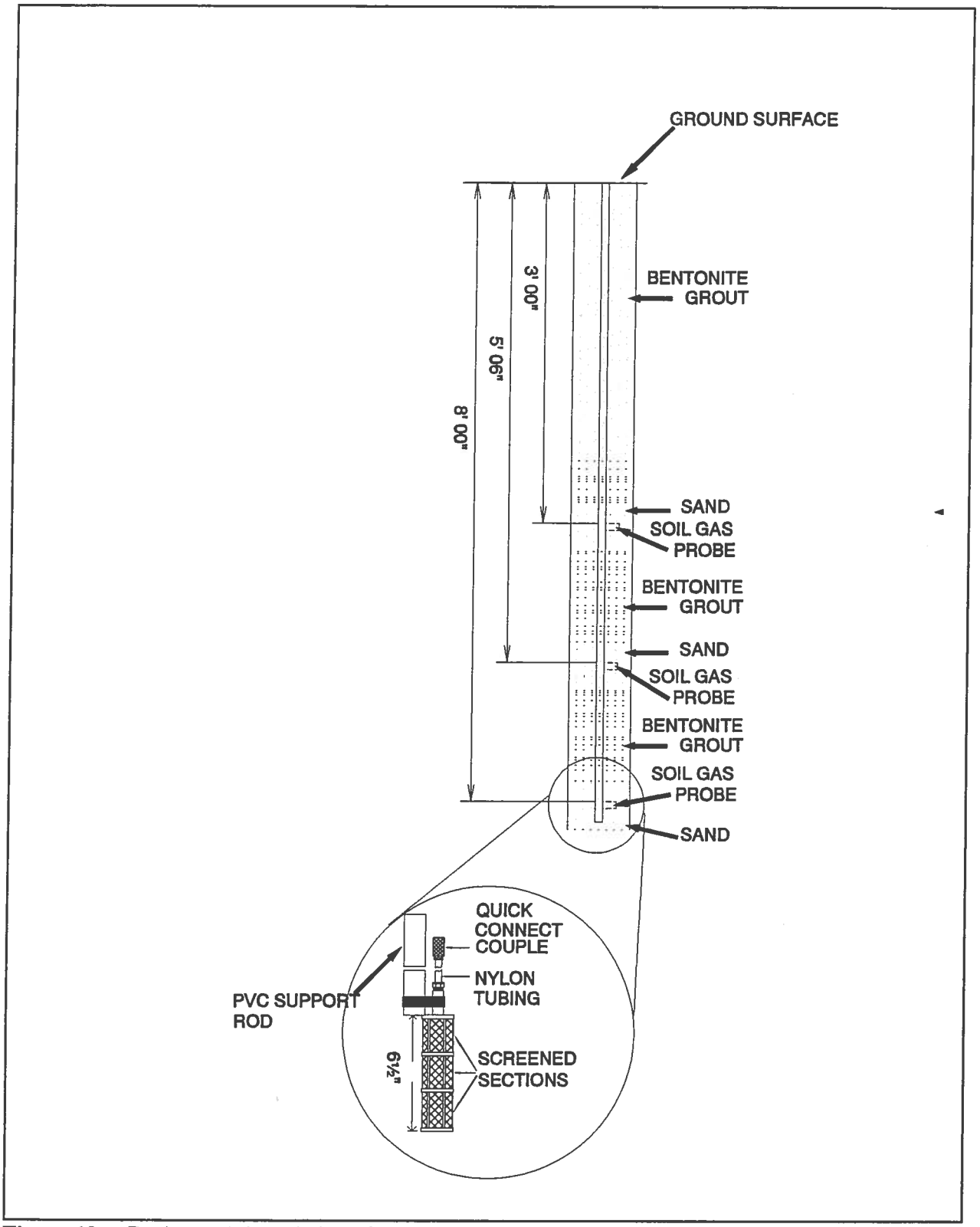


**Figure 12.** Design and Completion of the Soil Gas Monitoring Points Used for the Bioventing System at FPTA#1 at F.E. Warren AFB.

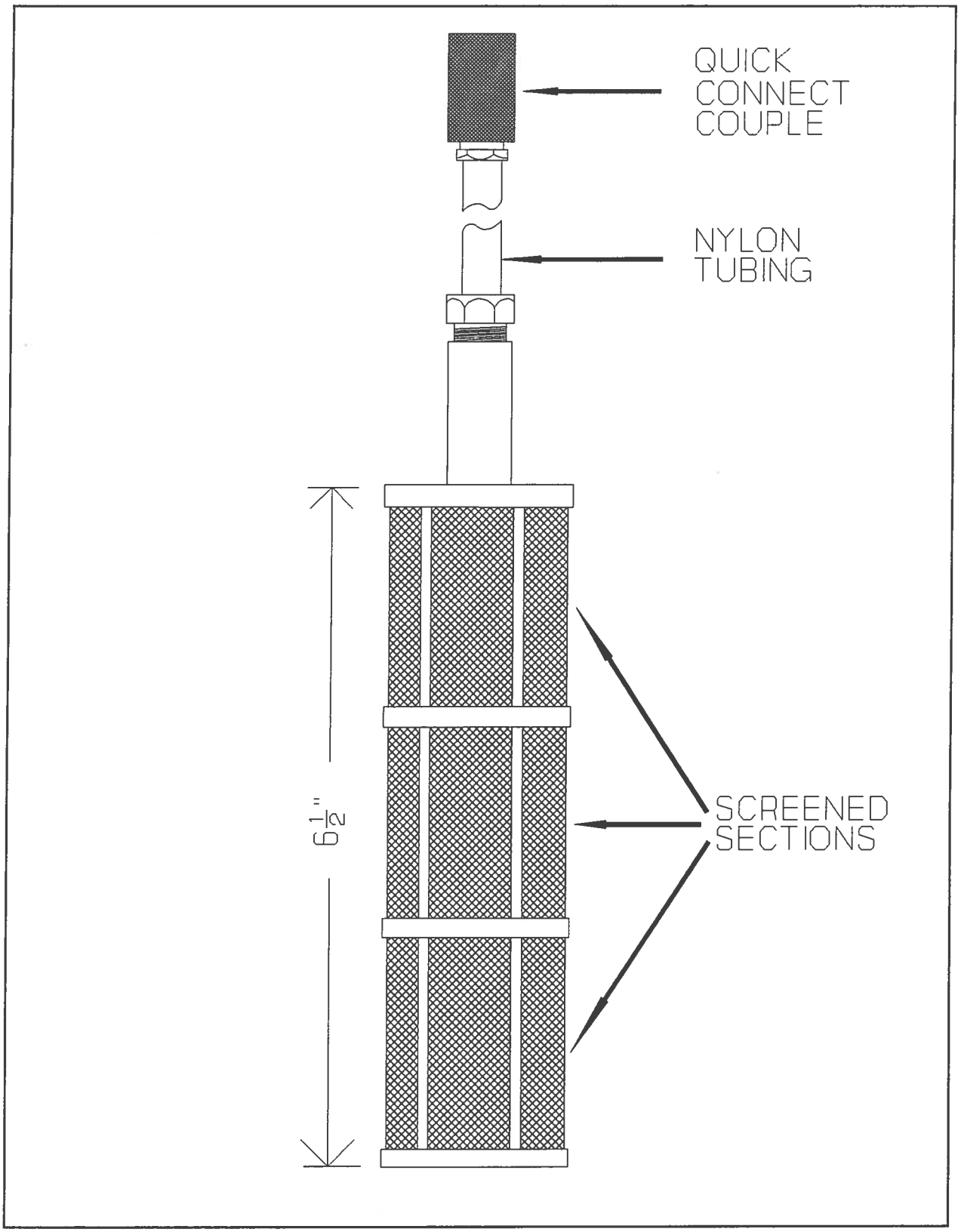


**Figure 13.** Soil Gas Probe Used in the Bioventing System at FPTA#1 at F.E. Warren AFB.

## C. SYSTEM OPERATION

The bioventing system was turned on in January, 1993 and was operated continuously for 26 months, except during the shutdown periods for respiration testing. The blowers were set to inject approximately 1.5 $ft^3$/minute of air into each of the 22 vent wells. Routine site visits were made on a monthly basis to monitor the performance of the system, and to make sure that the blowers were operating properly and that the integrity of the air distribution network was maintained.

The operation of the blowers was monitored by observing the total flow rate, temperature, and pressure. During the first month of operation, it was noticed that the blowers were running hotter than expected and there was softening of the PVC piping. The plumbing was modified to reduce the flow restriction around the flow meter, and the PVC pipe between the meter and the blower was replaced with galvanized pipe. There were no further problems associated with blower operation.

The integrity of the air distribution manifold system was checked by visual inspection and by monitoring the air flow rates in the manifold piping between each of the vent wells. During several visits, breaks were found in the manifold system. When a break was found, the system was shut off and the broken pipes were repaired. The system was then returned to normal operating conditions.

During each visit, soil gas was collected from all of the soil gas monitoring probes and was analyzed for $O_2$, $CO_2$, and TPH. The temperatures were measured at each of the thermocouple locations and recorded. The data were used to determine if the system was operating to deliver oxygen throughout the soils being treated, and to monitor bioactivity. The data collected during the monthly visits are presented in Appendix 2. The data show that the oxygen level has been maintained consistently above limiting concentration throughout most of the site. The only difficulty was oxygenating around the deep probes at monitoring points MP-32 and MP-33. The oxygen level in the soil gas collected from these probes often is below 5 percent. The air flow rate to the vent well in the area has been increased, but the oxygen levels remain low in this area of the system.

# SECTION III
# METHODOLOGY

The field tests included monthly system monitoring, approximately quarterly respiration tests, periodic surface emissions tests, initial and final soil sampling, and periodic groundwater sampling. Additional field activities were performed to better characterize the site and obtain data for site modeling. A summary of field activities undertaken by project personnel is shown in Table 1.

## A. MONTHLY MONITORING

Sampling trips to FPTA#1 were conducted on a nominal monthly basis to monitor the performance of the bioventing system. The main emphasis of these trips was to measure soil gas $O_2$, $CO_2$, and TPH, along with soil and injection air temperature, injection airflow rates, and vacuum readings in the monitoring probes during soil gas sampling. Locations of soil gas monitoring points with thermocouples, airflow and temperature monitoring points, and soil thermocouples are shown in Figure 9. Procedures followed for these measurements are described in Section III.D. "Analysis." Injection flow rates were adjusted according to the results of the soil gas sampling and airflow rate measurements to ensure the delivery of adequate oxygen in the subsurface. Any broken air delivery pipes were repaired during these trips.

## B. RESPIRATION TESTS

Respiration tests were conducted to monitor changes in respiration rates over the operational period of the bioventing system and were conducted approximately quarterly. These tests consisted of measuring initial soil gas concentrations with the injection system on, then shutting the system off and monitoring the soil gas concentrations over a 5-day period. The measurement frequency for each monitoring point depended on historical respiration rates and/or initial $O_2$ concentrations. Monitoring points with historically high rates and/or low initial $O_2$ concentrations were monitored frequently, i.e., up to four times daily; monitoring points with historically low rates and/or near-ambient $O_2$ concentrations were monitored less frequently, typically once per day. Soil gas monitoring points were monitored until the $O_2$ concentrations reached 2 percent. The soil temperature and vacuum also were measured during respiration tests.

TABLE 1. SUMMARY OF FPTA#1 FIELD ACTIVITIES.

| Date | Activity |
|---|---|
| 1/(14-21)/93 | Initial soil, groundwater, and soil gas sampling; respiration shutdown test |
| 4/(19-24)/93 | Respiration test, surface emissions test |
| 6/4/93 | Monthly monitoring trip |
| 6/(28-29)/93 | Monthly monitoring trip |
| 8/(16-20, 27)/93 | Respiration test, surface emissions test |
| 9/20/93 | Monthly monitoring trip, groundwater sampling |
| 10/16/93 | Monthly monitoring trip |
| 11/(15-19)/93 | Respiration test |
| 12/17/93 | Monthly monitoring trip |
| 1/15/94 | Monthly monitoring trip |
| 2/12/94 | Monthly monitoring trip |
| 2/24-3/1/94 | Respiration test |
| 3/26/94 | Monthly monitoring trip |
| 4/23/94 | Monthly monitoring trip |
| 6/3/94 | Monthly monitoring trip |
| 7/(5-13)/94 | Respiration test, surface emissions test, $O_2$ diffusion test, pressure distribution test; pure $O_2$ and pulsed system installed |
| 8/(24-27)/94 | Monthly monitoring trip, $O_2$ diffusion test |
| 9/23/94 | Monthly monitoring trip |
| 10/(13-17)/94 | Respiration test |
| 12/(3-8)/94 | Respiration test |
| 1/(18-19)/95 | Monthly monitoring trip |
| 3/(6-10)/95 | Respiration test |
| 3/(20-21)/95 | Monthly monitoring trip, surface emissions test, final soil sampling |

## C. SAMPLING

### 1. Soil Sampling

Soil samples were obtained during installation of the bioventing system and at the end of the project in order to determine changes in soil concentrations over the operational period of the system. Initial soil samples were collected from actual boreholes for monitoring point installation, whereas the final samples were collected within a distance of 1 foot away from the monitoring points. Soil boreholes were drilled to a depth of 8 feet, and soil samples collected using 2-foot split spoons segmented into 6-inch brass sleeves. Random sleeves from initial sampling were collected for analysis, while final samples matched the depths and locations of selected initial samples.

### 2. Soil Gas Sampling

Two different sampling procedures were used over the course of the field study. In the first, the analyzer was connected directly to the gas sampling probe so that the analyzer's internal pump could be used to withdraw the sample. When the analyzer reading had stabilized, the measurement was taken. This method was used from 1/93 to 10/93. In the second procedure, an external pump was used to withdraw a volume of gas into a 1-liter Tedlar™ bag. This volume was then flushed to ensure an unadulterated and undiluted sample. The Tedlar™ bag was then refilled with 1 liter of soil gas sample for TPH, $O_2$, and $CO_2$ analyses. This method was used from 11/93 to 3/95.

The methods described above were used when the soil gas $O_2$ concentrations were at ambient levels of $O_2$ or less. Samples with greater than 21 percent $O_2$ due to pure $O_2$ injection were quantified after mixing appropriate ratios of sample and $O_2$-free calibration gas in a 1-liter Tedlar™ bag. The soil gas $O_2$ concentration was then determined using Equation 1:

$$[O_2]_{sample} = [O_2]_{mix} \times \frac{V_{sample} = V_{cal}}{V_{sample}} \quad (1)$$

where $[O_2]_{sample}$ = $O_2$ concentration of soil gas, percent; $[O_2]_{mix}$ = $O_2$ concentration of mix, percent; $V_{sample}$ = volume of soil gas sample in mixture, milliliter (mL); and $V_{cal}$ = volume of $O_2$-free calibration gas in mixture, mL.

### 3. Surface Emission Sampling

Surface emission tests were conducted to quantify hydrocarbon emission rates due to injection of air into the subsurface during bioventing system operation. These tests entailed the use of surface emission isolation flux chambers to quantify TPH, boiling point splits (C-6 to C-15 *n*-paraffins), and specific *n*-paraffin and aromatic compounds released from the site. Test compounds of interest were collected from the effluent of the emission isolation flux chambers using Tenax™ solid sorbent media for the low- to medium-boiling-point-range compounds (two tubes in tandem with breakthrough tubes on each), and evacuated stainless steel canisters for the higher-molecular-weight fraction of the compound range of interest. Two evacuated canisters were used to collect whole air samples from each location before and during air injection.

An emissions isolation flux chamber encloses a defined headspace above a defined soil surface. Ambient air is introduced into the chamber at a known controlled rate to sweep volatile contaminants out of the chamber for collection and concentration. The flux chambers used in this study were identical to that presented by Dupont and Reineman (1986) without a Magnehelic for interior pressure measurements. They were constructed using modified clear acrylic double-domed skylights as shown in Figure 14. Their exterior dimensions are 68.7 centimeters (cm) × 68.7 cm (effective emissions surface area = 4,560 $cm^2$).

The acrylic double-dome interior was lined with opaque adhesive Teflon™ tape to provide a nonadsorbing, nonreactive interior surface, and to prevent contamination of the sampling system via outgassing from the chamber interior. Stainless steel was used for all bulkhead fittings, and Teflon™ was used for purge gas inflow and outflow lines to provide an inert surface in all areas of the chamber.

The sampling chambers were cleaned and pressure-checked for leakage prior to use in the field. The chambers were forced into the soil such that the bottom of the Teflon™-lined acrylic dome rested on the soil surface, and the aluminum dome rim made a tight seal with the soil surface.

The design and operation of the flux chamber used in this field study were based on the results of the system evaluation by Dupont and Reineman (1986). The Tenax™-based solid sorbent sampling system was chosen following an evaluation of collection and recovery efficiency of pure compounds and their mixtures identified in refinery wastes using Tenax™ sorbent tubes (Dupont, 1988).

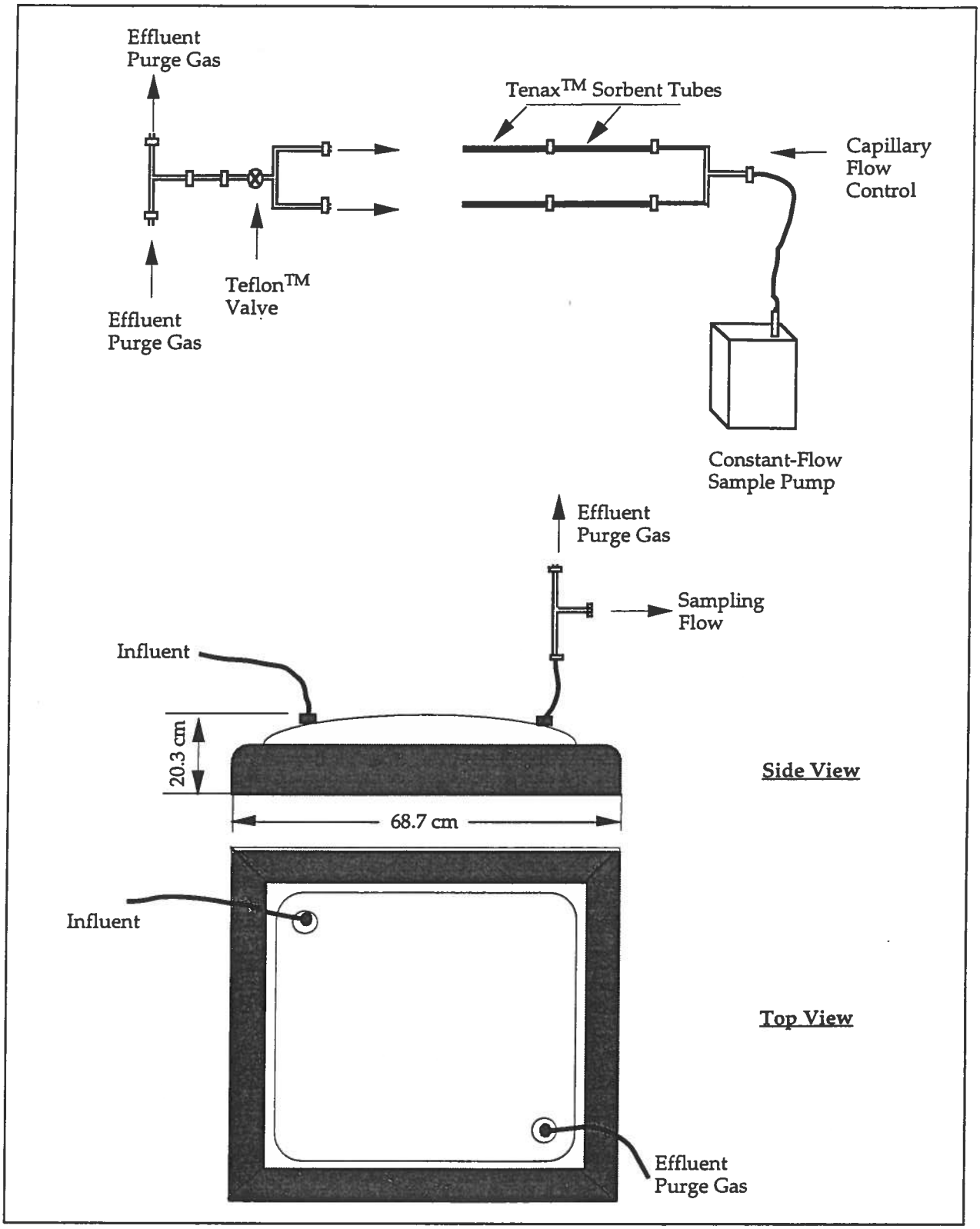


**Figure 14.** Surface Emission Test Apparatus Showing Flux Chamber and Flow System Using a Constant-Flow Sampling Pump.

Ambient air was passed through the flux chamber via constant-volume influent and effluent purge pumps operated at 2 liters/min during sampling events. Influent and effluent pump rates were set equal to one another prior to each sampling event. Each pump was calibrated using a Tekmar electronic bubble tube flowmeter.

Purge gas was supplied to the flux chambers, and the balanced effluent pumps were operated for approximately three retention volumes (15 minutes) prior to specific compound collection and concentration. Isolation flux chambers were removed from their sampling locations following sampling and were inspected for damage, leaks, etc., prior to being used for emissions sampling at the next designated sampling time or sampling location.

### 4. Groundwater Sampling

Groundwater samples were collected manually from the three monitoring wells in the vicinity of FPTA#1 shown in Figure 2. Samples were collected using a Teflon™ bailer after purging three well volumes. Well volumes were determined after measuring the water surface and well bottom elevations, and the well diameters. Volatile samples were collected in 40-mL VOA vials, whereas semivolatile samples were collected in 500-mL glass bottles.

## D. ANALYSIS

### 1. Total Petroleum Hydrocarbons (TPH) in Soil Gas

Soil gas TPH was measured using a GasTech TraceTechtor analyzer. After turning the analyzer on and allowing it to stabilize for 5 minutes, the analyzer was calibrated using air and 4,800 ppm hexane. Calibration checks were performed periodically during sampling using 4,800 and 500 ppm hexane calibration gas.

The analyzers were used outdoors when the temperature was above 20°F, and indoors when the temperature was less than 20°F. The sampling time was minimized with the external pump method, in order to minimize soil gas displacement because the pump flow rate was much higher than the flow rate of the analyzer internal pump. If $O_2$ concentrations were less than 12 percent, a 1:1 dilution fitting (GasTech) was used during the TPH measurements.

## 2. $O_2$ and $CO_2$ Concentrations in Soil Gas

$O_2$ and $CO_2$ concentrations in soil gas were measured using a GasTech model 3252OX analyzer. After the analyzer had warmed up, it was zeroed using $O_2$-free calibration gas and was calibrated for $O_2$ using air, and for $CO_2$ using air and 15 percent $CO_2$ calibration gas. Calibration gases of 7 percent $O_2$ and 5 percent $CO_2$ were used for calibration checks during sampling.

