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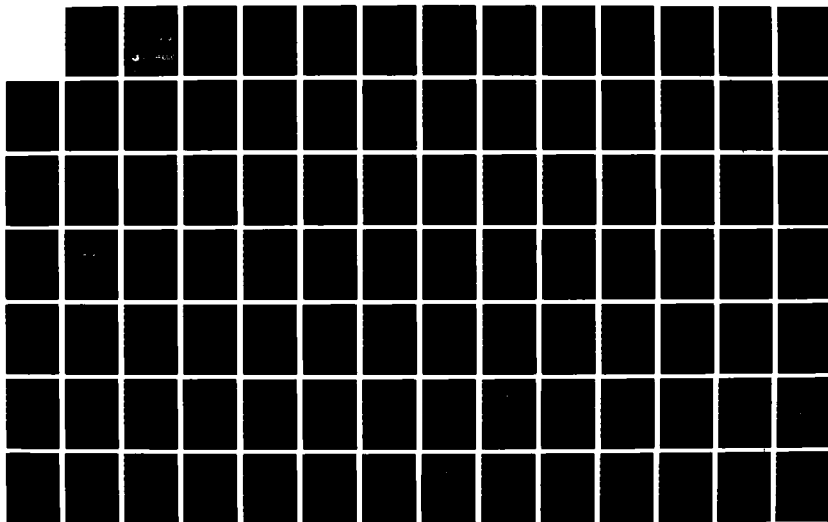
IN SITU BIOLOGICAL TREATMENT TEST AT KELLY AIR FORCE BASE, VOLUME II: FIELD TEST RESULTS AND COST MODEL

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The objective of this effort was to field test in situ biodegradation to treat aquifer contaminants. In situ biodegradation is enhanced by stimulating the indigenous subsurface microbial population by the addition of nutrients and an oxygen source to promote degradation of organic contaminants. In situ treatment affects contaminants sorbed to soil as well as dissolved in groundwater. It is potentially faster, and therefore cheaper, than conventional pump-and-treat technologies.

The test site, located at Kelly AFB, Texas, was contaminated with a mixture of organic and inorganic chemicals. The treatment system consisted of an array of nine pumping wells and four infiltration wells. These wells circulated groundwater and transported the treatment chemicals throughout the 2800 square feet treatment area. Oxygen was supplied by means of a hydrogen peroxide solution. Nutrients were principally ammonium and phosphate salts. The system was operated for 9 months.

Data showed evidence of both aerobic and anaerobic biodegradation. Decreases in tetrachloroethylene and trichloroethylene concentrations in groundwater correlate with anaerobic

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19.

microcosm tests. Aerobic biodegradation was indicated by acid and carbon dioxide production, and increases in petroleum hydrocarbon concentrations in groundwater. However, any biodegradation of these hydrocarbons was too small to be quantified. The main problems experienced during testing were caused by reactions between injected chemicals and sub-surface minerals. Calcium phosphate precipitation clogged infiltration wells and reduced the infiltration capacity of the test area by 90 percent. Metal sediments, primarily iron compounds, were found in the treatment system plumbing. These metals were probably mobilized by chemical reactions resulting from injecting high concentrations of hydrogen peroxide and nutrients, and may have been transported as small particles. The costs of the in situ treatment test were closely monitored. The technology was found to be no more expensive than conventional technologies.

    The study confirms that indigenous bacteria can be enhanced to degrade organic contaminants. The problems with in situ treatment are primarily those of delivery of chemicals and minimizing adverse reactions between injection chemicals and subsurface minerals.

ii

EXECUTIVE SUMMARY

The objective of this project was to field-test in situ biological degradation for removal of organic contaminants from soils and groundwater. In situ biological degradation involves stimulation of the indigenous subsurface microbial population by the addition of nutrients and an oxygen source (hydrogen peroxide) to promote degradation of organic contaminants present in soils and groundwater.

A site was selected for the test at Kelly AFB, Texas. This site, designated E-1 in the Phase I Installation Restoration Program (IRP) Report, was contaminated with a mixture of organic and inorganic compounds. A groundwater circulation system was installed within a 60-foot diameter portion of the site. This system consisted of nine pumping wells and four injection wells; groundwater was pumped to a central tank; nutrients and hydrogen peroxide were then added to the flow before reintroduction to the subsurface.

