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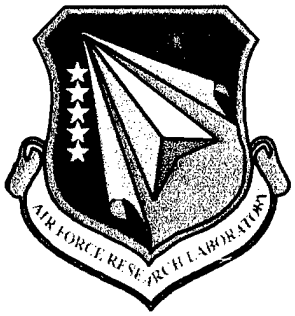


# DEMONSTRATION OF BIOVENTING FOR REMEDIATION OF CHLORINATED SOLVENT CONTAMINATION AT HILL AIR FORCE BASE OGDEN, UTAH

## VOLUME I

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This report describes the evaluation of the application of bioventing technology to non-petroleum hydrocarbon impacted soils. Bioventing has been thoroughly demonstrated to be a cost-effective remediation technology for a variety of petroleum hydrocarbons. This work included a laboratory column study and a field pilot-scale demonstration to evaluate the potential for applying bioventing to treat dichlorobenzenes in order to expand the list of contaminants impacting Air Force and other Department of Defense Installations beyond petroleum hydrocarbons. A pilot-scale bioventing system consisting of a single vent well and eight tri-level in situ soil gas monitoring points was installed at Hill Air Force Base, Utah. The system was designed to provide oxygen to an anoxic volume of soil and for monitoring the aeration effectiveness and conducting in situ respiration rates. Soil samples were collected at system installation and after approximately one year of system operation. Significant reductions in dichlorobenzene concentrations were observed over the one year demonstration, only a small portion of which could be accounted for by volatilization. In situ respiration tests indicated that significant biodegradation and supported the results observed in the field. The demonstration was supported by personnel in the Hill Air Force Base Environmental Management Office.

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## PREFACE

The work described in this report was performed by Battelle Memorial Institute of Columbus, Ohio, at Hill Air Force Base, Utah, for the Air Force Research Laboratory of Tyndall Air Force Base, Florida under contract number F08637-95-D-6004, Task 4B. The subject of the work is the evaluation of the use of bioventing technology to treat non-petroleum hydrocarbons.

# EXECUTIVE SUMMARY

## A. OBJECTIVE

The objective of this project was to design, install, operate, and monitor a pilot-scale bioventing system to evaluate the potential for using the technology to remediate non-petroleum hydrocarbon contaminants, primarily 1,2-dichlorobenzene (DCB).

## B. BACKGROUND

Bioventing is a remedial technology that has been proven successful for achieving in situ treatment of various types of hydrocarbon contamination at sites under varying geologic and climatic conditions. The effort described in this report focused on the use of bioventing to remediate soils contaminated with non-petroleum contaminants, primarily 1,2-DCB. The study was conducted in Chemical Disposal Pit (CDP) 1 at Operable Unit (OU) 1 at Hill Air Force Base (AFB), Utah. The base is located approximately 25 miles north of Salt Lake City and five miles south of Ogden. The project was performed for the Air Force Research Laboratory located at Tyndall AFB, Florida, by Battelle Memorial Institute of Columbus, Ohio.

## C. SCOPE

The demonstration included both field and laboratory components to achieve the project objective. Laboratory experiments were included as part of this treatability study to support any conclusions about the effect of biodegradation on any mass reductions of compounds of interest (COIs) observed in the field. These laboratory experiments allowed for more controlled tracking of the fate of the COIs, including volatilization and biodegradation removal mechanisms.

The field portion of this demonstration entailed installing separate bioventing systems into each of two plots. A fully operational bioventing system was designed and installed in the active plot, and a non-operational system was installed in the control plot. Because of the close proximity of both plots, five relief wells were placed between the two plots to hinder oxygenation in the control plot during air injection into the active plot.

This report includes descriptions of the bioventing system design, installation, operation, and monitoring procedures; laboratory monitoring and analytical methods; analytical results and data reduction procedures; and recommendations based on the results. The data from the analyses described in this report have been tabulated and graphed, and are included in a Data Package (Volume II) that complements this report. This report serves as an addendum to the Air Force's *Bioventing Principles and Practices Manual.*

## D. RESULTS

Based on respiration rates and stoichiometry, a total of 1,490 kg (3,400 lbs.) of organic degraded in one year of operation within the volume of soil that was monitored (10 to 20 ft bgs). Note that this value ignores removal in the upper soil layer, which was not represented by soil sampling. It should also be noted that the system delivered oxygen to a volume of soil greater than the volume that was monitored and that the presence of compound extended beyond the boundaries of the test cell. These facts suggest that bioventing probably supported degradation of more mass of compound than were estimated by these calculations.

The difference in mass between initial and final soil sampling indicated significant removal of 1,2-DCB. Soil sampling results indicated that dichlorobenzene compounds were removed at an average rate of 65.7% when analyzed individually, and 68% when quantified as a single compound by GC, over the one year of bioventing. It is noteworthy that tetrachloroethylene, which is volatile and known not to be aerobically biodegradable, either directly or by cometabolism, was removed at a rate almost one order of magnitude less than DCB.

The mass losses for the COIs that could be attributed to biodegradation were calculated as the difference between the total mass removed as measured through initial and final soil sample analyses and the mass volatilized from the system as determined through surface emission testing. Note that only the 12- and 17-ft bgs layers were included in the soil mass loss calculation because the soil-sampling interval was between 10 and 20-ft bgs; also, the fact that the surface emission test was conducted immediately following system startup when emission rates would be the highest. These factors suggest that these estimated biodegradation rate are conservative.

## VI. CONCLUSIONS

This study demonstrated that non-petroleum hydrocarbon organic compounds can be treated effectively using conventional bioventing technology. The focus in this demonstration was on 1,2-DCB, which was shown to be removed 74% over one year of operating a standard bioventing system. Other dichlorobenzene isomers were also effectively removed, with 1,3-DCB being removed at 42%, and 1,4-DCB being removed at 82%. Removal rates of the same order of magnitude were also demonstrated for many other compounds that were tracked.

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| AFB | Air Force Base |
| bgs | below ground surface |
| BNAE | base, neutral, and acid extractable |
| CAP | Corrective Action Plan |
| CDP | Chemical Disposal Pit |
| CFU | colony-forming unit |
| COI | compound of interest |
| DCB | dichlorobenzene |
| ECD | electron capture detection/detector |
| FID | flame ionization detection/detector |
| FS | Feasibility Study |
| FTA | Fire Training Area |
| GC | gas chromatograph/chromatography |
| hp | horsepower |
| HP | Hewlitt-Packard |
| I.D. | inside diameter |
| IDW | investigation-derived waste |
| IRP | Installation Restoration Program |
| IRPIMS | Installation Restoration Program Information Management System |
| LEL | lower explosive limit |
| LF | landfill |
| LNAPL | light, nonaqueous-phase liquid |
| lpm | liters per minute |
| MP | monitoring point |
| NA | not applicable |
| O.D. | outside diameter |
| OEMS | on-line environmental monitoring system |
| OU | Operable Unit |
| OUR | oxygen utilization rate |
| PAH | polycyclic aromatic hydrocarbon |
| PCE | tetrachloroethylene |
| PEL | permissible exposure limit |
| ppmv | parts per million by volume |
| psi(g) | pounds per square inch (gage) |
| RI | Remedial Investigation |

| | |
|---|---|
| scf(h)/(m) | standard cubic feet (per hour/minute) |
| SS | stainless steel |
| TCD | thermal conductivity detector |
| TCE | trichloroethylene |
| TLV | threshold limit value |
| TPH | total petroleum hydrocarbons |
| TWA | time-weighted average |
| VOC | volatile organic compound |
| WOST | waste oil storage tank |
| WPOP | waste phenol/oil pit |

# SECTION I
# INTRODUCTION

## A. BACKGROUND

Bioventing is a remedial technology that has been proven successful for achieving in situ treatment of various types of hydrocarbon contamination at sites under varying geologic and climatic conditions. Bioventing has been employed at numerous sites as a cost-effective treatment for contamination removal and eventual site closure. The contaminants at these sites typically are petroleum hydrocarbons such as gasoline, diesel fuel, JP-4 and JP-5 aviation fuels, and complex mixtures from fire protection training exercises. Few attempts have been made to bioremediate soils with kinds of hydrocarbon contamination other than petroleum hydrocarbons, but research emphasis recently has changed to focus on the effectiveness of bioventing for treating non-fuel hydrocarbons that can be directly metabolized. These non-fuel hydrocarbons include chlorobenzenes, acetone, and polycyclic aromatic hydrocarbons (PAHs), as well as compounds that can be degraded cometabolically such as trichloroethylene (TCE) and other chlorinated solvents.

The effort described in this report focused on the use of bioventing to remediate soils contaminated with non-petroleum contaminants, primarily 1,2-dichlorobenzene (DCB). The study was conducted in Chemical Disposal Pit (CDP) 1 at Operable Unit (OU) 1 at Hill Air Force Base (AFB), Utah. The base is located approximately 25 miles north of Salt Lake City and five miles south of Ogden. The project was performed for the Air Force Research Laboratory located at Tyndall AFB, Florida, by Battelle Memorial Institute of Columbus, Ohio.

A preliminary site characterization was conducted in the area of CDP 1 to determine whether (1) DCB concentrations were high enough to allow effective monitoring of its disappearance during bioventing; (2) the site was oxygen-limited; and (3) the limiting conditions were attributable to biological activity. Previous investigations in CDP 1 had shown that the soil was sufficiently permeable to allow vapor flow in the vadose zone soils (Montgomery, 1995).

Site characterization activities included conducting a soil gas survey and collecting soil and soil-gas samples for analysis to determine the concentrations of particular compounds of interest (COIs), which are listed in Table 1. The oxygen and carbon dioxide data from the soil gas survey showed that the area contained very low levels of oxygen (< 5%) and elevated levels of carbon dioxide. The results from soil-gas sample analyses are listed in Table 2. The soil-gas analysis data indicated the presence of 1,2-DCB in low concentrations, with an upper value of 11 parts per million by volume (ppmv) and an average of 2.5 ppmv; these results were expected because the vapor pressure of 1,2-DCB is 1.2 mm Hg at 25°C.

Concentrations of 1,3- and 1,4-DCB in soil-gas were also low, reflecting their low vapor pressures. Trichloroethylene, cis-1,2-dichloroethylene, and 1,1,1-trichloroethane were found to be the predominant contaminants present in the soil-gas, having average concentrations of 12.9, 299.1, and 18.8 ppmv, respectively.

The results from soil analyses are listed in Table 3. The soil analysis data indicated the presence of 1,2-DCB at an average concentration of 29.3 mg/kg, which is a concentration sufficiently high for a comprehensive bioventing study. The soil data also indicated that 1,2-DCB was the predominant contaminant in the soil, a characteristic that was desirable for the site selection process for this demonstration. The soil concentrations of the other COIs were also high enough to allow tracking their fate during treatment. Based on the results from these preliminary tests, it was determined that CDP 1 was a suitable site for a bioventing demonstration, and the demonstration proceeded.

**Table 1. List of Target Compounds for the Hill AFB Non-Petroleum Bioventing Study at CDP 1**

| Compound | Formula |
|---|---|
| *cis*-1,2-dichloroethylene | $C_2H_2Cl_2$ |
| 1,1,1-trichloroethane | $C_2H_3Cl_3$ |
| Trichloroethylene | $C_2HCl_3$ |
| Toluene | $C_7H_8$ |
| Tetrachloroethylene | $C_2Cl_4$ |
| Chlorobenzene | $C_6H_5Cl$ |
| Ethylbenzene | $C_8H_{10}$ |
| *m,p*-Xylene | $C_8H_{10}$ |
| *o*-Xylene | $C_8H_{10}$ |
| 1,3,5-trimethylbenzene | $C_9H_{12}$ |
| 1,2,4-trimethylbenzene | $C_9H_{12}$ |
| 1,2-dichlorobenzene | $C_6H_4Cl_2$ |
| 1,3-dichlorobenzene | $C_6H_4Cl_2$ |
| 1,4-dichlorobenzene | $C_6H_4Cl_2$ |
| 1,2,4-trichlorobenzene | $C_6H_3Cl_3$ |
| 1,2,3-trichlorobenzene | $C_6H_3Cl_3$ |
| Naphthalene | $C_{10}H_8$ |

**Table 2. Analytical Results from the Soil-Gas Samples Collected from CDP 1 at Hill AFB During Site Characterization Activities, March 1997**

| Compound | Concentration (ppmv) | | |
|---|---|---|---|
| | Minimum | Maximum | Average |
| *cis*-1,2-dichloroethene | 0.006 | 1,200 | 299.1 |
| 1,1,1-trichloroethane | 0.001 | 81 | 18.8 |
| Trichloroethylene | 0.001 | 220 | 13.9 |
| Tetrachloroethylene | 0.001 | 37 | 2.8 |
| Toluene | 0.001 | 28 | 4.8 |
| Chlorobenzene | 0.001 | 2 | 0.6 |
| Ethylbenzene | 0.001 | 2.3 | 0.7 |
| *m,p*-Xylenes | 0.001 | 9.2 | 1.4 |
| *o*-Xylenes | 0.001 | 3.3 | 1.0 |
| 1,3,5-trimethylbenzene | 0.001 | 2 | 0.7 |
| 1,2,4-trimethylbenzene | 0.001 | 2 | 0.7 |
| 1,2-dichlorobenzene | 0.001 | 11 | 2.5 |
| 1,3-dichlorobenzene | 0.001 | 2 | 0.6 |
| 1,4-dichlorobenzene | 0.001 | 2 | 0.7 |
| 1,2,4-trichlorobenzene | 0.001 | 2 | 0.6 |
| 1,2,3-trichlorobenzene | NT | NT | NT |
| *p*-Cymene | NT | NT | NT |
| Naphthalene | NT | NT | NT |
| Total petroleum hydrocarbons (TPH) | NT | NT | NT |

NT = Not Tested

**Table 3. Analytical Results from Soil Samples Collected from CDP 1 at Hill AFB During Site Characterization Activities, March 1997**

| Compound | Concentration (µg/kg) | | |
|---|---|---|---|
| | Minimum | Maximum | Average |
| *cis*-1,2-dichloroethene | 2.5 | 2,750 | 700 |
| 1,1,1-trichloroethane | 2.5 | 5,600 | 823 |
| Trichloroethylene | 2.5 | 2,750 | 722 |
| Tetrachloroethylene | 2.5 | 2,750 | 712 |
| Toluene | 2.5 | 18,000 | 2,701 |
| Chlorobenzene | 2.5 | 2,750 | 700 |
| Ethylbenzene | 2.5 | 6,200 | 987 |
| *m,p*-Xylenes | 5 | 34,000 | 4,818 |
| *o*-Xylenes | 2.5 | 14,000 | 2,233 |
| 1,3,5-trimethylbenzene | 2.5 | 3,000 | 746 |
| 1,2,4-trimethylbenzene | 2.5 | 58,000 | 8,442 |
| 1,2-dichlorobenzene | 2.5 | 140,000 | 29,263 |
| 1,3-dichlorobenzene | 2.5 | 2,750 | 856 |
| 1,4-dichlorobenzene | 2.5 | 17,000 | 4,891 |
| 1,2,4-trichlorobenzene | 2.5 | 14,000 | 3,557 |
| 1,2,3-trichlorobenzene | 2.5 | 22,000 | 1,563 |
| *p*-Cymene | 2.5 | 9,300 | 1,683 |
| Naphthalene | 2.5 | 24,000 | 4,047 |
| TPH (mg/kg) | 7 | 36,300 | 9,781 |

## B. OBJECTIVES AND SCOPE

The objective of this project was to design, install, operate, and monitor a pilot-scale bioventing system to evaluate the potential for using the technology to remediate non-petroleum hydrocarbon contaminants, primarily 1,2-DCB. The compounds (including 1,2-DCB) that were tracked during this demonstration are listed in Table 1.

The demonstration included both field and laboratory components to achieve the project objective. Laboratory experiments were included as part of this treatability study to support any conclusions about the effect of biodegradation on any mass reductions of COIs observed in the field. These laboratory experiments allowed for more controlled tracking of the fate of the COIs, including volatilization and biodegradation removal mechanisms.

This report includes descriptions of the bioventing system design, installation, operation, and monitoring procedures; laboratory monitoring and analytical methods; analytical results and data reduction procedures; and recommendations based on the results. The data from the analyses described in this report have been tabulated and graphed, and are included in a Data Package that complements this report. This report serves as an addendum to the Air Force's *Bioventing Principles and Practices Manual* (Battelle, 1995).

## C. SITE SELECTION

Personnel from the Airbase and Environmental Technology Division of the Air Force Research Laboratory (AFRL) conducted a comprehensive search of the Air Force's Installation Restoration Program Information Management System (IPRIMS) database to identify candidate sites for demonstrating non-petroleum hydrocarbon bioventing. During the site selection process, site data were solicited from Air Force Bases that previously had been identified as being contaminated with non-petroleum hydrocarbon compounds and where some level of site characterization already had been performed. The data were reviewed and the list of candidate sites was narrowed based on a set of criteria that included the following:

- Water table depth adequate for significant vadose zone thickness
- Soil permeability adequate to exchange air in vadose zone once in 2 days with typical regenerative bioventing blower
- Minimal soil heterogeneity
- Administrative environment at the installation that would support a study of this type
- Year-round, 24 hour per day access to the site is not problematic
- Installation support for disposal of investigation-derived waste (IDW), site clearances, base access, and supply of utilities (power, phone).

CDP 1 was ultimately selected for this project because the site met the most criteria and provided the most beneficial environment for study of all the sites reviewed. One slight drawback of CDP 1 is that the non-petroleum hydrocarbon of primary interest (1,2-DCB) was present at the site only in a mixture of other compounds and petroleum hydrocarbons. But data from the site selection process indicate that it is more common for non-petroleum hydrocarbons to impact a site as a part of a mixture than it is for them to occur in pure form.

## D. SITE HISTORY

Hill AFB is situated within the Lake Bonneville Basin, which is characterized by alternating, isolated, north-trending, block-faulted mountains and intermontane basins flanked by alluvial slopes. CDP 1 is part of OU 1, which is located close to the northeastern boundary of Hill AFB, approximately 300 feet above the Weber River on the edge of a steep hillside that forms the southern boundary of the Weber River Valley (Montgomery, 1995).

The near-surface geology of OU 1 is characterized by approximately 40 feet of interfingered sand, gravely sand, and gravel underlain by approximately 200 feet of silty clay containing interbeds of silt and very fine to fine sand (Montgomery, 1995). The northern boundary of OU 1 is a steep escarpment formed through the erosion of poorly consolidated sediments by the Weber River.

OU 1 is comprised of the following sites: Landfills (LFs) 3 and 4, CDPs 1 and 2, Fire Training Areas (FTAs) 1 and 2, the Waste Oil Storage Tank (WOST), the Waste Phenol/Oil Pit (WPOP), and a golf course. High concentrations of volatile organic compounds (VOCs) and base, neutral, and acid extractables (BNAEs) were detected in soil samples taken from CDPs 1 and 2 and FTA 1. The predominant contaminant transport pathway of these compounds is from the CDPs, LF 3, and FTA 1 through the unsaturated zone and into the light, nonaqueous-phase liquid (LNAPL) layer that exists on the water table and extends from the CDPs, FTA 1, and the eastern part of LF 3. The most frequent detections and highest concentrations of contaminants have been found downgradient of the CDPs. Based on these results and others obtained through Remedial Investigation/Feasibility Studies (RI/FSs), the predominant source areas at OU 1 for most contaminants are CDPs 1 and 2, LF 3, and FTA 1.

This study was performed in CDP 1, which was used as a disposal area for liquid industrial wastes from the early 1950s to 1973 (Montgomery, 1995). In 1981, Hill AFB initiated a base-wide Installation Restoration Program (IRP). Comprehensive RI/FSs were performed in 1991, 1993, and 1994, with the later study being completed in 1995. The investigations were performed to characterize the contaminants present, the extent of the contamination, and provide data that would support a Corrective Action Plan (CA) at OU 1.

Results from previous investigations revealed that the soils at CDP 1 were contaminated with VOCs including 1,2-DCB. Results from analyses of soil samples taken from throughout the area showed 1,2-DCB present at concentrations as high as 170 mg/kg. 1,2-DCB is a clear flammable liquid with a pleasant aromatic smell. Routes of entry include inhalation, ingestion, absorption, eye contact, and skin contact. Table 4 lists the physical/chemical properties for 1,2-DCB. It has been used by industry for a wide variety of purposes including the following (Montgomery and Welkom, 1990):

- Industrial solvent for a wide variety of organic compounds and for oxides of nonferrous metals
- A solvent carrier for products of toluene diisocyanate
- An intermediate for dye production
- A fumigant and insecticide
- Hide degreaser
- In metal polishes
- Industrial air control
- Disinfectant
- Heat transfer medium.

**Table 4. Physical and Chemical Properties of 1,2-Dichlorobenzene**

| Characteristic | Value |
|---|---|
| Chemical formula | $C_6H_4Cl_2$ |
| Molecular weight | 146.20 |
| Carbon content (%) | 49.0 |
| Hydrogen content (%) | 2.7 |
| Chloride content (%) | 48.3 |
| Density ($g/cm^3$) | 1.30 |
| TLV/TWA (ppmv) | 50 |
| PEL (ppmv) | 50 |
| Lower explosive limit (LEL) | 2.2% |
| Vapor pressure (mm Hg at 208 C) | 1.2 |

TLV/TWA = Threshold limit value/time-weighted average.
PEL = Permissible exposure limit.