## 3. Volatile Hydrocarbons

### a. Soil Samples

Soil samples were analyzed for volatile hydrocarbons through purge-and-trap extraction with GC analysis with a FID. Initial soil sample extracts were purged manually, whereas final soil extracts were purged using an autopurging system. The procedures followed are outlined below.

(1) Methanol Extraction of Soil Samples. Methanol extraction for purge-and-trap procedures involved placing 3 to 5 grams of a soil sample in a 40-mL volatile organic analysis (VOA) bottle containing a known mass of methanol. The vial was reweighed to determine the exact amount of soil placed in it. The vial was then completely filled with methanol to eliminate headspace and was weighed to determine the total volume of methanol used for this extraction procedure. The soil/methanol mixture was vortexed for approximately 2 minutes using a vortex stirrer, and the vials were stored in a refrigerator at $\leq 4°C$ overnight to allow the soil to settle completely.

(2) Manual Purge-and-Trap of Soil Methanol Extracts. From 0.5 to 1.0 mL of the settled methanol extract, and double distilled water (DDW) to reach a 5.0-mL volume, were placed in a Liquid Sample Concentrator, Model LSC-1 (Tekmar Company, Cincinnati, Ohio). The solution was then purged with 40 mL/min of compressed air for 12 minutes so that the VOCs could be collected on Tenax™ sorbent tubes. These sorbent tubes were prepared from 5-mm-inner diameter (ID), 10-cm-long glass tubes loosely packed in the interior 8 cm with 0.27 to 0.28 g of prepared Alltech Associates, Inc., 60/80 mesh Tenax™ GC solid sorbent material. These sorbent tubes were desorbed using either a Dynatherm Analytical Instruments, Inc. or an Envirochem Thermal Tube

Desorber, Model 850 interfaced to a Shimadzu GC-9A gas chromatograph equipped with a FID. The GC and thermal desorber operating conditions are outlined in Table 2.

TABLE 2. GC OPERATING CONDITIONS FOR VOC ANALYSIS.

| Parameter | Auto Purge-and-Trap Analysis Conditions | Manual Purge-and-Trap, Canister Gas and Tenax™ Sample Analysis Conditions |
|---|---|---|
| Instrument | Shimadzu GC-9A | |
| Detector type | FID | |
| Column | Petrocol 3710, fused silica capillary column, 5.0-μm film thickness; Supelco, Inc., 0.75 mm × 10 m | |
| Thermal desorber conditions | | |
| Trap type | Internal Tenax™ sorbent tube | External Tenax™ sorbent tube |
| Line heater | 145°C | 275°C |
| Valve heater | 150°C | 250°C |
| Desorber temperature | 270°C | 300°C |
| Desorb time | 8 minutes | 12 minutes |
| Temperature programming | | |
| Initial oven temperature | 37°C for 5 minutes | |
| Oven temperature program rate | 10°C/min to 77°C | 9°C/min to 77°C |
| | 3°C/min to 95°C | |
| | 18°C/min to 149°C | |
| | 3°C/min to 158°C | 3°C/min to 170°C |
| | 20°C/min to 210°C | 20°C/min to 200°C |
| Final oven temperature | 210°C for 5 minutes | 200°C for 5 minutes |
| Injector temperature | 200°C | |
| Detector temperature | 250°C | |
| Carrier gas | Helium | |
| Carrier flow | 4.5 mL/minute | |

(3) Autopurging of Soil Methanol Extracts. One mL of the methanol extract was injected into a purge chamber using a Dynatrap purge-and-trap system (Dynatech Precision Sampling, Baton Rouge, LA), along with DDW to reach a total volume of 10.0 mL. The solution was then purged with 40 mL/min of helium gas for 12 minutes, followed by a dry purge for 3 minutes. The volatile gases were focused on an internal Tenax™ trap and then desorbed into a Shimadzu GC-9A gas chromatograph equipped with a FID. The GC operating conditions are outlined in Table 1.

**b. Water Samples**

Water samples were analyzed for VOCs through purge-and-trap extraction with GC analysis using a FID. The initial water samples were manually purged, and the final water samples were purged using an autopurging system. The procedures followed are outlined below.

(1) Manual Purge-and-Trap of Water Samples. The procedure followed was identical to that described in Section III.D.3.a.(2), "Manual Purge-and-Trap of Soil Methanol Extracts," except 5.0 mL of the water sample was used as the total purge volume. The GC and thermal desorber operating conditions are outlined in Table 2.

(2) Autopurging of Water Samples. The procedure followed was identical to that described in Section III.D.3.a.(3), "Autopurging of Soil Methanol Extracts," except 5.0 mL of the water sample was injected into the purge chamber along with DDW to reach a total volume of 10.0 mL. The GC operating conditions are outlined in Table 2.

**c. Canister Samples**

Canister samples were analyzed for volatile hydrocarbons by injection through a thermal desorber and analyzed on a Shimadzu GC-9A with a FID. Evacuated canisters were moved from the 4°C cooler to an incubator maintained at 37°C and held there for approximately 0.5 hour prior to analysis. This procedure was carried out to ensure that the gas in the canister was above atmospheric pressure so that a sample could be removed from it for analysis. In addition, the 37°C holding temperature ensured that a representative sample of the collected gas was analyzed so that minimal compound sorption to the interior canister walls occurred under these storage conditions. Once the canister samples had remained in the 37°C incubator for the requisite time period, a 5-mL gastight syringe was used to remove a sample from it for analysis. The syringe was filled with

canister sample and flushed back into the canister three times before a 5-mL sample was withdrawn. The syringe sample was then injected directly into the thermal desorber connected to the Shimadzu GC-9A with a FID for analysis. The analysis conditions are shown in Table 2.

#### d. Tenax™ Samples

Tenax™ samples were analyzed for volatile hydrocarbons by thermal desorption using a thermal desorber connected to a Shimadzu GC-9A with a FID. The analysis conditions are shown in Table 2.

### 4. Semivolatile Hydrocarbons

#### a. Soxhlet Extraction of Soil Samples

Soil samples were analyzed for semivolatile hydrocarbons through methylene chloride soxhlet extraction using GC analysis with a FID. Approximately 10 grams of soil were mixed with approximately 10 grams of anhydrous sodium sulfate and placed in a cellulose thimble that was placed in a soxhlet extractor. Approximately 150 mL of methylene chloride were added to the soxhlet extractor and boiled for 16 to 24 hours at 45°C. The solution from the soxhlet extractor was then transferred to a K-D apparatus connected to a concentrator tube. The K-D apparatus was kept in a water bath maintained at 45°C until the extract volume was reduced to approximately 1 mL. The solution in the concentrator was then brought up to 5 mL by rinsing the walls of the K-D apparatus with methylene chloride before transferring the final solution to a 10-mL screw cap vial. The concentrate was analyzed using a Shimadzu GC-9A GC with a FID and an AOC-9 autoinjector. The GC operating conditions are outlined in Table 3.

#### b. Liquid-Liquid Extraction of Water Samples

Water samples were analyzed for semivolatile hydrocarbons using liquid-liquid extraction and GC analysis with a FID. A volume of approximately 500 mL of water sample was measured using a 1,000-mL graduated cylinder before being placed in a separatory funnel. Approximately 60 mL of methylene chloride were added to the separatory funnel and shaken

vigorously for 1 minute, with periodic venting of the funnel to release pressure buildup. The methylene chloride extract was drained into a beaker and set aside. This process was repeated twice with 30 mL of methylene chloride.

TABLE 3. GC OPERATING CONDITIONS FOR SEMIVOLATILE HYDROCARBON ANALYSIS.

| Parameter | Description |
|---|---|
| Instrument | Shimadzu GC-9A |
| Detector type | FID |
| Column | Petrocol 3710, fused silica capillary column, 5.0-$\mu$m film thickness; Supelco, Inc., 0.75 mm × 10 m |
| Temperature programming | |
| Initial oven temperature | 50°C for 5 minutes |
| Oven temperature program rate | 10°C/min to 77°C |
| | 3°C/min to 95°C |
| | 18°C/min to 149°C |
| | 3°C/min to 170°C |
| | 20°C/min to 230°C |
| Oven final temperature | 230°C for 5 minutes |
| Injector temperature | 200°C |
| Detector temperature | 200°C |
| Carrier gas | Helium |
| Carrier flow | 15 mL/min |

The 120-mL methylene chloride extract was dried by pouring the solution through a drying column containing sodium sulfate to a depth of approximately 20 cm. The extract was then concentrated using a K-D apparatus with concentrator tube and hot water bath as described above in Section III.D.4.a., "Soxhlet Extraction of Soil Samples." The concentrate was analyzed using a Shimadzu GC-9A GC with a FID and an AOC-9 autoinjector. The GC operating conditions are outlined in Table 3.

### 5. Polycyclic Aromatic Hydrocarbons (PAHs)

Soil samples were analyzed for PAHs using methylene chloride soxhlet extraction, as described in Section III.D.4.a., "Soxhlet Extraction of Soil Samples," with GC/MS analysis. The GC/MS conditions used are outlined in Table 4.

TABLE 4. GC/MS OPERATING CONDITIONS FOR PAH ANALYSIS.

| **Parameter** | **Description** |
|---|---|
| Instrument | Varian 3400 gas chromatograph |
| Detector | Finnegan ITD 700 |
| Ionization mode | Electron ionization |
| ITD scan mode | Selected ion monitoring |
| Column | HP-5MS, 0.25-$\mu$m film thickness; 0.25 m × 30 m |
| Temperature programming | |
| Oven initial temperature | 40°C for 2 min |
| Oven temperature program rate | 10°C/min to 300°C |
| Oven final temperature | 300°C for 12 min |
| Injector temperature | 280°C |
| Manifold temperature | 254°C |
| Carrier gas | Helium |
| Carrier flow | 20 cm/sec |

### 6. Chlorinated Solvents

#### a. Initial Soil Samples

Methanol extracts of initial soil samples were sent to an outside laboratory for chlorinated solvent analysis. Samples were analyzed using EPA Method 8240.

#### b. Final Soil Samples

Final soil samples were analyzed for chlorinated solvents using manual purge-and-trap of soil methanol extracts as described in Sections III.D.3.a.(2), "Methanol Extraction of Soil Samples" and III.D.3.a.(3) "Manual Purge-and-Trap of Soil Methanol Extracts," with the GC/MS analysis conditions shown in Table 5.

### 7. $O_2$ and $CO_2$

$O_2$ and $CO_2$ analyses of canister gas samples were conducted using a GC with a thermal conductivity detector (TCD). Evacuated canisters were moved from the 4°C cooler to an incubator maintained at 37°C and held there for approximately 0.5 hour prior to analysis. A 3.0-mL gastight syringe was filled with canister sample and flushed back into the canister three times before a 3.0-mL sample was withdrawn. The syringe sample was then injected into either a 0.5- or 1.0-mL gas sample loop for analysis. The GC operating conditions for this analysis are outlined in Table 6.

## E. DATA REDUCTION

### 1. Soil and Water Samples

(a) Hydrocarbon Mass Determinations. TPH analyses were calibrated using a 25-compound external standard containing C-5 to C-15 *n*-alkanes along with benzene, toluene, *m*-xylene, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, naphthalene, and methylnaphthalene (Table 7). The standard used for initial soil analysis did not include the trimethylbenzene isomers. Purge-and-trap extraction analysis was quantified from C-5 up

to but not including C-12, and soxhlet extraction analysis was quantified from C-12 through C-15. A five-point calibration curve was established over a three-log concentration range for each standard compound to quantify the mass of each compound in a sample.

TABLE 5. GC/MS OPERATING CONDITIONS FOR CHLORINATED SOLVENT ANALYSIS.

| Parameter | Description |
|---|---|
| Instrument | Varian 3400 gas chromatograph |
| Detector | Finnegan ITD 700 |
| Ionization mode | Electron ionization |
| ITD scan mode | Selected ion monitoring |
| Thermal desorber conditions | |
| Trap type | Tenax™ sorbent tube |
| Line heater | 275°C |
| Valve heater | 250°C |
| Desorber temperature | 270°C |
| Desorb time | 12 minutes |
| Column | DB-VRX, 0.14-$\mu$m film thickness; 0.25 m × 30 m |
| Temperature programming | |
| Oven initial temperature | 35°C for 10 minutes |
| Oven temperature program rate | 6°C/min to 47°C |
| | 18°C/min to 200°C |
| Oven final temperature | 200°C for 8 minutes |
| Injector temperature | 280°C |
| Manifold temperature | 254°C |
| Carrier gas | Helium |
| Carrier flow | 20 cm/sec |

TABLE 6. GC OPERATING CONDITIONS FOR RESPIRATION GAS ANALYSIS.

| Parameter | Description | |
|---|---|---|
| Instrument | Shimadzu GC-14A | Perkin-Elmer Sigma Model 4 |
| Detector type | Thermal conductivity detector (TCD) | |
| Column | Alltech CTR 1; outer 6-ft, 1/4-in. ID stainless steel molecular sieve packing; inner 6-ft, 1/8-in. ID stainless steel column Porapak packing | |
| Temperature program | 35°C isothermal | 25°C isothermal |
| Injector temperature | 25°C | |
| Detector temperature | 200°C | 125°C |
| Carrier gas | Helium | |
| Carrier flow | 65 mL/min | |

TABLE 7. SPECIFIC HYDROCARBONS IN THE EXTERNAL STANDARD USED FOR HYDROCARBON ANALYSIS.

| Hydrocarbons | | |
|---|---|---|
| 2-methylpentane | ethylbenzene | *n*-undecane |
| *n*-pentane | *p*-xylene | naphthalene |
| 2-methylpentane | *n*-nonane | *n*-dodecane |
| *n*-hexane | *n*-propylbenzene | *n*-tridecane |
| 2,4-dimethylpentane | 1,3,5-trimethylbenzene | 1-methylnaphthalene |
| benzene | 1,2,4-trimethylbenzene | *n*-tetradecane |
| *n*-heptane | *n*-decane | *n*-pentadecane |
| toluene | 1,2,3-trimethylbenzene | |
| *n*-octane | *n*-butylbenzene | |

The raw chromatographic data for hydrocarbon determinations were integrated using a Macintosh-based data reduction package, Dynamax™ HPLC Method Manager, Version 1.2 (Rainin Instruments Company, Inc., Woburn, Massachusetts). This package generated summary data identifying peak retention time, peak area, peak height, and compound mass if retention times matched one of the external standards. These data files were then transferred to Microsoft® Excel spreadsheet format for further data manipulation. From the spreadsheet format, all compound identification was verified by comparison with standard samples analyzed the day of sample analysis. Boiling point splits were determined based on the sum of integrated peak areas occurring between *n*-alkane compounds in the standard mixture. Total hydrocarbon data were determined from the total integrated area of each sample chromatogram.

After the appropriate areas were determined, the corresponding masses of the contaminants were determined using the response factors (RFs) for each of the known compounds in the standard mixture. The RFs were the slopes of the calibration curves for each compound, with the slopes determined using a linear regression of integrated area versus mass injected, forced through the origin. Mass values were then calculated as follows:

$$\text{Mass}_{\text{specific compound}} = \text{Area}_{\text{specific compound}} \times \text{RF}_{\text{specific compound}} \quad (2)$$

$$\text{Mass}_{\text{boiling pt. range}} = \text{Area}_{\text{boiling pt. range}} \times \text{RF}_{\text{boiling pt. range}} \quad (3)$$

$$\text{Mass}_{\text{TPH, hexane equivalent}} = \text{Area}_{\text{total}} \times \text{RF}_{\text{hexane}} \quad (4)$$

$$\text{Mass}_{\text{TPH, C-5 - C-15}} = \text{Area}_{\textit{total}} \times \text{RF}_{\text{MeanC-5 - C-15}} \quad (5)$$

(b) PAH Mass Determinations. PAH analyses were calibrated using a 16-compound standard containing the analytes listed in Table 8. A five-point calibration curve was established for each analyte, and internal standards were used to quantify the mass of each analyte in a sample. Calibration curves of the ratio of integrated area of analyte to integrated area of internal standard versus analyte mass injected were used to determine RFs. The RFs were the slopes of the linear

regressions of the calibration curves, forced through the origin. The mass of analyte in a sample was then calculated according to Equation 6:

$$\text{Mass}_{\text{analyte}} = \frac{\text{Area}_{\text{analyte, sample}}}{\text{RF}_{\text{analyte}}} \times \text{V}_{\text{inj}} \times \frac{\text{Mass}_{\text{IS}}}{\text{Area}_{\text{IS}}} \qquad (6)$$

where $\text{Mass}_{\text{analyte}}$ = mass of analyte in sample injection; $\text{Area}_{\text{analyte,sample}}$ = area of the analyte in the sample; $\text{RF}_{\text{analyte}}$ = analyte response factor; $\text{V}_{\text{inj}}$ = sample volume injected; $\text{Mass}_{\text{IS}}$ = mass of internal standard in sample; and; $\text{Area}_{\text{IS}}$ = area of the internal standard. In addition, surrogate compounds were used to evaluate extraction recoveries. Internal standards and surrogate compounds used in the PAH analyses are shown in Table 8.

TABLE 8. ANALYTES, INTERNAL STANDARDS, AND SURROGATES USED IN PAH ANALYSIS.

| Analytes | | Internal Standards | Surrogate Compounds |
|---|---|---|---|
| naphthalene | benzo(a)anthracene | naphthalene-d8 | 2-fluorobiphenyl |
| acenaphthylene | chrysene | acenaphthene-d10 | 2,4,6-tribromophenol |
| acenaphthene | benzo(b)fluoranthene | phenanthrene-d10 | p-terphenyl-d14 |
| fluorene | benzo(k)fluoranthene | chrysene-d14 | |
| phenanthrene | benzo(a)pyrene | perylene-d12 | |
| anthracene | indeno(1,2,3-cd)pyrene | | |
| fluoranthene | dibenzo(a,h)anthracene | | |
| pyrene | benzo(ghi)perylene | | |

(c) Chlorinated Solvent Mass Determinations. Chlorinated solvent analyses were calibrated using a 13-compound standard containing the analytes listed in Table 9. The calibration and quantitation methods used were identical to those described in Section III.A.6.a.(2), "PAH mass determinations," above. Internal standards and surrogate compounds used in chlorinated solvent analyses are shown in Table 9.

TABLE 9. ANALYTES, INTERNAL STANDARDS, AND SURROGATES USED IN CHLORINATED SOLVENT ANALYSIS.

| Analytes | | Internal Standards | Surrogate Compounds |
|---|---|---|---|
| carbon tetrachloride | chlorobenzene | bromochloromethane | 1,2-dichloroethane-d4 |
| trichlorofluoromethane | 1,1-dichloroethane | chlorobenzene-d5 | toluene-d8 |
| chloroform | 1,1-dichloroethylene | 1,4-difluorobenzene | 4-bromofluorobenzene |
| dibromochloromethane | 1,1,2-trichloroethane | | |
| methylene chloride | 1,2-dichlorobenzene | | |
| tetrachloroethene | 1,2-dichloropropane | | |
| trichloroethylene | | | |

(d) Concentration Determinations. Concentration calculations were based on the mass of each contaminant divided by either the dry weight of the soil or the volume of water extracted.

Soil concentrations were based upon the mass of soil extracted, the soil moisture content, the volume of soil extract, and the volume of extract purged or injected, for purge-and-trap (P+T) or soxhlet extractions, respectively. These concentration calculations were performed as shown in Equations 7 and 8:

$$\text{P+T Soil Conc.} = \frac{\text{Mass Injected}}{\text{Vol. Purged}} \times \frac{\text{Vol. Methanol Extract}}{\left[\frac{\text{Wet Wt. Soil}}{1 + \text{Decimal \% Soil Moisture}}\right]} \quad (7)$$

$$\text{Soxhlet Soil Conc.} = \frac{\text{Mass Injected}}{\text{Vol. Injected}} \times \frac{\text{Final MeCl Extract Vol.}}{\left[\frac{\text{Wet Wt. Soil}}{1 + \text{Decimal \% Soil Moisture}}\right]} \quad (8)$$

Water concentrations were based upon the volume of water purged or extracted for purge-and-trap or liquid-liquid (L-L) extractions. These concentration calculations were performed as shown in Equations 9 and 10:

$$\text{P+T Water Conc.} = \frac{\text{Mass Injected}}{\text{Vol. Purged}} \quad (9)$$

$$\text{L-L Water Conc.} = \frac{\text{Mass Injected}}{\text{Vol. Extracted}} \quad (10)$$

**2. Gas Samples**

(a) Canister Sample Hydrocarbon Concentrations. Hydrocarbon concentrations obtained from the canister samples were determined based on the ideal gas law knowing the volume of the canister, the vacuum measured in the canisters before and after sampling, the temperature during sample collection and sample analysis, and the volume of sample injected for quantification. These parameters were related as indicated in the following equations:

$$\text{Concentration} = \frac{\text{Mass Injected}}{\text{Vol. Injected} \times \left[\frac{\text{Actual Vol. Sample}}{\text{Canister Vol.}}\right]} \quad (11)$$

$$\text{Actual Vol. Sampled} = \text{Canister Vol.} - \text{Vol. Canister Before Sampling} \quad (12)$$

where:

$$\text{Vol. Canister Before Sampling} = \text{Canister Vol.} \times \left[\frac{\text{Atm. Pres.} - \text{Canister Vac.}}{\text{Atm. Pressure}}\right] \times \frac{T_{sampling}}{T_{analysis}} \quad (13)$$

(b) Respiration Gas Concentrations. Quantitation of soil gas $O_2/CO_2$ during atmospheric $O_2$ injection was based on a four-point calibration curve generated from standards (Scott Specialty Gases, Longmont, Colorado) and air containing from 1.0 to 21 percent $O_2$, and from 0.04 to 15 percent $CO_2$. Samples containing $O_2$ concentrations greater than 21 percent due to pure $O_2$ injection were quantified with two additional standards: a pure $O_2$ standard and a 1:1 mix of pure $O_2$ and pure $N_2$. Concentration values were based on calibration curves generated on the day each sample was run and the sample volume injected. A sample volume check was carried out based on the known volume injected, and data were rejected and reanalyzed if this sample volume deviated

from the known value by more than ±10 percent. An additional check was provided by summing the $N_2$, $O_2$, and $CO_2$ concentrations. This sum was within ±5 percent of 100 percent for an analysis to pass quality assurance/quality control (QA/QC) requirements.

### 3. Flux Chamber Results

Component surface emission flux rates were calculated for Tenax™ samples collected from isolation flux chambers. Surface emissions flux rate calculations were based on known values of flux chamber purge flow rates, sampled surface area (4,560 $cm^2$), sample flow rates, and total sampling times. These parameters are related as indicated in Equation 14:

$$\text{Flux Rate} = \frac{\text{Mass Collected}}{\text{Collection Area} \times \text{Total Sampling Time}} \times \frac{\text{Chamber Purge Flow Rate}}{\text{Sample Flow Rate}} \quad (14)$$

### 4. Temperature

Soil and air temperatures were measured to determine the impact of temperature on biodegradation rates and the effectiveness of the passive solar soil heating cover. Temperatures were determined using a Fluke model 51 K/J thermometer and Type K thermocouples.