Literature review, site characterization, treatability studies, design, installation, startup, and approximately 3 months of operation were conducted as an initial phase and are reported in Volume I. Operation of the system was continued for an additional 5 months. This Volume II report documents the data collected during the full field operations period, analysis of system performance, and general considerations and cost analysis for applications to future sites. Analytical data and methodologies are presented in Appendix form in Volume III.

The results of the test at Kelly AFB allowed for a number of conclusions regarding in situ treatment. The low and variable permeabilities at the test site resulted in a slower delivery of nutrients and oxygen source than anticipated, as well as difficult operating conditions, but did not prevent degradation from occurring.

Data collected during the test shows evidence of degradation of contaminants by both aerobic and anaerobic means. Decreases in concentrations of PCE, TCE, and hydrocarbons in the groundwater were observed. A number of other effects of in situ treatment were also observed as a result of this test. The precipitation of calcium phosphate began almost immediately upon the introduction of nutrients and hydrogen peroxide. This precipitation had a negative impact on the project by reducing the permeabilities of the soil surrounding the injection wells. A migration of some metal compounds (particularly iron) from soil was also observed and may have been caused by movement of fine-grained particles in the subsurface. Work performed on estimating the cost of in situ treatment showed that full-scale implementation would be no more expensive than conventional techniques. The cost of performing in situ treatment for the entire site at Kelly AFB, where the test was performed, was estimated to be approximately $100 per ton of soil in the saturated zone. The cost of removal and redisposal was estimated to be $121 per ton.

A number of recommendations were presented regarding the future of in situ treatment. Recommendations include suggestions for future testing to determine the cause of calcium phosphate precipitation, study aerobic vs. anaerobic treatment, develop optimum treatment systems and monitoring programs, determine the cause of metals mobilization, and develop optimal nutrient compositions and sources of oxygen. Specific attention was paid to the requirements that will be posed by applying in situ treatment at a full-scale installation.

PREFACE

This report was prepared by Science Applications International Corporation (SAIC), 8400 Westpark Drive, McLean, Virginia 22102, under EG & G Idaho, Inc. Subcontract C84-130562 for the Air Force Engineering and Services Center, Engineering and Services Laboratory, Tyndall Air Force Base, Florida, and the EPA Office of Research and Development, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio.
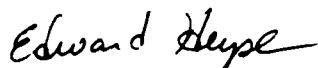
A number of subcontractors and consultants were used to provide specialized expertise for in situ biological degradation. These subcontractors include: FMC Corporation Aquifer Remediation Systems; Biosystems, Inc.; Dr. C. H. Ward, Rice University; Memphis State University; Environmental Research Group, Inc.; Hamilton Drilling and Engineering Testing, Inc.; K. W. Brown and Associates; Mr. Paul Rogoshewski; Shilstone Engineering Testing Laboratories; and Aqualab, Inc.

This technical report is divided into three volumes. Volume I presents work done between May 1984 and September 1985 and discusses in detail the site characterization, laboratory studies, and treatment system design and installation. Volumes II and III summarize the work performed between October 1985 and February 1987. Volume II discusses the system operation and performance, results of the field demonstration project, and the cost of in situ biological treatment. Analytical data and methodologies are presented in Appendix form in Volume III. Ms. Barbara Broomfield was the EG & G Idaho, Inc. Project Officer. Captain Edward Heyse was the AFESC Project Officer, and Mr. Stephen James was the EPA Office of Research and Development Project Officer.

This report discusses field demonstration using proprietary formulations of nutrients and hydrogen peroxide. It does not constitute an endorsement of these products by EG & G Idaho, Inc., the Air Force or EPA, nor can it be used for advertising the product.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to NTIS. At NTIS, it will be available to the general public including foreign nationals.

This technical report has been reviewed and is approved for publication.

EDWARD HEYSE, Capt., USAF, BSC
Project Officer

LAWRENCE D. HOKANSON, Col, USAF
Director, Engineering and
Services Laboratory

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USAF, BSC
Chief, Environics Division

v

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONCLUDED)

LIST OF FIGURES

LIST OF FIGURES (CONCLUDED)

LIST OF TABLES

SECTION I

INTRODUCTION

A. OBJECTIVE

The purpose of this project was to test in situ biological degrada-
tion under actual field conditions and to determine its applicability to
cleaning up hazardous waste sites and waste-contaminated soil and ground-
water. The technology was field-tested on a hazardous waste site at
Kelly AFB, San Antonio, Texas. In situ biological degradation can be at
least as effective as other remedial technologies at a lower overall
cost. In situ technology can treat those contaminants sorbed to soil
particles as well as those dissolved in groundwater. In situ treatment
may, therefore, be more effective for sorbtive contaminants than are con-
ventional pump-and-treat technologies which treat only groundwater.