Dichlorobenzene is known to undergo transformation under both aerobic and anaerobic conditions (Spain, 1997). Under anaerobic conditions, one of the chlorines is removed and replaced with a hydrogen atom. The result is the transformation of DCB into chlorobenzene. Anaerobic dehalogenation of chlorobenzene has been speculated but has not been demonstrated (Spain, 1997). Aerobic degradation of chlorobenzenes is well studied and degradation pathways have been determined: a DCB molecule undergoes dihydroxylation to form a *cis*-dihydrodiol, that in turn undergoes dehydrogenation to form a catechol, which finally undergoes ring opening (Reineke and Knackmuss, 1984; de Bont et al., 1986)

While aerobic degradation of chlorobenzenes has been documented, several studies have shown that bacteria with the capability of carrying out chlorobenzene degradation are not ubiquitous in nature (Nishino et al., 1994; Spain, 1997; van der Meer et al., 1998). Bacteria with the capability of degrading chlorobenzenes have been isolated from soils that have had a history of chlorobenzene exposure, but not from soils within the same vicinity that were not exposed to the contaminant. Bacteria isolated from a contaminated site at Kelly Air Force Base in Texas appeared to have acquired chlorobenzene-degrading capabilities through horizontal gene transfer and genetic recombination involving two separate gene clusters (van der Meer et al., 1998). One cluster carries the genes that encode production of an aromatic dioxygenase and the other appears to carry the genes that regulate the production of dihydrodiol dehydrogenase.

Dichlorobenzenes contaminating CDP 1 have been there for many years. The success of the bioventing demonstration described in this report depended on whether or not the bacteria were able to acquire dichlorobenzene-degrading genes required for production of the required enzymes over the time that the site was contaminated.

## SECTION II
## PRELIMINARY INVESTIGATIONS

Before proceeding with bioventing at CPD 1, a soil gas survey was conducted and a round of soil samples was collected as preliminary measures to ensure that the site was amenable to the planned bioventing demonstration. Soil gas was collected and analyzed to determine whether the oxygen in the vadose zone was depleted to the point where aerobic biological activity was affected, a crucial consideration for the success of aerobic bioventing. Soil samples were collected and analyzed to determine whether compounds of interest were still present at the levels indicated by previous site investigations. The following sections provide more detail on the methods followed for these preliminary investigations along with a summary of the analytical results.

### A. SOIL GAS SURVEY

The preliminary soil gas survey was conducted in CDP 1 in March 1997. A sampling grid was staked out over the area of interest within the surface of CDP 1. A previous investigation indicated that the area was contaminated with elevated levels of 1,2-DCB. Soil gas samples were collected in Tedlar™ bags for field analysis of oxygen, carbon dioxide, and total petroleum hydrocarbons (TPH). (While DCB is not a petroleum hydrocarbon, it does elicit a response on the field TPH meter.) The soil gas samples were collected using a GeoProbe® system from depths up to 20 feet below ground surface (bgs) across the grid area. The probe was advanced to the desired sampling depth and the gas withdrawn under vacuum directly into a Tedlar™ bag. The withdrawn gas was analyzed for $O_2$ and $CO_2$ using a Gas Tech Model 3252OX analyzer and for TPH using a TraceTechtor™ hydrocarbon analyzer calibrated against hexane. The results showed that the site was oxygen limited, with $O_2$ concentrations ranging between 0 and 3.5%. Elevated carbon dioxide levels ranging between 6.5 and 16% were observed, indicating that the depressed $O_2$ levels were a result of biological activity.

Additional soil-gas samples were collected in Summa™ canisters from various points around the grid area. These samples were sent to an analytical laboratory (Lancaster Laboratories, Lancaster, PA) for contaminant analysis using EPA Method TO-14. The results from these analyses verified the presence of the contaminants listed in Table 1. The summarized analytical results can be found in the Final Work Plan for Bioventing of Non-Petroleum Hydrocarbon Contamination at Hill Air Force Base, Utah (Battelle, 1997).

### B. SOIL SAMPLING

A preliminary set of soil samples was collected immediately following the preliminary soil gas survey and sent to an analytical laboratory for contaminant analysis. EPA SW-846 Method 8260 was used to quantify the 18 individual compounds and EPA Method 418.1 was used to measure TPH. The results indicated that all 18 compounds were present throughout the site, with higher concentrations of the compounds found between 15 and 20 feet bgs. 1,2-DCB concentrations ranged from 2.4 to 140 mg/kg, with an average concentration of 29.3 mg/kg. Levels of 1,2-DCB at the site were similar to those previously reported, and it was determined that DCB concentrations were sufficient to conduct the bioventing study described in this report.

The remaining COIs were detected at concentrations that were sufficiently high to allow monitoring of their fate during bioventing. Because many of these compounds are volatile and can be displaced from soils during air injection, a laboratory study was conducted under controlled conditions using undisturbed soil cores from CDP 1 to verify the biodegradation potential of the soils.

## SECTION III
## SYSTEM DESIGN, INSTALLATION, AND OPERATION

The objective of this demonstration was to evaluate the effectiveness of bioventing for remediating non-petroleum hydrocarbon contaminants, primarily dichlorobenzene. The bioventing demonstration took place in an area of CDP 1 that previous site investigations identified as being contaminated with DCB. In order to achieve the objective, the demonstration was designed to compare the reduction in the mass of DCB between an actively vented plot, and a non-vented control plot.

## A. SYSTEM LAYOUT, DESIGN AND INSTALLATION

The demonstration entailed installing separate bioventing systems into each of two plots. A fully operational bioventing system was designed and installed in the active plot, and a non-operational system was installed in the control plot. Because of the close proximity of both plots, five relief wells were placed between the two plots to hinder oxygenation in the control plot during air injection into the active plot.

Soil samples were collected from each plot during system installation for contaminant analysis. One of the plots was actively vented and one of the plots remained untreated. Microbial activity was monitored through respiration measurements. Oxygen concentrations in the control plot were also monitored. After approximately 1 year of system operation, a final set of soil samples was collected for contaminant analysis. The following sections describe the bioventing system in greater detail.

### 1. System Layout

The bioventing system layouts in the actively vented and non-vented control plots are shown in Figure 1. The system in the actively vented plot consisted of eight soil-gas-monitoring points placed along two crossed axes at right angles to each other and one vent well centered at the cross point. The layout was designed to evaluate the degree of soil aeration, oxygen utilization rates, and biodegradation rates at various distances and directions from the vent well.

The system in the non-vented control plot consisted of one vent well and four tri-level soil gas monitoring points (see Figure 1). The soil gas monitoring points each were placed 20 feet from the vent well, and at right angles to each other.

### 2. System Components

Both bioventing systems included a single vent system designed for air injection and a set of tri-level soil gas monitoring points installed at discrete distances from the vent well for soil gas sampling and respiration monitoring. The system in the actively vented plot also included thermocouples placed with each soil gas probe, and six in situ oxygen sensors. The following sections provide more detail on the individual components of the bioventing systems.

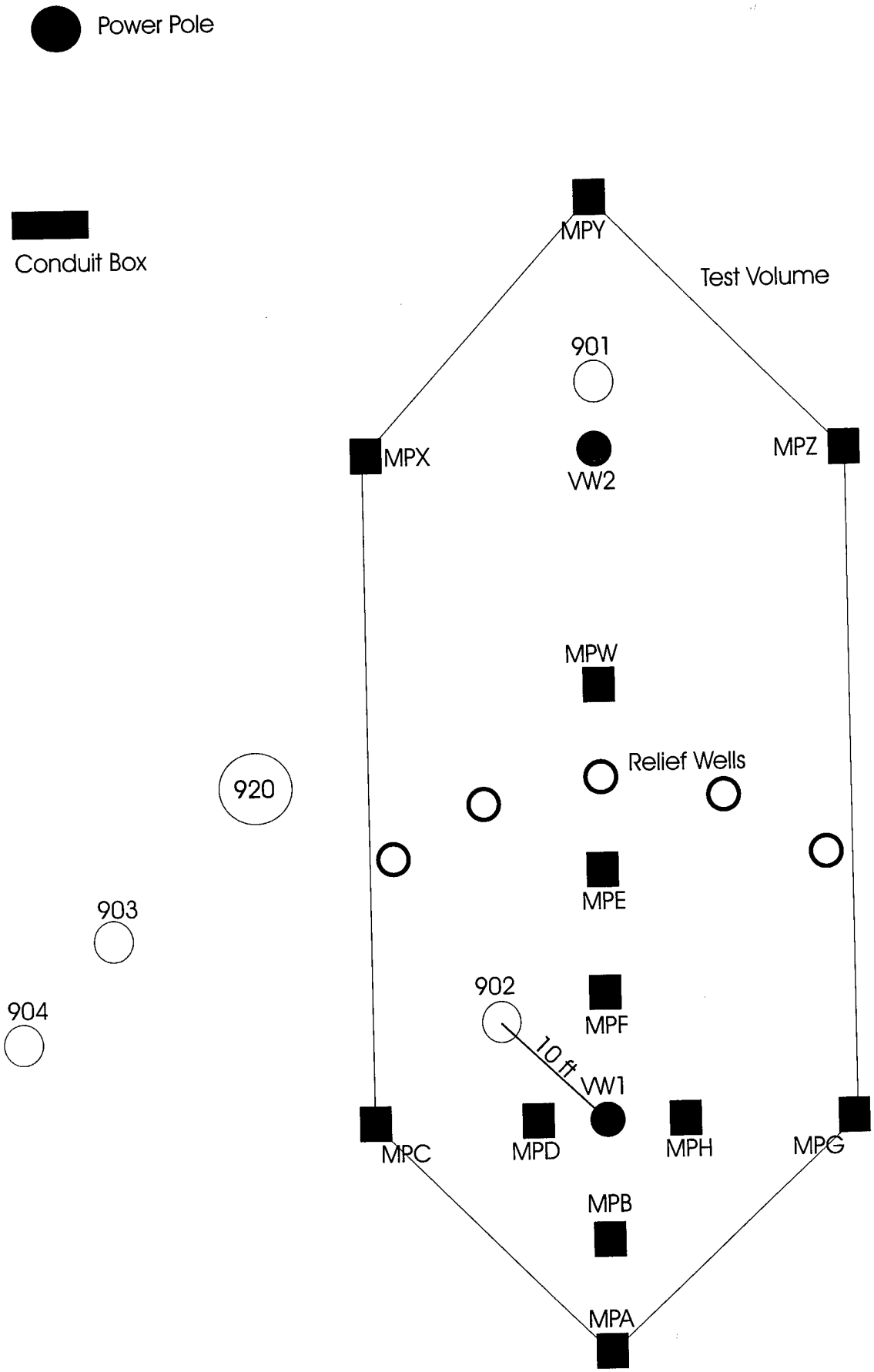


**Figure 1. Layout of the Bioventing Systems in the Actively Vented Plot and the Non-Vented Control Plot**

### a. Vent Wells

The design of the vent wells in the vented and non-vented plots were identical, and a schematic diagram of the vent well design is provided as Figure 2. Each vent well was constructed of 2-in.-outside diameter (O.D.) stainless steel with a 0.010-in. slot screen extending from 10 to 20 feet bgs. A sand pack was set in the borehole around the screened section of the vent wells and the annulus of the borehole above the screen was filled with hydrated bentonite chips to provide an airtight seal to prevent short-circuiting of air around the well casing. A 2-foot concrete pad was constructed around the riser pipe in the control plot to secure the vent well in place, and the well subsequently was capped and unused. The top of the vent well in the active plot was connected to an air supply line and completed below grade in the central manhole.

### b. Soil Gas Monitoring Point Assemblies

The tri-level soil-gas monitoring point assemblies consisted of three soil-gas probes, three Type K thermocouples, Teflon™ sample lines, and a PVC support rod; a schematic diagram of the assemblies is provided as Figure 3. The probes were 6-in.-long, ½-in.-diameter stainless steel screen sections. Each probe was connected to ¼-in. diameter Teflon™ tubing. The probes and tubing were fastened to a 1-in. diameter PVC rod to facilitate their proper placement and completion. A Type K thermocouple was attached to the PVC support rod adjacent to each soil-gas probe location.

The tubing from the probes and the thermocouple wires in the vented plot were fed underground through PVC conduit to a panel located in the field trailer. A heat trace was installed along the tubing in the conduit to prevent potential problems with condensation and freezing in the soil gas sampling lines. The ends of each tube were connected to female quick-connect couplings, which were mounted to the central sampling panel in the trailer. The thermocouple wires were connected to a data logger to record temperatures automatically. The tubes from the soil gas probes in the non-vented control plot were fed to a flush-mount well cover. The ends of the tubing were fitted with pneumatic quick couples to facilitate sampling.

Six in situ oxygen sensors (Datawrite Research Co., Model XT252SP) were installed at selected locations to compare and confirm field meter values. The sensors were equipped with gas lines to facilitate in situ calibration. The gas lines and the signal wires were run along with the sample lines from the soil gas probes and into the trailer. The signal lines were connected to a data logger housed inside the field trailer.

Originally, the soil-gas monitoring probes were to be set at 10, 15, and 20 feet bgs. However, because groundwater was encountered at shallower than expected depths around the site, the soil gas probes were set at 7, 12, and 17 feet bgs. The soil-gas-monitoring points were completed with 18 inches of sand pack placed in the borehole so that the sand extended 6 inches above and below each probe. Bentonite was placed in the borehole between each sand pack, and above the shallowest sand pack, to approximately 1-foot below grade.

### c. System Air Supply

A 1-horsepower (hp) regenerative air blower (Gast REGENAIR Model R4110-2) was used to supply the air to the vent well in the active plot. The blower was wired for single-phase 120V electrical service. The starter switch was fitted with a heater overload to cut the power in the event of increased amperage draw. The blower was placed in the back corner of the field trailer closest to the vent well in the active plot.

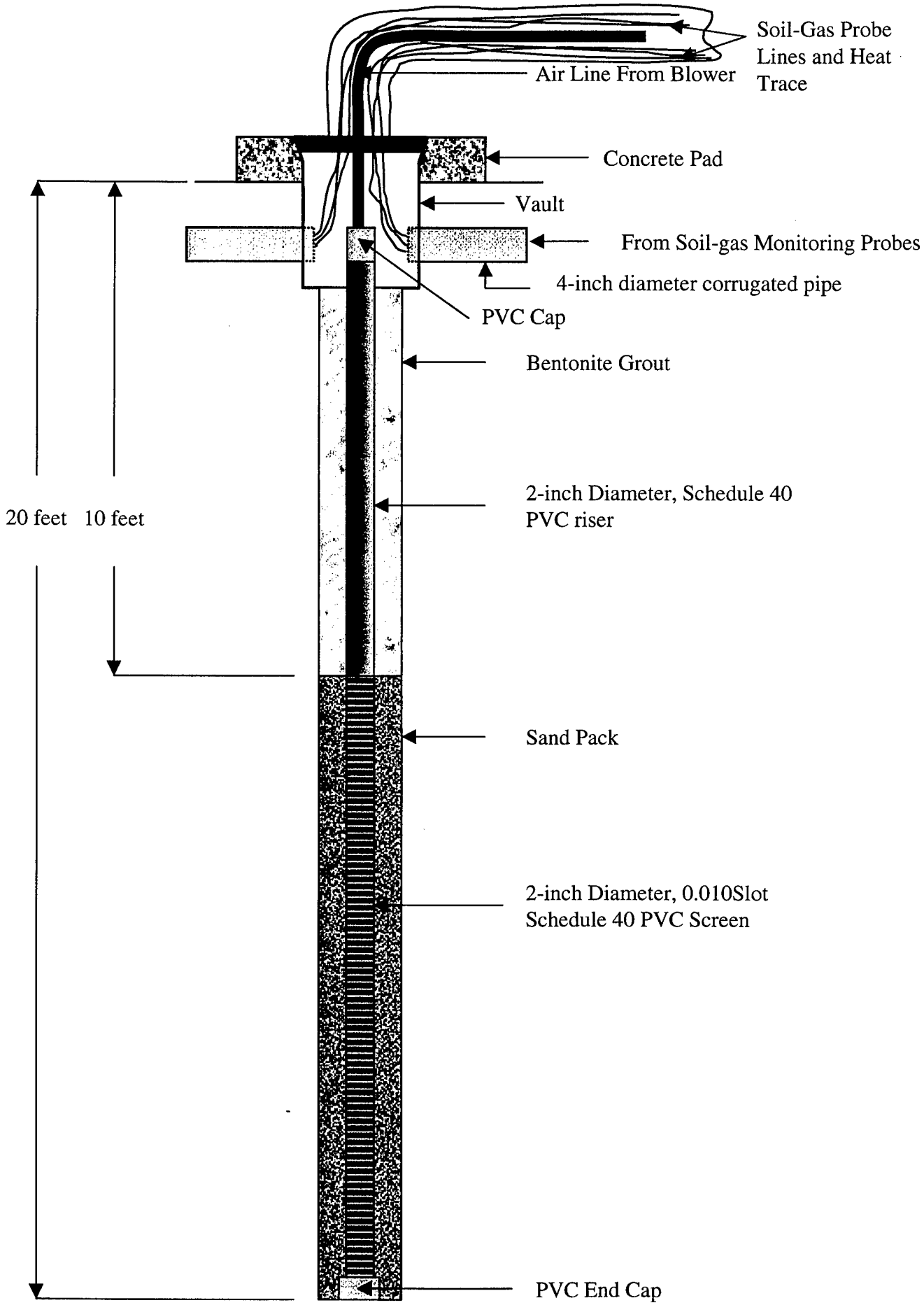


**Figure 2. Schematic Diagram of the Vent Wells Used at CDP 1**

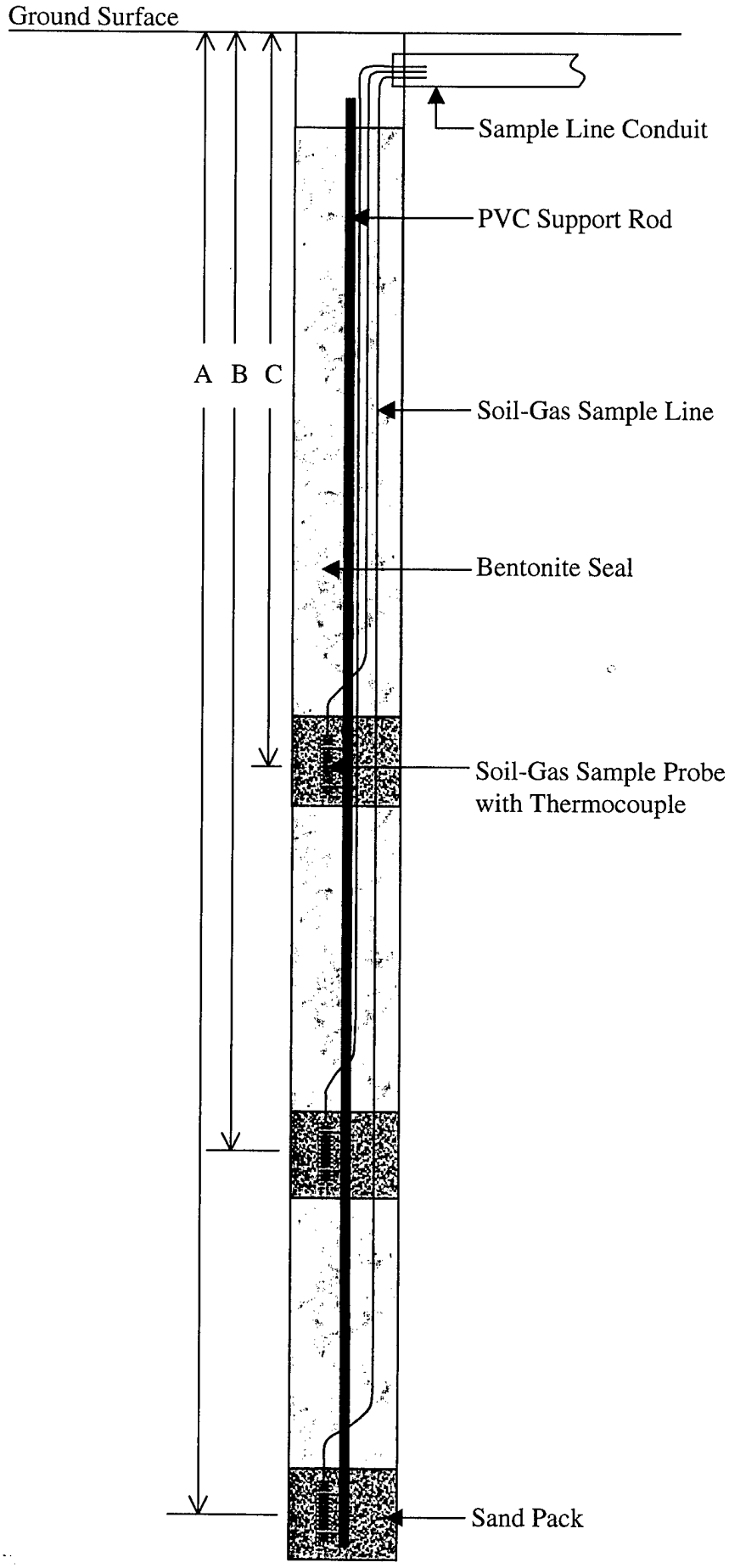


**Figure 3. Schematic Diagram of the Soil Gas Monitoring Point Assemblies Used at CDP 1**

The plumbing between the blower and the flow meter was made of galvanized steel. A tee section was inserted approximately 6 inches from the blower outlet. The 180° side of the tee served as the bypass line and was fitted with a ball valve to control the pressure and flowrate of the injected air stream. The 90° side served as the supply line to the vent well and was also connected to a flow control valve. A rotameter and an inline thermometer were plumbed into the supply line to monitor system airflow and temperature, respectively. The output side of the rotameter was fitted with a Magnehelic™ pressure gauge to monitor system pressure. The supply line from the pressure gauge was connected to 1-in. diameter heater hose that was fed through the floor of the trailer to the head of the vent well and then connected to the well.

**d. Automated Monitoring System**

An on-line environmental monitoring system (OEMS) provided by Battelle was used to track oxygen, carbon dioxide, and TPH in soil gas from each of the 24 monitoring probes in the active plot. An OEMS consists of a vacuum pump, a vacuum chamber, and a sample chamber containing a variety of sensors. For the bioventing demonstration, a galvanic oxygen sensor, an infrared carbon dioxide sensor, and an infrared TPH sensor were used. The system was connected to each of the soil gas lines at the sample panel using 1/8-in. diameter Teflon™ tubing and was programmed to perform an automated calibration both prior to and following each sampling event. The oxygen and carbon dioxide sensors were calibrated against a calibration gas of known concentration and ambient air. The TPH sensor was calibrated against a hexane standard. The system was programmed to collect and analyze samples on a daily basis, except during respiration tests, when the sampling frequency was increased to every 4 hours. The system had remote capabilities so that it could be accessed from Battelle via modem, which enabled monitoring of the system without requiring a site visit.