### 5. Air Flow

Air flow rates from the bioventing blowers and pure $O_2$ injection system were measured using flowmeters calibrated in standard cubic feet per minute (scfm). Flowmeter readings were converted from scfm to actual cubic feet per minute (acfm) using Equation 15:

$$Q_{acfm} = Q_{scfm} \times P_{meas} \times \frac{288K}{T_{meas}} \quad (15)$$

where $Q_{acfm}$ = corrected flow rate, acfm; $Q_{scfm}$ = measured flow rate, scfm; $P_{meas}$ = barometric pressure, atmospheres; and $T_{meas}$ = absolute temperature of air in pipe, K.

Air flow velocities were measured in air delivery pipes between injection vent wells to determine air injection rates. Air velocity was measured using a Dwyer thermal anemometer and

converted to a flow rate using the area of the delivery pipe. The anemometer was inserted through a one-hole rubber stopper, and then inserted into the air delivery pipe at measurement locations between injection vent wells. The velocity was converted to a flow rate according to Equation 16:

$$Q = v \times A \tag{16}$$

where Q = air flow rate, actual cubic feet per second (acfs); v = air velocity, ft/s; and A = cross-sectional area of air delivery pipe = 0.0218 $ft^2$.

### 6. Vacuum

Vacuum was measured during pumping of soil gas samples to determine the permeability of the soil to gas flow at the sampling point. Vacuum was measured using a vacuum gauge with a range of 0 to 30 inches of Hg, connected to the inlet line of the soil gas sampling pump.

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## SECTION IV
## TEST RESULTS

### A. SOIL ANALYTICAL RESULTS

#### 1. Petroleum Hydrocarbon Results

##### a. Initial Soil Analytical Results

During the drilling and installation of 34 soil gas monitoring wells, 130 initial soil samples were collected. The analytical results from the initial soil samples are presented in Appendices 1 and 2. All soil concentrations are reported as $\mu$g/g on a dry weight of soil basis, with TPH concentrations expressed on a hexane-equivalent basis. Semivolatile ($C_{12}$ - $C_{15}$) TPH soil concentrations ranged from below method quantitation limits (MQLs) (0.45 $\mu$g/g for TPH) to 17,801 $\mu$g/g. The highest semivolatile TPH occurred at 1.0 to 1.5 feet below grade at MP-11. The volatile ($C_6$ - $C_{12}$) TPH soil concentrations ranged from below MQLs (0.10 $\mu$g/g for TPH) to 597 $\mu$g/g. The highest volatile TPH occurred at 1.0 to 1.5 feet below grade at MP-33. The results showed that the highest contaminant levels at the site were found at monitoring points MP-11, -29, -32, and -33. Among the dominant compounds in the initial soil extracts were 2,4-dimethylpentane, hexane, toluene, xylene, decane, undecane, propylbenzene, butylbenzene, naphthalene, and pentadecane.

##### b. Final Soil Analytical Results

During the final soil sampling trip, 121 soil samples were collected. These analytical results are presented in Appendices 3 and 4. The semivolatile TPH concentrations ranged from below MQLs to 15,475 $\mu$g/g. The highest semivolatile TPH concentration occurred at 7.5 to 8.0 feet below grade at MP-29. The volatile TPH concentrations ranged from below MQLs to 1,198 $\mu$g/g. The highest volatile TPH concentration also occurred at 7.5 to 8.0 feet below grade at MP-29. Final soil concentration results show that the highest contaminant levels at the site were found at monitoring points MP-29, -32, and -33, as was true from initial soil sampling results. Final soil samples from MP-11 did not show the high semivolatile concentrations at 1.0 to 1.5 feet below grade

found during initial soil sampling; all three final semivolatile samples from 0.0 to 2.5 feet below grade had TPH concentrations less than 35 $\mu$g/g.

The final soil analytical results showed that 1,2,4-trimethylbenzene was detected at roughly the same concentration in all the collected soil samples. The chromatograms show a significantly larger peak for 1,2,4-trimethylbenzene than for the other compounds in the soil extracts. Blank checks for water and methanol blanks showed that contamination from 1,2,4-trimethylbenzene did not occur in the laboratory. No peak similar to that of 1,2,4-trimethylbenzene appeared in any of the chromatograms for the initial soil samples collected in January 1993. Based on the consistent pattern of 1,2,4-trimethylbenzene present in all of the final soil samples at generally the same concentration, it appears likely that field contamination of the samples occurred during final soil sampling, storage, and transport to the UWRL. Based on this conclusion, the 1,2,4-trimethylbenzene peak was eliminated from all final soil sample chromatograms prior to any further data reduction. Appendix 3 contains the volatile hydrocarbon analysis results both with and without the 1,2,4-trimethylbenzene peak; however, only the results without 1,2,4-trimethylbenzene were used in subsequent mass calculations.

Dominant contaminants in the final soil samples other than 1,2,4-trimethylbenzene included 2,4-dimethylpentane, toluene, xylene, decane, undecane, butylbenzene, naphthalene, and pentadecane, much the same list as that seen in the initial soil results.

### c. Initial Soil Hydrocarbon Mass Estimates

Soil contaminant mass estimates were made by dividing the bioventing test area into 35 soil blocks centered on each of the monitoring points (MP-0 through MP-34). An area of 1,275 $ft^2$ was used for each block in MP-0 through MP-5; an area of 2,125 $ft^2$ was used for each block in MP-6 through MP-34. An average soil concentration was calculated for each individual soil block, assuming a contaminated soil depth of 9 feet. An average soil bulk density of 90 $lb/ft^3$ and soil moisture content of 17 percent were assumed. Details of these mass calculations are presented in Appendix 5.

The initial TPH mass in the bioventing test area was estimated to be 10,567 pounds, of which 1,199 pounds were volatile and 9,368 pounds were semivolatile. The initial masses of benzene, toluene, ethylbenzene, and xylenes were estimated to be 64.4, 18.0, 14.7, and 23.1 pounds, respectively. The initial naphthalene mass was estimated to be approximately 49 pounds.

### d. Final Soil Hydrocarbon Mass Estimates

The TPH mass based on the final soil analyses was calculated using the same assumptions as for the initial soil TPH mass calculations. This resulted in a TPH mass of approximately 6,099 pounds remaining in the bioventing test area at the end of the study. Of the remaining contaminants, 4,462 pounds were in the semivolatile fraction and 1,637 pounds were found in the volatile fraction of the soil extracts. The final BTEX masses were estimated to be 15.2, 11.3, 11.9, and 36.3 pounds, respectively. The final naphthalene mass was approximately 40 pounds. Detailed calculations for final soil mass estimates are included in Appendix 5. The initial and final mass estimates for TPH, BTEX, and naphthalene are summarized in Table 10.

TABLE 10. SUMMARY OF INITIAL AND FINAL SOIL MASSES ESTIMATED FROM SOILS COLLECTED FROM BIOVENTING TEST AREA, FPTA#1.

| | TPH | | | | | | |
|---|---|---|---|---|---|---|---|
| Mass, pound (lb) | C-6 to C-12 | C-12 to C-15 | Benzene | Toluene | Ethylbenzene | Xylenes | Naphthalene |
| Initial Mass, lb | 1,199 | 9,368 | 64.4 | 18.0 | 14.7 | 23.1 | 49.0 |
| Final Mass, lb | 1,637 | 4,462 | 15.2 | 11.3 | 11.9 | 36.3 | 40.2 |
| Percent change, % | +36.5 | −52.4 | −76.4 | −37.2 | −19.0 | +57.1 | −18.0 |

Note: Final mass of C-6 to C-12 does not include 1,2,4-trimethylbenzene.

### e. TPH Mass Removal Estimate

Based on the analytical soil results, TPH mass removal is:

$$\Delta M = M_{initial} - M_{final} \quad (17)$$

$$= 10{,}822 \text{ pounds} - 6{,}543 \text{ pounds} = 4{,}279 \text{ pounds} \quad (18)$$

Using this total mass removal, the average TPH removal rate during the study period (approximately 790 days) is 5.42 lb/day.

An estimate was made of the hexane-equivalent of the oxygen uptake rates measured throughout the site over the duration of the study. These calculations were based on the averaged significant rates of all monitoring points observed during each respiration test at the bioventing test area over the period of field study. The averaged rate for each monitoring point was corrected for background bioactivity using an average background respiration rate of 0.007 percent/hour observed at background wells MP-20 through MP-26. These monitoring points were selected as background points because of low contaminant concentrations and generally low to nonsignificant respiration rates. A respiration rate of 0.0 percent/hour was used for those points having respiration rates equal to or less than the background respiration rate. Mass removal in the soil block covered by each monitoring point was calculated as follows:

$$\Delta M_i = -K_0 V_a D_O M_S C \div (100T) \quad (19)$$

where $\Delta M_i$ = TPH mass removal in soil block, kilogram (kg) or pound (lb); $K_0$ = oxygen utilization rate, percent/day; $V_a$ = volume of air/kg of soil, liter/kg (a soil density of 1,440 kg/m$^3$ $\approx$ 90 lb/ft$^3$ and 30 percent soil porosity are assumed); $D_0$ = density of oxygen gas, mg/L (assuming ideal gas of 32 g/22.4 liters); $M_S$ = mass of soil in each soil block, lb; C = mass ratio of hydrocarbon to oxygen required for mineralization (using hexane's ratio of C:O = 1:3.5); and T = total time, days. Based on the averaged significant respiration rate, approximately 14,800 pounds of TPH mass has been removed from the site over the course of the study. Details of these calculations are summarized in Appendix 6.

Data for soil TPH and BTEX constituents as well as naphthalene were submitted for preliminary statistical analysis. The data consisted of contaminant calculated mass values, in pounds, before and after bioventing, calculated over the 35 grid blocks into which the bioventing demonstration site at FPTA #1 at F.E. Warren was separated. These calculated mass values represent the initial and final data sets used in the analysis. The data were reviewed for quality assurance purposes prior to the statistical analysis. It was noted during this quality check that the initial masses of volatile and semivolatile TPH at M11 and M29, and the final mass of benzene at M18 and M21 were inadvertently transposed, probably due to challenging field conditions at the time of sample collection and recording. These transpositions were corrected before statistical analysis.

Paired t-tests were performed on the initial and final calculated mass values. In addition, the differences (initial - final) were plotted against the initial mass values. It was determined, based on the plots of the differences against initial values, that the amount of decrease in

the contaminant was a function of the initial mass of the contaminant in the grid block. One possible explanation for this trend is the limited opportunity for a decrease in contaminant mass which corresponds to a very low initial mass value. In addition, the initial masses of some contaminants, such as toluene and xylenes, were so low that a larger measurement after treatment could be attributable to measurement error. For these reasons, the analyses were performed using only grid blocks having initial masses that were above specified threshold values, based on regulatory cleanup goals for TPH constituents in concentration units (100 mg/kg), and on approximately 10 percent of the highest mean concentration for benzene, ethylbenzene, xylenes, and naphthalene. A slightly greater threshold was used for toluene in order to avoid omitting a potentially significant portion of the data which fell near the 10 percent level. The thresholds for the various contaminant species are listed in Table 11.

TABLE 11. THRESHOLD MASSES FOR EACH CONTAMINANT BELOW WHICH LOCATIONS WERE ASSUMED CLEAN AND NOT INCLUDED IN THE STATISTICAL ANALYSIS

| Contaminant | Threshold Concentration |
|---|---|
| TPH | 100 mg/kg |
| Volatile TPH | 100 mg/kg |
| Semivolatile TPH | 100 mg/kg |
| Benzene | 100 μg/kg |
| Toluene | 35 μg/kg |
| Ethylbenzene | 23 μg/kg |
| Xylenes | 57 μg/kg |
| Naphthalene | 30 μg/kg |

Table 12 shows the lower confidence bounds for the changes in contaminant concentrations at both the 90% and the 95% levels of significance for TPH, benzene, toluene and ethylbenzene. It is notable that the statistical analysis reveals that the bioventing demonstration produced decreases in TPH at the 95% level of statistical significance for those grid blocks which

were above the regulatory cleanup goal for TPH concentration prior to treatment. One omitted grid block was below the goal prior to the demonstration, and slightly above the cleanup goal (112 mg/kg) after bioventing. It is suspected that this apparent increase is due to the inherent variability at the site, and that its effect on the statistical analysis results would be insignificant. Benzene, toluene, and ethylbenzene were also reduced according to the analysis, but only at the 90% statistical significance level.

TABLE 12. SUMMARY OF STATISTICAL ANALYSIS OF CONTAMINANT MASS DATA BEFORE AND AFTER BIOVENTING AT FPTA#1, F.E. WARREN AFB

| Contaminant | Number of Observations | Average Decrease (lb) | Average Decrease (%) | Standard Error of Decrease | 95% Lower Confidence Bound | 90% Lower Confidence Bound |
|---|---|---|---|---|---|---|
| TPH | 9 | 603 | 40 | 271 | 98 | 224 |
| Semivolatile TPH | 5 | 1,156 | 52 | 319 | 475 | 666 |
| Benzene | 8 | 7 | 76 | 4 | −1.2 | 0.8 |
| Toluene | 24 | 0.33 | 37 | 0.2 | −0.03 | 0.06 |
| Ethylbenzene | 26 | 0.24 | 19 | 0.15 | −0.005 | 0.05 |

### f. Discussion

Contaminant mass removal estimates based on the soil analytical results and field-observed respiration rates were substantially different. It is felt that there is more uncertainty in the soil analytical results due to the heterogeneity of the soil at the former landfill site. The soil analytical results show that discrepancies exist at many sampling points between the initial and final soil samples, and that significant differences in TPH concentrations detected from adjacent soil sampling locations are common. The accuracy of mass removal based on soil analytical results is largely dependent upon the representativeness of the soil samples collected from the site which, in turn, is affected by site heterogeneity. The field-observed respiration rates are considered a more reliable indicator of mass removal because they are less affected by soil heterogeneity. The respiration results are averaged over the large soil volumes associated with each soil gas probe,

whereas the soil analytical results are determined from a much smaller soil volume. To illustrate, if 3 liters of soil gas are withdrawn during sampling soil with 30 percent air-filled porosity, this soil gas represents the sampling of 10 liters of soil. A 6-inch-long, 2-inch-diameter soil core represents only 0.3 liter of soil, of which only 5 to 10 grams are analyzed. The averaging from soil gas sampling would therefore tend to average over heterogeneous soil textural and concentration conditions, giving a more integrated, representative picture of respiration rates and contaminant distribution throughout the site than is possible from discrete soil core samples.

Using the soil data, concentration contour plots were developed to illustrate the contaminant distribution over the test area before and after treatment. Figures 15 and 16 show the contours of TPH concentration prior to and following, respectively, the bioventing demonstration project. The reduction in the area contaminated as well as the concentrations encountered is graphically evident in the plot. The removal efficiency achieved by the demonstration is illustrated by the reduction of the initial TPH concentrations near three of the monitoring points (MP-11, -13, and -31) to below the value represented by the lowest contour line (200 mg/kg). While significant contamination remains near MP-29, the TPH concentration in that area was very high initially and was greatly reduced by the demonstration.

Figure 17 represents the extent of contamination before treatment. Figure 18 shows a dramatic reduction in area and concentration of BTEX contamination following the demonstration. The figures show particular improvement in the area around MP-18, where there was initially a relatively high concentration of BTEX. (Similar contour plots for volatile- and semivolatile-TPH, individual BTEX constituents, and naphthalene are presented in Appendix 7.)

The TPH boiling point ranges in the soil samples also were analyzed for trends in the shift in compound distribution over the course of the study. The boiling point range concentration and concentration normalized data from each sampling point were plotted to compare the initial and final results, as shown in Appendix 8. Averaged concentration values for each boiling point range were calculated using results from 30 sampling locations where both initial and final soil analytical results were available. These averaged initial and final boiling point range soil concentrations are plotted in Figure 19 with percent change shown in Table 13. Figure 19 indicates that an approximately 50 percent decrease in concentration occurred for the C-12 and heavier boiling point range components. Figure 19 also indicates no significant changes in the lighter-molecular-weight constituents in the test soils during the study. The boiling point range data were normalized as a percentage of the total concentration in the sample and were plotted in Figure 20. The normalized

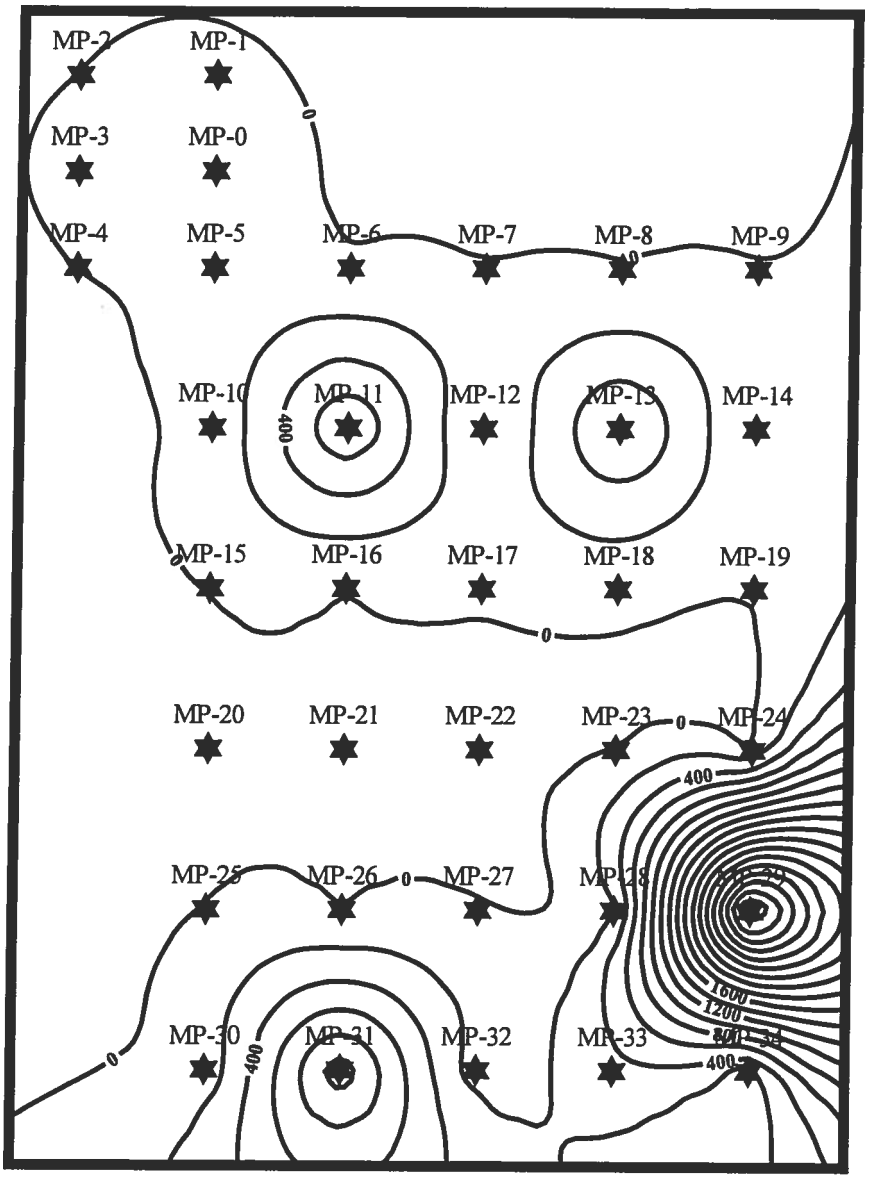


**Figure 15.** Initial TPH Concentration Profile at the Bioventing Demonstration Site at FPTA#1 at F.E. Warren AFB, in January 1993 Prior to Bioventing.

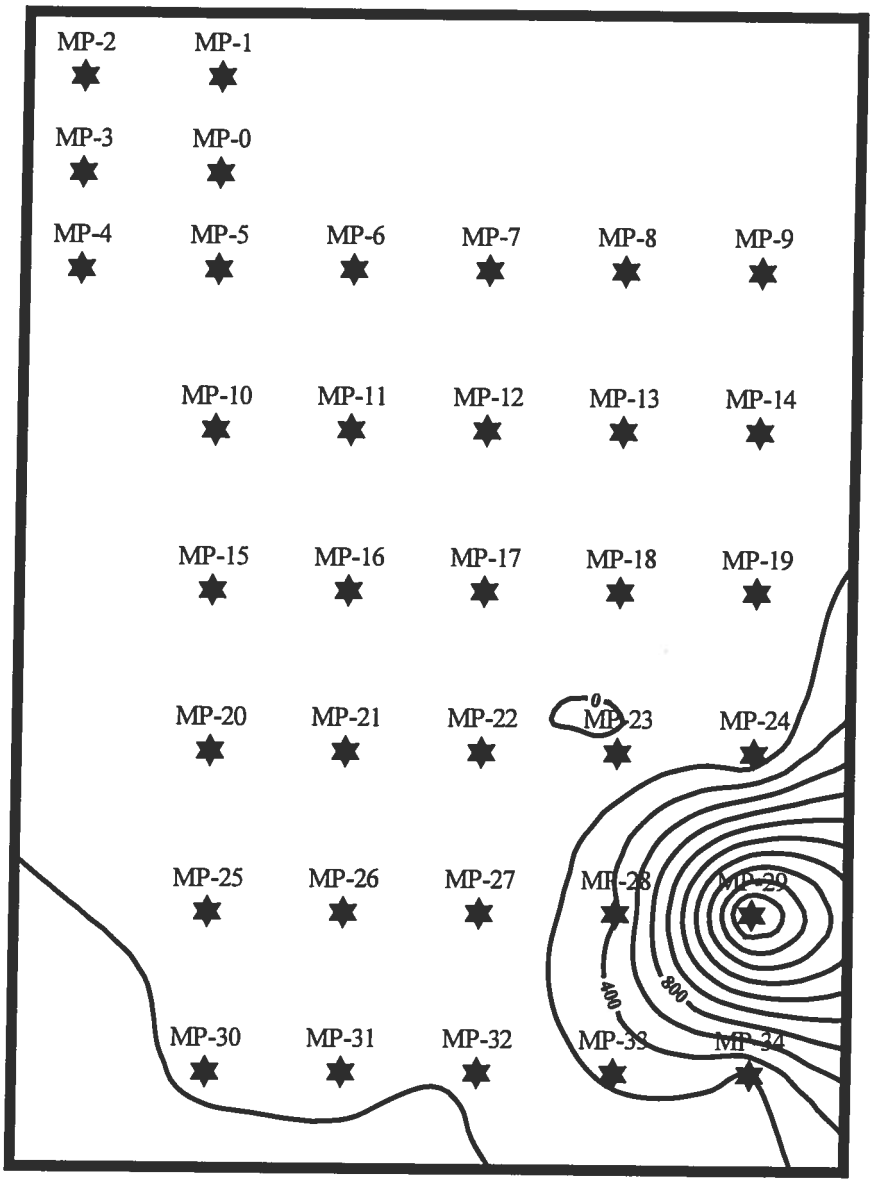


**Figure 16.** Final TPH Concentration Profile at the Bioventing Demonstration Site at FPTA#1 at F.E. Warren AFB, in March 1995 After Bioventing.