B. BACKGROUND

In situ biological degradation of contaminants in soil and ground-
water involves stimulation of the indigenous subsurface microbial popu-
lation to promote degradation of organic contaminants. The tested pro-
cess uses aerobic degradation pathways requiring that a source of oxygen
be supplied to the subsurface environment to maintain aerobic conditions.
Previous studies have shown that conventional aeration techniques cannot
consistently supply an adequate amount of oxygen for in situ treatment.
Thus, the amount of degradation that occurs is limited. The field test
at Kelly AFB will help evaluate the effectiveness of using hydrogen
peroxide as an oxygen source; hydrogen peroxide can provide as much as 50
times the level of oxygen provided by conventional aeration. Nutrients,
such as nitrogen and phosphorus, are also added to the subsurface to en-
hance the growth of the microbial population.

1

C. SCOPE

The field test was performed within a 60-foot diameter area located on waste site E-1 in the Installation Restoration Program (IRP) Phase I study at Kelly AFB. Within this area, nine pumping wells and four gravity injection wells were placed to circulate groundwater. A specially formulated nutrient solution and stabilized hydrogen peroxide were added to the groundwater flow and transported to the subsurface to enhance the ability of the indigenous microbes to degrade contaminants.

This project included a feasibility study and a laboratory treatability study to evaluate potentially applicable in situ treatment options and to optimize their design. A pilot-scale in situ treatment system was installed, operated, and monitored for 8 months at a waste site at Kelly Air Force Base.

Volume I of this report included project activities from May 1984 through September 1985 as well as detailed site characterization activities. These activities included the determination of site stratigraphy, soil permeability, and hydraulic conductivity. Enumeration of both soil and groundwater microbes was conducted to determine if an adequate population was present for successful biodegradation of the organic contaminants. A full inorganic and organic contaminant profile of the subsurface soils and groundwater was derived. Treatability studies were conducted to determine the effect of treatment to onsite soils. Nutrients and hydrogen peroxide were added to columns containing soil from the Kelly AFB site to determine biodegradability of contaminants using soil/groundwater microcosms. Volume I also discusses design, implementation, startup, and 3 months of operation.

Volume II, focuses on the operation of the system, conclusions, and recommendations for future applications of in situ biological degradation. Section II gives a brief summary of previous project activities. Section

III discusses operational procedures followed, including system operation, sampling schedule and procedures, analytical procedures, health and safety procedures, plan for mitigating spills and any uncontrolled releases of contaminants during the operation of the system, and system shutdown procedures. Section IV discusses system performance, operational problems and data relating to hydrogeological, chemical, and microbiological changes observed during the 8 month demonstration period. Section V includes project Quality Assurance/Quality Control (QA/QC) procedures followed. Section VI discusses the planning and cost associated with full-scale implementation of in situ treatment. Section VII presents a summary of observations at the Kelly AFB test. Sections VIII and IX present Conclusions and Recommendations, respectively.

Volume III contains appendixes A-E with additional information, including analytical data and methodologies.

SECTION II

PRELIMINARY ACTIVITIES

The field test was preceded by a literature review, site character-
ization, and treatability studies. Information gained from these studies
was used to design the treatment system. The results of these studies and
detailed descriptions of system design and installation were presented in
Volume I and are summarized in this section.

A. LITERATURE REVIEW

In situ biodegradation is a technical outgrowth of land-spreading
technology, a process primarily used by petroleum refineries to dispose
of oily sludges from storage and processing facilities. Land-spreading
involves the mixing of biodegradable sludge and fertilizer into the
soil using a tiller or dozer and allowing the indigenous soil micro-
organisms to multiply and degrade the waste material. Exxon's Baytown
refinery has been disposing of oily wastes by land farming since 1953
(Reference 1).