3. System Construction and Installation

The vent wells and soil gas monitoring points were installed using a 4-in.-inside diameter (I.D.). hollow-stem auger. Prior to drilling, a trencher was used to dig a 6-in.-wide trench along the axis of the bioventing system. The boreholes for the vent well and soil-gas monitoring points were advanced at desired spacing along each leg of the trench, and the tubing and thermocouple lines were fed through the conduit that was placed underground in the trench.

Once the vent well and soil gas monitoring points were installed, the 4-in.-diameter flex pipe conduit was installed in the trench. The tubing and wiring from each monitoring point were fed through the pipe. The trenches were backfilled with the soils removed during trenching.

After all below-grade installation was completed, a field trailer (8 ft by 20 ft) was delivered to the site and positioned adjacent to the vent well. The tubing and thermocouple wire were fed into the trailer and connected to the appropriate terminals on the sampling board and the data loggers, respectively. The blower was plumbed to the vent well and the electrical service was connected. The flush-mount well covers were installed over each soil gas monitoring point in the control plot, and a 2-foot square concrete pad was constructed to secure them in place. The lip of each flush mount was stamped with the monitoring point identification.

The installation activities resulted in generation of approximately 150 $ft^3$ of soil. The soil was placed in a lined roll-off bin and labeled for disposal in accordance with Hill AFB's Investigation-Derived Waste (IDW) Management Plan.

## B. OPERATION AND MONITORING

The bioventing system was operated to aerate the vented test plot. Aeration was designed to enhance aerobic biodegradation in the vadose zone without excessively volatilizing organics. Various parameters were monitored to evaluate system status, aeration effectiveness, biological activity, temperature changes, and vapor-phase concentrations of COIs. The following sections describe operation and monitoring procedures in more detail.

### 1. System Startup

After installation, the bioventing system was visually inspected to ensure that the blower and all piping were installed properly. Once the integrity of the system was verified, the blower was turned on and the air flowrate was set at approximately 78 standard cubic feet per hour (scfh) (1.3 standard cubic feet per minute [scfm] or 36.8 liters per minute [lpm]), which is the calculated rate necessary to exchange one complete pore volume every 2 days within the assumed 20 foot radius of influence. The air delivery pipe and the injection vent well were inspected to ensure that air was not leaking or short-circuiting. The blower was initially operated for one week while the temperature and pressure were monitored to ensure that the blower was operating properly. Periodic soil gas samples were collected from the soil gas monitoring points to monitor the aeration efficiency of the blower. Soil gas samples also were collected from the non-vented control plot to determine if the blower was affecting the soils in this area of CDP 1. After the initial one-week operating period, the system was shut off, and the initial in situ respiration test was performed. The test was conducted according to the procedure described in the Air Force Bioventing Principles and Practice Manual (Battelle, 1995) and continued for 5 days. The blower was then turned on, and the system was put into standard operating mode.

The original target $O_2$ level in the actively vented plot was 10% or greater at all monitoring points. Soil gas monitoring performed in August 1997, one month after installation was completed, revealed that the vented plot was not aerated as thoroughly as intended. On September 2, 1997 the air flowrate was increased to 200 scfh (3.3 scfm or 93.4 lpm) to improve the delivery of oxygen to the actively vented plot. This higher flowrate resulted in an exchange of one pore volume of soil gas approximately every 2 days. This estimate assumes air was exchanged throughout the treatment volume, including the volume that was originally intended as a control plot. Other parameters affecting the estimate were taken as follows:

- Test volume = 32,000 $ft^3$ (906 $m^3$) (within polygon formed by MPs)
- Air-filled porosity = 0.32.

### 2. System Operating and Performance Monitoring Procedures

The bioventing system was operated in a continuous injection mode. The air flowrate was maintained at approximately 200 scfh (3.3 scfm or 93.4 lpm) throughout one year of operation. System parameters, including blower temperature, feed air temperature, manifold pressure, air flowrate, ambient temperature, soil gas $O_2$ concentration, soil gas $CO_2$ concentration, soil gas TPH concentration, soil gas contaminant concentrations, and microbial respiration were monitored periodically during operation of the bioventing system. The procedures used for monitoring these parameters are described in the following sections.

### 3. System Operation Monitoring Procedures

The OEMS was used to automatically monitor the system temperatures, pressures, and flowrates, and also measured concentration in soil gas of oxygen, carbon dioxide, and TPH in the vented

plot. Battelle performed monthly site visits to collect soil-gas samples manually from every in situ soil gas monitoring point. Soil gas was extracted from each monitoring probe and analyzed for $O_2$, $CO_2$, and TPH concentrations using field meters. The $O_2$ data were evaluated in the field to determine whether the air flowrate needed to be adjusted. In addition, a complete set of soil gas samples from each monitoring probe was collected and sent to Battelle's Columbus, Ohio, laboratory for gas chromatography (GC) analysis to confirm field meter data.

### 4. System Performance Monitoring Procedures

Battelle conducted five quarterly in situ respiration tests (initial, Q1, Q2, Q3, final) to monitor system performance during the 12 months of operation. The tests entailed turning off the blower and collecting respiration data used to calculate biodegradation rates. Both the OEMS and manual sampling and analysis were used to monitor respiration during the shutdown period.

Prior to turning off the blower, all system-operating parameters were recorded. An initial set of soil-gas samples were collected from each monitoring probe and analyzed for $O_2$, $CO_2$, and concentrations of the organic COIs. Once the initial samples were collected, the blower was turned off and the valve on the injection line was closed. Following shutdown, periodic sets of soil gas were collected and analyzed for the $O_2$, $CO_2$, and COI concentrations. All measurements were recorded in a field notebook. The tests were continued for 5 days or until the $O_2$ level dropped below 5%.

# SECTION IV
# DATA COLLECTION

## A. DATA COLLECTION

Three soil sampling events were conducted during the course of the bioventing demonstration to evaluate the effectiveness of the technology for reducing the mass of the targeted compounds at CDP 1. The three sampling events included:

- Preliminary sampling: for verification of the presence and location of COIs
- Initial sampling: conducted after installation and before bioventing was initiated to provide baseline data against which to evaluate contaminant reduction and technology performance
- Final sampling: performed after 1 year of bioventing to determine the mass of contaminant remaining within the treated volume of soil.

### 1. Preliminary Sampling

The preliminary soil-sampling event was conducted to determine whether the CDP 1 site could support the non-petroleum bioventing study. Soil samples were collected from various depths at points on a grid laid out over the area reported to contain COIs. Soil samples were collected in stainless steel (SS) sleeves using a GeoProbe® system and sent to an independent analytical laboratory for analysis.

### 2. Initial Sampling

Pre-bioventing soil samples were collected while drilling boreholes for system installation. Sampling locations included each vent well and in situ soil-gas monitoring point as shown in Figure 1. Soil was collected in SS sleeves using a split-spoon sampler. Samples were preserved in the field according to the requirements for analysis by EPA Method 5021 (headspace analysis). Approximately 70 soil samples were collected and analyzed. The preliminary soil sampling results indicated that most of the COIs were in the 10 to 20 ft bgs interval; therefore, the initial soil samples were collected from within that interval. A 2-ft long spoon loaded with two 6-in. SS sleeves and one 1-ft SS sleeve was used to collect each of the five 2-ft cores from 10 to 20 ft bgs. Soil sample recovery in the sleeves varied from complete to very poor due to the presence of cobble, or gravel, in the soils. After recovery from each sample was noted, samples were preserved, capped, sealed, labeled, and stored on ice prior to shipment to Battelle for headspace analysis. Selected sleeves having nearly complete recovery were capped, sealed, labeled, and sent to Battelle for property analysis. Properties determined were moisture content, specific gravity, dry density, and porosity.

### 3. Final Sampling

Post-bioventing soil samples were collected using the same procedure as the initial sampling, but locations were offset approximately 1 ft from the initial borehole. Each of the 14 initial locations was resampled during the final sampling. Each initial borehole was located by removing surficial soil prior to marking the location for drilling. Approximately 140 soil samples were collected in duplicate (more than 280 total samples) and analyzed. Soil recovery was similar to that observed during the initial round of sampling. Four 6-in. SS sleeves were used to collect the soils within the split-spoon sampler. Efforts were made to collect duplicate soil samples from the interfaces between the top two and between the bottom two sleeves; however, these efforts were impacted by the relative recovery of soil in each of the sleeves. Typically, four soil samples were preserved from each 2-ft soil interval between 10 and 20 ft bgs.

## B. MONTLY MONITORING

The site was visited on a monthly basis to collect soil gas samples for field analysis of TPH, $O_2$, and $CO_2$, and for laboratory analysis of COIs. Soil gas was collected from each probe using a vacuum chamber containing a 1-L Tedlar™ bag. This apparatus establishes conditions in which the in situ pressure exceeds that surrounding the bag, forcing soil gas into the bag. A valve was used to control the flow into the bag to prevent rupture. Calculations of the total tubing bore volume showed that one 1-L flush was adequate to flush the entire tubing volume completely. Each bag was flushed with one volume of soil gas, prior to collection of the sample for TPH, $O_2$ and $CO_2$ analyses. A second bag was then collected and sent via overnight express to Battelle for GC analysis. The bags to be shipped were not filled to capacity, to allow for expansion during air transport.

During the monthly visits, the system hardware was inspected and necessary adjustments or repairs were made. Blower temperature, injection flowrate, and injection pressure were recorded in the field logbook. The system was inspected for leaks, signs of wear, and general operating condition. The datalogger storing in situ oxygen sensor data was downloaded onto disk using a laptop computer.

On two occasions, site visits were cancelled because system parameters monitored remotely indicated that the system was operating properly and no adjustments were required.

## C. QUARTERLY RESPIRATION TESTS

In situ respiration rate tests were performed quarterly using the procedure given in the Air Force *Bioventing Principles and Practice Manual* (Battelle, 1995). A total of five tests were performed over the year of operation, each separated by approximately three months time. The initial test was performed immediately after installation (and a brief aeration period) in July 1997, and the last test was performed approximately one year later in August 1998.

A complete set of soil-gas samples was collected from all of the soil-gas monitoring probes within the vented plot and the control plot at the beginning of each test. The data were reviewed to ensure that the soils had been sufficiently aerated and that the oxygen concentrations were high enough to adequately monitor respiration. For the initial respiration test, the blower was operated at approximately 80 scfh (1.3 scfm or 38 lpm) for approximately 5 days. The blower was then turned off, and frequent in situ soil gas sampling was conducted to track $O_2$ and $CO_2$ concentrations over time.

The soil gas oxygen data revealed that the oxygen utilization rates (OURs) at the 7- and 12-ft depths were much slower than that observed at 17 ft bgs. The frequency of soil gas sampling was adjusted based on the observed data to eliminate over-sampling. The $O_2$ levels in the soil gas from the outermost probes at the 17-ft depth were below 5%, indicating that the soils in this vicinity were not adequately aerated to perform respiration testing. These probes were not monitored during this respiration test.

## D. ON-LINE ENVIRONMENTAL MONITORING SYSTEM

The OEMS system was programmed to collect and measure soil gas samples once per day. During respiration tests the frequency of sampling was increased to evaluate whether the system could be used to perform remote respiration tests. The data stored in the OEMS were downloaded by modem weekly to ensure that data was preserved.

The OEMS system monitors soil gas by evacuating a sealed chamber using a small diaphragm pump (as described further in Section 3.1.2.4).

## E. IN SITU SENSORS

Six oxygen sensors were installed at selected monitoring probe locations. The probes were installed to allow continuous monitoring of $O_2$ levels in the vadose zone without the need for removing gas for analysis. The sensors use a basic galvanic cell that respond to $O_2$ and produce a current that is recorded as a millivolt signal. The data were recorded using an automatic data logger that was programmed to collect readings from the six sensors every 12 hours. During the site visits, the data were downloaded using software and an interface card on a laptop computer. The data were entered into a Microsoft® Excel spreadsheet for graphing and evaluation.

## F. SURFACE EMISSIONS TESTING

One concern over the implementation of air injection as a means of soil remediation is the possibility of transferring toxic compounds from the soil to the atmosphere. Surface emission measurements were made following system startup to determine whether VOCs were being released to the atmosphere during bioventing at CDP 1.

An area of soil was enclosed under a Teflon™ box that was designed to allow the purging of the enclosure with high-purity air. The soil voids contain a mixture of atmospheric air that has diffused in over time mixed with contaminant vapors and respiration gases from microbial activity. The use of high-purity air mimicked the in situ concentration gradients between the soil voids and the atmosphere, and allowed for sample collection with minimal disturbance of the existing equilibrium between the two reservoirs. The purging activity removed ambient air from the region above the soil to allow equilibrium to be established between the VOCs emitted from the soil and the organic compound-free purge air. The air stream was sampled by drawing a known volume of the VOC/pure air mixture through a tube packed with sorbent materials known to retain the organic compounds previously identified at the site. Following collection, the sample tubes were shipped to Battelle where the sorbed compounds were thermally desorbed and resolved and then quantified by gas chromatography. The measured concentrations were converted to a flux value to indicate the rates of emission of the VOCs from the soil to the atmosphere.

A schematic diagram of the sampling system used is shown in Figure 4. It consisted of a Teflon™ box that covered a surface area of 0.453 $m^2$. The box was fitted with inlet and outlet ports for entry and exit of the high-purity purge gas. The inside of the box contained a manifold system that delivered the air supply uniformly across the soil surface. The surface emission sampling system was inert with all components made from either Teflon™ or stainless steel. This ensured that there was no contribution to, or removal of, organics from the air stream.

A three-phased carbon-based sorbent bed (Supelco, Carbotrap 300 Cat.#2-0370) was used to effectively capture the suite of organic compounds efficiently. This sorbent trap had been evaluated extensively at Battelle (Pollack, 1993) in conjunction with ambient air sampling and had been shown to be very efficient at capturing and retaining a wide range of VOCs. This carbon-based sorbent bed typically displays very low background artifact levels. One limitation of this sorbent configuration is that it is not able to retain methane, ethane, or ethylene at ambient temperatures; however, those particular compounds were not of interest in the bioventing demonstration.

Surface emission samples were pulled through the sorbent trap using a personal monitoring pump (SKC, Model #224-PCXR7) so that the air passed from the weakest sorbent (Carbotrap C) to the moderately strong material (Carbotrap) and finally onto the strongest sorbent (Carbosieve S-III). This three-phased arrangement made it possible to capture a wide range of molecular weight VOCs, yet still allowing for efficient desorption. Contaminant desorption was accomplished by back-flushing the organics off the sorbent bed with helium while heating the tube.

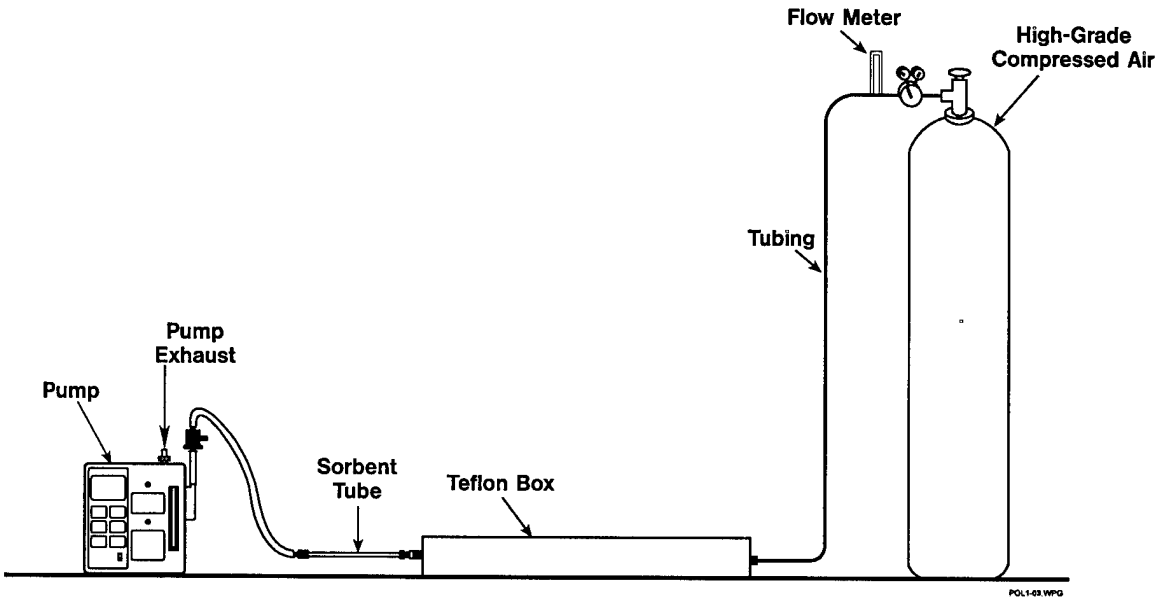


**Figure 4. Schematic Diagram of the Apparatus Used at Hill AFB**

Prior to use, the sorbent tube, it was baked at 350°C for one hour with an ultra-high-purity helium purge flow of 50 $cm^3$/minute. This ensured that the sorbents were clean prior to their use.

During surface emission sampling, the Teflon™ box was positioned in three locations at 5-, 12-, and 20-foot distances from the injection vent well. The collection of each surface emission sample involved the following activities:

1. Ensuring that the sorbent tubes had been properly conditioned.
2. Setting the flow of the SKC pump to approximately 50 $cm^3$/minute using a Mini-Buck gas flow calibrator (Model #APB-M5). Connecting the Mini-Buck calibrator to the inlet end of a spare sorbent tube and the outlet end of this tube to the SKC pump. Adjusting the pump flowrate so that the air flowrate through the tube was 50 $cm^3$/minute. Removing the sorbent tube and measured the pump flowrate again (this flowrate was determined to be the flowrate necessary to pull 50 $cm^3$/minute through the packed tube). The sorbent tube used to determine the required pumping rate was sacrificed, and was not used for sampling.
3. Installing a pressure regulator and flow meter to the high-purity air cylinder and set the flowrate to 2 L/minute using the Mini-Buck calibrator. The cylinder delivery pressure was set at 60 pounds per square inch gage (psig) prior to establishing this flow.
4. Checking all tubing and fittings on the Teflon™ box and repairing or replacing any parts necessary.
5. Positioning the Teflon™ box at the location where the sampling was to be done. Because of gravel and vegetation at the site, it was necessary to loosen the soil and remove ground cover around the perimeter of the box to allow it to be in continuous contact with the soil. The surface of the soil under the box was left undisturbed as much as possible during this process.

6. Connecting the inlet port on the box to the air cylinder with Teflon™ tubing and starting a 2-hour purge to obtain equilibrium between surface emissions and the high-grade air.
7. At the end of the 2-hour purge time, connecting a clean sorbent tube to the exit tubing on the box and the SKC pump. Starting the pump and running it for 6 minutes so that 300-$cm^3$ of air passed through the sorbent sampling tube.
8. Removing the sorbent tube from the sampling line, capping it, and then returning it to its storage tube. Recording the sample tube number, sampling location, date, time, and any observations in the field notebook.
9. Repositioning the Teflon™ box at the next sampling location, and repeating the purge/sampling procedure.
10. In addition to the three surface emission samples, collecting a duplicate emission sample, a sample of the high-grade cylinder air, an ambient air sample, a sample from the relief wells, and a trip blank. These additional samples served as the quality control samples.

## G. LAB STUDY

A laboratory-scale column study was performed to track the fate of the COIs under more controlled conditions to provide support to the results obtained in the field. The study used soil cores collected from CDP 1 during installation of the bioventing system. The following sections describe the methods used to set up and monitor the columns.

### 1. Column Setup

Soil cores collected in 12-in.-long, 1.5-in.-diameter SS sleeves during system installation were brought back to the laboratory and set up as follow-through columns (Figure 5). The ends of each sleeve were fitted with a stainless steel cap that was tightened to provide an airtight seal. Each end cap had a single port tapped into the center and the inside surface was beveled. Glass wool was packed into the bevel to facilitate gas flow and minimize channeling and/or short-circuiting. The columns were mounted in an upright position in an incubator maintained at 20°C.

### 2. Column Operation

The columns were operated in three different modes: closed system, continuous flow-through, and batch fed. During each of these modes of operation, influent and effluent gas samples were collected from each column and analyzed for oxygen, carbon dioxide, and COI concentrations. The gas sampling method depended on the configuration of each reactor at the time of sampling. Each sampling method is described below.

#### a. Closed System Mode

For the initial mode, all six columns were operated as closed systems. Gas samples were drawn directly from the valve on the end of each column using a 5-mL Gastight™ syringe fitted with a syringe valve to monitor the $O_2$ levels in the columns. The syringe was attached to a two-way valve at the top of the column and the two valves were opened. Five milliliters of gas was drawn into the syringe and the syringe valve and reactor valves were closed. The syringe was removed and the gas sample was injected into a GC for analysis of the respiratory gases $O_2$ and $CO_2$. If the concentration of $O_2$ dropped below 10%, the column was flushed with 500 ml of clean air by attaching a 1-L Gastight™ syringe to the bottom port on each column. The oxygen in each column was measured following each flush.