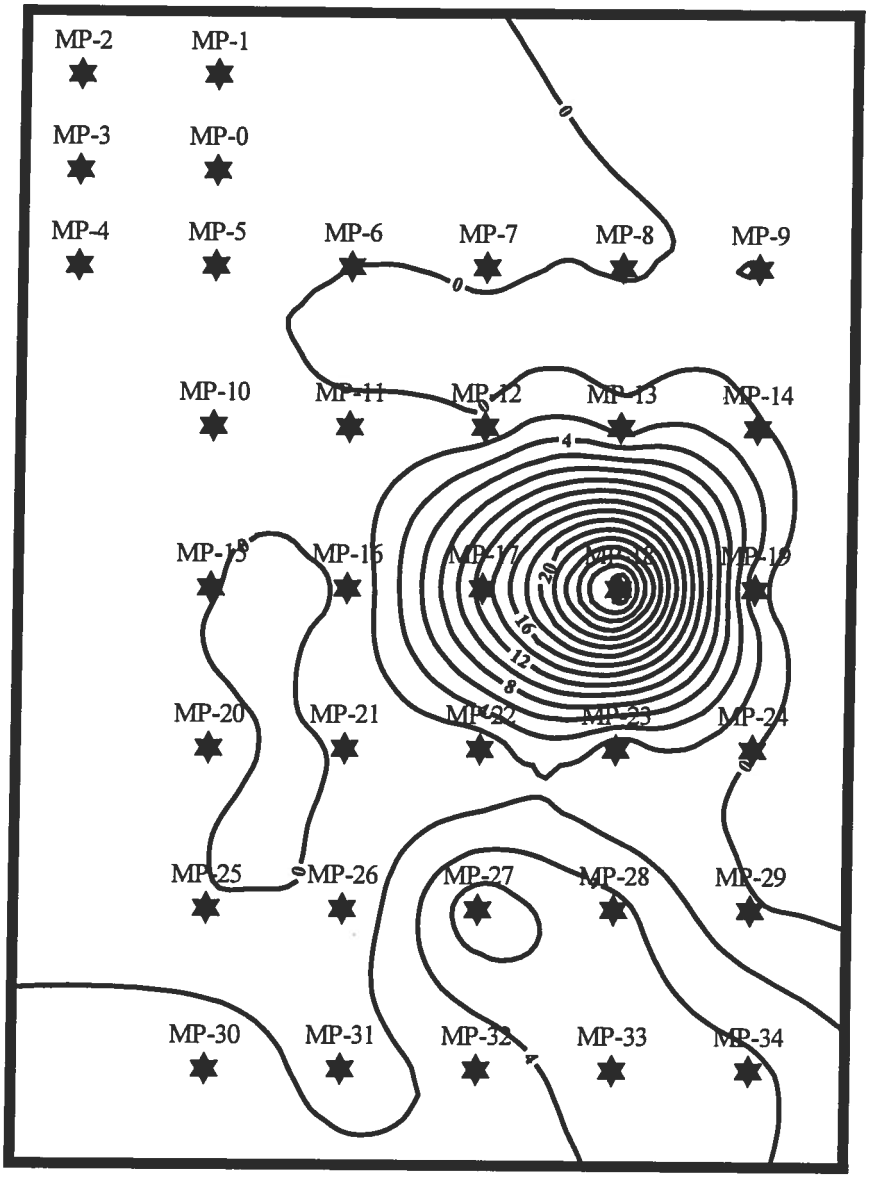


**Figure 17.** Initial BTEX Concentration Profile at the Bioventing Demonstration Site at FPTA#1 at F.E. Warren AFB, in January 1993 Prior to Bioventing.

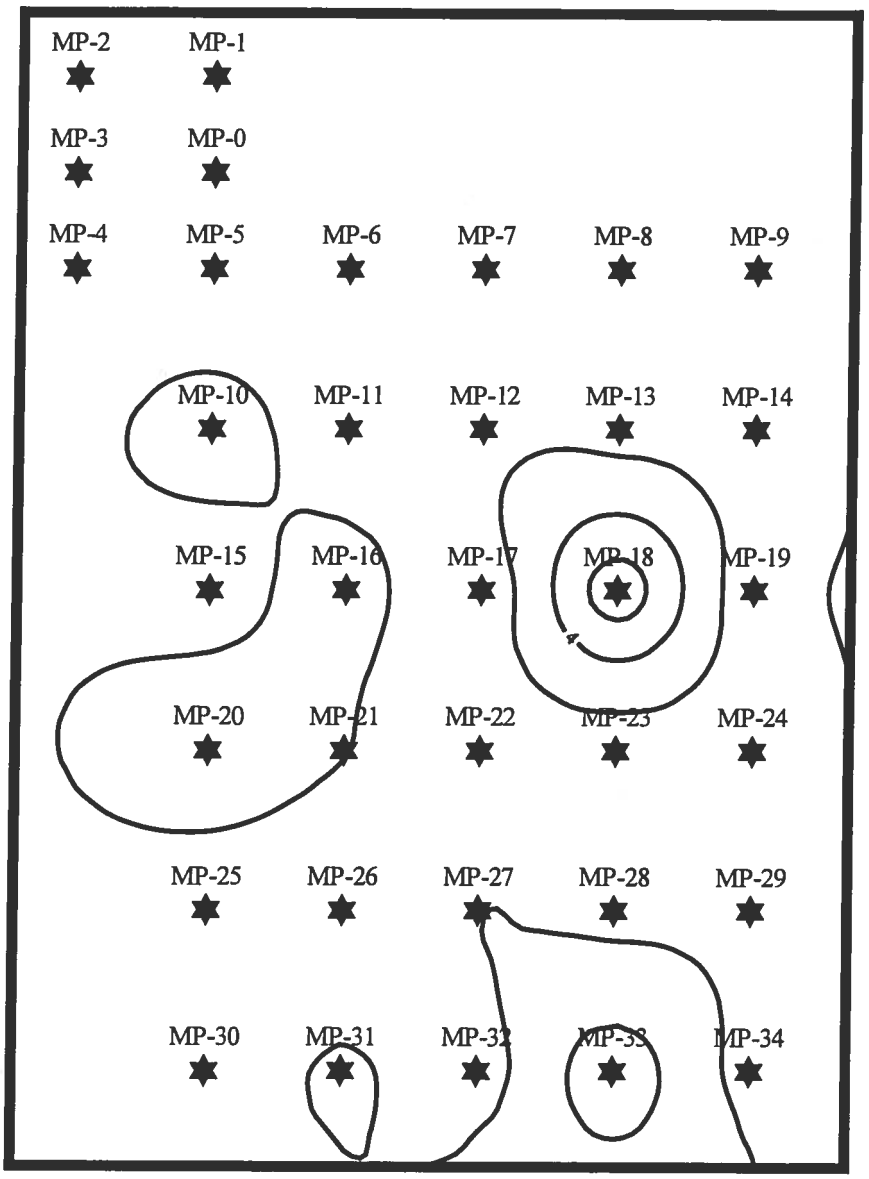


**Figure 18.** Final BTEX Concentration Profile at the Bioventing Demonstration Site at FPTA#1 at F.E. Warren AFB, in March 1995 After Bioventing.

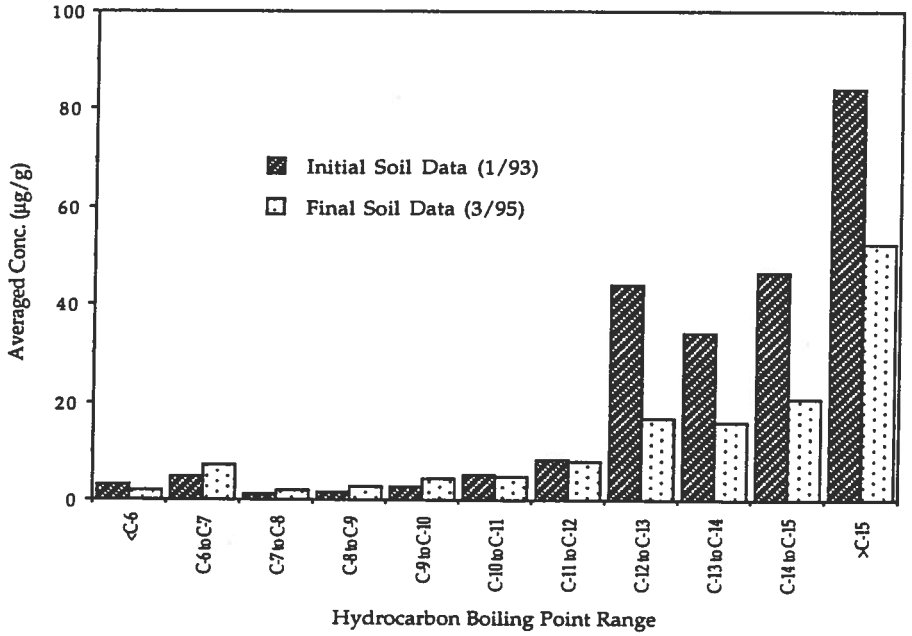


**Figure 19.** Plot of the Overall Averaged Concentrations of Hydrocarbons in Boiling Point Ranges from Soil Samples Collected from the Bioventing Area in FPTA#1 at F.E. Warren AFB.

results suggest a general trend of decreasing concentrations in the $C_8$ and lower boiling point range and an enrichment in middle boiling point range ($C_8$ to $C_{10}$) and high boiling point range ($C_{13}$ and higher) soil contaminants.

## 2. PAH Results

The initial and final soil samples analyzed for PAHs show little PAH contamination, with only one sample exceeding the detection limits for PAH analysis (Appendix 9). MP-15 showed a pyrene concentration of 2.4 $\mu$g/g at a depth of 5.0 to 5.5 feet below grade from initial soil analysis, with all other samples below the detection limit of 2.3 $\mu$g/g. The final soil analysis revealed no PAH concentrations above the detection limits ranging from 0.5 to 1.2 $\mu$g/g.

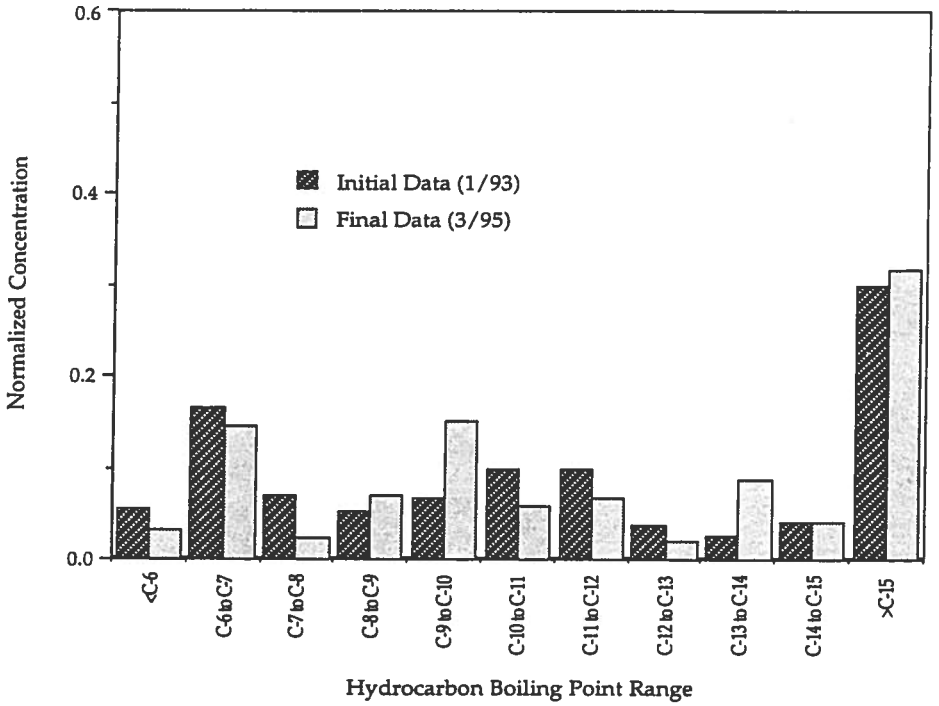


**Figure 20.** Plot of Normalized Overall Boiling Point Range Hydrocarbon Concentrations in Soil Samples Collected from the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

TABLE 13. PERCENTAGE CHANGE IN AVERAGED HYDROCARBON BOILING POINT RANGES.

| Boiling Point Range | Averaged Initial Soil Concentration, μg/g | Averaged Final Soil Concentration, μg/g | Percentage Change, % |
|---|---|---|---|
| <C-6 | 3.1 | 2.1 | −30.4 |
| C-6 to C-7 | 5.0 | 7.2 | +46.1 |
| C-7 to C-8 | 1.2 | 1.8 | +52.4 |
| C-8 to C-9 | 1.8 | 2.8 | +61.2 |
| C-9 to C-10 | 2.9 | 4.4 | +49.3 |
| C-10 to C-11 | 5.3 | 4.7 | −12.7 |
| C-11 to C-12 | 8.2 | 8.0 | −2.4 |
| C-12 to C-13 | 43.9 | 16.6 | −62.2 |
| C-13 to C-14 | 34.0 | 16.0 | −53.0 |
| C-14 to C-15 | 46.4 | 20.4 | −56.0 |
| >C-15 | 84.3 | 52.4 | −37.8 |

### 3. Chlorinated Solvent Results

The principal chlorinated solvent contaminants identified in the initial and final soil samples were methylene chloride, trichloroethylene (TCE), and tetrachloroethylene (PCE) (Appendix 10). Methylene chloride was detected in all soil samples, with initial soil sample concentrations ranging from 0.61 to 168 $\mu$g/g. The final soil sample methylene chloride concentrations were significantly lower, however, with concentrations ranging from 0.08 to 0.57 $\mu$g/g. Quality assurance/quality control (QA/QC) data were not available from the commercial laboratory analysis of the initial samples to evaluate potential sources of methylene chloride in the samples. It is likely that the methylene chloride represents laboratory contamination during extraction and analysis because prior soil investigations found only low methylene chloride concentrations ($\leq$0.16 mg/kg; Peterson et al., 1993), and the final soil methylene chloride results from UWRL analysis also were low ($\leq$0.57 $\mu$g/g).

Because TCE and PCE were the only other chlorinated solvents detected during the initial soil sample analysis, they were the only other chlorinated compounds quantified during the final soil sample analysis. The initial TCE concentrations in most samples ranged from below detection limits to 14 $\mu$g/g, whereas PCE was detected in only one sample at 4.2 $\mu$g/g. The final soil analysis showed most TCE concentrations less than 0.1 $\mu$g/g, with a maximum of 5.3 $\mu$g/g, whereas PCE was detected in only one sample at 0.001 $\mu$g/g.

## B. SURFACE EMISSIONS TEST RESULTS

Four in situ surface emission tests were conducted at the site during the field study. The first three tests were conducted under conditions both with and without atmospheric air injection. The last test was conducted to investigate the effect of low-rate pure oxygen injection on surface emission rates with and without active injection. The following data analyses were performed on the emissions flux data, with all raw data located in Appendix 11:

1. Specific compound and boiling point split data for all samples including field and trip blanks were summarized.
2. Total hydrocarbon hexane-equivalent emission flux rates for all samples collected during the four tests were organized by sampling location and air/oxygen injection flow rate.

The sample mass detected on sorbent tubes was corrected by subtracting out the averaged mass detected in the field and trip blanks.

3. Breakthrough results for the sorbent tubes were organized by sampling locations. Those data with breakthrough rates greater than 50 percent were excluded from further analysis. This resulted in the summary data shown in Table 14.
4. Analysis of variance (ANOVA) calculations were performed using the data summarized in Table 14 to evaluate the statistical significance of differences between total contaminant surface emission rates under various air/oxygen injection flow rates and at different soil contaminant levels.

The first surface emissions test was conducted on April 23 and 24, 1993. During the test, four flux chambers were placed near MP-11, -17, -28, and -30. Surface emission fluxes were measured both with and without air injection to the vadose zone soils. The air injection flow rate to each injection well was estimated to be 1 to 2 (acfm). The emission flux rates ranged from $1.3 \times 10^{-7}$ to $7.33 \times 10^{-7}$ g/m$^2$-s (0.011 to 0.063 g/m$^2$-day).

The second emissions test was conducted on September 22, 1993. Surface emission rates were measured at MP-11, -28, -30, and -32, both with and without air injection. Injection airflow rates up 2 acfm were applied for the injection mode. The observed emissions flux rates after background correction ranged from 0 to $2.24 \times 10^{-7}$ g/m$^2$-s (0 to 0.02 g/m$^2$-day).

The third emissions test was conducted at the site during July 7 through 11, 1994. The test was carried out with various air injection flow rates ranging from 0 to 50 acfm to the injection vent well I1. Surface emission rates were measured at I1 and at MP-26, -28, and -29. The measured emission flux rates ranged from 0 to $2.72 \times 10^{-7}$ g/m$^2$-s (0.0 to 0.024 g/m$^2$-day).

The last emissions test was conducted on March 21, 1995. The main purpose of the test was to investigate the effect of pure oxygen injection on measured surface emission rates. Surface emission rates were measured at MP-30 and -32, both with and without pure $O_2$ injection. The oxygen injection rate was 0.5 to 1.0 scfm (0.47 to 0.94 acfm). The measured emission flux rates ranged from 0 to $1.38 \times 10^{-7}$ g/m$^2$-s (0.0 to 0.01 g/m$^2$-day).

A two-factor ANOVA (Appendix 11) indicated that neither the soil contaminant level nor the injection flow rate had a statistically significant impact on surface total hydrocarbon emission rates at the 95 percent confidence level (CL). The p-values for the ANOVA for injection flow rate and soil contaminant level were 0.198 and 0.438, respectively. The mean of emission rates ($1.99 \times 10^{-7}$ to

TABLE 14. SUMMARY OF OBSERVED EMISSIONS DATA WITH BREAKTHROUGH VALUES LESS THAN 50 PERCENT.

| Sample Name | Sample Date | Sample Location | Injection Flow Rate (acfm) | Injection Medium | Breakthrough (%) | $C_6$ Emission Flux ($g/m^2$-s) | Soil Contaminant Level |
|---|---|---|---|---|---|---|---|
| MP11-2 | 4/24/93 | MP-11 | 1-2 | air | 32.0 | $6.60 \times 10^{-7}$ | HIGH |
| FC17-1NF | 4/23/93 | MP-17 | 0.0 | ~ | 32.0 | $3.87 \times 10^{-7}$ | LOW |
| FC17-1NF | 4/23/93 | MP-17 | 0.0 | ~ | 47.0 | $1.30 \times 10^{-7}$ | LOW |
| MP28-2NF | 4/23/93 | MP-28 | 0.0 | ~ | 18.0 | $5.51 \times 10^{-7}$ | HIGH |
| MP30-1NF | 4/23/93 | MP-30 | 0.0 | ~ | 3.6 | $2.10 \times 10^{-7}$ | LOW |
| MP30-2NF | 4/23/93 | MP-30 | 0.0 | ~ | 1.5 | $7.33 \times 10^{-7}$ | LOW |
| MP30-1 | 4/24/93 | MP-30 | 1-2 | air | 18.8 | $1.75 \times 10^{-7}$ | LOW |
| MP30-2 | 4/24/93 | MP-30 | 1-2 | air | 42.1 | $1.64 \times 10^{-7}$ | LOW |
| FC30-1-1 | 9/22/93 | MP-30 | 0.0 | ~ | 35.6 | 0.00 | LOW |
| FC11-1-1NF | 9/22/93 | MP-11 | 0.0 | ~ | 3.5 | 0.00 | HIGH |
| FC30-1-1 | 9/22/93 | MP-30 | 1-2 | air | 43.4 | 0.00 | LOW |
| FC32-1-2 | 9/22/93 | MP-32 | 1-2 | air | 21.7 | $2.24 \times 10^{-7}$ | HIGH |
| M26-1 | 7/7/94 | MP-26 | 1-2 | air | 47.1 | $5.42 \times 10^{-8}$ | BCKGRND |
| M26-2 | 7/7/94 | MP-26 | 1-2 | air | 1.3 | $4.97 \times 10^{-7}$ | BCKGRND |
| TC1 | 7/10/94 | I1 | 32 | air | 14.7 | $8.10 \times 10^{-8}$ | HIGH |
| M29-1 | 7/10/94 | MP-29 | 32 | air | 30.0 | 0.00 | HIGH |
| TC1 | 7/10/94 | I1 | 32 | air | 12.8 | $1.01 \times 10^{-7}$ | HIGH |
| TC1-2 | 7/10/94 | I1 | 32 | air | 37.8 | $1.44 \times 10^{-7}$ | HIGH |
| TCA2 | 7/11/94 | I1 | 50 | air | 30.0 | $2.89 \times 10^{-8}$ | HIGH |
| M29-1 | 7/11/94 | MP-29 | 50 | air | 0.0 | 0.00 | HIGH |
| TC1-2 | 7/11/94 | I1 | 50 | air | 35.5 | 0.00 | HIGH |
| TCA-1 | 7/11/94 | I1 | 50 | air | 24.2 | $6.98 \times 10^{-8}$ | HIGH |
| TCA-2 | 7/11/94 | I1 | 50 | air | 22.8 | 0.00 | HIGH |
| M32-1NF | 3/1/95 | MP-32 | 0.0 | ~ | 33.0 | $1.16 \times 10^{-8}$ | HIGH |
| M32-1 | 3/1/95 | MP-32 | 0.5 | oxygen | 17.0 | $1.38 \times 10^{-8}$ | HIGH |
| M30-2 | 3/1/95 | MP-30 | 0.5 | oxygen | 35.3 | 0.00 | LOW |

Note: 1. ~ indicates no injection flow
2. HIGH: TPH concentration = 200 to 17,000 $\mu$g/g; LOW: TPH concentration = 20 to 200 $\mu$g/g; BACKGROUND: TPH concentration < 20 $\mu$g/g.

$2.52 \times 10^{-7}$ g/m$^2$-s) for the lower injection flow rates (0 to 2 cfm) were actually slightly higher than the mean of the emission rates ($1.77 \times 10^{-8}$ to $5.87 \times 10^{-8}$ g/m$^2$-s) for the higher injection flow rates (32 to 50 cfm). In addition, the comparison with soil contaminant levels indicated that there was no statistically significant difference among the surface total hydrocarbon emission rates as a function of soil concentration. The mean TPH emission rates for these background, low-TPH, and high-TPH-concentration soils were found to be $2.76 \times 10^{-7}$, $2.25 \times 10^{-7}$, and $1.11 \times 10^{-7}$ g/m$^2$-s, respectively.