Formal research on the land spreading technique began in the 1970s.
In 1972, a report for the U.S. EPA was prepared by Shell Oil Company,
summarizing 18 months of research on land-spreading of three types of
oily wastes: crude oil tank bottoms, Bunker C fuel oil, and waxy
raffinate wastes (Reference 2). Biodegradation rates were found
to be about 70 barrels per acre of soil per month. The population of
soil microbes was found to increase during the study period to over
10^8 organisms per grain of soil. Major species of microorganisms in-
cluded members of the genus Pseudomonas, Flavobacterium, Nocardia,
Corynebacterium, and Arthrobacter.

4

Sun Ventures, Inc., a subsidiary of Sun Oil Company, also conducted research on oily waste land farming (Reference 3). Their 18-month project involved three field sites and six types of oily wastes. Results indicated a naturally occurring hydrocarbon-utilizing bacterial population that reached levels of about 10 million organisms per grain of soil 1 year after the initial application. Removal efficiencies of oil ranged from 48.5 to 90 percent depending on the type of waste and location.

In the early 1970s, Sun Ventures developed the _in situ_ biodegradation process as a means of treating contaminated subsurface soils and groundwater. In 1971, Sun Pipe Line Company experienced a gasoline pipeline break in Ambler, Pennsylvania, which spilled more than 3,000 barrels of high-octane product into the groundwater (Reference 4). Gasoline recovery by pumping was effective for removing only about 50 percent of the gasoline. Additional pumping to remove residual contamination proved futile. The problem was referred to Sun Ventures, which proposed _in situ_ biodegradation as a means of removing the remaining gasoline contamination.

After conducting a series of treatability studies, Sun Ventures confirmed that the active bacterial population present in the subsurface could degrade the gasoline when provided with certain nutrients and oxygen. The actual cleanup was conducted by adding nitrogen and phosphorus to the groundwater in the form of $(NH_4)_2 SO_4$, $Na_2 HPO_4$, and NaH_2PO_4. Oxygen was provided by injecting air into the groundwater via a series of diffuser wells connected to paint-sprayer type compressors. The flow of groundwater was controlled by a series of injection and extraction wells. An estimated 744 to 944 barrels of gasoline were degraded. Ten months after the addition of nutrients, no gasoline was found in water from extraction wells (Reference 5).

In 1976, a leak was discovered in an underground gasoline storage tank in Millville, New Jersey, which contaminated a shallow sandy

aquifer and caused gasoline vapor problems in the basements of nearby houses. Again, physical recovery efforts could only remove a portion of the spilled product. In situ biodegradation of the contaminated aquifer was carried out by SunTech, Inc. (Sun Ventures, Inc.) using addition of nutrients and oxygen. Air was injected, using diffuser wells connected to an air compressor. Nutrients were added in the form of ammonium sulfate, disodium phosphate, monosodium phosphate, sodium carbonate, calcium chloride-dihydrate, magnesium sulfate hepta-hydrate, manganese sulfate-monohydrate, and ferrous sulfate hepta-hydrate (Reference 5). The in situ biodegradation program was carried out for 6 months. At the end of the study period, no free hydrocarbons were observed in groundwater from any of the wells. However, some gasoline residuals were observed in subsurface soil samples, indicating that cleanup was less than 100 percent complete.

In situ biodegradation was also used to clean up a 1980 gasoline and diesel fuel spill in La Grande, Oregon, in which leaking storage tanks from a bulk plant contaminated a high-permeability shallow aquifer and caused explosive concentrations of gasoline fumes in two nearby restaurants. Environmental Emergency Services Company carried out a physical recovery and in situ biodegradation program from October 1981 to September 1982 (Reference 6). Several hundred pounds of ammonium chloride, monosodium phosphate, and disodium phosphate were injected into the groundwater while oxygen was provided by injecting air into porous stone diffusers located at the bottom of an injection trench. A physical recovery system was installed for the collection of floating fuel, and a ventilation system was installed to eliminate the vapor problem in the restaurants. At the end of 1 year of operation, over 3000 gallons of free hydrocarbons were recovered by physical means. No free product was present in groundwater after the study period, however, subsurface soil contained gasoline residuals of 100 to 500 ppm. The dissolved organic carbon concentrations in groundwater had decreased to the point that 71 percent of the measurements were below 5 ppm and 50 percent were below 2 ppm.

A number of other subsurface gasoline spills have been treated by
in situ biodegradation, and several companies specializing in the
process have been formed. Most cleanups have been for industrial clients
and are not well-publicized.