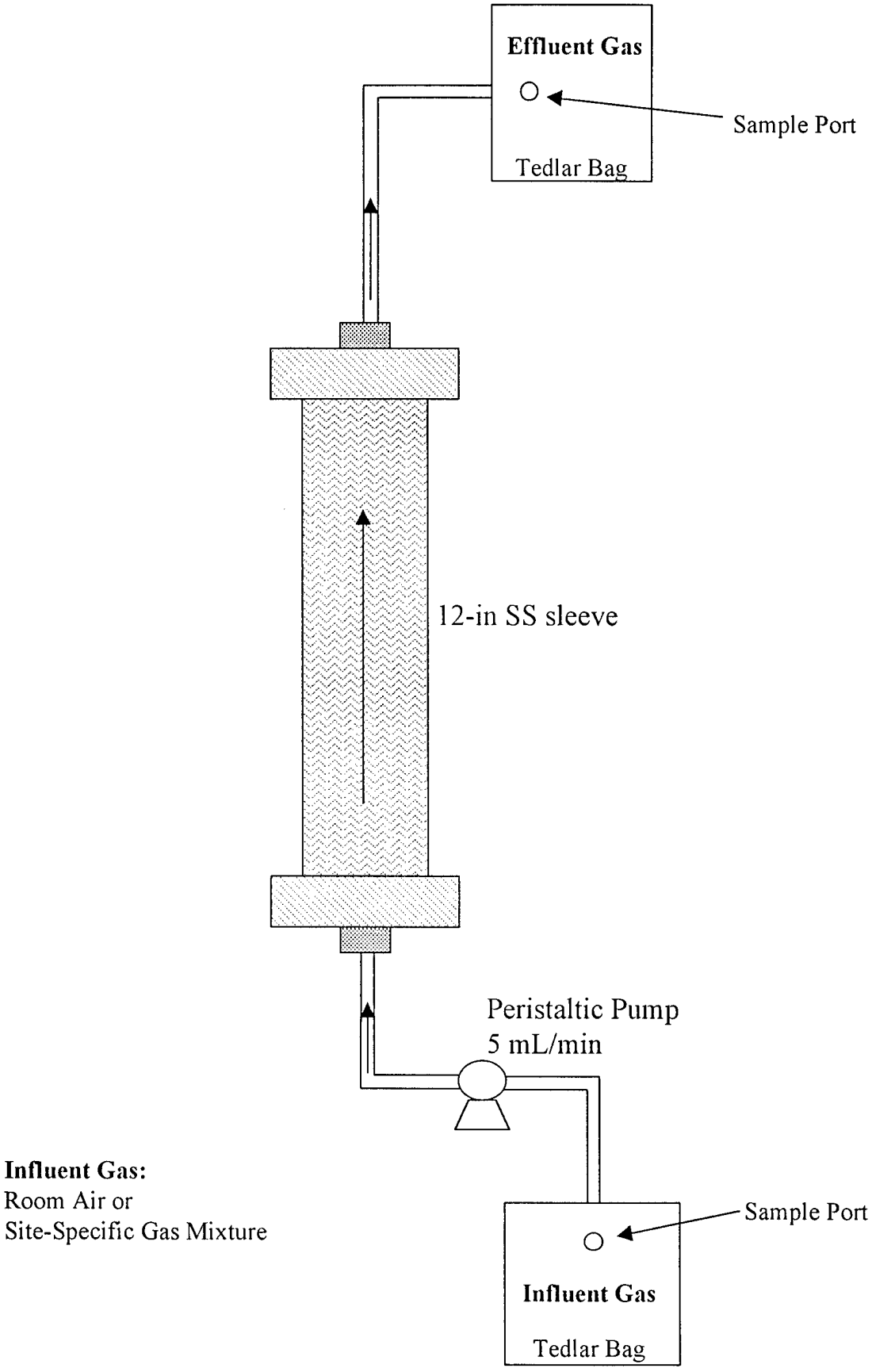


**Figure 5. Experimental Setup of Soil Column Reactors for Laboratory Study**

During each flush, a 1-L Tedlar™ gas-sampling bag was attached to the top port, and the effluent gas was collected for analysis of COI concentrations. The data were used to keep track of the mass of contaminant removed from the columns and for calculating mass balances at the end of the experiment.

### b. Continuous Flowthrough Mode

A peristaltic pump was plumbed using Viton™ tubing to the bottom of each column and operated to provide a flowrate of 1 ml/min. The air flowrate for each column was monitored with a digital flow meter. If the flowrate varied by more than 0.2 mL/min, the Viton™ tubing was replaced and the pump was reset. The off gas from each column was collected in a 3L Tedlar™ bag. The gas collected in the bags was analyzed for $O_2$, $CO_2$, and COI concentrations.

### c. Batch Fed Mode

For the final phase of laboratory testing, a 3-liter Tedlar™ bag was filled with 3 liters of a gas blend and connected to each column. The bag was connected to the intake side of the peristaltic pump that was then plumbed to the bottom of to the bottom of a column. The bags were filled with 2.4 liters of a specialty gas containing the compounds at the concentrations listed in Table 5, and 600 mL of oxygen. The gas was pumped through the columns at 5 ml/min and the effluent was collected in 3-liter Tedlar™ bags connected to the port at the top of the column. $O_2$, $CO_2$, and COI concentrations were measured in gas samples from both the influent and effluent bags.

**Table 5. Composition of Site-Specific Gas Mixture Used in Laboratory Column Study**

| Component | Concentration, ppmv |
|---|---|
| *cis*-1,2 dichloroethylene | 1,069 |
| 1,1,1-trichloroethane | 86 |
| trichloroethylene | 192 |
| tetrachloroethylene | 31 |
| toluene | 27 |
| chlorobenzene | 2.6 |
| ethylbenzene | 2.8 |
| *m*-xylene | 5.4 |
| *p*-xylene | 5.4 |
| *o*-xylene | 3.6 |
| 1,3,5-trimethylbenzene | 2.3 |
| 1,2,4-trimethylbenzene | 2.6 |
| 1,2-dichlorobenzene | 13.4 |
| 1,3-dichlorobenzene | 2.7 |
| 1,4-dichlorobenzene | 2.6 |
| 1,2,4-trichlorobenzene | 2.5 |
| nitrogen, pre-purified | balance |

## 3. Performance Monitoring

The sleeves used for the lab study were collected in conjunction with two 6-in. long sleeves, each at opposite ends of the split spoon sampler. The soil at the end of the 6-in. sleeve that was adjacent to the effluent end of a 12-in. sleeve was sampled and analyzed for COI and TPH concentrations. Because the soils were in intimate contact in the ground and during the sampling process, the resulting

concentrations from the 6-in. sleeves were assumed to be representative of the concentrations in the associated 12-in. sleeve. Sampling the 6-in. sleeves allowed the soil cores in the 12-in. sleeves to remain undisturbed.

A simulated soil gas mixture was injected into the bottom of the columns and the effluent vapor was collected in either 1- or 3-L Tedlar™ gas sampling bags. The influent gas to, and the effluent gas from, the columns were analyzed for $O_2$, $CO_2$, TPH, and COI concentrations over time. The $O_2$ and $CO_2$ data were used to monitor biological activity in each column. The TPH and COI data were used to calculate the mass removed from the column through volatilization and advective transport.

The concentrations of the COIs remaining in the soil in the columns at the end of the experiment were determined by sacrificing each column. The columns were dismantled and soil samples were removed from the effluent end (which had been in immediate contact with the 6-in sleeve face sampled for initial concentrations) for contaminant analysis. Triplicate soil samples were collected from each column for enumeration of total heterotroph and 1,2-DCB-degrading bacterial populations.

## H. ANAYLTIC METHODS

Soil-gas and soil samples were collected during the field and laboratory components of this demonstration and analyzed to determine the concentrations of $O_2$, $CO_2$, COIs, and TPH. The data from the field samples provided information on the effectiveness of the air injection system for delivering oxygen, the microbial activity as measured by respiration, and the changes in the composition of the organic mixture present over the course of the demonstration. The data from the laboratory sample analyses were used to monitor biological activity and to track the fate of the organic mixture present under more controlled conditions than could be achieved in the field. The following sections provide the analytical methods used for soil and soil gas samples from both the field and laboratory efforts.

### 1. Gas-Phase Oxygen and Carbon Dioxide Analysis

A SRI GC equipped with a CTR-I concentric column (Alltech) connected to a thermal conductivity detector (TCD) was used to analyze the gas-phase samples for oxygen and carbon dioxide concentrations. An isothermal method at 35°C was used, with helium serving as the carrier gas. A 5-mL gas sample was injected through a multi-port valve injector assembly fitted with a 1-mL sample loop. The concentrations of oxygen and carbon dioxide were calculated using response factors generated based on the response to injections of standards of known concentrations.

### 2. Gas-Phase COI and TPH Analysis

The concentrations of the 17 compounds listed in Table 1were measured, and TPH concentrations were calculated in soil gas samples collected in the field during the in situ respiration tests and monthly site visits, and in influent and effluent samples during the laboratory study. Total petroleum hydrocarbon (TPH) was not a major focus of this study, but was tracked as an indicator of the effectiveness of aeration, and because it is a known substrate for microbial respiration.

Two methods were used to measure the concentrations of COIs in influent and effluent gas samples collected during column operation. Samples collected in Tedlar™ bags were analyzed using a gas bag autosampler/GC system. The valve on the bag was opened, and the sample was injected into a Hewlett-Packard (HP) 5890 GC equipped with a 60-m SPB-1 wide-bore capillary column (Supelco) attached to a flame ionization detector (FID).

Gas-phase samples that were drawn into a gas-tight syringe were injected directly into a Varian Star 3400 GC equipped with a 60-m HP-1 wide-bore capillary column (Hewlett-Packard) attached

to a FID. Contaminant concentrations were calculated using Chrom Perfect® by multiplying area counts by a response factor generated from a single point calibration from injections of a standard of known concentrations of contaminants.

### 3. Soil-Phase COI and TPH Analysis

COI analyses on both soil samples from the field, and soil samples from the laboratory columns was accomplished using a GC procedure developed based on EPA Method 5021, a method for the analysis of VOCs in soils. The developed method employed gas chromatography with flame ionization detection (FID) and electron capture detection (ECD). A Tekmar Model 7000 Equilibrium Headspace Autosampler with a Tekmar 7050 Carousel and a HP 5890 GC equipped with a 60-m SPB-1 fused silica capillary column (Supelco) split between a FID and an ECD was used.

The samples were processed in the field during sample collection, or in the laboratory upon sacrificing the columns. At least two grams of soil were weighed into a crimp-seal glass headspace vial and 10 mL of a matrix modifying solution, consisting of an acidic brine solution. The solution served as the aqueous phase for establishing equilibrium and also preserved the sample. The samples from the field were shipped to the laboratory in the sample vial in this solution. Upon receipt at the lab, the sample vials were placed in the autosampler carousel on the headspace analyzer. Prior to analysis, the autosampler moved the individual vials to a heated platen set at 95°C where it was equilibrated for 55 min. The autosampler then mechanically mixed the sample for 3 min then pressurized the vial with helium carrier gas to 10 psi. The pressure in the vial forced a portion of the headspace gas mixture through a heated 1-mL sample loop set at 110°C. The headspace gas mixture inside the 1-mL sample loop then passed through the heated transfer line set at 105°C and onto the GC column. The initial column temperature was held at 35°C for 2 min then ramped to 200°C at 8°C/min and held there for 2 min.

The resulting chromatographic information was recorded and stored as computerized files using the Chrom Perfect® for Windows data acquisition package. Chrom Perfect® calculated the contaminant concentrations by multiplying area counts for each COI by a response factor generated from a 5-point calibration curve made from triplicate injections of standards of known COI concentrations.

It must be noted that TPH in soil samples was measured using a headspace equilibrium method that was developed to effectively detect the COIs listed in Table 1, not TPH. Even though the samples were equilibrated at an elevated temperature of 95°C, the analytical method was more effective at detecting the lower molecular weight fraction of the overall hydrocarbon contamination, and the reduction of TPH observed in soil samples was not representative of the total reduction in TPH at the site.

### 4. Microbial Enumeration

Microbial enumeration assays were performed on soil samples collected during field installation of the bioventing system, in soil samples collected in the field after one year of venting, and from the laboratory columns after approximately 8 months of treatment. Microbial populations were enumerated using the serial dilution and spread plate technique described in Standard Method 9215 (Greenberg et al., 1992).

Total heterotroph bacteria were enumerated by spreading appropriate dilutions of soil onto standard plate count agar (supplied by Difco, Detroit, MI). The plates were inverted and placed in an incubator maintained at 25°C. The plates were examined on a daily basis and when colony formation was observed, the plates were counted. The number of colony forming units (CFUs) were calculated by

taking the count from plates with between 30 and 300 colonies, applying the appropriate dilution factor for those plates, then dividing by the dry weight of soil that was added to the first dilution tube.

1,2-DCB-degrading bacteria present in soil samples collected in the field and from the laboratory columns were enumerated using a method based on a procedure described by Nishino et al (1994). The procedure involved minimal salts medium solidified with 1.8% (w/v) noble agar, and supplemented with yeast extract (10 mg/L) and dilute tryptic soy agar (1:10 w/v). These plates were maintained in a sealed desiccator and supplied 1,2-DCB in the vapor phase by adding 10 mL of pure 1,2-DCB to a 25-ml glass beaker positioned in the center of the desiccator.

Each series was incubated for 3 weeks at 25°C. Plates were examined for growth approximately two times per week and numbers of colonies were reported. After 3 weeks, select colonies that grew on the 1,2-DCB were streaked onto medium containing bromthymol blue (30 mg/L) to indicate acid production.

# SECTION V
# DATA ANALYSIS

It is not possible using currently available field techniques to isolate the metabolic destruction (i.e., biodegradation) rate of a single compound that exists in a mixture with many other compounds that are also metabolized. Therefore, any evaluation of the effectiveness of the bioventing process must rely on determining the net decrease in soil concentration of a particular chemical species by sampling.

Evaluating the effectiveness of using bioventing to treat the compounds listed in Table 1 required the analysis of the large amount of data collected and generated from sampling of both soil and soil gas over the one-year period of this demonstration. This section describes analysis methods used to identify trends in the data and to determine the value of various parameters that are useful in understanding conditions and changes at the site over that one-year period. The summary and interpretation of results from data analysis are presented in Section 6.0 of this report.

## A. RELATIONSHIP OF BIODEGRADATION AND VOLATILIZATION

Decreases in soil organic concentration typically occur in two forms in bioventing applications: biodegradation and volatilization. Biodegradation is the only removal mechanism that results in the destruction of the chemical; other mass transfer mechanisms simply move it among environmental matrices. For volatilization to be regarded as a significant removal mechanism, a chemical would have to be transported out of the treatment area, and into surrounding soils or the atmosphere.

In the case of 1,2-DCB, which has a low vapor pressure (1.2 mm Hg), it is likely that a significant fraction of the decrease in soil concentration observed during bioventing is a result of biodegradation. The net change in soil concentration of 1,2-DCB is a measure of the loss of mass of that compound from the water film surrounding soil particles and from sorption sites in the soil matrix. Local volatilization of 1,2-DCB is likely to be followed by re-solution (as shown in Figure 6), at least by a fraction of the original mass that volatilized, for potential subsequent biodegradation. Extensive vapor-phase transport of chemical mass is less likely in low vapor pressure compounds like 1,2-DCB than it is in compounds with higher vapor pressures; and re-solution of 1,2-DCB returns it to the site of biodegradation in the water film surrounding soil particles.

## B. CONCEPTUAL MODEL OF MASS BALANCES

As air is forced under pressure from the vent well and through the soil column, pressure and concentration gradients are imposed on the subsurface environment, disturbing equilibrium. These gradients induce advective (pressure-induced) and diffusive (induced by clean air) mass transfer, as well as volatilization. The conceptual model shown in Figure 6 illustrates these mass transfer mechanisms, which impact the mass balance on the interstitial soil water (where most biodegradation occurs). These relationships are rendered in abstract terms in the following conceptual equation:

$$\text{Desorption} + \text{Re-solution} - \text{Volatilization} - \text{Sorption} - \text{Biodegradation} = 0 \qquad (1)$$

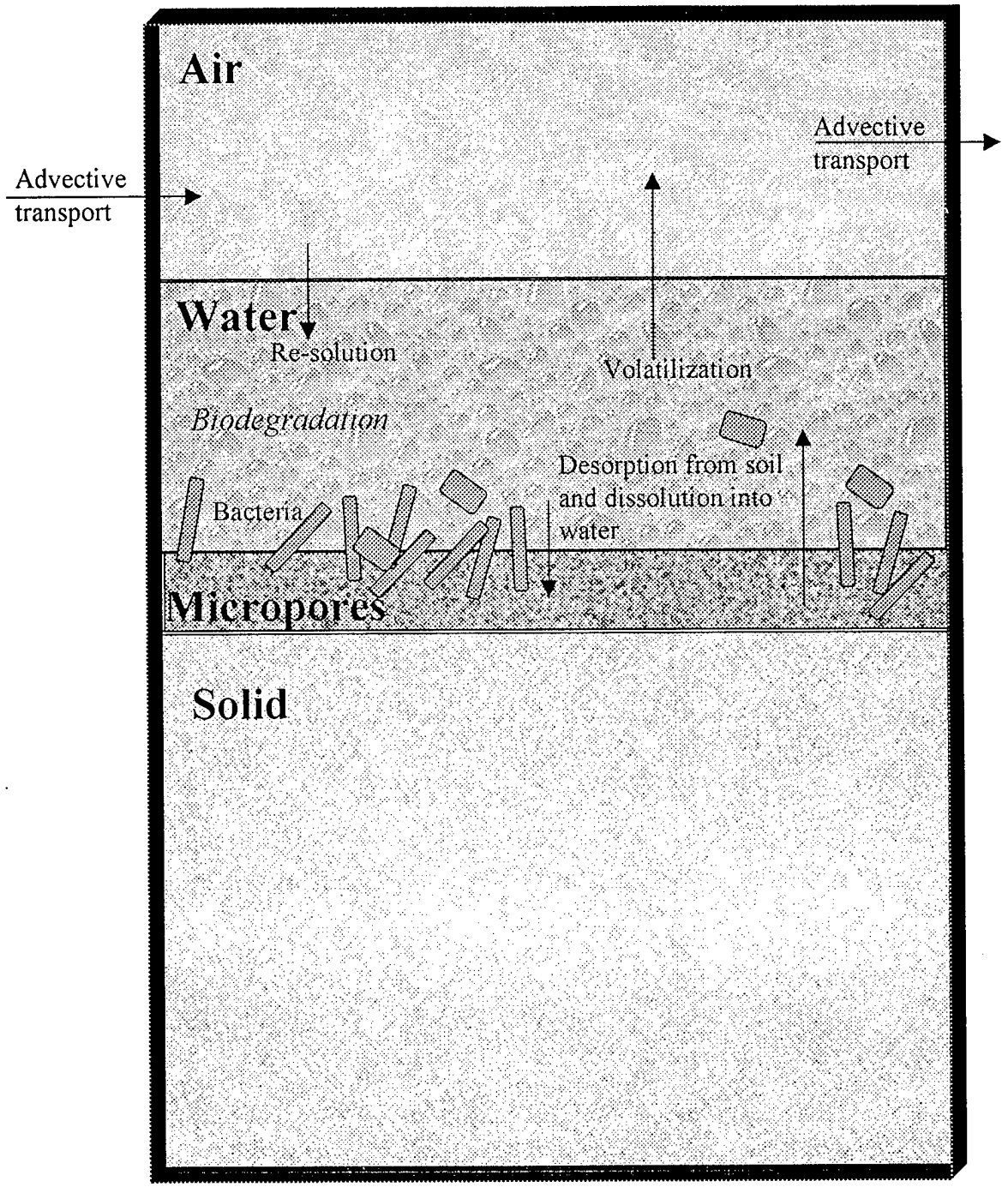


**Figure 6. Conceptual Model for the Mass Balance of Contaminants in the Soil System During Bioventing**

As shown in the conceptual model, air from the vent well immediately encounters soils containing organic compounds and begins to accumulate organic vapors as it travels through the soil air-filled void spaces. Adjacent to the air-filled void space is the water film that covers most soil particles in most climates. Compounds are exchanged between the air and the water film in the direction toward the equilibrium described by Henry's Law. Typically, near the vent well and in highly contaminated soil, the direction of this transfer is from the water into the vapor phase. In the expanded bioreactor commonly formed in bioventing applications, the dominant direction of transfer is into the water out of the vapor phase.

The major points to be noted in the conceptual model are that 1) volatilization and re-solution occur together at different rates with dominance changing from volatilization (nearer the vent well) to re-solution (in the expanded bioreactor), and 2) that biodegradation occurs primarily in the water film surrounding soil particles.

## C. IN SITU BIODEGRADATION RATE CALCULATIONS

### 1. Mass Ratios and Biodegradation Rates

In typical petroleum hydrocarbon bioventing applications, the mass of hydrocarbon degraded per unit mass of oxygen utilized is approximately 1/3.5 or 0.283. This ratio is given as C in the following Equation (1) used to calculate biodegradation rate from the oxygen utilization rate measured during an in situ respiration test.

$$k_b = \frac{-k_o \cdot \theta_a \cdot \rho_{O_2} \cdot C \cdot (0.01)}{\rho_k} \qquad (2)$$

where:

| | | |
|---|---|---|
| $k_b$ | = | In situ biodegradation rate, in mg/kg-d |
| $k_o$ | = | Oxygen utilization rate, in %/d |
| $\theta_a$ | = | Air-filled pore space |
| $\rho_{O2}$ | = | Density of oxygen, in mg/L |
| $\rho_k$ | = | Bulk density of soil, in g/cm$^3$. |

This project addressed the potential for applying bioventing to non-petroleum hydrocarbons; therefore, a new mass ratio comparing the mass of compounds being degraded versus the mass of oxygen utilized was calculated. Each of the compounds present at the site has a distinct stoichiometric ratio to oxygen in the oxidation reaction. That ratio was determined from the balanced oxidation reaction and using the molecular weights of the compounds involved.

The mass ratio for each compound was calculated as the mass of compound degraded per unit mass of oxygen utilized. These mass ratios were then weighted by the mass fraction and summed. The following Equation (2) was used:

$$C_{ave} = \sum_{i=1}^{n} (X_i \cdot C_i) \qquad (3)$$

where:

| | | |
|---|---|---|
| $C_{ave}$ | = | Average ratio of compound mass to oxygen mass in oxidation reaction |
| $X_i$ | = | Mass fraction of compound in total contaminant mass (see comments below) |
| $C_i$ | = | Compound-to-oxygen mass ratio for compound *i* |

Because the flame ionization detector (FID) is insensitive to chlorine, the total mass of organic compounds measured, including chlorinated compounds, is underestimated. The mass of chlorine must be added to the TPH mass value (measured by FID) to get the total mass of contaminants. This was done by finding the product of the chlorine content and the mass fraction for each organic species and adding that mass to the TPH mass as calculated from measurement with the FID. That total contaminant mass, including chlorine, was used as the basis for finding $X_i$ (mass fraction) for each constituent compound.