The results of these statistical analyses indicate that no significant increase in contaminant surface emission flux rates occurred at the bioventing test area under various injection flow rates during air injection compared to soil emissions with the air turned off. In addition, the results indicate that emission rates at the site were not significantly different between background and contaminated soils, indicating that under the range of operating conditions used in this study, no measurable contaminant soil surface emissions occurred due to operation of the air injection bioventing system.

## C. GROUNDWATER RESULTS

Groundwater samples were taken at the beginning of the project (January 1993) and in September 1993 from the three wells in the immediate vicinity of FPTA#1 shown in Figure 2. The results of the groundwater sampling indicate that TPH concentrations decreased from the first to second sampling event, although concentrations were below 1 mg/L for all samples (Appendix 12). Examination of BTEX concentrations show that nearly all samples were below U.S. EPA Drinking Water Maximum Contaminant Levels (MCLs) of 5; 700; 2,000; and 10,000 $\mu$g/L, respectively (U.S. EPA, 1990). The only sample that exceeded the BTEX MCLs was from monitoring well M-90, where benzene was found at 13.1 $\mu$g/L in January 1993. No benzene was detected in a duplicate sample from January 1993 nor in the September 1993 sample.

## D. SOIL GAS MONITORING RESULTS

Results from the nominal monthly soil gas monitoring events are shown in Appendix 13, with results up to July 1994, under the influence of continuous air injection. Subsequent measurements reflected the impacts of pure $O_2$, pulsed air, continuous air, or no injection, depending on a specific

sampling location and time of measurement. There was adequate oxygenation at most monitoring points for the duration of the monitoring period, with many of the monitoring points remaining at approximately ambient $O_2$ concentrations, including some points experiencing no injection (MP-20 to -26, -30, and -31). Exceptions include MP-32, -33, and -11, and the monitoring points surrounding the plastic-covered area. Oxygen depletion at MP-32 and -33 was most likely due to high-$O_2$ demand caused by high soil contaminant levels and to inadequate $O_2$ delivery caused by subsurface high-water-content conditions. The latter reason is supported by the inability to elevate $O_2$ concentrations even with pure $O_2$ injection, and the lack of elevated $CO_2$ due to $O_2$ consumption observed during pure $O_2$ injection (see Section IV.G.2. "Effectiveness of Pure $O_2$ Injection"). Oxygen depletion at MP-11 was seen primarily during the summer months, when temperatures were elevated, resulting in an increase in $O_2$ utilization. The monitoring points in the plastic-covered area experienced fluctuating $O_2$ levels due to frequent breaks in the air supply pipe in the vicinity of I20 (Figure 9).

Comparison of the two different soil gas sampling methods used showed no statistical difference in measurement of $O_2$ , $CO_2$, and TPH (Appendix 14). Comparison of field measurements and laboratory GC analyses of canister samples also shows no statistical difference in measurement of $O_2$ and $CO_2$ (Appendix 15).

Soil gas TPH levels typically were in the range of 10 to 250 ppmv (hexane equivalent). Exceptions include MP-32D and -33D, which generally ranged between 1,000 and 5,000 ppmv, with MP-32D concentrations usually higher than those in MP-33D.

## E. SOIL TEMPERATURE AND AIR FLOW RESULTS

The soil and injection air temperatures measured for the monitoring period are shown in Appendix 16. Soil temperatures ranged from approximately $-2°C$ in the winter to 25°C in the summer, with shallow-depth temperatures typically warmer in the summer and colder in the winter than temperatures at the deeper depths.

Air flow velocities were measured in delivery pipes between injection vent wells to estimate the injection flow rate and adjust the flow rates to each injection vent well (data in Appendix 16). Typical air injection flow rates ranged from approximately 3 to 5 acfm. Several sections of pipe broke during the operational period, most frequently near I20 (Figure 9), temporarily disrupting the flow of air to the subsurface.

## F. RESPIRATION RATES

Oxygen utilization and $CO_2$ production data were evaluated for zero- and first-order relationships by plotting concentration and ln(concentration), respectively, versus time. Appendix 17 contains the measured soil gas concentration data obtained from the nine respiration tests conducted during the site monitoring period. Appendix 18 contains the zero- and first-order rates with regression statistics generated from these measured soil gas data. In general, more respiration rates determined from $O_2$ uptake data were significant at the 95 percent CL than those generated from $CO_2$ production data, and thus rates from $O_2$ uptake data were used in all data evaluations. Only negative respiration rates (indicating a decrease in $O_2$ concentrations during the test period) that were significant at the 95 percent CL were examined for effects due to changes in system operation and over time. Respiration rate plots and temperature transformations used the absolute value of statistically significant rates for ease of comparison in plots and to allow logarithmic transformation during temperature transformation analyses. The numbers of significant zero- and first-order rates determined during each respiration test were approximately equal, and zero-order rates were used to examine the effects of operational changes and time due to the inherent simplicity of zero-order-rate expressions.

Oxygen utilization rates measured at the site typically were low, 0.1 percent/hour or less, with rates usually highest in the summer months and lower in the winter. Some monitoring probes had higher rates, up to 0.4 percent/hour (MP-11D, -28D, -29M, and -29D). Other probes (MP-32D and -33D) likely would have had high rates due to high soil contaminant concentrations, but they were not adequately oxygenated (initial $O_2$ concentrations were typically less than 4 percent and frequently nondetectable) to allow rate determinations.

Respiration rates would be expected to change over time due to changes in both temperature and contaminant concentration in the soil. It would be expected that respiration rates would increase with an increase in temperature, and vice versa, due to temperature effects on biological reactions. Respiration rates also would be expected to decrease with decreases in contaminant concentration, and therefore with increasing treatment time, if soil contaminants are being degraded.

## 1. Temperature Effects.

To examine the effect of temperature on respiration rates, only those monitoring probes that had significant rates during at least the first several respiration tests were used for comparison purposes, resulting in 58 of 102 monitoring probes examined for temperature effect. Respiration rates and temperatures for each respiration test were plotted for each monitoring point selected, with missing data points indicating nonsignificant rates for that respiration test. Figures 21 through 23 show plots from selected monitoring probes at different depths; all of the plots of monitoring probe data used to evaluate temperature effects on respiration rates are included in Appendix 19.

To determine if respiration rates changed over time, the effect of temperature on respiration rates was quantified using the Arrhenius relationship. It has been found that many biological reactions follow this relationship over a limited temperature range as shown in Equation 20 (Benefield and Randall, 1985):

$$\frac{d(\ln K)}{dT} = \frac{E_a}{R}\frac{1}{T^2} \qquad (20)$$

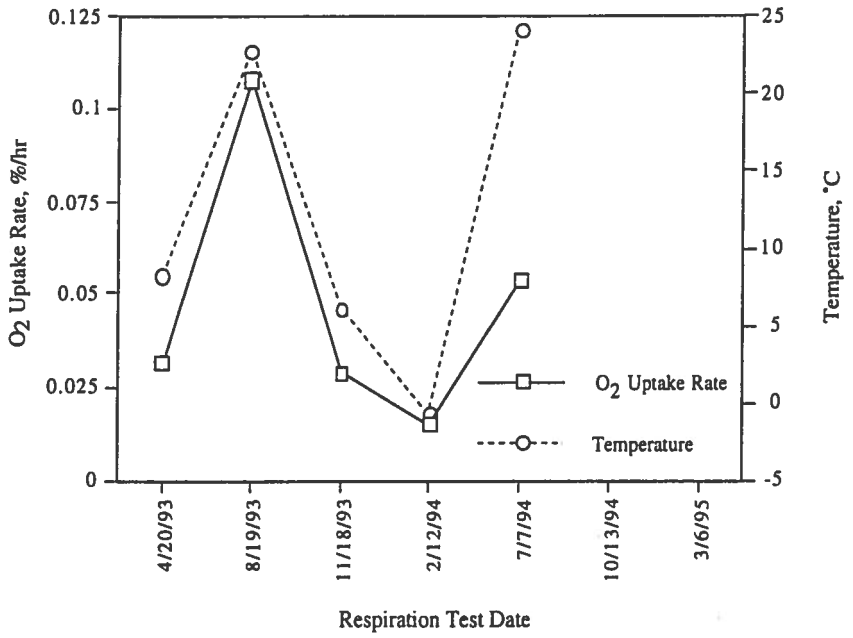


**Figure 21.** Significant Zero-Order $O_2$ Uptake Rates and Subsurface Temperatures at MP-13S in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

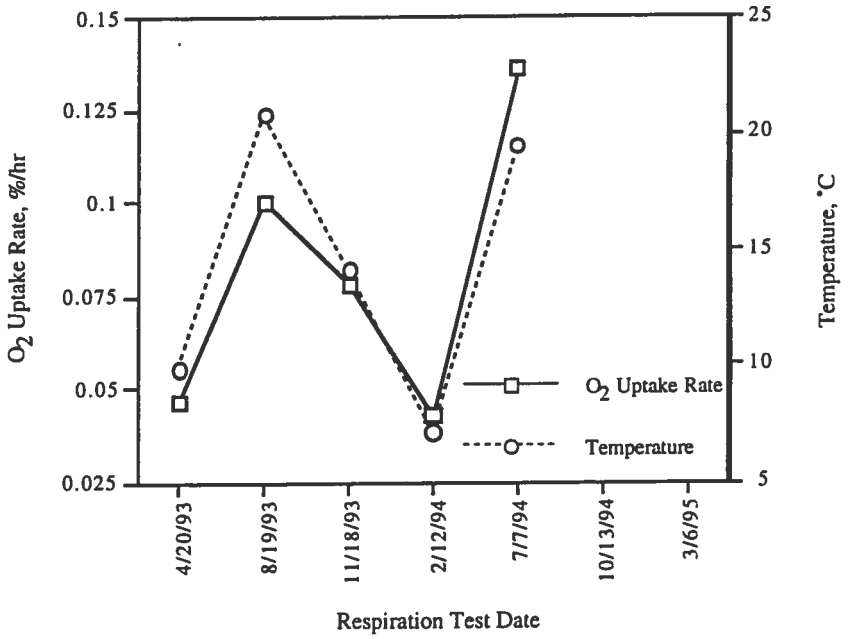


**Figure 22.** Significant Zero-Order $O_2$ Uptake Rates and Subsurface Temperatures at MP-34M in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

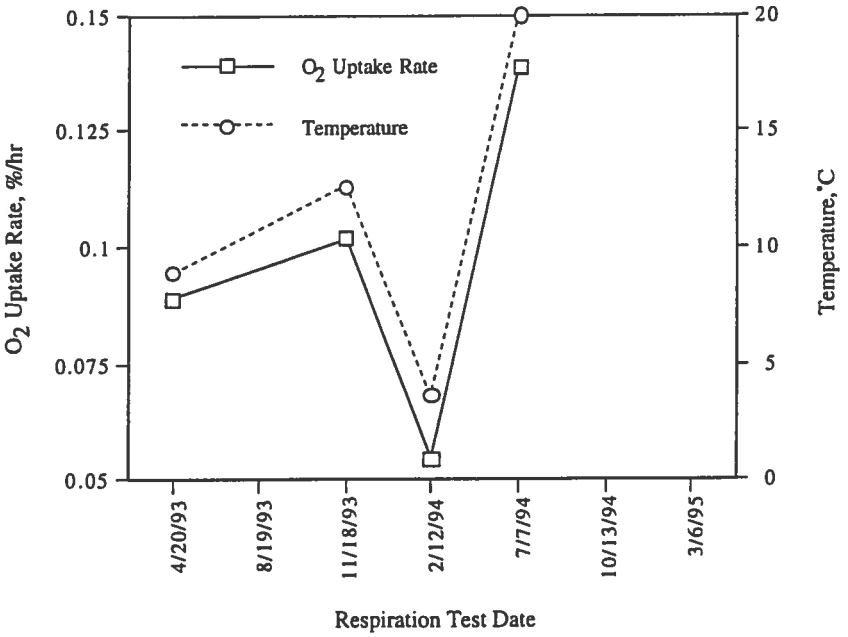


**Figure 23.** Significant Zero-Order $O_2$ Uptake Rates and Subsurface Temperatures at MP-4D in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

$$\frac{d(\ln K)}{dT} = \frac{E_a}{R}\frac{1}{T^2} \quad (20)$$

where K = reaction-rate constant, percent/hour; T = absolute temperature, K; $E_a$ = activation energy, calorie/gmol; and R = ideal gas constant = 1.98 cal/gmol-K.

Integrating Equation 20 produces the following relationship:

$$\ln K = -\frac{E_a}{R}\frac{1}{T} + \ln B \quad (21)$$

where B represents a constant. A plot of lnK versus $T^{-1}$ allowed the determination of $E_a/R$ as the slope of the regression line. Fifteen of the 58 monitoring probes examined had at least three significant respiration rates and produced Arrhenius regressions significant at the 95 percent CL. The data from these 15 monitoring probes were then combined and a regression was performed, resulting in an $E_a/R$ value of 5,570 K. Figure 24 shows the plot of the regression with the regression statistics shown in Appendix 20. This value predicts a doubling of rate with an increase of approximately 10.3°C (over a temperature range from 5°C to 25°C), which is comparable to the van't Hoff rule of a doubling in rate for every 10°C (Benefield and Randall, 1985).

### 2. Change Over Time.

To determine whether there was a decrease in respiration rates over the period of system operation, transformation to a common temperature was first required. The respiration rates were transformed to 12°C, the average annual temperature at a depth of 5.5 feet measured at the bioventing test area during the monitoring period (Appendix 21). The respiration rates from the 15 monitoring probes used in the temperature correction regression were transformed; these 15 probes represented 11 monitoring point locations from throughout the site. The respiration rates of seven additional monitoring probes (MP-11D, -18D, -19M, -29S, -29M, -29D, and -34D) not used in the temperature correction regression, but of interest due to their high soil TPH concentrations and/or relatively high respiration rates measured at these probes during the study, were also temperature-transformed. MP-32D and -33D were also of interest due to their high soil TPH concentrations; however, no significant respiration rates were determined for these probes because $O_2$ concentrations typically were below 5 percent (usually nondetectable) prior to initiation of each

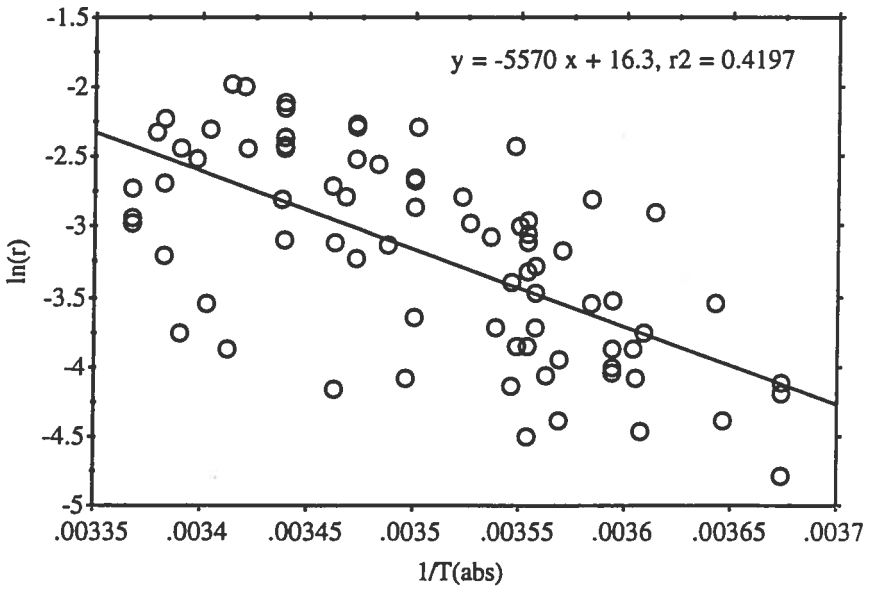


**Figure 24.** Regression Results from Respiration Rate-Temperature Data Used to Determine $E_a/R$ for Respiration Rate Temperature Corrections.

respiration test. Although MP-32D and -33D each had one respiration test event with initial $O_2$ concentrations greater than 15 percent, the $O_2$ was depleted before enough data were gathered to produce a regression that was statistically significant.

The respiration rate data were corrected to 12°C using Equation 22:

$$K_{12°C} = K_{meas} e^{\frac{E_a}{R}\left(\frac{1}{T_{meas}} - \frac{1}{285K}\right)} \quad (22)$$

where $K_{12°C}$ = respiration rate transformed to 12°C, percent/hour; $K_{meas}$ = respiration rate determined at field temperature, percent/hour; and $T_{meas}$ = subsurface temperature during respiration test, K. Mean $K_{12°C}$ rates were determined using the best-fit slope from the ln(K) versus $T^{-1}$ regression.

Upper and lower CLs (UCL and LCL, respectively) were determined for these adjusted rates by combining the $E_a/R$ CI and the individual respiration rate CI. Because the exponent in the temperature correction equation could be either positive or negative, depending on the measured temperature, the corrected rate confidence intervals must be calculated differently for rates determined

at temperatures below and above 12°C. Equations 23 and 24 were used for rates determined at temperatures below 12°C; Equations 25 and 26 were used to correct rates determined at temperatures above 12°C.

$$K_{12°C(T<12°C),UCL} = K_{meas} e^{\left[\left(\frac{E_a}{R}\right)_{UCL} \times \left(\frac{1}{T_{meas}} - \frac{1}{280K}\right)\right]} + CI_{meas} \quad (23)$$

$$K_{12°C(T<12°C),LCL} = K_{meas} e^{\left[\left(\frac{E_a}{R}\right)_{LCL} \times \left(\frac{1}{T_{meas}} - \frac{1}{280K}\right)\right]} - CI_{meas} \quad (24)$$

$$K_{12°C(T>12°C),UCL} = K_{meas} e^{\left[\left(\frac{E_a}{R}\right)_{LCL} \times \left(\frac{1}{T_{meas}} - \frac{1}{280K}\right)\right]} + CI_{meas} \quad (25)$$

$$K_{12°C(T>12°C),LCL} = K_{meas} e^{\left[\left(\frac{E_a}{R}\right)_{UCL} \times \left(\frac{1}{T_{meas}} - \frac{1}{280K}\right)\right]} - CI_{meas} \quad (26)$$

The respiration rate CI was added to that generated for the temperature correction after the rate transformation in Equations 23 through 26 under the assumption that the uncertainty due to the respiration rate was independent of the temperature at which it was measured. Transformation of the rates resulted in unequal upper confidence interval (UCI) and lower confidence interval (LCI) values due to the exponential transformation, and the confidence intervals were averaged to facilitate comparison among rates. Spreadsheet results for these calculations for the 15 monitoring probes used in the temperature correction regression are shown in Appendix 22; results for the additional selected monitoring probes are shown in Appendix 23.

Background monitoring probes were selected, based on low soil contaminant levels and generally low to nonsignificant respiration rates, for comparison with contaminated monitoring probes. Respiration rates for the background monitoring probes were transformed to 12°C according to Equation 22, and mean rates with 95 percent CIs were calculated for each respiration test using values of 0 for rates that were not significant. The background monitoring probe rates were temperature-transformed even though they were not included in the determination of $E_a/R$ for

temperature transformation, because many of them lacked an adequate number of significant rates for regression and due to the relatively temperature-insensitive nature of the low respiration rates. Spreadsheet results for these background rate temperature corrections are shown in Appendix 24.

The temperature-corrected respiration rates for monitoring probes used in the Arrhenius correction, along with the average background monitoring probe rates, were then plotted with 95 percent CIs to determine trends in these rates over time. Figures 25 through 27 are corresponding temperature-corrected plots for the same shallow, medium, and deep monitoring probes that were shown in Figures 21 through 23. The plots for all 15 monitoring probes that were temperature-transformed are provided in Appendix 25. Similar plots for the additional temperature-transformed monitoring probes are shown in Appendix 26. Missing data points indicate measured rates that were not significantly different from 0 at the 95 percent CL. Some measured respiration rates that were significant at the 95 percent CL became nonsignificant after temperature transformation due to the uncertainty associated with the temperature transformation regression. These rates were plotted, even though they were not significant, to show their relationship to background rates. Confidence interval error bars and results in Appendices 22, 23, and 24 can be used to identify the nonsignificant rates.

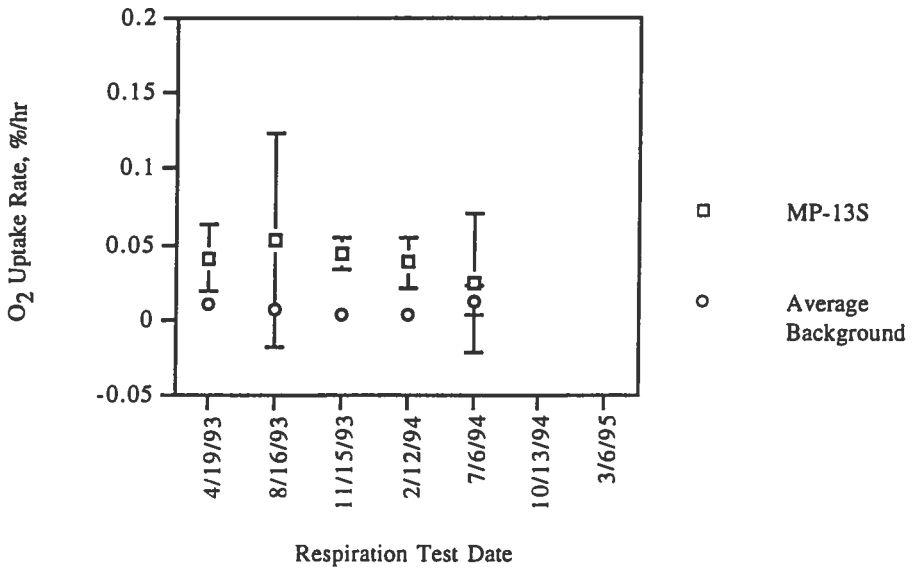


**Figure 25.** Temperature-Corrected Significant Zero-Order $O_2$ Uptake Rates for MP-13S and Average Background Monitoring Probes in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB. Error Bars Represent 95 Percent CIs.