In situ biodegradation has also been employed to clean up subsur-
face contamination by substances other than gasoline. In 1975, Biocraft
Laboratories traced a pollution problem to a leak in an underground tank,
which had resulted in contamination of the subsurface with an estimated
33,000 gallons of methylene chloride, acetone, n-butyl alcohol, and
dimethylanaline (Reference 7). After efforts to pump and dispose of
the contaminated water became cost-prohibitive, Biocraft researched otner
options, including biodegradation of contaminated water. Initial treat-
ability studies indicated the indigenous subsurface microflora could be
stimulated to degrade the contaminants. Biocraft designed a combined
aboveground in situ treatment system consisting of a groundwater collec-
tion trench, a series of aboveground treatment tanks, two reinjection
trenches, and a series of nine aeration wells located in the contaminant
plume. Nutrients were added to contaminated groundwater, which was then
pumped to the treatment tanks and aerated at about 20°C for 16 to 18
hours before being reinjected. An in situ aerobic treatment zone was
presumably set up in the subsurface by aeration from the nine wells.
After 1 1/2 years of operation, concentrations of all contaminants were
dramatically reduced in most of the observation wells. Some pockets of
contamination still exist and treatment is continuing. Biocraft origi-
nally estimated it could take as long as 5 years to remove all traces of
contamination.

A number of other cases exist in which mutant bacteria were used to
enhance in situ biodegradation of organics in the subsurface (Reference
5). Most of the mutant bacteria in situ work was combined with other
processes such as aboveground biological treatment, air stripping, and
carbon adsorption. Chemicals that were successfully removed from the
subsurface include acrylonitrile, phenol, o-chlorophenol, etnylene

7

glycol, propyl acetate, and dichlorobenzene. The contribution of bio-
degradation by mutant bacteria to the success of these projects was not
rigorously studied in most cases.

A common problem encountered in past in situ biodegradation work
has been the limited amount of oxygen that can be supplied by aeration
to the subsurface microorganisms (Reference 8). The use of hydrogen
peroxide as an alternate source of oxygen has recently been investigated
(Reference 9). Although hydrogen peroxide is cytotoxic at higher con-
centrations, studies indicate it can be added to groundwater at concen-
trations up to 100 ppm without being toxic to microbial populations.
This amount is five times greater than the amount of oxygen tnat can be
introduced by aeration alone. Concentrations as high as 1000 ppm H_2O_2
can be added to microbial populations without toxic effects if the
proper acclimation period is provided for the bacteria (Reference 10).
Decomposition of hydrogen peroxide was a concern, but experimental evi-
dence indicates that the rate of decomposition can be effectively con-
trolled using a phosphate buffered solution at a pH of 7.0 (Reference
10).

All of the previous in situ biodegradation projects were associated
with gasoline leaks or spills of one or relatively few chemicals. In
situ biodegradation at hazardous waste sites presents the problem of
dealing with many different compounds with varying degrees of biodegrada-
tion. Chlorinated compounds are almost always present in hazardous waste
sites and, as a class, are generally more resistant to biodegradation.
Thus, much of the current research on in situ biodegradation is
focusing on methods to biodegrade chlorinated organics.

Much research centers on using anaerobic pathways to degrade low
concentrations (<200 ppb) of various chlorinated species as well as other
organics. A number of aromatic compounds are anaerobically degradable,
including phenols, benzoate, aromatic amino acids, cresols, phthalic acid
esters, pentachlorophenol, and chlorobenzoate (Reference 11). Researchers