Once $C_{ave}$ was determined, that value was substituted for C in the equation used to relate the biodegradation rate, $k_b$, to the oxygen utilization rate, $k_o$. Site-specific soil properties of bulk density and air-filled porosity were used with the site-specific C factor to develop the following relationship, represented by the Equation (3):

$$k_b = -0.871 \cdot k_o \tag{3}$$

Oxygen utilization rates measured at each monitoring probe location (those at which initial oxygen concentrations were adequately elevated to perform a respiration rate test) during each respiration test were used to calculate the biodegradation rate at each location for each test. The resulting rates were used to evaluate biodegradation at the three levels within the test plot and to identify changes in the rates over the year of operation. Changes in biodegradation rate were also compared to in situ temperature changes throughout the year.

### 2. Mass Removals

The degree to which compounds were removed or destroyed was measured by both direct and indirect approaches. The direct approach involved collecting and analyzing soil samples from multiple depths at 14 locations within the test area. The indirect approach involved calculating the estimated mass of organic compounds that would have been destroyed if all of the oxygen utilized within the site had been used to metabolize these compounds.

#### a. Soil Sampling

The total mass of each COI within the treatment volume was calculated by summing the mass contained within selected volumes of soil of similar concentration. A three-dimensional (3D) grid model of the contaminant distribution in the soil was generated using EarthVision® Software by Dynamic Graphics. A 3D grid model defines a region in three-dimensional, Cartesian space. The EarthVision® 3D minimum tension gridding algorithm calculates a smooth surface that closely fits the input data values using a bicubic spline technique. All figures from 3D grids used in this report have a unit rectangular lattice or grid cell size of 2 feet in the X direction, 2 feet in the Y direction, and 0.5 feet in the Z (depth) direction. A total of 95 data points were used in the calculation of each grid. Any non-detect sample points were used in the gridding process as one-half the lowest detected value for that constituent.

EarthVision® software was used to contour soil volumes of similar concentration in three dimensions, and then calculate the volume of soil within each contour shell. An example graphic representation of the three-dimensional shells is shown in Figure 7. Each volume of soil was converted to a mass of soil using the average dry bulk density calculated from selected soil samples obtained during system installation. The COI concentration (on a mass/mass basis) for each volume of soil was multiplied by the mass of soil within each concentration shell, and then the individual masses were summed to

# Three Dimensional Isoconcentration Shell Volume Calculation

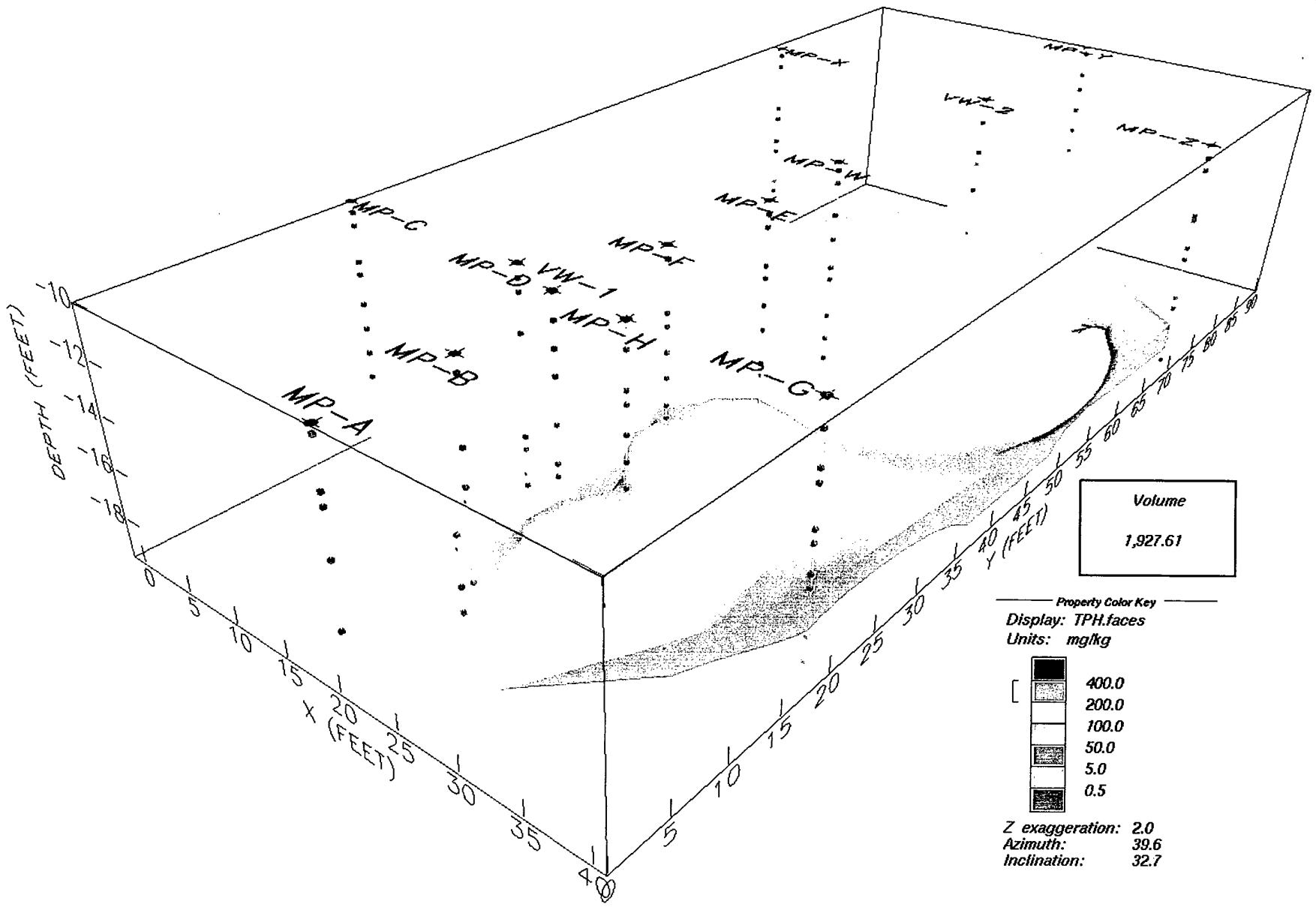


**Figure 7. Example of the 3-Dimensional Shells Generated by the EarthVisions Software Geostation Modeling Package**

obtain the total mass of that compound. The following Equation (4) was used:

$$M_{COI} = \sum_{i=1}^{n} \frac{C \cdot V_i \cdot \rho_d}{10^6} \quad (4)$$

where:

| | | |
|---|---|---|
| $M_{COI}$ | = | Total mass of COI before or after bioventing, in kg |
| $C_i$ | = | Concentration of COI within shell *i*, in mg/kg |
| $V_i$ | = | Volume of soil within shell *i*, in $m^3$ |
| $\rho_d$ | = | Dry bulk density of soil, in $kg/m^3$ |
| $10^6$ | = | Conversion factor, mg/kg.The total mass of COIs was calculated twice for this project: once before the one-year bioventing period began, and once after it ended. |

**b. In Situ Biodegradation**

The total mass of aerobically biodegradable organic compounds destroyed in situ was estimated by calculating in situ biodegradation rates for each of three 5-ft-thick soil layers at CPT 1: 4.5 to 9.5 ft bgs, 9.5 to 14.5 ft bgs, and 14.5 to 19.5 ft bgs. Soil-gas monitoring probes placed in those layers collected representative data from the midpoint depths of each layer, at levels of 7, 12, and 17 ft bgs, respectively.

The total volume of soil was estimated as the product of the area defined by the perimeter of all exterior monitoring point locations and of the deepest soil layer at which soil-gas samples were collected. The total volume of soil was divided into thirds to obtain soil volumes corresponding to the three soil layers described above, from which biodegradation rates were calculated.

The total mass of biodegraded compound was estimated using the following Equation (5):

$$M_b = \left( \sum_{i=2}^{3} k_{bi} \cdot V_i \right) \cdot \rho_d \cdot t \quad (5)$$

where:

| | | |
|---|---|---|
| $M_b$ | = | Mass of organic compounds biodegraded in one year of bioventing, in kg |
| $k_{bi}$ | = | Average in situ biodegradation rate within layer *i*, in mg/kg-d |
| $V_i$ | = | Volume of soil within layer *i*, in $m^3$ |
| $\rho_d$ | = | Dry bulk density of soil, in $kg/m^3$ |
| t | = | Duration of bioventing, in days. |

The duration of bioventing was defined as 360 days, to account for the five weeks of respiration testing during which the blower was not in operation. This summation was performed on only the middle (9.5 to 14.5 ft bgs) and lower (14.5 to 19.5 ft bgs) soil layers, because only these layers were represented by soil sampling (i.e., soil samples were collected at a depth of at least 10 ft bgs). Because soil sampling was only performed at depths below 10 ft bgs, the total mass estimated may not account for all biodegradation that actually occurred in the upper soil layer (4.5 to 9.5 ft bgs).

## D. SURFACE EMISSIONS

Surface emission testing was performed to ensure that minimal mass flux occurred from the soil surface into the atmosphere during bioventing system operation. The full procedure for surface emissions

testing is described in the *Work Plan* (Battelle, 1997). In summary, a high-purity air stream is passed through a box open only to ground surface and collected onto a sorbent tube after accumulating any organic compounds that may have volatilized from ground surface. The mass collected on the sorbent tube is quantified using GC. Surface emissions (i.e. flux) are calculated using the quantity of mass on the sorbent tube, the known ground surface area under the box, the air flowrate through the box, and the duration of air stream sampling onto the sorbent tube. The following general Equation (6) is used:

$$F = \frac{C \cdot V_r}{S} \tag{6}$$

where:

| | | |
|---|---|---|
| F | = | Flux, in mass/area-time |
| C | = | Concentration of the gas, in mass/volume |
| Vr | = | Volumetric flowrate of sweep gas |
| S | = | Soil surface covered by enclosure (McVeety, 1993). |

## E. LABORATORY STUDY

Oxygen data collected during closed-system operations were used to calculate average initial $O_2$ utilization rates. Oxygen concentrations were plotted against time, and the linear portion of the utilization curve was regressed to determine the zero-order $O_2$ utilization rate for each column.

The initial and final soil data and all gas-phase data for all COIs collected during the operation of the reactors were used to construct a mass balance for the compounds 1,2-DCB; 1,3- and 1,4-DCB; and 1,2,4-trichlorobenzene. These mass balances were used to quantify the fraction of total removal of TCB and DCBs by volatilization, absorption, and/or biodegradation. The biodegraded masses of TCB and DCBs were then determined by using the following Equation (7):

$$M_{bc} = M_{si} - M_{sf} - M_v + M_a \tag{7}$$

where:

| | | |
|---|---|---|
| $M_{bc}$ | = | Mass biodegraded in the column, in kg |
| $M_{si}$ | = | Initial mass of COIs in soil, in kg |
| $M_{sf}$ | = | Final mass of COIs in soil, in kg |
| $M_v$ | = | Total mass volatilized during aeration or captured in effluent during feeding, in kg |
| $M_a$ | = | Mass of vapor-phase COIs added to each reactor during feeding, in kg. |

# SECTION VI
# RESULTS AND DISCUSSION

The data from the analyses of soil-gas and soil samples described in section 4.8 were tabulated and graphed and the results have been compiled into a Data Package that complements this report. Although information about and discussion of the analytical data generated for the other compounds along with their implications also are provided in this section, the primary focus of the information provided in this section is on the effectiveness of bioventing for remediating the primary target contaminant, 1,2-DCB. The results from the analyses of the data collected during both the field and laboratory components of this demonstration are presented to facilitate the discussion and to support the results.

## A. ASSESSMENT OF SYSTEM OPERATION

The performance of the bioventing system was assessed based on system parameters including blower temperature, air flowrate, line pressure, and aeration efficiency.

### 1. System Parameters

System parameters were monitored during each site visit to ensure that the bioventing system was operating properly. After the initial air injection rate was found to be insufficient to provide oxygen to some of the soil-gas monitoring probes, the rate was increased to 200 scfh. From this point forward, the blower temperature remained around 120°F, the flowrate held at 200 scfh, and the line pressure was consistent at 1.1 psig. Also, the only downtime over the course of the year was during the intentional shutdown for the respiration testing. Consistency of operation and of system parameters therefore indicate that the bioventing system operated properly throughout the demonstration.

### 2. Aeration Efficiency

One of the most useful monitoring parameters for any aerobic bioventing system is in situ soil-gas oxygen concentration. Oxygen in soil gas is a good indicator of the effectiveness of aeration, and its uptake rate during respiration testing is used to calculate in situ biodegradation rates. Changes in oxygen concentration in soil gas can indicate the following conditions:

- Increased aeration effectiveness resulting from increased soil permeability caused by soil drying
- Increased aeration effectiveness resulting from decreased oxygen use along the flow path from the vent well
- Decreased aeration effectiveness resulting from decreased soil permeability caused by moisture infiltration
- Decreased aeration effectiveness resulting from increased oxygen use along the flow path from the vent well.

The last condition on that list could be caused by acclimation of microbial populations to a new substrate source and greater populations supported by a new, rich oxygen supply.

Oxygen concentrations in soil gas samples collected in the field were monitored by four distinct methods: (1) manual sampling and analysis with field meters, (2) manual sampling and analysis by GC, (3) monitoring by the OEMS, and (4) monitoring by the in situ oxygen sensors. Results from the

two analytical methods associated with the manual sampling (field meters and GC) were compared to results from the other two methods to confirm that field meters were producing representative results.

The OEMS measured and recorded daily in situ soil gas $O_2$, $CO_2$, and TPH concentrations from every probe in the monitoring array. The data were downloaded weekly by modem and the $O_2$ data were plotted over the entire study period of 1 year. The data plot showed the effectiveness of oxygenation during air injection. While some trends in changing concentration were observed over the course of the demonstration, the day-to-day data values were very consistent, showing little variability.

The in situ oxygen sensors installed at six selected probe locations also measured and recorded daily soil-gas oxygen concentrations. The results were stored on a datalogger (Data Electronics Model Datataker DT505) and then downloaded periodically during site visits by Battelle onto floppy disk using laptop computers. These data also were plotted over the 1-year study period. Trends in data taken by the in situ sensors over the year was similar to the trends indicated by data taken by the OEMS at the selected probe locations. The trends indicated the effectiveness of the bioventing system for aerating those locations.

Oxygen concentrations were found to have increased significantly throughout most of the soil test volume, as measured by the devices and methods described in Section 4. Figure 8 shows the volume within the test plot that was oxygenated to >5% $O_2$ before air injection was initiated. Only the upper soil layer (nearer the surface) was oxygenated to >5%. These soils were not impacted by COIs. Figures 9 through 11 show the volume oxygenated >5%, >10%, and >20%, respectively after bioventing started and was assumed to reach semi-steady state. As can be seen in the figures, the bulk of the oxygenated volume surrounded the active vent well. Aeration did extend into what was originally intended to be the non-biovented control volume as shown in Figure 12. Respiration in this area was evident during respiration testing when the blower was turned off. It can also be seen that some of the 17-ft bgs soil gas monitoring probes farthest away from the vent well were not thoroughly oxygenated. This is the typical geometry of an oxygenated volume around a vent well. The air follows the path of least resistance, which tends to be more vertical father away from the vent well due to flow paths terminating at the ground surface.

Once bioventing began, oxygen concentrations increased rapidly in most of the treatment volume around the vent well. Both the OEMS system and the in situ oxygen sensors revealed that this rapid increase was followed by a more gradual increase, as shown in Figures 13 and 14, respectively. The gradual increase in oxygen was likely due to a decrease in oxygen demand closer to the vent well as substrate was consumed over time.

## B. TECHNOLOGY PERFORMANCE ASSESSMENT

### 1. Field Assessment

#### a. Respiration Testing and Calculated Biodegradation Rates

One initial and four subsequent quarterly in situ respiration rate tests were performed over the course of the demonstration to monitor biological activity and to calculate biodegradation rates at the site. The biodegradation rates were calculated based on the stoichiometric oxidation rate of an organic compound that was formulated using the weight-averaged composition of the known contaminants. These calculated biodegradation rates reflected the overall microbial activity and could not be used to extrapolate a biodegradation rate for any single contaminant.