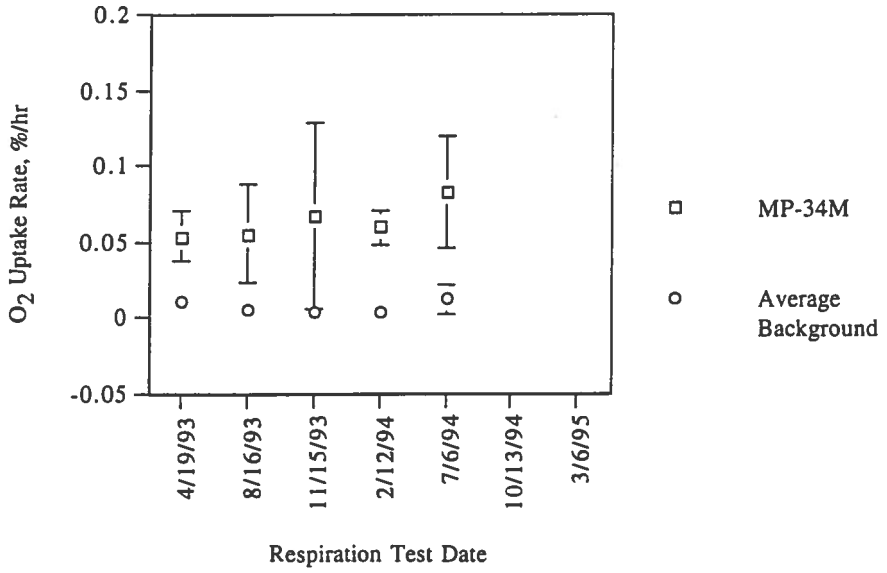


**Figure 26.** Temperature-Corrected Significant Zero-Order $O_2$ Uptake Rates for MP-34M and Average Background Monitoring Probes in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB. Error Bars Represent 95 Percent CIs.

There was a general trend toward nonsignificant rates at the end of the operational period for the monitoring probes used in the temperature transformation regression, as indicated in Figures 25 and 27. Nine of the 15 monitoring probes had nonsignificant rates measured during the last two respiration tests, with an additional monitoring probe (MP-13D) showing a statistically significant decrease in rate from the initial to the final respiration test. The other three monitoring probes (MP-18D, -19S, and -27M) had statistically significant differences in some rates without a decreasing trend between the initial and final sampling periods.

The temperature-transformed respiration rates for the monitoring probes examined reveal that the rates were relatively low (0.11 percent/hour or lower), with initial background rates 10 times lower. Initially, 9 out of 15 of the monitoring probes had rates significantly higher than background rates; however, by the end of the study, only 6 of 15 rates remained significant.

Several of the additional temperature-corrected monitoring probes had relatively high transformed respiration rates ($\geq$0.18 percent/hour). There was an overall decrease in respiration rates over time, with all 7 of these monitoring probes having nonsignificant rates at the last respiration test. In all cases this was not due just to a large uncertainty in the regression, but rather to low oxygen consumption.

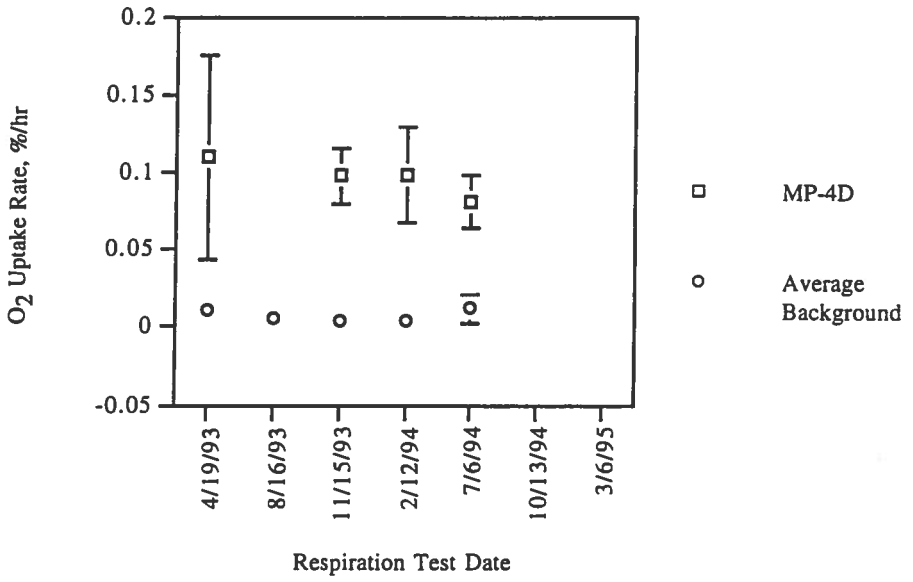


**Figure 27.** Temperature-Corrected Significant Zero-Order $O_2$ Uptake Rates for MP-4D and Average Background Monitoring Probes in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB. Error Bars Represent 95 Percent CIs.

Comparison of untransformed respiration rates for all monitoring probes reveals that there was a decrease in the percentage of significant rates over the period of operation, particularly the October 1994 and March 1995 respiration tests, as shown in Figure 28. The percentage of significant rates decreased from an average of 62.1 percent for the first four respiration tests to 15.7 percent for the March 1995 respiration test.

### 3. Influencing Subsurface Temperatures Through the Use of Surface Plastic Cover.

A portion of the bioventing injection area at FPTA#1, as shown in Figure 9, was covered from January 1993 through July 1994 to determine the effectiveness of a surface cover for increasing subsurface temperatures. The soil surface was covered with black plastic and weighted with tires and lumber to hold the cover in place. The plots in Appendix 19 show that increased temperature resulted in increased respiration rates for most of the monitoring points examined. If respiration rates are indicative of contaminant degradation rates, raising the temperature of the subsurface can result in reduced remediation times. In addition, biological activity essentially ends

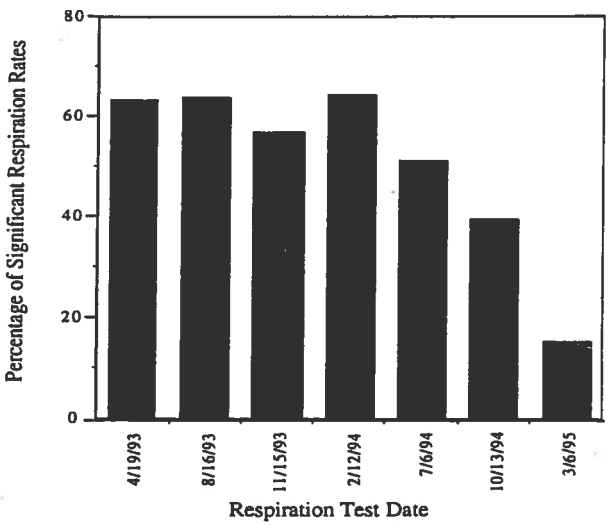


**Figure 28.** Percentage of Monitoring Probes with Respiration Rates Significant at the 95 Percent CL for Each Respiration Test Conducted in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

when soil freezes, so prevention of freezing through the use of surface covering also may be beneficial as it can reduce the length of biologically inactive operating periods.

Two sets of data were available from monitoring the plastic-covered area at FPTA#1: one temperature data set from monitoring points inside and outside the plastic-covered area (Appendix 13), and one set from thermocouples installed within the soil inside the plastic-covered area (Appendix 16). Each data set contains measurements made while the cover was in place (January 1993 through July 1994) and after its removal (August 1994 through March 1995). However, the data sets are not directly comparable because the monitoring point thermocouples were installed at depths of 3, 5.5, and 8 feet, whereas the soil thermocouples were installed at the depths listed in Table 15, approximately 4 and 7 feet BGS. The monitoring point data were examined independently in order to assess cover effectiveness as a function of soil depth. The data sets were combined to examine seasonal effects on the cover effectiveness.

TABLE 15. INSTALLATION DEPTHS OF THERMOCOUPLES IN THE PLASTIC-COVERED AREA.

| Thermocouple Number | Depth, ft bgs |
|---|---|
| t1 | 7 |
| t2 | 4 |
| t3 | 3.8 |
| t4 | 7 |
| t5 | 4 |
| t6 | 4.3 |
| t7 | 6.4 |
| t8 | 3.7 |
| t11 | 6.8 |
| t12 | 6 |
| t13 | 4 |
| t14 | 3.2 |
| t15 | 7 |
| t16 | 4 |
| t17 | 3.3 |
| t18 | 6 |
| t19 | 3.7 |
| t20 | 6.9 |
| t21 | 3.5 |

### a. Monitoring Point Temperature Results

The monitoring point temperature data set can be compared using MP-1, -2, -5, and -6, which were outside the plastic-covered area, and MP-3 and -4, which were within the plastic-covered area (Figure 9). In addition, data exists for the monitoring points both when the plastic cover was in place and after it had been removed. The labels on the thermocouples at MP-6M and -6D, and -4M and -4D appear to have been reversed, based on temperature plots of other monitoring points at similar depths and locations (Appendix 27), so these data were eliminated in the subsequent data analysis.

Figure 29 shows the mean temperatures at each depth for monitoring points inside and outside the covered area over the period of monitoring. Several conclusions are apparent from the plot of the data: (1) at a depth of 3 feet, the mean temperatures of the monitoring points inside the covered area were generally warmer than the mean temperatures of the monitoring points outside the covered area; (2) at a depth of 5.5 feet, the mean temperatures of the monitoring points inside the covered area were warmer than those outside during cold weather, but cooler during warm weather; (3) there is no apparent trend in the temperature differences at a depth of 8.0 feet; and (4) these trends for the shallow and medium monitoring points continued even after the plastic cover was removed. This last point suggests that the differences were not due to the presence of the cover.

To determine if the temperature differences due to the covered surface were significant, mean temperatures at monitoring points inside the covered area were plotted against temperatures outside the covered area, with data separated according to depth and whether the cover was present or removed (Figure 30). Data falling above a line with a slope of 1 and intercept 0 indicate that the temperature was warmer in the covered area; data falling below the line indicate that the temperature was cooler in the covered area. Figure 30 shows that the data are clustered around the line of no effect, both before and after the cover was removed.

To determine if the effectiveness of the cover was a function of depth, regressions were performed on mean temperatures inside versus outside the covered area for each of the three thermocouple depths. Interpretation of the regressions must take into account both the slope and intercepts of these regression lines. The slope is an indication of whether the temperature effect is a function of seasonal soil temperature, and the intercept indicates whether inside temperatures were warmer or cooler than outside temperatures.

Table 16 shows the statistics from the regressions. The results for the shallow depth with cover present indicate that the temperature was higher inside the covered area than outside by 0.84 $\pm$ 0.63°C over the full range of temperatures, because the regression slope was 1.00 $\pm$ 0.05. There was no difference in soil temperatures inside and outside the covered area after the cover was removed, because the intercept was statistically identical to 0, and the slope was identical to 1.0. These values indicate that there was a beneficial effect of the cover on increasing soil temperatures at a depth of 3 feet. Figure 31 shows these results graphically. With the cover absent, 95 percent CL lines overlapped 0; with the cover present, confidence lines did not overlap 0.

The results using the slope and intercept for the medium depth with cover present indicate the temperatures of the monitoring points inside and outside the covered area were equal at

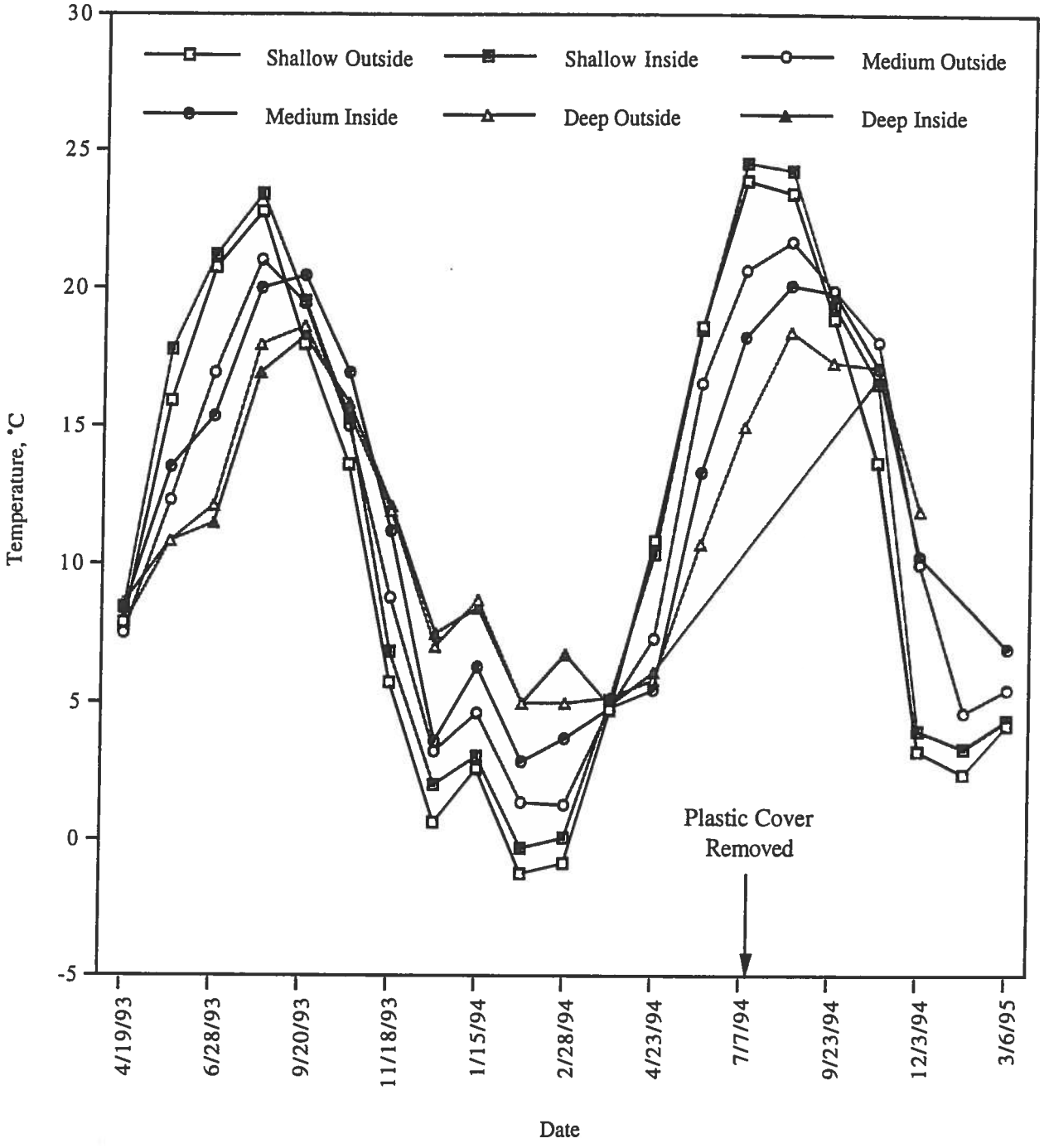


**Figure 29.** Mean Subsurface Temperatures for Monitoring Points at Each Depth Inside and Outside the Plastic-Covered Area in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

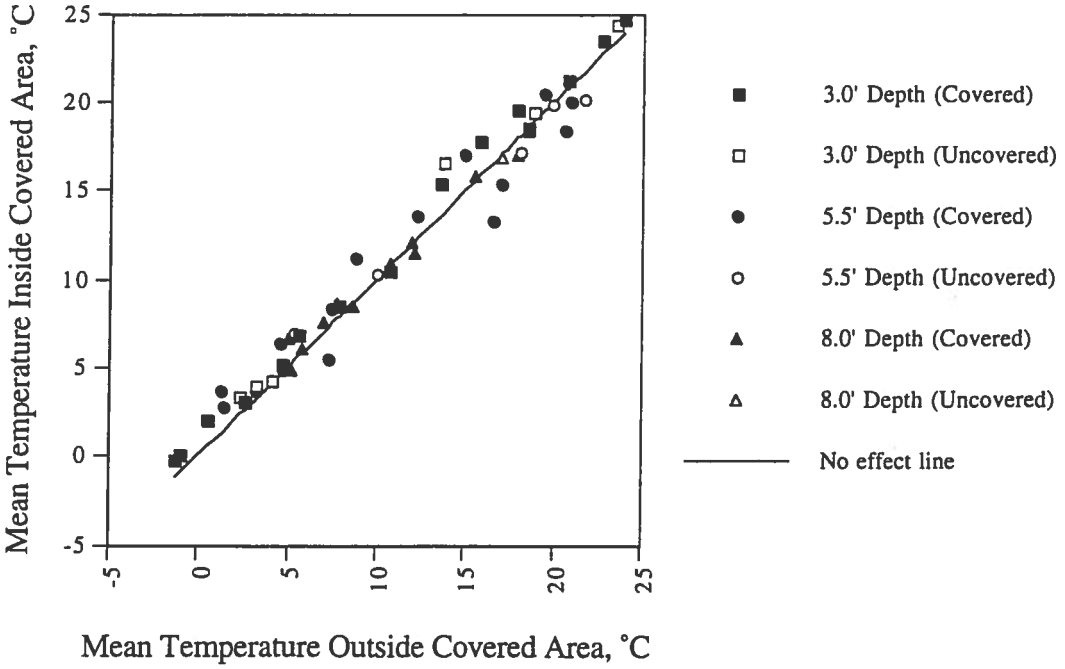


**Figure 30.** Mean Subsurface Temperature at MP-1 through MP-6 in the Plastic-Covered Area Before and After Cover Removal in the Bioventing Test Area in FPTA#1 at F.E. Warren AFB.

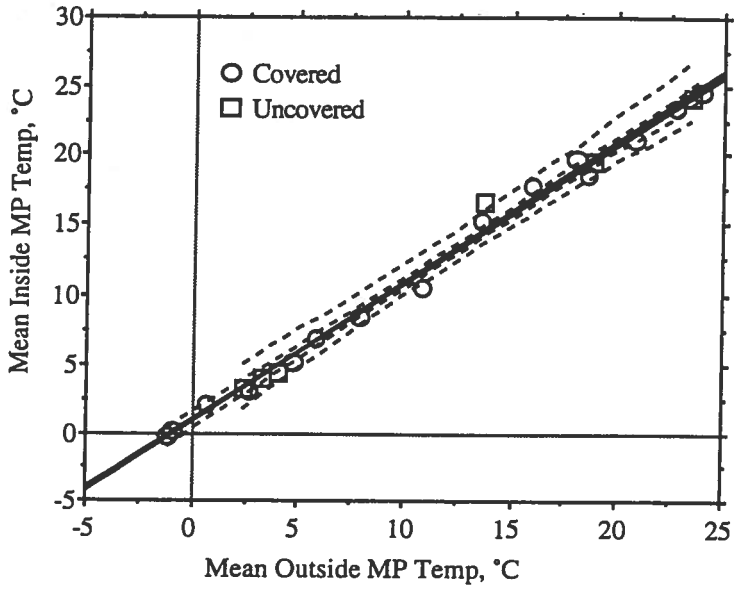


**Figure 31.** Solar Heating of Subsurface Soils due to the Plastic Cover as Measured at the Shallow Monitoring Points. Dashed Lines Represent 95 Percent CI of Mean.

13.7°C. At temperatures above 13.7°C (generally June through November), monitoring points inside were cooler than those outside the covered area, but were warmer at temperatures below 13.7°C. This same pattern occurred when the cover was removed with the isothermal point at 13.3°C. There was no significant difference between the cover present and absent, however, because both the slopes and confidence intervals overlapped as shown in Figure 32.

TABLE 16. RESULTS OF REGRESSIONS EXAMINING EFFECT OF PLASTIC COVER ON SUBSURFACE MONITORING POINT THERMOCOUPLE TEMPERATURES.

| Depth | Cover | Slope | 95% CI | p-value | Intercept | 95% CI | p-value | $r^2$ |
|---|---|---|---|---|---|---|---|---|
| Shallow | Present | 1.00 | 0.05 | <0.0001 | 0.84 | 0.63 | 0.0114 | 0.994 |
| Shallow | Absent | 1.02 | 0.15 | <0.0001 | 0.86 | 2.04 | 0.2921 | 0.989 |
| Medium | Present | 0.89 | 0.15 | <0.0001 | 1.51 | 1.75 | 0.0814 | 0.936 |
| Medium | Absent | 0.82 | 0.15 | <0.0001 | 2.39 | 2.52 | 0.0462 | 0.983 |
| Deep | Present | 0.93 | 0.076 | <0.0001 | 0.84 | 0.85 | 0.0497 | 0.985 |
| Deep | Absent | Insufficient data | | | | | | |

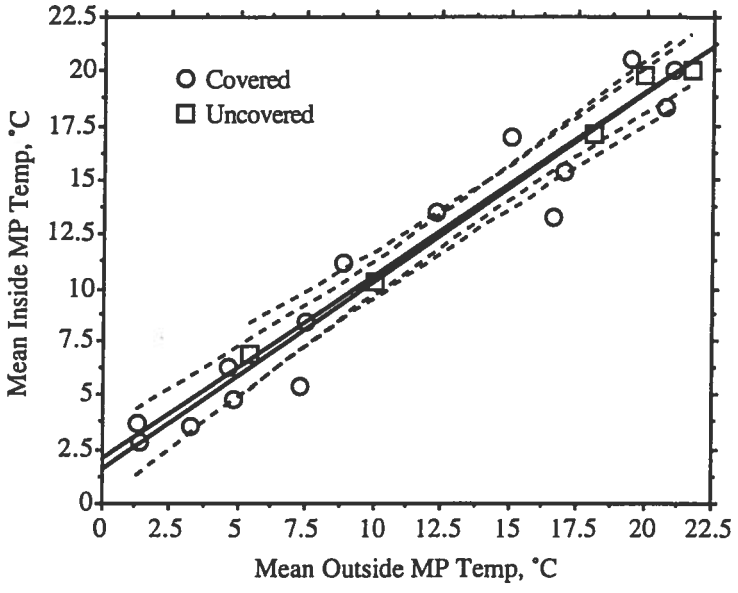


**Figure 32.** Solar Heating of Subsurface Soil due to the Plastic Cover as Measured at the Medium Depth Monitoring Points. Dashed Lines Represent the 95 Percent CI about the Mean.

The results for the deep monitoring points with the cover present indicate that there was no statistically significant difference between points inside and outside the covered area because the slope overlapped 1.0 and the intercept overlapped the origin. It was not possible to perform a regression on the deep temperature data after the cover was removed because there was only one temperature data point after eliminating data from the suspected mislabelled sampling probes. The results of the deep monitoring point analyses are shown in Figure 33.

These results agree with the conclusions drawn from Figure 28, except that the regression results indicate that the temperature differences at the shallow monitoring points were not significant when the cover was absent.