8

have produced some evidence of reductive dehalogenation of aliphatic chlorinated organics, however, results have been sporadic. Bower, Rittman, and McCarty (Reference 12) demonstrated anaerobic degradation of chloroform, dichloromethane, and dibromochloromethane in the presence of mixed methanogenic bacterial cultures, but found no significant anaerobic degradation of trichloroethylene or tetrachloroethylene. Later studies by Bower and McCarty (References 13, 14) indicated almost complete mineralization of chloroform, carbon tetrachloride, and 1,2-dichloroethane under continuous-flow methanogenic conditions and evidence of reductive dehalogenation of tetrachloroethylene and 1,1,2,2-tetrachloroethane to less chlorinated intermediates in anaerobic batch studies with a mixed methanogenic culture. Parsons, Wood, and DeMarco (Reference 15) observed transformation of 100 ppb tetrachloroethene to less chlorinated ethenes after 21 days in batch anaerobic microcosms consisting of Florida groundwater and Everglades muck. Less chlorinated transformation products included trichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, and chloroethene. Attempts to reproduce the study with different types of sediments yielded sporadic results. Wilson, et al. (Reference 16) conducted a similar experiment using enclosed microcosms of sterile water mixed with samples of subsurface sediment from Lula, Oklahoma. No significant biotransformation occurred for tetrachloroethene, trichloroethene, 1,2-dichloroethane, or 1,1,2-trichloroethane, although significant degradation occurred for toluene, chlorobenzene, and bromodichloromethane. In a subsequent study, Wilson, et al. (Reference 17) performed a similar experiment using microcosms of sterile water mixed with subsurface sediments from two different aquifers. No degradation of chloroform, 1,1,1-trichloroethane, or 1,1-dichloroethane was detected. However, tetra- and trichloroethene were found to slowly degrade in these studies. Parsons, Wood, and DeMarco (Reference 15) attribute the variability of such studies to a number of factors, which include differences in the native microflora (population and species), nutrient levels, and level or quality of organic carbon present, all which may significantly affect the enzymatic or cometabolic processes that may be associated with transformation of these compounds.

9

In summary, significant recent developments have occurred in the field of in situ biodegradation, which show potential for application of the process to the cleanup of selected hazardous waste sites. In situ biodegradation of underground gasoline spills, by the addition of oxygen and nutrients to the groundwater, has shown considerable success. The main problem encountered is that, although concentrations are substantially reduced, residuals are still present in the subsurface. This may be a result of poor hydraulic contact and oxygen transfer. The use of hydrogen peroxide rather than air may increase process performance by increasing the amount of oxygen available in the subsurface.

Use of in situ biodegradation has not been reported in a hazardous waste site situation, although chemicals such as acrylonitrile, phenol, methylene chloride, dimethylaniline, and dichlorobenzene have been removed from soils and groundwaters contaminated by industrial spills. A hazardous waste site cleanup using the in situ process presents some unique problems, i.e., a wide variety of chemicals may be present as subsurface contaminants, and different methods of treatment may be required at the same site. Of particular concern are chlorinated organics, which have been shown to be generally resistant to aerobic biodegradation. Anaerobic degradation of chlorinated species shows some promise, however, laboratory results have been sporadic because of differences in bacterial population, nutrients, and carbon sources.

B. SITE CHARACTERIZATION

Site characterization data were collected from soil borings, chemical and microbiological analysis of groundwater and soils, and hydrologic field testing. Samples and observations were taken at various locations over the entire area of Site E-1 at Kelly AFB. Figure 1 shows the locations of boreholes, monitoring wells, and the demonstration area. Boreholes 1 through 5 were drilled in June 1984 to collect soil samples for determining contamination concentrations and microbial populations. Priority pollutant analyses were also performed on ground-