# Hill AFB, UT OU1 CDP1
## Volume Aerated to >5 % Oxygen Before Bioventing

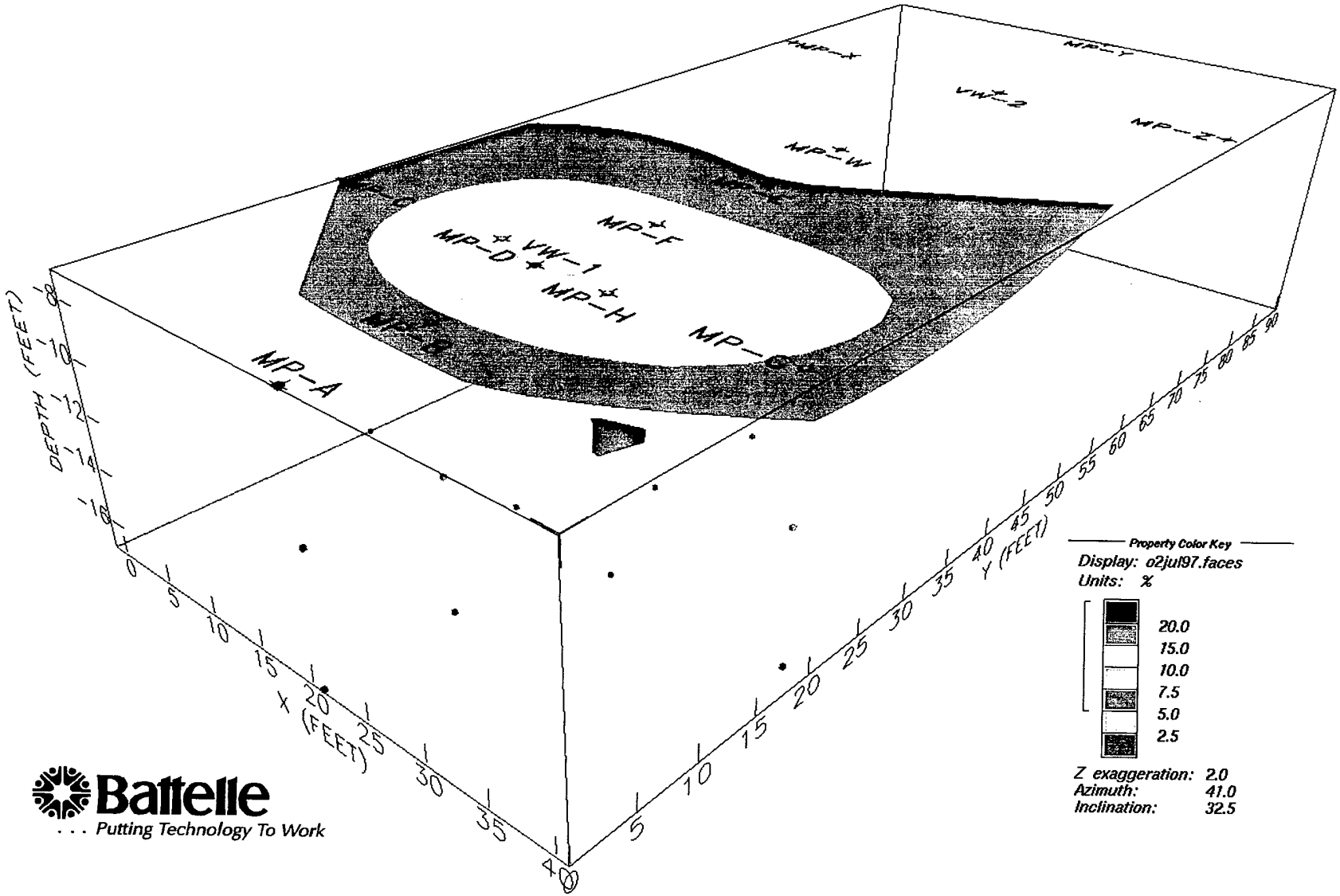


**Figure 8. Volume of Soil Oxygenated to >5% Before Bioventing**

# Hill AFB, UT OU1 CDP1
## Volume Aerated to >5 % Oxygen During Bioventing

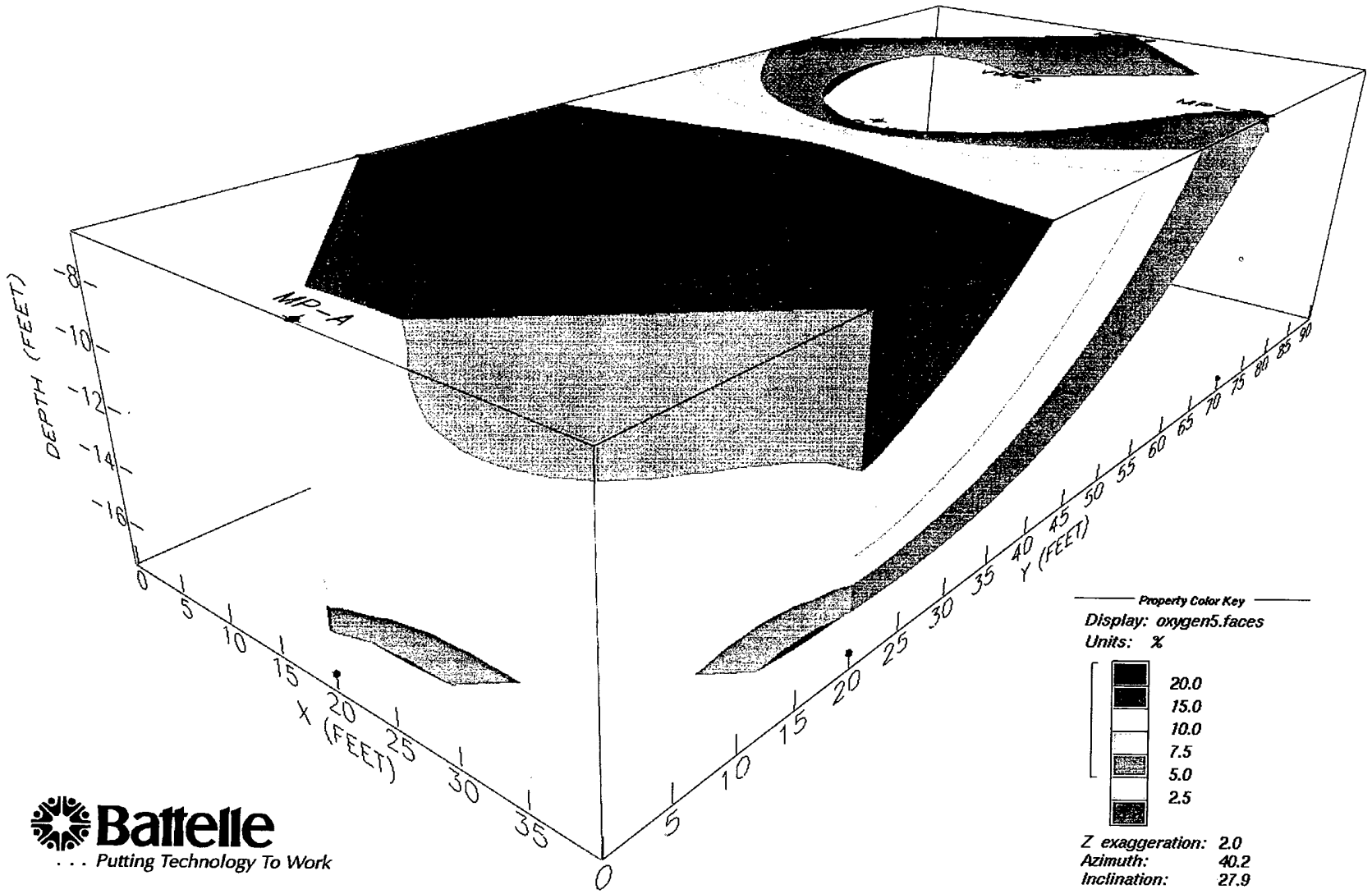


**Figure 9. Volume of Soil Oxygenated to >5% During Bioventing**

# Hill AFB, UT OU1 CDP1
## Volume Aerated to >10 % Oxygen During Bioventing

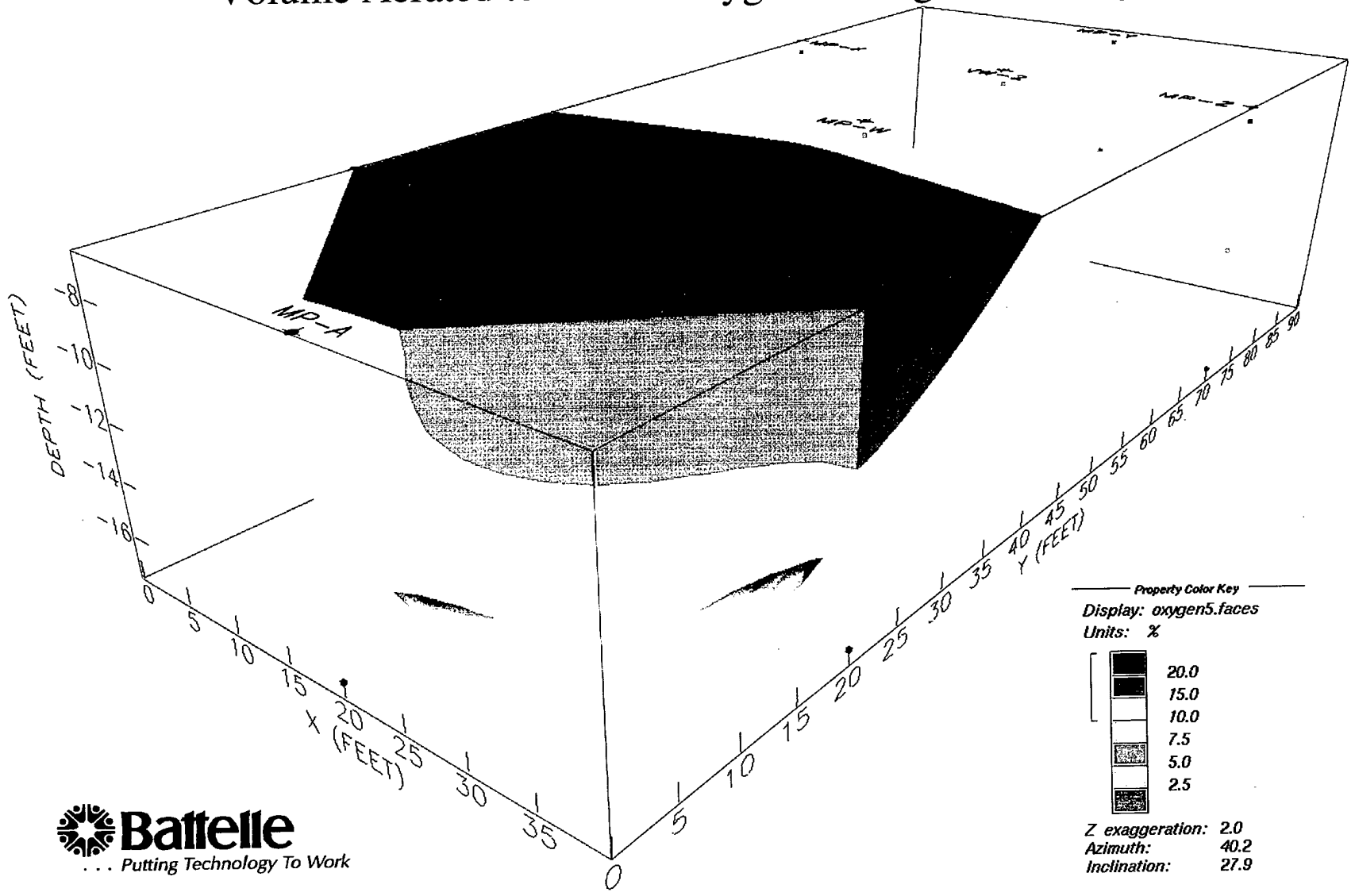


**Figure 10. Volume of Soil Oxygenated to >10% During Bioventing**

# Hill AFB, UT OU1 CDP1
# Volume Aerated to >20 % Oxygen During Bioventing

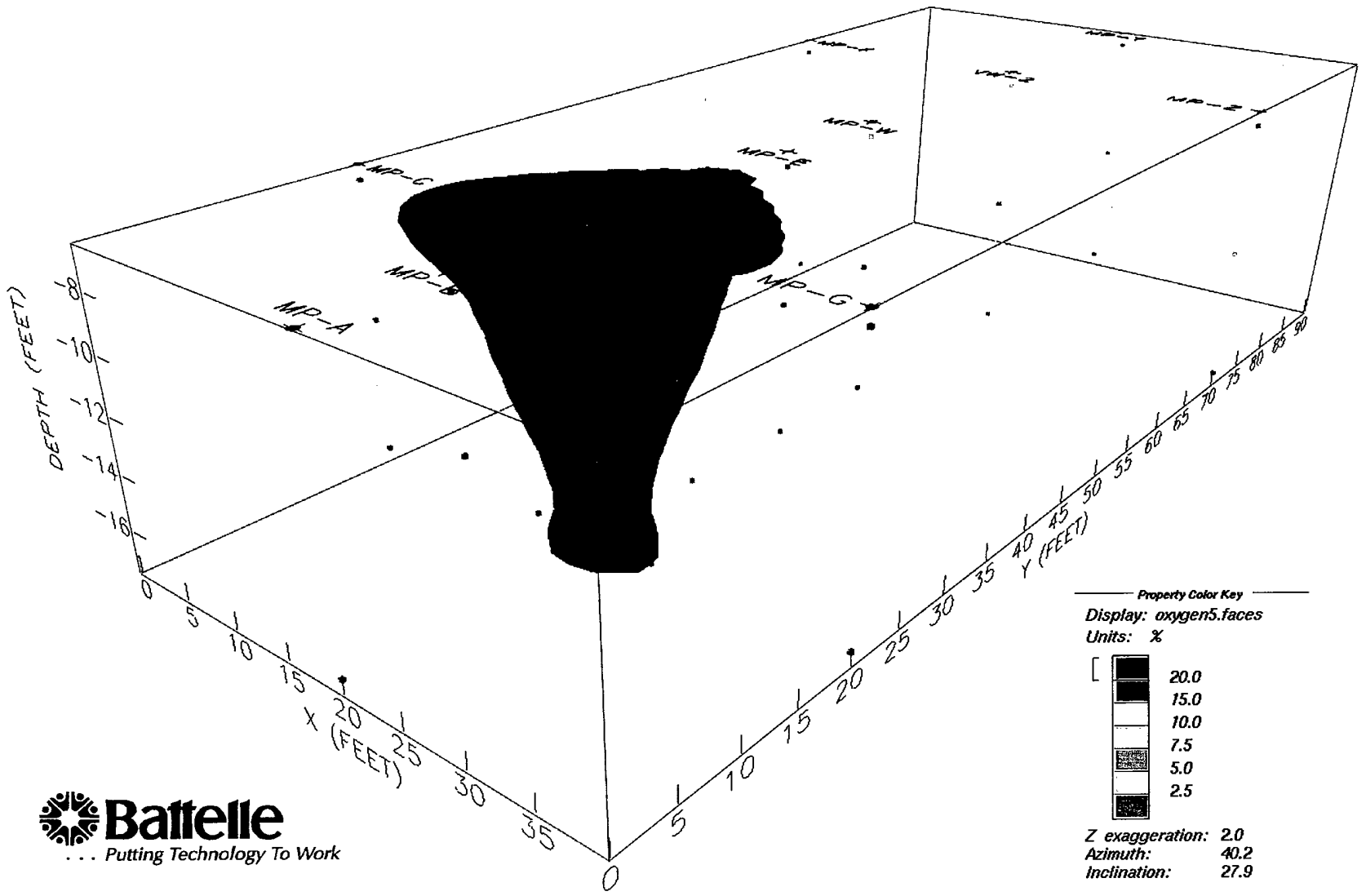


**Figure 11. Volume of Soil Oxygenated to >20% During Bioventing**

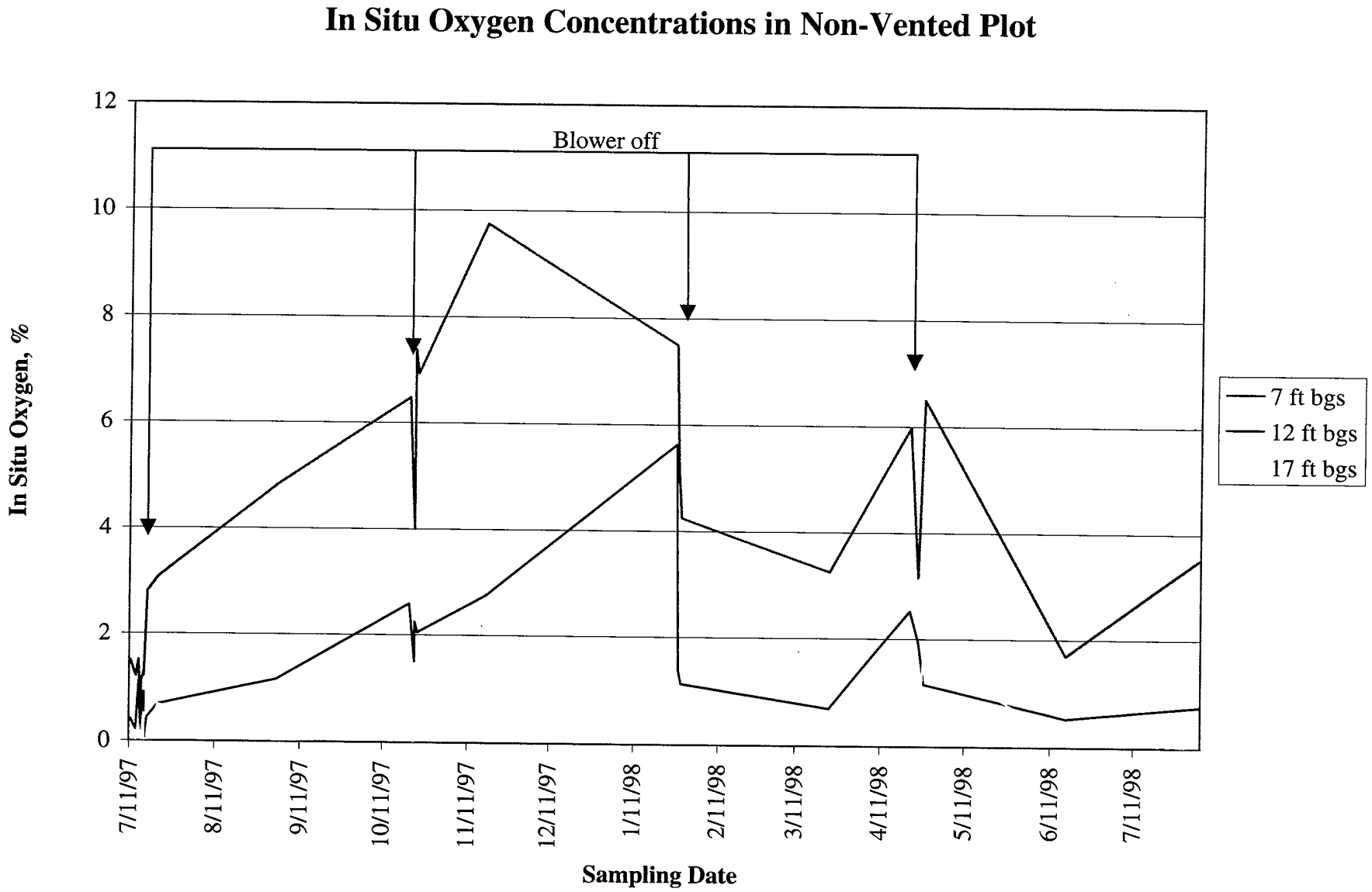


**Figure 12. Soil Gas Oxygen Concentrations in Non-Vented Plot**

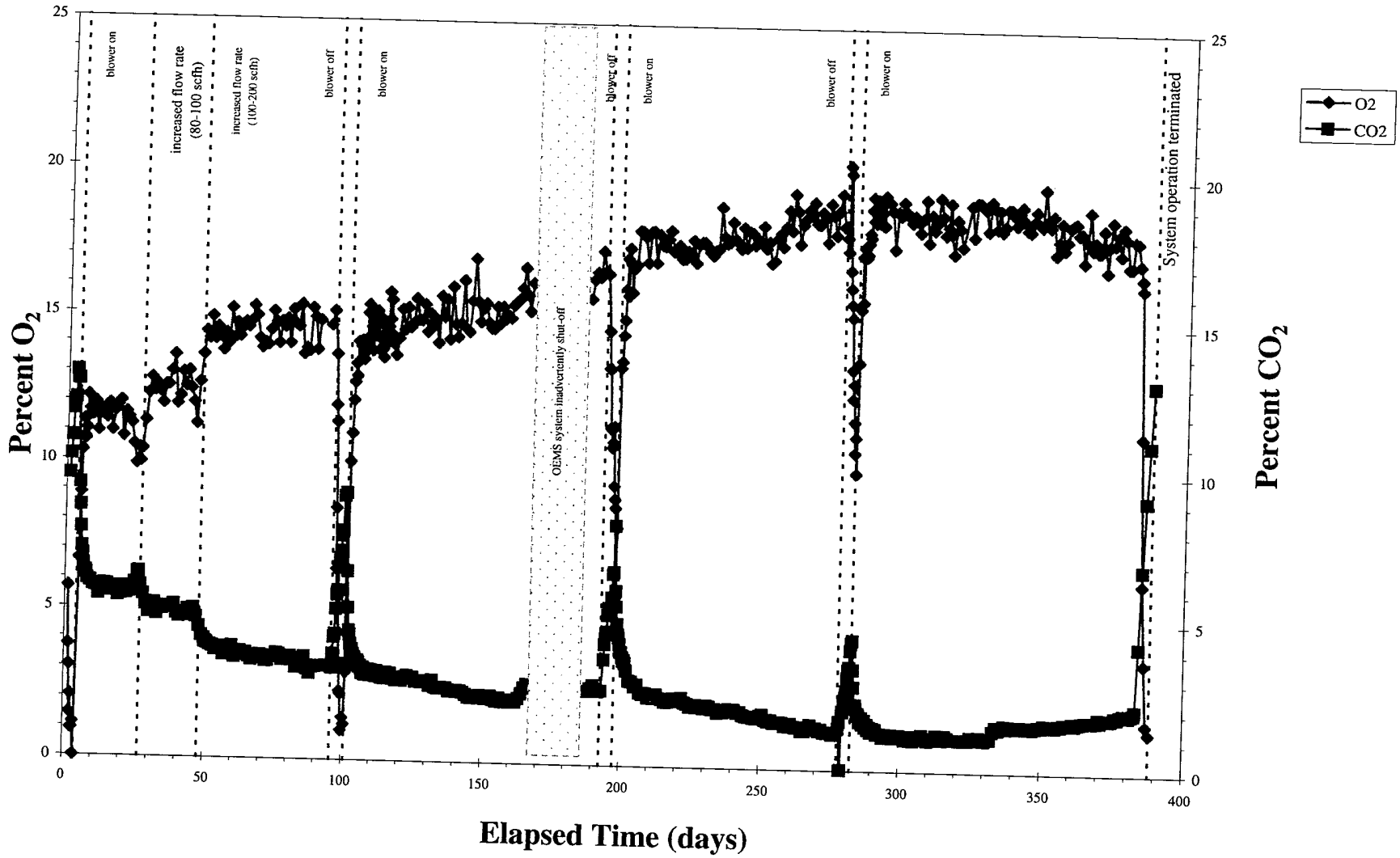


**Figure 13. Soil Gas Oxygen Concentrations Over One Year of Bioventing as Measured by OEMS**

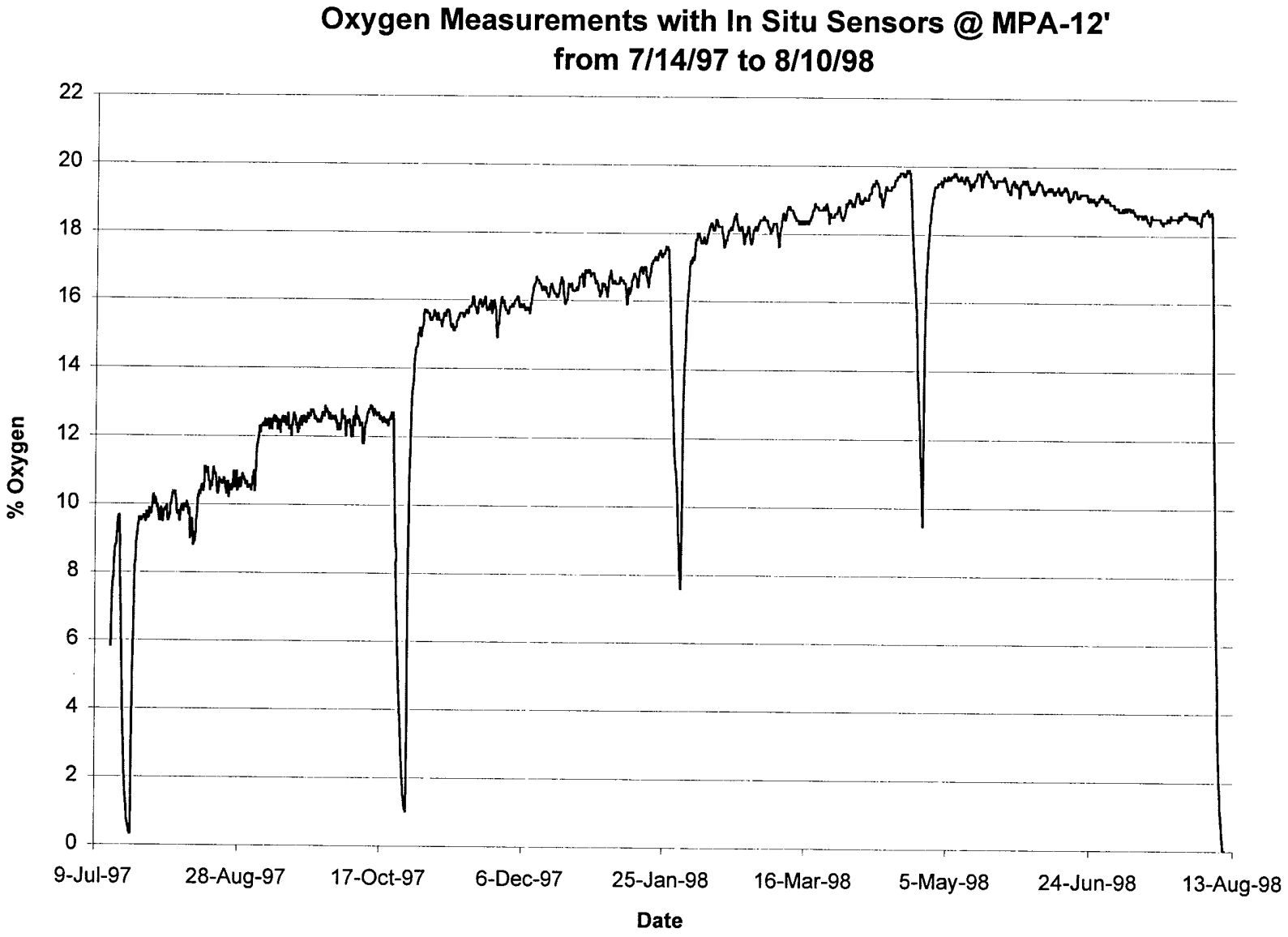


**Figure 14. Soil Gas Oxygen Concentrations Over One Year of Bioventing as Measured by In Situ Oxygen Sensors**

During the test, soil-gas $O_2$ concentrations were monitored by using a field meter, by the OEMS, and by the in situ $O_2$ sensors. Soil-gas $O_2$ data collected by the manual method were used to calculate the OUR at each soil gas monitoring probe location. Soil-gas $CO_2$ and TPH concentrations were monitored using field meters and by the OEMS. If soil gas measurements indicated that the $O_2$ level at any monitoring probe location was not above 5%, that location was excluded from the test.