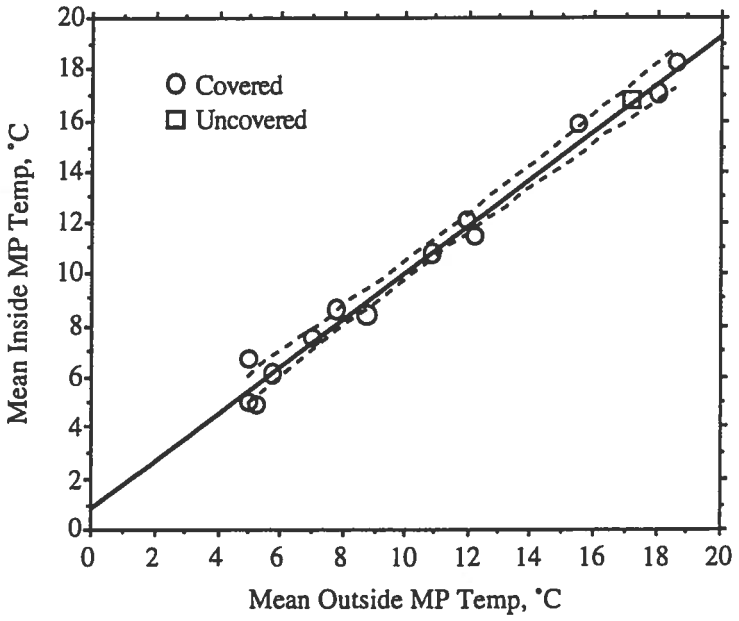


**Figure 33.** Solar Heating of Subsurface Soil due to the Plastic Cover as Measured at the Deep Monitoring Points. Dashed Lines Represent 95 Percent CI about the Mean.

### b. Monitoring Point and Soil Thermocouple Temperature Results

To combine both monitoring point and soil thermocouple temperature data in evaluating the effectiveness of the plastic cover, the influence of depth was examined because there were no thermocouples outside of the covered area at depths comparable to those of the soil thermocouples within the covered area. To determine if any effect was seasonal, the data were compared for each measurement event. Regressions of both inside and outside subsurface temperatures versus depth were first performed to determine if the temperature-depth relationships were linear. If both sets of data showed significant linear relationships (slope $p \leq 0.05$), plots of the regressions with 95 percent CIs of the mean were examined for overlapping CIs to determine if temperature differences did exist for thermocouples inside versus outside the covered area. If at least one of the regressions was not significant, a one-way ANOVA was performed on each set of temperature data (inside and outside the covered area) versus depth to determine if the temperature was independent of depth ($p > 0.05$). If this was true for both sets of data, a one-way ANOVA was performed on temperature data for all depths outside versus all depths inside the covered area to determine if temperature differences existed due to the presence of the cover. If only one of the data sets showed no difference in temperature with depth, each data set was examined more closely using a one-way ANOVA to determine what depths had statistically identical temperatures. Statistically identical temperature data from inside the covered area were then compared with statistically identical temperature data from outside the covered area, with only approximately equivalent depths compared (e.g., shallow depths would not be compared with deep depths; however, shallow and medium depth data would be compared with medium depth data).

The results of the statistical analyses are summarized in Table 17, and the regression plots and ANOVA output are provided in Appendix 28. The general trend that is apparent from examination of Table 17 is that, when the cover was present, temperatures inside the covered area were significantly warmer than temperatures outside the covered area at the depths monitored during colder months (September through March). This difference persisted to some extent, however, after the cover was removed. This apparent persistence of differences suggests that it was the location, and not the cover, that was responsible for the observed temperature differences between locations inside and outside the covered area.

TABLE 17. RESULTS OF STATISTICAL ANALYSES OF IMPACT OF PLASTIC COVER ON SUBSURFACE TEMPERATURES, COMBINED TEMPERATURE DATA SET.

| Measurement Date | Type of Analysis | Depth Comparison | | Results |
|---|---|---|---|---|
| | | Inside | Outside | |
| April 1993 | ANOVA | All | All | SD, inside warmer |
| Early June 1993 | Regression | --- | --- | SD < 5.5 ft, inside warmer |
| Late June 1993 | Regression | --- | --- | NSD |
| August 1993 | Regression | --- | --- | NSD |
| September 1993 | ANOVA | All | All | SD, inside warmer |
| October 1993 | ANOVA | S MP | S MP | SD, inside warmer |
| | ANOVA | All except S MP | M & D MP | SD, inside warmer |
| November 1993 | ANOVA | All | S MP | SD, inside warmer |
| | ANOVA | All | M MP | NSD |
| | ANOVA | All | D MP | NSD |
| December 1993 | Regression | --- | --- | SD, inside warmer |
| January 1994 | Regression | --- | --- | SD, inside warmer |
| Mid-February 1994 | Regression | --- | --- | SD, inside warmer |
| Late February 1994 | Regression | --- | --- | SD, inside warmer |
| March 1994 | ANOVA | All | All | SD, inside warmer |
| April 1994 | Regression | --- | --- | NSD |
| June 1994 | Regression | --- | --- | NSD |
| July 1994 | Regression | --- | --- | NSD |
| August 1994 | ANOVA | S MP & TC | All | SD, inside warmer |
| | ANOVA | M MP & D TC | All | NSD |
| September 1994 | ANOVA | All | S & M MP | NSD |
| | ANOVA | All | D MP | SD, inside warmer |
| October 1994 | ANOVA | All | All | SD, inside warmer |
| December 1994 | ANOVA | S & M MP | S MP | NSD |
| | ANOVA | S &M MP | M & D MP | SD, inside warmer |
| January 1995 | ANOVA | S MP & TC | S & M MP | SD, inside warmer |
| March 1995 | ANOVA | S MP | S & M MP | NSD |
| | ANOVA | S TC & M MP | S & M MP | SD, inside warmer |

S = Shallow; M = Medium; D = Deep; MP = Monitoring Point; TC = Soil Thermocouple
SD = Significant difference at the 95 percent CL.
NSD = No significant difference at the 95 percent CL.
Shaded area represents period with cover present.

### c. Discussion of Passive Solar Effectiveness

Analysis of the temperature data on a depth basis (monitoring point only analysis) revealed (1) that the plastic cover increased temperatures by 0.84°C during all seasons at a depth of 3.0 feet bgs; (2) deep monitoring points showed no effect of the cover; and (3) medium monitoring points showed moderated temperatures that were not due to the presence of the cover. Analysis of the combined monitoring point and soil thermocouple data showed a seasonal effect, with temperatures inside the covered area warmer than those outside at similar depths from September to March. This pattern continued to be observed after the cover was removed.

The observed temperature differences that persisted after removal of the cover may have been due to subsurface heterogeneities in soil properties such as soil moisture or bulk density that varied with location. Differences in soil moisture content were observed in initial and final soil samples, with samples from inside the covered area having higher mean soil moisture contents (12.6 percent) than samples from outside the covered area (5.8 percent) (data in Appendix 29). ANOVA results indicate that this difference was significant at a 95 percent CL (Appendix 29). A higher moisture content inside the covered area, resulting in a higher soil heat capacity, could explain the temperature moderation observed at medium-depth monitoring point thermocouples inside the plastic-covered area whether the cover was present or not. This effect of soil moisture appears to have taken precedence over any temperature differences due to subsurface heating from the plastic cover.

The limitations of the available data set must be considered when evaluating the impact of the plastic cover at this site. Ideally, (1) more data should have been gathered during later measurement events, (2) more thermocouples should have been installed outside the covered area, and (3) the thermocouple depths outside and inside the plastic-covered area should have been matched. Without these limitations, comparisons could have been made on a depth and time basis with adequate statistical power to distinguish differences resulting from the presence of the plastic cover.

## G. EFFECT OF PURE $O_2$ INJECTION

A pure oxygen system was installed in July 1994 to evaluate the effects of pure $O_2$ on subsurface respiration rates. Pure $O_2$ injection may be desirable because it can (1) achieve more effective oxygenation in fine-grained or high-water-content soils; (2) allow decreased flow rates to

reduce surface emissions of volatile contaminants; or (3) allow longer times between pulse cycles in pulsed injection systems.

Pure $O_2$ was injected through selected injection vent wells from July 1994 through March 1995. Mechanical problems occurred with the injection system, however, and the data acquired to evaluate the effectiveness of this system are limited. Results from laboratory experiments involving pure $O_2$ atmospheres were examined to shed further light on the effect of pure $O_2$ environments on resultant microbial respiration.

### 1. Effect on Respiration Rates

#### a. Field Results

Table 18 summarizes the monitoring dates and system status of the field injection of the pure $O_2$ injection system. The first pure $O_2$ injection vent well was at I13 (Figure 9). Monitoring of the pure $O_2$ injection system indicated that the system was operating consistently over the first 3 months following system operation; however, most monitoring point $O_2$ concentrations were below ambient, and high levels of $CO_2$ had accumulated at monitoring points adjacent to I13. The system was turned off prior to the October 1994 respiration test, and $O_2$ concentrations were well below ambient, with elevated $CO_2$ levels observed once again throughout most of the monitoring points surrounding I13.

F.E. Warren AFB personnel were contacted to monitor the pure $O_2$ injection system and restart it if necessary, prior to the next monitoring trip. The system was operating prior to the December 1994 monitoring event, with near-ambient $O_2$ concentrations at most points, and a respiration test was conducted at the monitoring points surrounding the pure $O_2$ injection vent well at this time. During the December 1994 respiration test the injection vent well was moved to MP-26 and I1. MP-26 was chosen to see if high concentrations of $CO_2$ could also be observed to accumulate at a background monitoring point. Injection at I1 was used to determine if $O_2$ concentrations could be increased in soil adjacent to MP-33, which had never had measurable $O_2$ concentrations at the maximum depth and was located in highly contaminated soil.

TABLE 18. SUMMARY OF MONITORING ACTIVITY AND SYSTEM STATUS FOR PURE $O_2$ INJECTION SYSTEM.

| Date | Activity | System Status | Results |
|---|---|---|---|
| 7/94 | Pure $O_2$ system installed at I13 | In prep | N/A |
| 8/94 | Monitoring trip | Operating | Most $O_2$ below ambient (highest = 23.6 percent), elevated $CO_2$ (>25 percent); increased flow from 0.3 to 0.4 cubic feet per minute (cfm) |
| 9/94 | Monitoring trip | Operating | Most $O_2$ below ambient (highest >25 percent), elevated $CO_2$ (>25 percent) |
| 10/94 | Respiration test | Off | Depressed $O_2$ (<15 percent), elevated $CO_2$ (>25 percent) |
| 12/94 | Respiration test, pure $O_2$ system moved to I1 and MP-26 | Operating | Near ambient $O_2$ (MP-13D = 44.5 percent), elevated $CO_2$ (≤15.5 percent) |
| 1/95 | Monitoring trip, pure $O_2$ system moved from MP-26 to MP-32, continued at I1 | Operating | Elevated $O_2$ at MP-s 25, 28, & 34 (highest = 50 percent), $CO_2$ ≤7.5 percent) |
| 3/95 | Respiration test | Off | No elevated $O_2$ except MP-32 |

The system was operating during the January 1995 monitoring event, and high $O_2$ concentrations (but not high $CO_2$ concentrations) were measured in the monitoring points surrounding both MP-26 and I1. At this time, the injection vent well was moved from MP-26 to MP-32, while injection was continued at I1. The system was off again, however, prior to the March 1995 monitoring event.

Because of the mechanical problems with the pure $O_2$ injection system, the principal field data concerning the effect of pure $O_2$ on respiration rates come from the four monitoring points surrounding I13. Comparison was made of zero-order respiration rates for these monitoring points determined from eight respiration tests, with the October and December 1994 rates considered to be influenced by the pure $O_2$ injection. Rates that either were not significant or were positive were not examined for effect, with the significant rates transformed to 12°C using procedures identical to those described in Section IV.F.1., "Temperature Effects" (spreadsheet results in Appendix 30). Temperature transformation was performed on respiration rates for MP-14S, -18M,

and -19M, although they were not included in the temperature transformation regression. Differences between pure $O_2$ and atmospheric $O_2$ rates were distinguished using nonoverlapping 95 percent CIs.

The results are summarized in Table 19, with plots showing 95 percent CI error bars shown in Appendix 30. Of the six monitoring probes examined, the pure $O_2$ rates for two probes (MP-14S and -18M) became nonsignificant through the rate-transformation procedure. A total of 18 of the 32 atmospheric $O_2$-influenced rates were statistically identical to rates measured during pure $O_2$ injection. Of the rates that were statistically different, six atmospheric $O_2$-influenced rates were lower than the pure $O_2$-influenced rates, whereas eight rates were higher than the pure $O_2$-influenced rates.

TABLE 19. SUMMARY OF SIGNIFICANT TEMPERATURE-CORRECTED RESPIRATION RATES USED TO EXAMINE THE INFLUENCE OF PURE $O_2$ INJECTION AT I13. (Page 1 of 2)

| Monitoring Probe | Respiration Test Date | Temperature-Corrected $O_2$ Uptake Rate, %/hr | Temperature Corrected 95% CI | Statistically Identical to Pure $O_2$ Rate? |
|---|---|---|---|---|
| 13D | 4/93 | -0.0563 | 0.0133 | no |
| | 8/93 | -0.0766 | 0.0348 | yes |
| | 11/93 | -0.0547 | 0.0066 | no |
| | 2/94 | -0.0334 | 0.0125 | no |
| | 7/94 | -0.0831 | 0.0495 | yes |
| | **12/94** | **-0.1124** | **0.0036** | --- |
| | 3/95 | -0.0267 | 0.0153 | no |
| 14S | 4/93 | -0.0091 | 0.0067 | no |
| | 8/93 | -0.0098 | 0.0109 | yes |
| | 11/93 | -0.0160 | 0.0096 | no |
| | 2/94 | -0.0159 | 0.0087 | no |
| | 7/94 | -0.0056 | 0.0078 | yes |
| | **10/94** | **-0.0047** | **0.0056** | --- |
| | 3/95 | -0.0132 | 0.0032 | no |

TABLE 19. SUMMARY OF SIGNIFICANT TEMPERATURE-CORRECTED RESPIRATION RATES USED TO EXAMINE THE INFLUENCE OF PURE $O_2$ INJECTION AT I13. (Page 2 of 2)

| Monitoring Probe | Respiration Test Date | Temperature-Corrected $O_2$ Uptake Rate, %/hr | Temperature Corrected 95% CI | Statistically Identical to Pure $O_2$ Rate? |
|---|---|---|---|---|
| 18M | 4/93 | -0.0301 | 0.0244 | no |
| | 8/93 | -0.0348 | 0.0578 | yes |
| | 11/93 | -0.0486 | 0.0068 | no |
| | 7/94 | -0.0415 | 0.0143 | no |
| | **10/94** | **-0.0230** | **0.0441** | --- |
| 19S | 4/93 | -0.0490 | 0.0151 | yes |
| | 8/93 | -0.0329 | 0.0318 | yes |
| | 11/93 | -0.0880 | 0.0185 | no |
| | 2/94 | -0.0395 | 0.0230 | yes |
| | 7/94 | -0.0294 | 0.0162 | yes |
| | **12/94** | **-0.0401** | **0.0273** | --- |
| | 3/95 | -0.0359 | 0.0187 | yes |
| 19M | 4/93 | -0.0531 | 0.0148 | yes |
| | 8/93 | -0.0521 | 0.0407 | yes |
| | 11/93 | -0.0772 | 0.0272 | yes |
| | 7/94 | -0.0519 | 0.0245 | yes |
| | **12/94** | **-0.0463** | **0.0403** | --- |
| | 3/95 | -0.0334 | 0.0165 | yes |
| 19D | 4/93 | -0.0595 | 0.0138 | no |
| | 8/93 | -0.0584 | 0.0246 | yes |
| | 2/94 | -0.0472 | 0.0272 | yes |
| | 7/94 | -0.0669 | 0.0171 | yes |
| | **12/94** | **-0.1124** | **0.0391** | --- |
| | 3/95 | -0.0404 | 0.0179 | no |

Bold numbers indicate $O_2$ uptake rates under the influence of pure $O_2$.

The single respiration rate determined at an $O_2$ concentration significantly higher than ambient (MP-13D, December 1994) was statistically higher than four of the atmospheric $O_2$-influenced rates at that monitoring probe, and was statistically identical to the remaining two rates.

### b. Laboratory Results

Laboratory batch studies were conducted using FPTA#1 soil, spiked with a 1:1 JP-4 jet fuel/diesel #2 mixture at 100-, 1,000-, and 10,000-$\mu$g/g dry weight soil, and maintained at 75 percent field capacity and 11°C. The batch studies were performed with atmospheric and pure $O_2$ headspace conditions at each of the three soil contaminant levels. Experimental microcosms were purged when atmospheric $O_2$ batches fell to approximately 5 volume percent $O_2$, and pure $O_2$ batches reached approximately 85 volume percent $O_2$ in the headspace. Table 20 shows the zero-order $O_2$ uptake rates and regression output from sequential purge events for each batch, with lag phase data not included in the first purge rate determinations (subsequent purges exhibited no lag phase). Because there were significant differences in some of the calculated rates (particularly between the 1,000-$\mu$g/g batches), and rates decreased with purge event, cumulative $O_2$ consumption was plotted for additional analyses (Figures 34 through 36; data in Appendix 31). These plots show $O_2$ consumption as a relatively smooth curve of decreasing slope after an extended lag phase. The 1,000- and 10,000-$\mu$g/g batches had lag phases that were approximately 100 hours longer in the pure $O_2$ batches than in the atmospheric batches. These data were offset to match the end of their lag phases. Upon doing this (Figures 35 and 36), the cumulative $O_2$ consumption plots show no apparent difference in $O_2$ consumption rate, particularly for the 1,000- and 10,000-$\mu$g/g batches between pure $O_2$ and atmospheric $O_2$ batches. The 100-$\mu$g/g batch results, shown with outliers removed (Figure 34), are less conclusive because the error in measuring high $O_2$ concentrations overwhelmed the low-$O_2$ consumption rate observed in these reactors.

To verify that addition of $O_2$ consumed over several purges to form cumulative plots is a valid analysis technique, data from a 1,000-$\mu$g/g pure $O_2$ batch maintained at 20°C without purging were plotted with the 1,000-$\mu$g/g pure $O_2$ batch maintained at 11°C with two purges (Figure 37; data in Appendix 31). The 20°C batch had a higher $O_2$ uptake rate than the 11°C batch, as a consequence of the temperature difference, and confirmed the general curved shape of $O_2$ uptake over time for these batches.

TABLE 20. ZERO-ORDER $O_2$ UPTAKE RATES FROM LABORATORY BATCH STUDIES USING FPTA#1 SOIL IN 1:1 JP-4 JET FUEL/DIESEL #2 CONTAMINANT MIXTURE.

| Treatment Concentration, μg/g dry soil | Atmospheric $O_2$ | | | | | Pure $O_2$ | | | | | Statistically Identical ? |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Purge Interval | $O_2$ Uptake Rate, %/hr | 95% CI | $r^2$ | p-value | Purge Interval | $O_2$ Uptake Rate, %/hr | 95% CI | $r^2$ | p-value | |
| 100 | 1st | −0.0117 | 0.00085 | 0.946 | <0.0001 | 1st | −0.00649 | 0.00227 | 0.252 | <0.0001 | No |
| 1,000 | 1st | −0.127 | 0.00817 | 0.983 | <0.0001 | 1st | −0.174 | 0.0747 | 0.729 | 0.0003 | Yes |
| | 2nd | −0.0376 | 0.00373 | 0.945 | <0.0001 | 2nd | −0.0925 | 0.0143 | 0.866 | <0.0001 | No |
| | | | | | | 3rd | −0.0352 | 0.00709 | 0.821 | <0.0001 | No |
| 10,000 | 1st | −0.192 | 0.0487 | 0.735 | <0.0001 | 1st | −0.210 | 0.126 | 0.215 | 0.0017 | Yes |
| | 2nd | −0.311 | 0.0348 | 0.912 | <0.0001 | 2nd | −0.250 | 0.0543 | 0.613 | <0.0001 | Yes |
| | 3rd | −0.157 | 0.0319 | 0.695 | <0.0001 | 3rd | −0.204 | 0.0406 | 0.705 | <0.0001 | Yes |
| | 4th | −0.0766 | 0.00474 | 0.952 | <0.0001 | 4th | −0.142 | 0.0329 | 0.784 | <0.0001 | No |

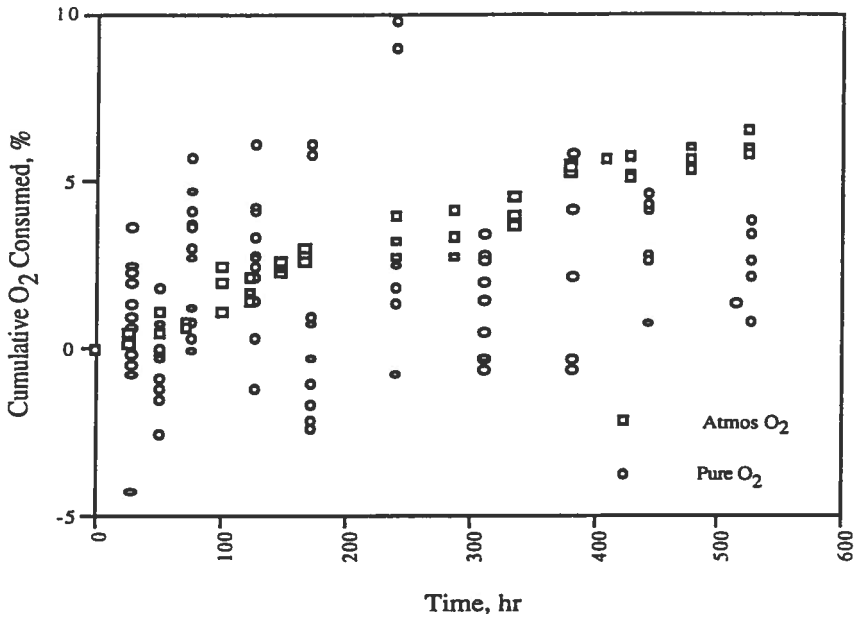


**Figure 34.** 100-$\mu$g/g TPH Batch Reactor Cumulative $O_2$ Uptake for Atmospheric and Pure $O_2$ Experiments over a Single Purge Event.

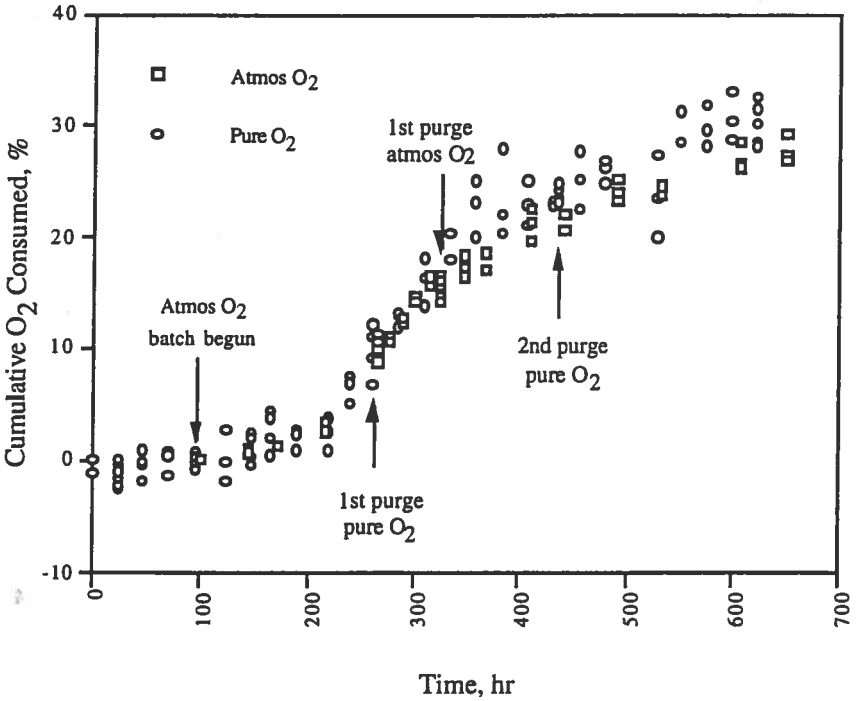


**Figure 35.** 1,000-$\mu$g/g TPH Batch Reactor Cumulative $O_2$ Uptake for Atmospheric and Pure $O_2$ Experiments over Several Purge Events.