10
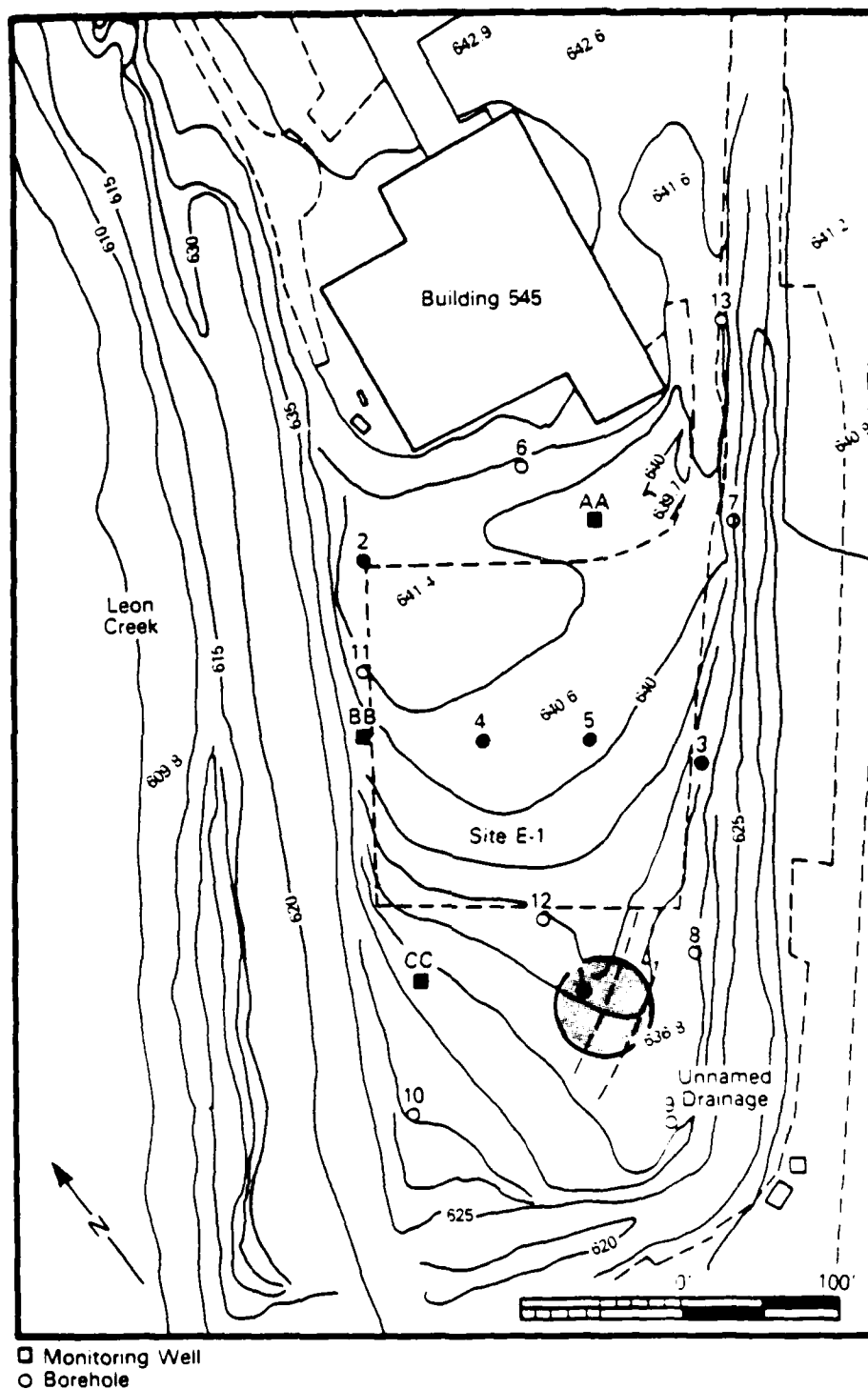
Figure 1.   Area of Site Showing Boreholes, Monitoring
Wells and Demonstration Site

11

water samples from Wells AA, BB, and CC. These wells were previously
installed at the site during IRP Phase II (Confirmation Phase of the Air
Force Installation Restoration Program). Additional soil and groundwater
samples were collected in September 1984 for use in laboratory micro-
cosm studies. Boreholes 6 through 13 were then drilled in October 1984
to provide a fuller geological characterization of the site and to help
resolve variability in strata described in the previous soil borings.
Hydrologic field testing was conducted in January 1985 within the chosen
demonstration area to provide hydrogeologic data for the underlying
saturated zone.

This information was used to design the well layout for the demon-
stration, assess any potential impact on the nearby creek, and set
the initial pumping rates for the demonstration. Three test wells,
TP-01, TO-01, and TO-02, were installed for this purpose (Wells TP-01
and TO-02 were later incorporated into the treatment system and re-
designated I1 and P2, respectively). Finally, additional samples and
hydrogeologic tests were performed during installation of the 13
additional wells to be used for the treatment system. This informa-
tion provided a baseline for assessment of fluid movement during the
demonstration. The results of these site characterization activities
are discussed in the following sections.

1. Geology

Site E-1 at Kelly AFB consists of a heterogeneous mixture of
gravels and sands in a silt and clay matrix typical of alluvial (river-
laid) deposits. These interlayered deposits comprise approximately
the first 30 feet of sediment. Below this lies the Navarro Forma-
tion consisting of homogeneous layer of sandy clay which prevents the
downward movement of the shallow aquifer.

12

2. Hydrology

A shallow aquifer with a continuous groundwater surface sub-
ject to seasonal variations lies beneath Site E-1. The gradient is
toward Leon Creek which suggests a possible hydrologic connection
between the saturated zone and the creek. Groundwater movement in
the saturated zone is generally slow because of the predominant silt
and clay matrix. Preconstruction field tests showed hydraulic con-
ductivities of between 0.3 and 0.6 feet per day, but this varies
widely throughout the site area. Postconstruction hydraulic conduc-
tivities in the wells used for the demonstration varied from 0.11 to
9.26 feet per day.