The $O_2$ data taken during the first quarterly respiration test and using the three monitoring methods were plotted together (see Figure 15) and showed very good agreement, indicating that all three methods were effective for monitoring $O_2$ concentrations during in situ respiration rate tests.

The $O_2$ data collected by the field meters were plotted against time and a linear regression analysis was performed on the linear portion of each curve to determine the zero-order $O_2$ utilization rate. This rate was representative of the rate at which $O_2$ was consumed during active venting when $O_2$ was above the rate-limiting concentration. The $CO_2$ concentration data were plotted against time along with the oxygen concentration data, and supported the result that reductions in $O_2$ concentrations observed during respiration testing were a result of microbial activity and not of other abiotic reactions. Respiration plots and the results of the linear regression analyses are provided in the data package that accompanies this report.

The oxygen utilization rate was then converted to an in situ biodegradation rate, using methods described in Section V-C. The average biodegradation rate for each monitoring probe depth and the associated volumes and soil bulk densities that were used to calculate the compound masses removed over the one year that the system was operated are listed in Table 6. The average in situ biodegradation rates for the soil layers increased with increasing depth, as did the apparent concentration of organics as observed during initial and final soil sampling activities. The rates of $CO_2$ production also followed this trend. The correlation in trends between these parameters indicated that the microbial activity observed at CDP 1 during bioventing resulted from the degradation of the target compound, 1,2-DCB.

Based on respiration rates and stoichiometry, a total of 1,490 kg (3,400 lbs.) of organic degraded in one year of operation within the volume of soil that was monitored (10 to 20 ft bgs). Note that this value ignores removal in the upper soil layer listed in Table 6. It should also be noted that the system delivered oxygen to a volume of soil greater than the volume that was monitored and that the presence of compound extended beyond the boundaries of the test cell. These facts suggest that bioventing probably supported degradation of more mass of compound than were estimated by these calculations.

**Table 6. In Situ Biodegradation Rates and Bioreactor Properties**

| Average Depth and Interval for Each Soil Layer, ft bgs | Average In Situ Biodegradation Rate, mg/kg-d | Volume, $m^3$ ($ft^3$) | Bulk Dry Density, $kg/m^3$ ($lb/ft^3$) | Estimated Mass Biodegraded, kg (lb) |
|---|---|---|---|---|
| 7 (4.5 to 9.5) | 1.7 | 260 (9,100) | 1,521 (95) | 240 (540) |
| 12 (9.5 to 14.5) | 3.5 | 260 (9,100) | 1,521 (95) | 490 (1,100) |
| 17 (14.5 to 19.5) | 7.4 | 260 (9,100) | 1,521 (95) | 1,000 (2,300) |

### b. Reduction of 1,2-DCB Mass

The more critical method for assessing the performance of the bioventing technology includes analysis of the reduction of the contaminants in the vadose zone soils. To effectively track the fate of the COIs, both soil and surface emission analyses were conducted. The results from these analyses

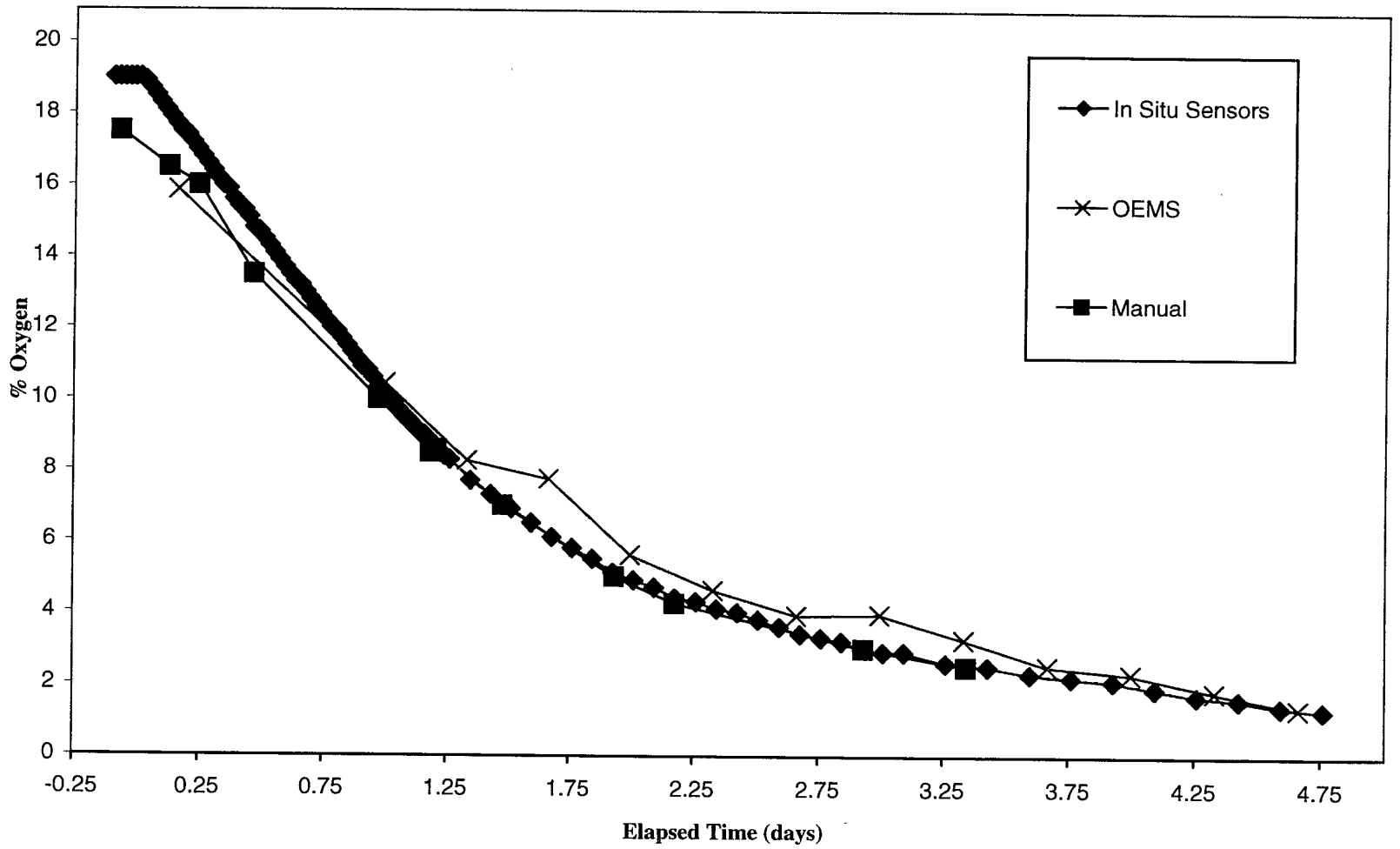


**Figure 15. Correlation Among Three Methods of Oxygen Measurement During In Situ Respiration Test**

provide the data necessary to determine whether the compounds were biodegraded or simply lost from the system through volatilization and advective transport.

***Soil Sampling.*** Table 7 lists the total mass for each compound tracked within the treatment volume before and after bioventing for one year. Each of the masses listed was calculated using methods described in Section V-C-2a. The difference in mass between initial and final soil sampling indicated significant removal of 1,2-DCB. Soil sampling results indicated that dichlorobenzene compounds were removed at an average rate of 65.7% when analyzed individually, and 68% when quantified as a single compound by GC, over the one year of bioventing. These comparisons were performed because of the similar elution times of 1,3- and 1,4-DCB, which could potentially interfere with quantification of the mass of the individual isomers. Other COIs were also removed insignificant masses, as data in Table 7 indicates. It is noteworthy that tetrachloroethylene, which is volatile and known not to be aerobically biodegradable, either directly or by cometabolism, was removed at a rate almost one order of magnitude less than DCB. In total (including TPH), 61.7 kilograms of the COIs were removed; and 16.5 kg of target compounds, neglecting TPH, were removed during the year of bioventing.

***Surface Emissions.*** Surface emissions were measured to quantify the mass of contaminant that was lost from the site to the atmosphere as a result of volatilization and advective transport. The measurements were made following system startup when emission rates would be expected to be the highest. The emission measurements were made for hydrocarbon and chlorinated compounds under non-vented (no bioventing) and vented (active bioventing) conditions.

**Table 7. Mass Removal of Compounds of Interest from One Year of Bioventing at CDP-1 Hill AFB**

| Compound | Initial Mass, kg | Final Mass, kg | Mass Removed, kg | % Removal |
|---|---|---|---|---|
| *cis*-1,2-dichloroethylene | 0.003 | 0.062 | -0.059 | NA |
| 1,1,1-trichloroethane | 0.20 | 0.14 | 0.06 | 28 |
| Trichloroethylene | 1.88 | 1.09 | 0.79 | 42 |
| Toluene | 0.72 | 0.53 | 0.19 | 27 |
| Tetrachloroethylene | 0.42 | 0.38 | 0.04 | 9 |
| Chlorobenzene | 0.36 | 0.25 | 0.11 | 30 |
| Ethylbenzene | 0.18 | 0.12 | 0.06 | 36 |
| *m* + *p*-Xylene | 0.37 | 0.27 | 0.10 | 27 |
| *o*-Xylene | 0.49 | 0.21 | 0.28 | 56 |
| 1,3,5-trimethylbenzene | 2.45 | 0.88 | 1.57 | 64 |
| 1,3-dichlorobenzene | 2.62 | 1.52 | 1.10 | 42 |
| 1,2,4-trimethylbenzene | 1.43 | 0.60 | 0.83 | 58 |
| 1,2-dichlorobenzene | 12.30 | 3.14 | 9.16 | 74 |
| 1,4-dichlorobenzene | 1.69 | 0.33 | 1.36 | 81 |
| 1,2,4-trichlorobenzene | 4.28 | 1.15 | 3.13 | 73 |
| 1,2,3-trichlorobenzene | 1.81 | 0.38 | 1.43 | 79 |
| Naphthalene | 5.89 | 0.41 | 5.48 | 93 |
| Total DCBs | 20.50 | 6.57 | 13.9 | 68 |
| TPH | 98.5 | 62.4 | 36.1 | 37 |

Flux values were calculated from the measured concentrations to quantify the mass losses for each COI. The results from these calculations are presented in Table 8. All values are reported as grams of COI lost from the surface of the plot (3,200 $ft^2$) over the year that the bioventing system was operated. The surface emission data showed that the nature of the volatile contaminants, combined with the loose

soil type and environmental parameters (e.g., elevation and barometric influences), contributed to a low-level migration of contaminants from the soil to the atmosphere even under non-vented conditions. The data showed that bioventing did have an impact on the discharge of vapors from the ground surface as the introduction of air into the soil profile caused a general trend of increase in the measured flux rates. This increase was expected, because under static non-vented conditions some soil gas tends to migrate to the atmosphere; any additional physical pressure to the subsoil would increase this tendency. It is unlikely that lower air flowrates would have permitted emission levels equal to the non-vented conditions.

**Table 8. Summary of Surface Emissions Testing Results**

| Compound | Average Emissions During Bioventing, g/yr | Average Emissions Without Bioventing, g/yr | Average Net Emissions, g/yr |
|---|---|---|---|
| 1,1-dichloroethylene | 6.28 | 4.01 | 2.28 |
| *cis*-1,2-dichloroethylene | 410.68 | 403.57 | 7.12 |
| 1,1,1-trichloroethane | 129.78 | 107.70 | 22.08 |
| Trichloroethylene | 910.89 | 549.85 | 361.03 |
| 1,1,2-trichloroethane | 0.00 | 0.00 | 0.00 |
| Toluene | 2.48 | 2.40 | 0.08 |
| Tetrachloroethylene | 66.06 | 29.16 | 36.90 |
| Chlorobenzene | 1.66 | 0.00 | 1.66 |
| Ethylbenzene | 0.00 | 0.50 | -0.50 |
| *m,p*-Xylenes | 0.91 | 0.45 | 0.46 |
| *o*-Xylene | 1.34 | 0.00 | 1.34 |
| 1,3,5-trimethylbenzene | 1.40 | 0.41 | 0.99 |
| 1,2,4- trimethylbenzene | 3.08 | 9.26 | -6.18 |
| 1,3-dichlorobenzene | 0.00 | 0.00 | 0.00 |
| 1,4-dichlorobenzene | 0.00 | 1.53 | -1.53 |
| 1,2-dichlorobenzene | 76.7 | 41.5 | 35.2 |
| 1,2,4-trichlorobenzene | 7.51 | 0.72 | 6.78 |
| Total | 1619 | 1151 | 468 |

The COIs monitored at CDP 1 exhibit a wide range of vapor pressures listed in Table 9, that, when combined with their solubilities, are good indicators of their tendency to be lost through volatilization and advective transport. Overall, this tendency was reflected in the surface emission data, because a larger percentage of the loss of the compounds with vapor pressures greater than toluene was attributed to emissions from the ground surface. Losses through volatilization of compounds with vapor pressures equal to or lower than toluene were generally a much smaller percentage of the total mass removed. The loss through volatilization of 1,2-DCB was estimated to be 76.7 g over the one-year demonstration period. Although this is a worst-case estimate, this level of volatile loss represents just over 0.8% of the loss measured through the soil analyses. Interestingly, the flux of 1,3-DCB was below the detection limit and the flux of 1,4-DCB was greater before the bioventing system was turned on. The latter flux is probably a result of to the dilution effect of air injection causing the concentration in the emitted vapor to be below the analytical detection limit. This trend also was observed with ethylbenzene and 1,2,4-trimethylbenzene.

**Table 9. COI Vapor Pressures**

| Compound | Vapor Pressure | | Compound | Vapor Pressure | |
|---|---|---|---|---|---|
| | (Pa) | (mm Hg) | | (Pa) | (mm Hg) |
| Naphthalene | 12 | 0.09 | *m,p*-Xylene | 1,140 | 8.55 |
| 1,2,3-trichlorobenzene | 28 | 0.21 | Ethylbenzene | 1,280 | 9.60 |
| 1,2,4-trichlorobenzene | 39 | 0.29 | Chlorobenzene | 1,600 | 12.00 |
| 1,4-dichlorobenzene | 173 | 1.30 | Tetrachloroethylene | 2,479 | 18.59 |
| 1,2-dichlorobenzene | 196 | 1.47 | Toluene | 3,800 | 28.50 |
| 1,2,4-trimethylbenzene | 270 | 2.02 | Trichloroethylene | 7,753 | 58.14 |
| 1,3-dichlorobenzene | 287 | 2.15 | 1,1,1-trichloroethane | 13,149 | 98.61 |
| 1,3,5-trimethylbenzene | 330 | 2.47 | *cis*-1,2-dichloroethylene | 21,767 | 163.24 |
| *o*-Xylene | 493 | 3.70 | | | |

The estimated losses through volatilization take into account the loss of contaminant from above the 10- to 20-ft bgs interval over which the soil mass removal was calculated. Coupled with the timing of the surface emission measurements, this suggests that the calculated estimates overstate the percentage of loss that was attributable to volatilization.

***In Situ Biodegradation.*** The mass losses for the COIs that could be attributed to biodegradation were calculated as the difference between the total mass removed as measured through initial and final soil sample analyses and the mass volatilized from the system as determined through surface emission testing. The results of these calculations are presented in Table 10. Note that only the 12- and 17-ft bgs layers were included in the soil mass loss calculation because the soil-sampling interval was between 10 and 20-ft bgs; also, the fact that the surface emission test was conducted immediately following system startup when emission rates would be the highest. These factors suggest that these estimated biodegradation rate are conservative.

The data presented in Table 10 indicate that the large majority of the mass removal of the various chlorobenzene isomers was a result of biodegradation. Information on the biodegradation of *cis*-1,2-dichloroethylene, 1,1,1-trichlorooethane, and TCE was not available, because volatilization accounted for all or more of the mass loss that was determined through soil analyses. The mass of PCE, which is not biodegraded under aerobic conditions, was reduced by approximately 9% over the course of the demonstration. Surface emission data were in close agreement with the amount of PCE mass lost as determined by the soil analyses, thus providing further evidence that the reduction in mass of the compounds with lower vapor pressures than PCE was a result of biodegradation rather than volatilization.

The estimated mass of TPH biodegraded over the year of operation based on respiration measurements was greater than that calculated from observed results of direct soil sampling and analysis. Results were consistent even when the top layer was excluded from the mass removal calculation. The difference in mass attributed to biodegradation and the mass observed by came about because the analytical method used (headspace analysis), is unlikely to pick up many longer chain hydrocarbons because it is based on an equilibrium established between liquid and vapor within the assay vial. It is likely that longer chain hydrocarbons missed by this test method offered significant oxygen demand in the soils. It is unlikely that chemical oxygen demand was significant after the first few days of bioventing, except perhaps at the margin of the aerated soil volume.

**Table 10. COI Mass Balances During Bioventing at CDP 1, Hill AFB**

| Compound | Total Mass Removed, g | Mass Volatilized, g | Mass Biodegraded, g |
|---|---|---|---|
| *cis*-1,2-dichloroethylene | -59.0 | 410 | -- |
| 1,1,1-trichloroethane | 60.0 | 130 | -- |
| Trichloroethylene | 790 | 910 | -- |
| Toluene | 190 | 2.48 | 188 |
| Tetrachloroethylene | 40.0 | 66.1 | -- |
| Chlorobenzene | 110 | 1.66 | 108 |
| Ethylbenzene | 60.0 | 0[(a)] | 60 |
| *m, p*-Xylene | 100 | 0.91 | 99 |
| *o*-Xylene | 280 | 1.34 | 279 |
| 1,3,5-trimethylbenzene | 1,570 | 1.4 | 1,569 |
| 1,3-dichlorobenzene | 1,100 | 0[(b)] | 1,100 |
| 1,2,4-trimethylbenzene | 830 | 3.08 | 827 |
| 1,2-dichlorobenzene | 9,160 | 76.7 | 9,083 |
| 1,4-dichlorobenzene | 1,360 | 0[(a)] | 1,360 |
| 1,2,4-trichlorobenzene | 3,130 | 7.51 | 3,122 |
| 1,2,3-trichlorobenzene | 1,430 | 0[(b)] | 1,430 |
| Naphthalene | 5,480 | 0[(b)] | 5,480 |
| Total DCBs | 13,900 | 76.7 | 13,823 |
| TPH | 36,100 | NA | NA |

-- = Volatilization accounted for ≥100% of the mass loss for this COI.
NA = not available because TPH is not included in EPA Method TO-14.
(a) = Concentrations were below detection limits during venting.
(b) = Compounds were not detected during surface emission testing.

### c. Temperature Effects

The temperature fluctuated over the year at the various depths at which in situ thermocouples were installed as shown in Figure 16. As expected, the shallowest depth (7 ft bgs) experienced the greatest temperature fluctuations. The deeper thermocouples (12 and 17 ft bgs) showed temperature fluctuations that were both lagged and dampened compared to the 7 ft thermocouples.

Biodegradation rates appeared to be correlated with in situ temperature. Figure 17 shows the average site-wide biodegradation rate changing over the year and the trend line of temperature at the various soil-probe depths. It is commonly estimated that an enzyme-regulated reaction rate will double with every 10°C increase in temperature within the enzyme's effective temperature range. The correlation between in situ temperature and biodegradation rate is an illustration of this temperature effect on reaction rate. Of course, substrate concentration also affects reaction rates. While a van't Hoff-Arrhenius relationship could be calculated to determine the activation energy of the biodegradation reaction, only temperature effects should be considered for this relationship to be valid. Within the soil test volume and over the study period both temperature and substrate concentration changed with depth and time, making it impossible to identify the specific effects of each on reaction rate.