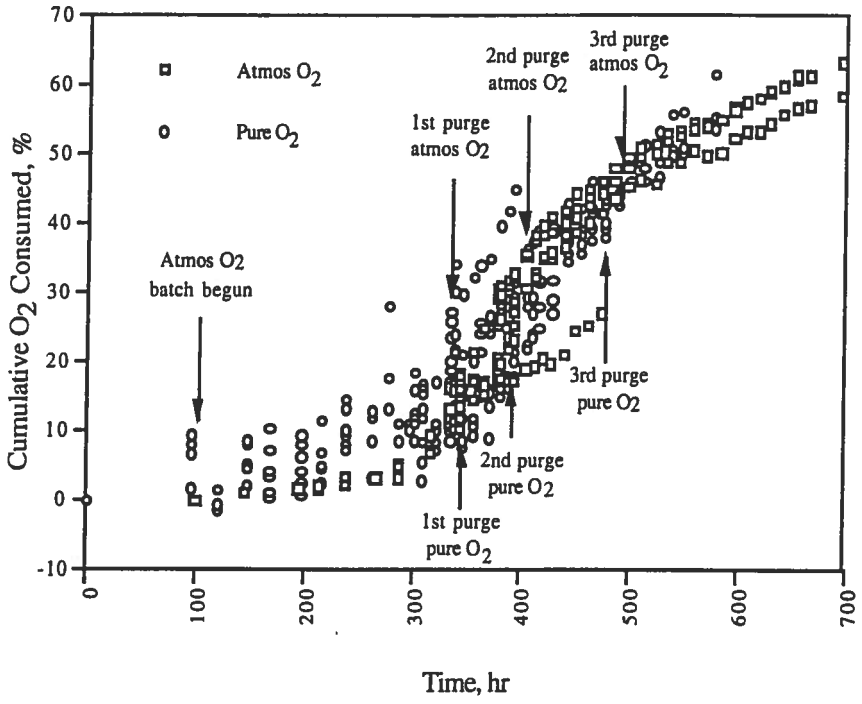


**Figure 36.** 10,000-μg/g TPH Batch Reactor Cumulative $O_2$ Uptake for Atmospheric and Pure $O_2$ Experiments over Several Purge Events.

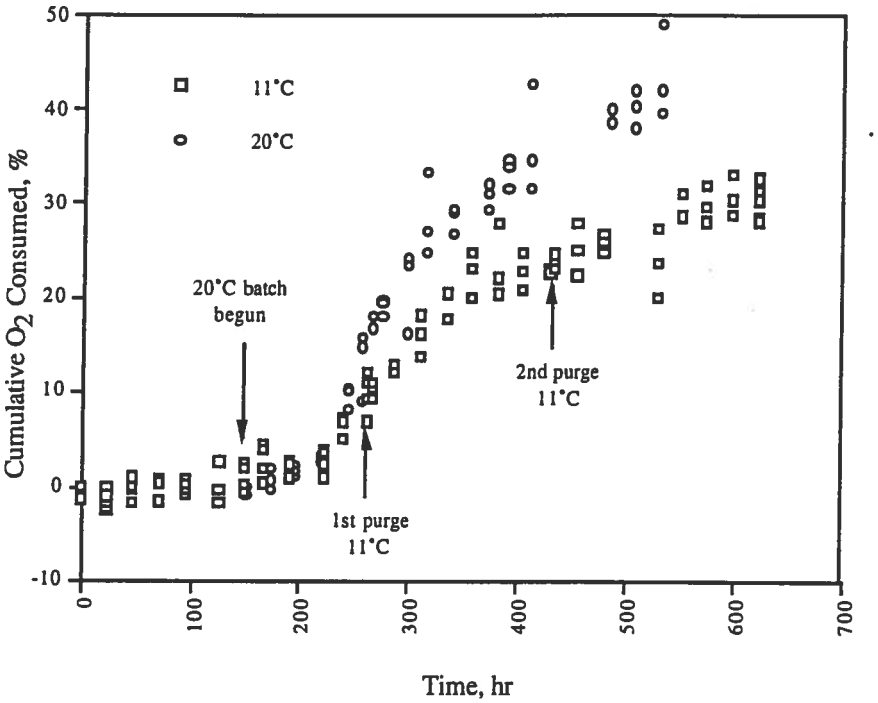


**Figure 37.** 1,000-μg/g TPH Batch Reactor Cumulative $O_2$ Uptake for 11°C and 20°C Pure $O_2$ Experiments.

These results suggest that the differences in the $O_2$ uptake rates determined for a single purge interval in the laboratory pure $O_2$ and atmospheric $O_2$ batches with identical contaminant concentrations could be due to the timing of the purge events and length of the purge interval. This was particularly evident in the 1,000-$\mu$g/g batch results, where the atmospheric $O_2$ and pure $O_2$ batch purge events did not occur at similar points in the cumulative $O_2$ consumption curves. A different length of purge interval would include a different portion of the cumulative $O_2$ uptake curve, resulting in a different set of data being used for respiration rate determinations. This could result in $O_2$ uptake rates which appear statistically different only because of the portion of the cumulative uptake curve used in their determination.

### 2. Effectiveness of Pure $O_2$ Injection

Because of the mechanical problems with the pure $O_2$ injection system, monitoring point $O_2$ concentrations did not significantly increase in many cases, and sometimes decreased substantially. Appendix 32 shows plots of $O_2$ and $CO_2$ concentrations over the period of operation at monitoring points adjacent to I13. These plots for MP-13, -14, -18, and -19 show the influence of pure $O_2$ injection at I13 from 7/94 to 12/94.

All of the monitoring points surrounding I13 show elevated $CO_2$ concentrations (20 percent and higher at MP-13, -18, and -19) with few $O_2$ concentrations above ambient. The reason for the dip in the $O_2$ concentrations in October 1994 is that the pure $O_2$ injection system was off upon arrival of field personnel. More effective delivery occurred between October and December when F.E. Warren AFB personnel were monitoring the injection system and ensuring that it was operating. Some $O_2$ depletion and $CO_2$ accumulation should be expected due to seasonal variations in respiration rates from temperature variation, as can be seen during summer months of 1993; however, the principal explanation for inadequate delivery of $O_2$ when the system was operating, particularly delivery to MP-18, is that the mass flow rate of $O_2$ was less from the pure $O_2$ injection than from the air injection. The pure $O_2$ injection system flow rate was measured at 0.3 scfm (0.29 acfm) in August 1994 and increased to 0.4 to 0.5 scfm (0.38 to 0.49 acfm) for the duration of the injection period. However, air injection rates, determined as the difference in flow rates in the manifold pipe between flow rate monitoring points, increased from 4 acfm in October 1993 to approximately 10.5 acfm prior to installation of the pure $O_2$ system (data in Appendix 16). Allowing for the approximately 4.2 times greater $O_2$ content of the pure $O_2$ system ($O_2$ concentration of 88 percent

measured December 1994) produces an air-equivalent flow rate of 1.6 to 2.1 acfm, 1.9 to 6.6 times less than during ambient air injection. MP-18 appeared to be the most impacted monitoring point from this lower $O_2$ delivery rate, because it had higher soil contaminant concentrations than adjacent monitoring points.

Pure $O_2$ injection occurred at MP-26 from 12/94 to 1/95 and at I1 from 12/94 to 3/95. Oxygen delivery was effective in reaching some of the surrounding monitoring points, with substantial increases in $O_2$ concentrations recorded at MP-25, -28, and -34 (Figures 38 through 40) during the January 1995 sampling trip, with slight increases at MP-21, -27, and -29 (data in Appendix 13). During the approximate month of pure $O_2$ injection, $O_2$ concentrations increased to as high as 50 percent (MP-28). Elevated $O_2$ concentrations were not observed at monitoring points surrounding I1 during the March 1995 sampling trip because the pure $O_2$ injection system was not operating.

Examination of the monitoring point and injection vent well locations (Figure 9), along with vacuum readings during soil gas collection (Appendix 13), helps explain the pure $O_2$ distribution results. Because injection at MP-26 was done through a monitoring point, the distance to the nearest

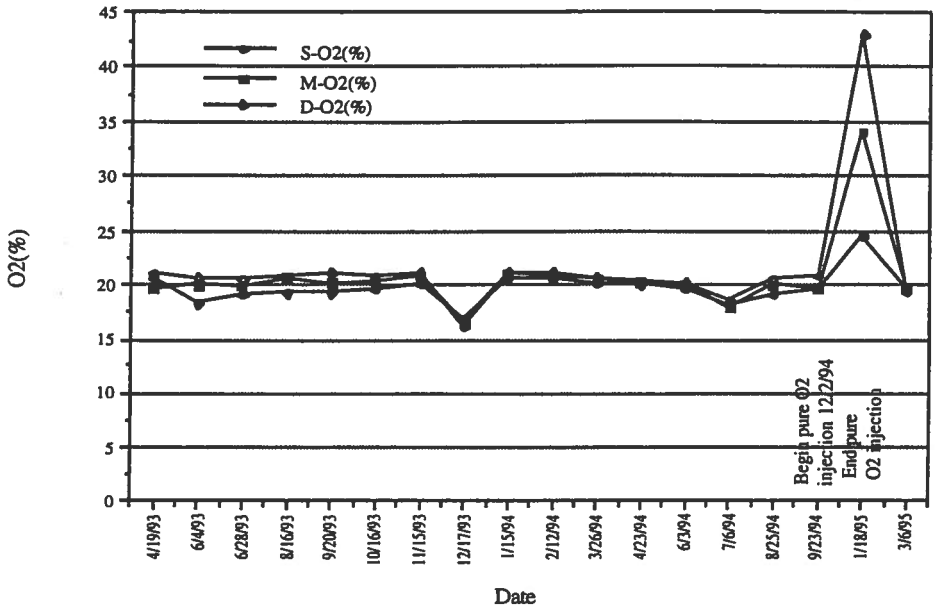


**Figure 38.** Measured $O_2$ Concentrations at MP-25 Showing the Effect of Pure $O_2$ Injection at MP-26.

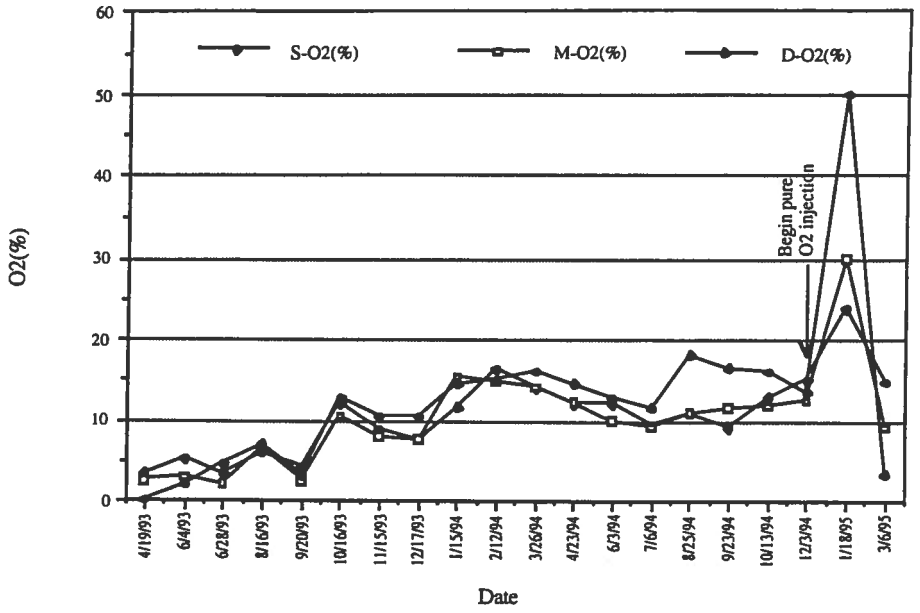


**Figure 39.** Measured $O_2$ Concentrations at MP-28 Showing the Effect of Pure $O_2$ Injection at I1.

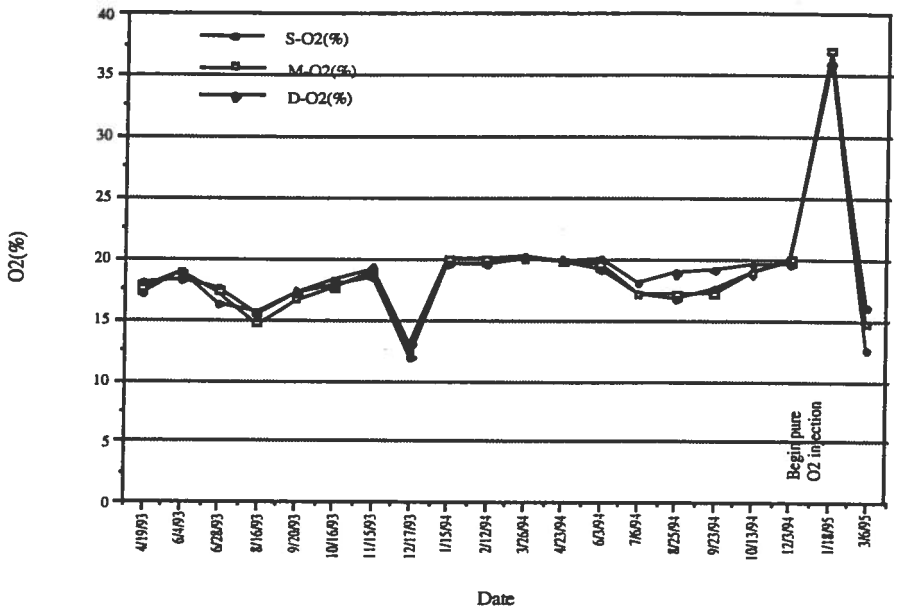


**Figure 40.** Measured $O_2$ Concentrations at MP-34 Showing the Effect of Pure $O_2$ Injection at I1.

monitoring points was farther than if injection had occurred through an injection vent well, as at I1. With $O_2$ consumption and diffusion to the surface, the $O_2$ concentration would decrease as the distance from the injection vent well increased, offering one reason why the monitoring points surrounding I1 showed a greater influence from pure $O_2$ injection than those surrounding MP-26.

The uneven distribution of pure $O_2$ influence surrounding the injection vent wells also could be due to the heterogeneous subsurface conditions. Vacuum readings measured during the soil gas sampling at MP-25M, -30M, -31M, -32S, and -32M surrounding MP-26 and I1 were consistently high (Appendix 13). The occurrence of several monitoring probes with high vacuum readings on the south side of the bioventing test area suggests that there could be subsurface lenses of low permeability due to fine-grained material or high water content in this area, preventing distribution of $O_2$ to these locations. Although not all of the monitoring probes in this area exhibited high vacuum readings, low-permeable lenses between the injection vent well and monitoring probes also could have prevented effective $O_2$ transfer.

The final pure $O_2$ injection vent well utilized was MP-32, a highly contaminated and $O_2$-depleted area. The pure $O_2$ injection system was not operating when personnel arrived at the site, and it subsequently was restarted. After operating for less than 2 minutes, the system once again shut down. Initial soil gas $O_2$ concentrations were high at all depths at MP-32 (up to 54.9 percent) following this 2-minute pure $O_2$ injection period and decreased over the 5-day respiration test (Appendix 17). This $O_2$ reduction was likely due to removal through sampling and diffusion, because elevated $CO_2$ levels did not accompany the observed declines in $O_2$ concentrations.

## H. EFFECT OF PULSED AIR INJECTION

Injection vent wells I16 and 17 (Figure 9) were changed from continuous to pulsed operation in July 1994. Appendix 33 shows plots of $O_2$ and $CO_2$ for the project duration for the adjacent MP-5, -6, -10, -11, -15, and -16. The concentrations measured were impacted by the timing of monitoring, because the system was frequently off when field personnel arrived. Data from August and October 1994, however, were collected while the blower was operating, and within 3 and 7 hours, respectively, of the end of the pulse cycle. Based on observations in March 1995, the blower operated for 48 hours during each pulse cycle, indicating the August and October measurements were made 94 and 85 percent through the operational cycle. These measurements would not represent

maximum $O_2$ concentrations, however, as flow from the injection vent well to the monitoring points would continue for some time after the blower shut off.

In general, $O_2$ and $CO_2$ concentrations were lower during pulsed operation than with continuous injection. For several monitoring points (MP-6, -15, and -16), there was relatively little impact, with $O_2$ concentrations generally at or above 15 percent and $CO_2$ concentrations less than 7.5 percent. The rest of the adjacent monitoring points (MP-5, -10, and -11), while not showing substantially greater impact due to pulsing, showed considerable $O_2$ depletion (completely depleted at MP-11D) and significant $CO_2$ accumulation (greater than 20 percent at MP-11D) during summer operation. Although neither pulsed nor continuous operation delivered adequate $O_2$ to MP-5 and -11 during the summer months, the pulsed system was slightly less effective in maintaining $O_2$ levels and would require either a higher flow rate or longer operating times in the pulse cycle during the summer months to meet observed oxygen consumption rates at these monitoring points.

# SECTION V
# CONCLUSIONS

Based on the results obtained from the large-scale bioventing system operated under a variety of flow rate and system configurations, the following conclusions can be reached:

1. There was a decrease of 4,468 pounds of TPH observed at the site over the 26-month operating period. There were total BTEX and naphthalene reductions of 28 percent and 18 percent, respectively. Benzene showed the most significant mass removal of the BTEX compounds, with 76 percent (49 pounds) mass removal during the study. There were no significant changes in the soil contaminant boiling point distribution for low-boiling-point compounds (< C-6 to C-12), but higher-boiling-point compounds (C-12 to > C-15) showed average reductions of 52 percent by the end of the study. Soil TPH removal of 14,842 pounds was estimated based on oxygen uptake rates measured within the site during the study.

2. No significant increases in hydrocarbon surface emission rates were measured under a variety of flow conditions, nor were differences in emission rates significant between background and contaminated soil locations. Air injection during operation of the bioventing system had no measurable impact on air quality at the F.E. Warren AFB site from uncontrolled soil emissions.

3. No significant hydrocarbon concentrations were measured in groundwater samples, with maximum TPH concentrations of less than 1 mg/L. Only one sample exceeded BTEX MCL concentrations.

4. Respiration rates typically were low (< 0.1 percent/hour), with higher rates during summer months and lower rates during the winter. After correcting these rates to 12°C for selected monitoring points, rates were either statistically the same or showed a slight decrease over the period of operation. The percentage of nonsignificant rates increased for the last two respiration tests, confirming the removal of contaminant mass throughout the site by the end of the study.

5. Thermocouple data from monitoring points in the plastic-covered area indicated that there was a statistically significant increase in temperature of 0.84°C due to the plastic cover at a depth of 3 ft bgs. This effect was not observed when the monitoring point and soil thermocouple temperature data were combined and analyzed at each sampling event. This analysis indicated that the temperatures were warmer inside the plastic-covered area during the colder months, but the increased temperatures were not due to the presence of the plastic cover. Because of higher background soil water contents in the area where the plastic cover was placed compared to the area immediately surrounding the covered area, the effect of the cover on subsurface soil temperatures was likely greatly moderated.

6. Mechanical problems with the pure $O_2$ injection system limited the quantity of data obtained to evaluate the impact of pure $O_2$ injection on in situ soil respiration rates. Examination of respiration rates at monitoring points adjacent to the first pure $O_2$ injection point, I13, indicated that there were no significant differences in rates under either air injection or the elevated $O_2$ concentrations achieved at this site. The effectiveness of pure $O_2$ injection in increasing subsurface $O_2$ concentrations was limited due to mechanical problems and subsurface heterogeneity, although soil gas oxygen concentrations as high as 50 percent were measured at some points in the site.

7. Pulsed air injection occurred for a period of 9 months and achieved oxygenation of subsurface soil comparable to continuous air injection at the adjacent monitoring points. Oxygen depletion occurred at several monitoring points under both injection strategies, however, particularly during the warmer temperatures of summer.

# SECTION VI
# RECOMMENDATIONS

Based on the findings of this study, the following recommendations can be made regarding the application of air injection bioventing systems at other Air Force sites.

1. Surface emission rates appear insignificant from even the shallow surface soil represented by the F.E. Warren AFB site investigated in this study. Concern for enhanced surface emission impacts to ambient air quality appears unwarranted, and continued monitoring of surface emissions appears unnecessary at most sites. The decision to carry out costly surface emission tests should be the exception, not the rule, at air injection bioventing sites. Site-specific characteristics, particularly close proximity to subsurface structures, should drive the decision to monitor gas migration away from the air injection system.

2. Contaminant removal using bioventing was successful at the F.E. Warren AFB site, despite the generally low hydrocarbon concentrations observed there. No indication of inhibition or toxicity associated with chlorinated solvents was evident from the field respiration data. It appears that bioventing should be pursued by the Air Force as a long-term approach for fire training pit site remediation.

3. Passive soil warming using the black plastic surface cover employed in this study was generally ineffective in significantly increasing overall contaminant removal rates over the course of the study. Alternative cover material should be considered, or a more active approach should be applied to take advantage of the increasing respiration rates observed with increasing soil temperatures.

4. Application of pure oxygen to the F.E. Warren AFB site was plagued by mechanical problems. Pure oxygen soil environments did not appear to affect soil respiration rates in either a positive or a negative way based on both laboratory and field respiration rate results. The cost and complexity of pure oxygen injection at bioventing sites must be a major consideration in its adoption, because based on Recommendation 1, above, the

major advantage of pure oxygen injection, i.e., the reduction in required gas flow and corresponding reduction in potential contaminant emission rates, may be of minor importance at most sites. The general application of pure oxygen injection at bioventing sites cannot be recommended based on the results of this study.

5. Pulsed air injection appeared to be less than optimized at the F.E. Warren AFB site based on depressed oxygen levels measured at some soil gas sampling points surrounding the pulsed air injection well. To take advantage of the pulsed air injection operating mode at a site, it appears that the sequencing of the air injection periods should be based on monitoring of soil gas oxygen response to air injection rather than on a fixed on/off cycle. Either feedback from an oxygen sensor at a location within the flow field or routine adjustments of the cycle based on ongoing manual soil gas monitoring should improve the overall efficiency of oxygen transfer of bioventing systems operated in a pulse venting mode.

## SECTION VII
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