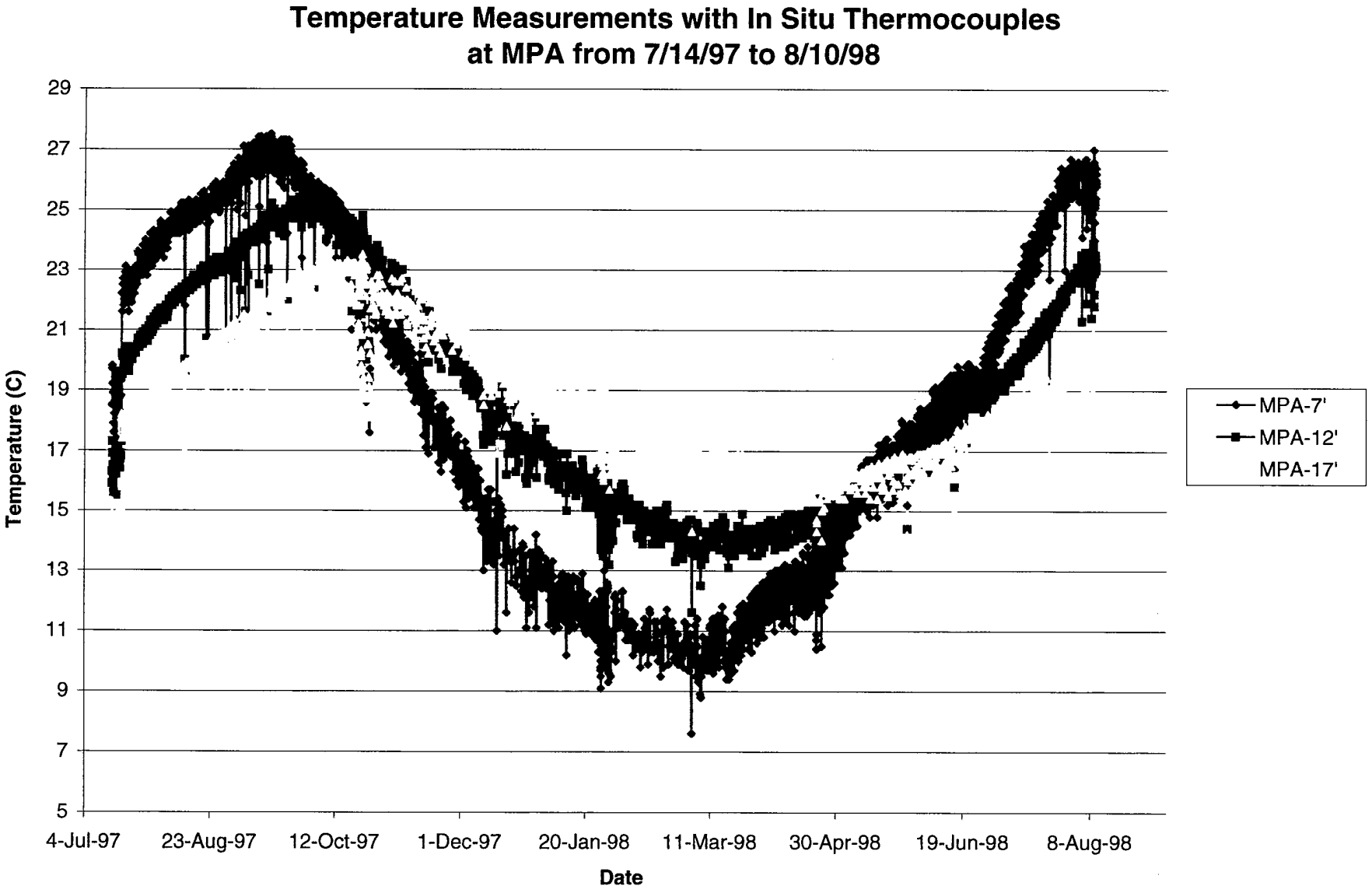


**Figure 16. Temperature Fluctuations in Subsurface Soils Over One Year of Bioventing**

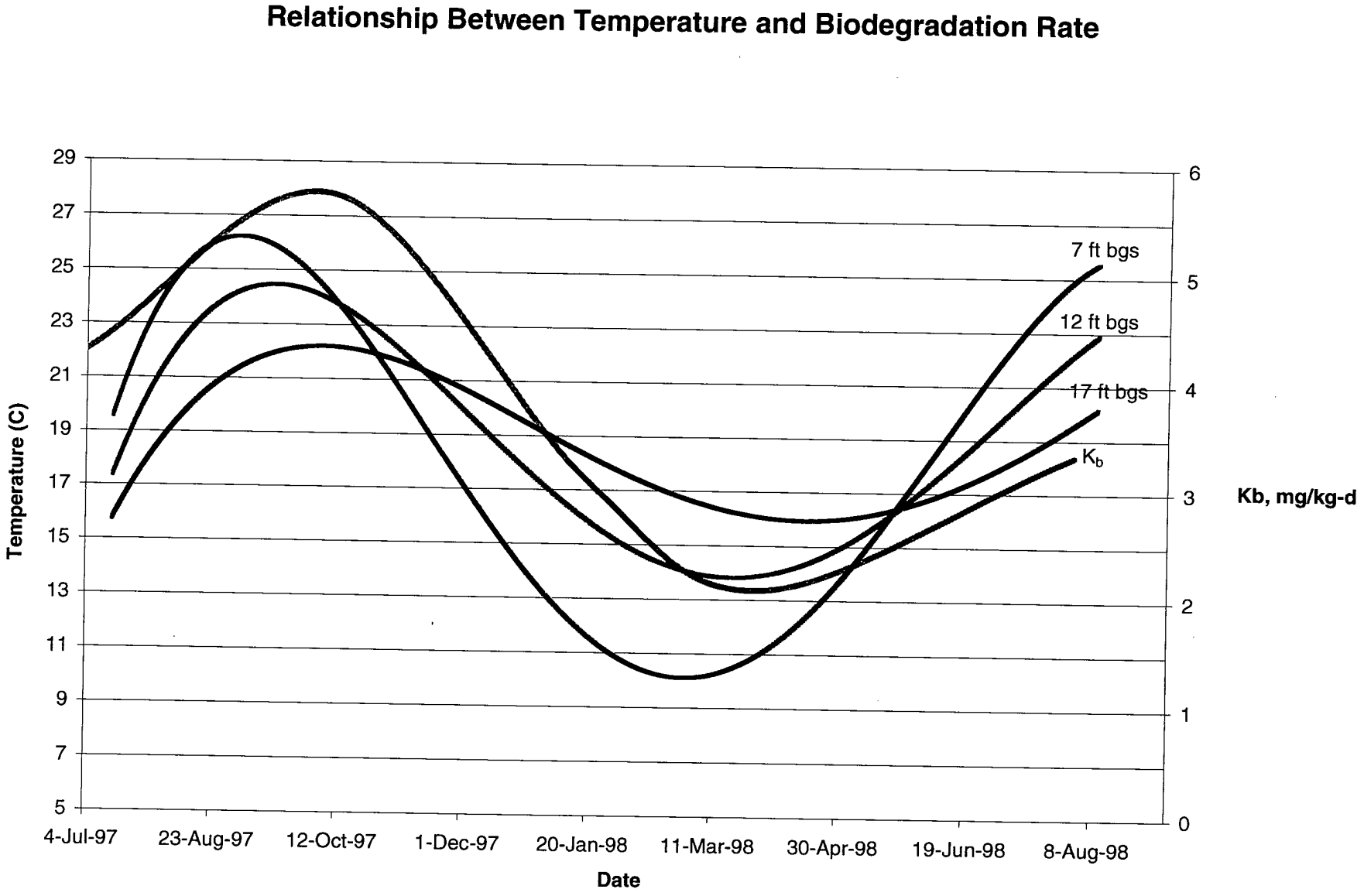


**Figure 17. Relationship Between Temperature and Biodegradation Rate**

## 2. Laboratory Assessment

A laboratory column experiment was conducted to collect evidence of biodegradation under more controlled conditions than could be achieved in the field to provide support to the conclusions based on the field observations. During the laboratory test, respiration, contaminant concentrations, and bacterial populations were monitored in six columns that contained undisturbed soil cores collected during installation of the bioventing system. The following discussion summarizes the results from these analyses and their implications for assessing the effectiveness of the bioventing technology.

### a. Respiration Testing

Respiration measurements were made by sampling the column off-gas and measuring the $O_2$ and $CO_2$ concentrations by GC/TCD. The data were analyzed to determine OURs using the same method described for the respiration data from the field. The oxygen utilization rates were used to monitor biological activity in the columns, not to calculate biodegradation rates. Biodegradation rates were determined instead based on the COI mass balances, as described in Section 6.2.2.2.

Initial and final respiration measurements (Table 11) indicate that the biological activity at the end of the laboratory experiment was significantly lower than at the beginning. The columns were maintained at 25°C, suggesting that a change had occurred in the columns that was affecting the microbial activity. One possibility was that the more readily biodegradable compounds were exhausted after 8 months and that the microbial population was becoming substrate-limited. Another possibility was that an essential nutrient may have limited microbial activity. A final possible explanation for the decreased activity is that a toxic byproduct had formed and accumulated in the soils.

**Table 11. Average of Initial and Final Respiration Rates**

| Column ID | Initial | | Final | |
|---|---|---|---|---|
| | Oxygen Utilization Rate (%$O_2$/hr) | Carbon Dioxide Production Rate (%$CO_2$/hr) | Oxygen Utilization Rate (%$O_2$/hr) | Carbon Dioxide Production Rate (%$CO_2$/hr) |
| 1 | 0.76 | 0.41 | 0.0242 | 0.0179 |
| 2 | 1.97 | 0.88 | 0.0318* | 0.0220* |
| 3 | 1.12 | 0.48 | -- | -- |
| 4 | 1.07 | 0.47 | 0.0091* | 0.0076* |
| 5 | 0.76 | 0.35 | -- | -- |
| 6 | 0.61 | 0.25 | -- | -- |
| **Mean** | **1.04** | **0.47** | **0.0217** | **0.0158** |
| **Standard Deviation** | **0.49** | **0.22** | **0.0116** | **0.0074** |

* Reactor 2 and 4 represent average values of 2 respiration tests.

### b. Contaminant Mass Reduction

Contaminant concentrations were monitored in initial and final soil samples, and in column-gas samples collected over the course of laboratory testing. The data from these analyses were used to construct a mass balance. The results of the analyses and the mass balance are discussed in the following sections.

***Soil Sampling.*** The mass of each COI initially present in the soil columns was determined based on the concentrations measured in soil samples collected from the ends of sleeves that

were collected in conjunction with and were adjacent to the sleeves used in the laboratory. The final mass remaining in the columns after treatment was determined from the analysis of soil samples collected from each column. Masses were calculated using the porosity and soil bulk density determined from triplicate analysis of cores collected from the same depth interval and the weight of soil in each soil column. The results of these calculations are provided in Table 12.

***Column Influent and Effluent Gas Sampling.*** Gas-phase monitoring was conducted to quantify the mass of COIs that was added to (or removed from) the soil columns for purposes of constructing the mass balances. The masses added (or removed) were calculated by multiplying the measured concentrations of each COI by the volumetric flowrate and time. The results are presented in Table 12.

**Table 12. COI Mass Balances From Laboratory Columns From CDP 1, Hill AFB**

| Compound | Initial Mass (mg) | Mass Added (mg) | Mass Volatilized (mg) | Final Mass (mg) | Mass Removal Attributed to Biodegradation (mg) |
|---|---|---|---|---|---|
| *cis*-1,2-dichloroethylene | 2.87 | 67.8 | 38.2 | 0.05 | 32.4 |
| 1,1,1-trichloroethane | 0.88 | 6.34 | 5.79 | 0.04 | 1.39 |
| Trichloroethylene | 9.41 | 14.1 | 32.6 | 0.18 | (9.27) |
| Toluene | 3.58 | 1.36 | 10.34 | 0.02 | (5.42) |
| Tetrachloroethylene | 1.17 | 2.83 | 6.57 | 0.08 | (2.65) |
| Chlorobenzene | 1.51 | 0.17 | 4.34 | 0.01 | (2.67) |
| Ethylbenzene | 0.53 | 0.17 | 1.24 | 0.01 | (0.55) |
| *m,p*-Xylene | 1.63 | 0.63 | 3.08 | 0.01 | (0.83) |
| *o*-Xylene | 1.50 | 0.21 | 2.14 | 0.02 | (0.41) |
| 1,3,5-trimethylbenzene | 7.35 | 0.15 | 6.90 | 0.16 | 0.44 |
| 1,3- and 1,4-DCBs | 26.5 | 0.44 | 16.0 | 1.10 | 9.84 |
| 1,2,4-trimethylbenzene | 5.67 | 0.18 | 0.65 | 0.26 | 4.94 |
| 1,2-dichlorobenzene | 35.2 | 1.08 | 7.18 | 0.87 | 28.2 |
| 1,2,4-trichlorobenzene | 9.98 | 0.33 | 0.66 | 3.26 | 6.39 |
| 1,2,3-trichlorobenzene | ND | -- | -- | -- | -- |
| Naphthalene | ND | -- | -- | -- | -- |
| TPH (as hexane) | 214.8 | 25.0 | 182 | 37.3 | 20.5 |

***Biodegradation.*** COI mass calculations were used to construct a mass balance with the missing term being assumed to be biodegradation. The results revealed that the ≥100% of the mass reductions of compounds with vapor pressures equal to or greater than *o*-Xylene (including chlorobenzene) was accounted for by volatilization. Only a small fraction of 1,3,5-trimethylbenzene was attributable to biodegradation. Tetrachloroethylene did not serve as a suitable tracer as it did in the field results as greater than 93% of its mass was removed with ≥100% of the loss accounted for through volatilization. The increased degree of volatilization is attributable to an air exchange rate approximately 45 times greater in the laboratory than the air exchange rate in the field.

The mass balance did provide favorable results for 1,2-DCB, 1,3- and 1,4-DCBs, and 1,2,4-TCB, with mass reductions of 82.1, 38.7, and 95.1 attributable to biodegradation, respectively. These results provided strong evidence to back the claim that the majority of the reductions of these COIs observed in the field was caused by biodegradation.

### c. Microbial Enumeration

As a final piece of evidence for biodegradation, microbial enumeration assays were performed to determine the numbers of total heterotroph and 1,2-DCB degrading microorganisms in the soil before and following bioventing. The initial analyses were performed on soil samples collected from the sleeves collected during system installation and used for initial COI analyses. The final analyses used soil samples collected from soil borings within 1 foot of the initial samples and soil samples collected from each of the laboratory columns. The initial and final total heterotroph enumeration assays were performed using the same analytic procedure, and the initial and final 1,2-DCB-degrading microbial enumeration assays were performed using different analytic procedures. The results from these assays are presented in Table 13.

**Table 13. Plate Count Results for Total Heterotroph and 1,2-DCB-Degrading Bacteria**

| Sample ID | CFUs per g-dry soil | | |
|---|---|---|---|
| | Initial | Final (field) | Final (laboratory) |
| **Total Heterotroph Counts** | | | |
| MP-E | 1.43 E+04 | 4.35 E+04 | 5.71 E+05 |
| VW-2 | 1.25 E+04 | 5.56 E+04 | 4.03 E+05 |
| MP-F | 4.90 E+03 | 1.08 E+04 | 5.94 E+05 |
| MP-H | 6.15 E+04 | 1.24 E+06 | 6.21 E+05 |
| MP-W | 1.43 E+04 | 3.26 E+06 | 4.36 E+07 |
| MP-Z | 1.80 E+04 | 7.64 E+04 | 8.45 E+05 |
| Mean | 2.09 E+04 | 7.81 E+05 | 7.77 E+06 |
| **1,2-DCB-Degrading Bacteria Counts** | | | |
| MP-E | 5.96 E+05 | 5.14 E+04 | 2.91 E+04 |
| VW-2 | 4.79 E+04 | 5.80 E+03 | 6.38 E+03 |
| MP-F | 8.31 E+05 | 7.69 E+03 | 5.14 E+04 |
| MP-H | 2.91 E+04 | 2.91 E+04 | 5.45 E+03 |
| MP-W | 5.02 E+04 | 6.38 E+03 | 5.80 E+03 |
| MP-Z | NA | 5.45 E+03 | 7.69 E+03 |
| Mean | 3.76 E+05 | 1.76 E+04 | 1.76 E+04 |

NA = Not applicable.

The initial population of total heterotrophic microorganisms averaged 2.09 $\times 10^4$ CFUs per gram of dry soil. This number was considered to be on the low side when compared to other sites at which TPH is present, but sufficient to support bioremediation. Because the site was anaerobic when the soil samples were collected and the enumeration assay was performed under aerobic conditions, a low number was expected. It also was anticipated that the number would increase as bioventing proceeded and as oxygen levels were maintained at sufficient levels to support aerobic growth. Increases of approximately 1.5 and 2.5 orders of magnitude were observed in the field and laboratory, respectively. It was not certain whether the final numbers represented the maximum bacterial concentrations in either the field or the lab, because the respiration rates in both were significantly below the maximum levels observed over the course of treatment.

The 1,2-DCB-degrading microorganism enumeration data from the initial soil samples suggested that the number of these specific microorganisms was greater than the number of total heterotrophs. This result did not make sense and the data were determined to be invalid. The colonies on the mineral salts plates took approximately 4 weeks to develop to a noticeable size. The colonies all appeared similar, were very small, and remained very small over a longer incubation period with 1,2-DCB supplied in the vapor phase. It appeared that the media formulation in the plates lacked a critical

growth factor, and that the colonies that did form used what little growth factor was transferred during plate inoculation.

Because poor results were achieved using the first 1,2-DCB-enumerating procedure, a modification of the method by Nishino et al. as described in Section IV-H4 was used for the final enumeration assay. Final assay results are presented in Table 13. The results from this method proved more reliable than the data from the first method. The colonies developed after approximately one week of incubation at 25°C, were much larger than those from other assays, and displayed approximately six colony morphologies. With the exception of one location in the field, the numbers of 1,2-DCB-degrading microorganisms were consistently less than the number of total heterotrophs.

Select colonies representing the six distinct colony morphologies were plated onto minimal salts agar containing the color indicator bromthymol blue, and then incubated at 25°C in a desiccator with 1,2-DCB supplied in the vapor phase. The objective of this procedure was to confirm that the different colony types were capable of degrading 1,2-DCB. This ability was indicated by a color change from blue to yellow, caused by the production of acid. Only one of the six colony morphologies, described as "whitish, round, smooth and shiny," consistently produced this color change. The other colonies showed no apparent growth, perhaps because of a lack of a critical growth factor in the minimal salts agar, but probably not because of an inability of the bacteria from other colonies to utilize 1,2-DCB. It was inferred that at least one of the bacterial types was capable or degrading 1,2-DCB, adding support to the claim that biodegradation of this compound occurred during bioventing.

# SECTION VII
# CONCLUSIONS AND RECOMMENDATIONS

## A. CONCLUSIONS

This study demonstrated that non-petroleum hydrocarbon organic compounds can be effectively treated using conventional bioventing technology. The focus in this demonstration was on 1,2-DCB, which was shown to be removed 74% over one year of operating a standard bioventing system. Other dichlorobenzene isomers were also effectively removed, with 1,3-DCB being removed at 42%, and 1,4-DCB being removed at 82%. Removal rates of the same order of magnitude were also demonstrated for many other compounds that were tracked (see Table 7).

Tetrachloroethylene removal rates were much lower (at 9%) than most of the other compounds tracked. This is especially noteworthy because tetrachloroethylene is considered a VOC, but is known not to biodegrade under aerobic conditions. If the bulk of mass removal of COIs had been accomplished by volatilization and subsequent forced convection from the test soil volume, then the removal rate of tetrachloroethylene would be expected to be more similar to the observed removal rates of dichlorobenzenes and other compounds tracked. This demonstration indicated that it is likely that a substantial portion of the observed removal rates were caused by in situ biodegradation of COIs.

The attempt to sequester a proximal soil volume to be used as a control plot was not successful. Although relief vent wells were installed with the intent of providing an escape path for air flowing laterally toward the control plot, significant oxygen impact was observed in the control plot (see Figure 12). The separation of the control plot was abandoned, and the theoretical treatment volume was expanded to include all soil within the perimeter drawn around the exterior monitoring point locations in both plots.

The automated oxygen monitoring devices used in this demonstration were useful in tracking the condition and progress of the system, making frequent site visits unnecessary. The OEMS system enabled monitoring of the blower temperature, thus enabling remote knowledge of the status of the blower (on or off). The in situ oxygen sensors were also valuable in tracking soil gas oxygen concentrations, and appeared to have less variability in the data than the OEMS. This could be related to the fact that the OEMS actively withdraws a vapor sample from the monitoring point, while the in situ oxygen sensors are passive.

## B. RECOMMENDATIONS

The results from this data provided valuable information on the fate of several contaminant compounds commonly found at sites requiring remediation. These sites are common to the Air Force and other branches within the United States Department of Defense, and include chemical disposal pits such as the one where this demonstration took place, fire training areas, spill and leak sites, and other sites where historic disposal practices did not take the impact to the environment into account. The combination of data from the field and laboratory components of this demonstration provides conclusive evidence that 1,2-DCB and other COIs were biodegraded during bioventing at CDP 1, Hill AFB. Based on the results from this demonstration, the following recommendations are made to serve as an addendum to the Air Force's *Bioventing Principles and Practice Manual* (Battelle, 1995).

1. It is recommended that DCB be added to the list of candidate compounds for bioventing applications. This recommendation specifically includes the addition of the three isomers 1,2-, 1,3- and 1,4-DCB. Field data showed mass reductions of 9.083, 1.100, and 1.360 kg for each of these isomers attributable to biodegradation, respectively. The laboratory data

showed that on average, 82.1, 38.7, and 95.1% of the mass reduction of 1,2-, 1,3- and 1,4-DCB attributable to biodegradation, respectively. Because DCB degrading capabilities are not inherent in soil bacteria (see Nishino et. al., 1994; van der Meer et. al., 1998), it is recommended that the age of the DCB spill be taken into account when considering the application of bioventing for DCB remediation.

2. The masses of trichloroethylene, TCA, and *cis*-dichloroethene were significantly reduced by over the one-year duration of the demonstration; however, the majority of the reduction was attributed to volatilization. The laboratory results indicated that significant biodegradation of trichloroethane and *cis*-dichloroethene occurred. It is recommended that a more detailed study be conducted to focus on the fate of these compounds during bioventing at sites co-contaminated with compounds such as toluene that are known to support cometabolism.

3. PCE is known to be biologically transformed only under anaerobic conditions. As expected, the results from this demonstration verified that PCE was not treated by aerobic bioventing. Because of the potential for misapplication of the bioventing technology, it is recommended that a list of compounds that should be excluded from aerobic bioventing be initiated, and that PCE should be included on the list.

4. Finally, it is recommended that the following considerations should be taken into account, if bioventing is considered for application at CDP 1.

    - Anaerobic bioventing may prove useful for reducing PCE and the other chlorinated solvents. The technology is an innovative approach for remediation of chlorinated compounds that are recalcitrant under aerobic conditions. The U.S. Environmental Protection Agency has demonstrated that the technology is effective for PCE dechlorination on a laboratory scale, and efforts are underway to demonstrate the technology in the field. CDP 1 was anoxic prior to aerobic bioventing and the indications from the oxygen utilization rates observed during the respiration tests suggest that the site will return to anaerobic conditions shortly after the air injection is stopped. Anaerobic bioventing at an anoxic site will require less nitrogen and should be economically feasible. It is recommended that a 6-to-9-month demonstration be conducted to monitor the effectiveness of anaerobic bioventing at CDP 1.

    - The analyses conducted during this demonstration were designed to monitor the COIs of interest, primarily the DCBs. The other compounds included in the list of analytes were compounds that had been identified in previous site investigation activities. Although the headspace method proved useful for measuring the soil concentrations of the COIs, it was not effective for measuring the concentration of heavier molecular weight compounds. It is recommended that if bioventing is pursued for remediation at CDP 1, an analytical program should be included that more effectively recovers and quantifies heavier contaminants that are of interest, including TPH.

## SECTION VIII
## REFERENCES


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