3. Contaminants

The depth of concentration of contamination together with bore-
hole location indicate the extent of contaminant migration. Boreholes
4 and 5 were located within the perimeter of the former evaporation
pit. Consequently, samples from Boreholes 4 and 5, taken at 5 and 9
feet, respectively, exhibited relatively high contaminant concentrations.
Lower contaminant concentrations at lower depths in Boreholes 4 and 5
indicate the lack of significant vertical migration, probably due to
the high clay content of the soils. Boreholes 2 and 3, which were
located outside the perimeter of the former evaporation pit, showed
low-contaminant concentrations at all sampling depths. The low con-
centrations suggest that horizontal migration is not significantly
aided by the presence of gravels in the silty clay matrix, which was
evident in Boreholes 2 and 3.

High concentrations of hydrocarbons in a sample of Borehole 1
taken at a depth of 18 feet, together with the absence of measurable
hydrocarbons in samples of Borehole 1 taken at 7 and 12 feet, suggest
that horizontal migration of contaminants has occurred from beneath
the former evaporation pit. The lack of any vertical migration ob-

13

served in Boreholes 4 and 5 suggests that the contaminants detected in Borehole 1 migrated from a section underlying the former evaporation pit which has a higher vertical permeability. Contamination evident in Borehole 1 could have been transported from beneath the former evaporation pit by advection or dispersion in the shallow aquifer. A summary of contaminants present at the Kelly AFB site is shown in Table 1.

4. Microbiology

Subsurface samples were collected at three depths from the initial set of five boreholes and direct and viable cell counts were performed. Results of these preliminary microbial analyses indicated that a substantial microbial population (10^7 to 10^8 organisms/gram soil) exists in the subsurface of site E-1. Viable cell counts on seven different growth media indicated a diverse or highly adaptive population capable of metabolizing a large variety of substrates.

C. TREATABILITY STUDIES

Treatability studies were conducted before the field investigation to: (1) determine if biodegradation of the organic contaminants present at the site would occur and (2) quantify the permeability of the subsurface materials and determine the effects of nutrient and hydrogen peroxide addition on soil permeability.

1. Biodegradation Study

A laboratory treatability study was conducted with soil and groundwater collected from the Kelly AFB site to determine if biodegradation of the organic contaminants present would occur. The following microcosms were prepared with soil and groundwater from the Kelly AFB site:

- Aerobic: stabilized H_2O_2 (Restore® 105) + nutrients
- Sterile aerobic control: stabilized H_2O_2 + nutrients

TABLE 1. REPRESENTATIVE CONCENTRATIONS OF CONTAMINANTS PRESENT AT THE DEMONSTRATION SITE

	Soil					Groundwater						
	Borehole #1	Borehole #2	Borehole #3	Borehole #4	Borehole #5	P-1	P-2	P-4	P-6	P-8	P-9	CC
Tetrachloroethylene	0.001	--	--	--	0.019	0.0081	0.70	2.30	0.50	2.90	3.65	0.13
Trichloroethylene	0.01	0.016	0.022	0.91	0.082	0.0248	2.65	1.65	1.10	3.00	5.05	6.7
1,1,1-Trichloroethane	0.10	0.97	--	--	--	--	--	0.001	--	0.60	--	--
1,1,2-Trichloroethane	--	--	--	--	--	--	--	--	--	0.0047	--	--
Trans 1,2-Dichloroethylene	--	--	--	--	--	0.0289	0.0944	--	--	0.0216	0.0142	2.2
Cis 1,2-Dichloroethylene	--	--	--	--	--	2.35	2.80	1.10	8.50	2.35	5.10	--
1,1-Dichloroethylene	--	--	--	--	--	--	0.0346	0.004	--	--	0.147	--
1,1-Dichloroethane	--	--	--	--	--	0.0291	0.0577	0.0034	0.0185	1.15	--	--
1,2-Dichloroethane	--	--	--	--	--	0.0019	0.0031	0.0013	0.0024	0.0057	--	--
Vinyl Chloride	--	--	--	--	--	0.753	0.0525	--	0.499	0.239	0.0231	--
Chloroethane	--	--	--	--	--	--	--	--	--	0.0354	--	--
Chloroform	--	--	--	--	--	--	--	--	--	--	0.0118	--
Benzene	0.093	--	--	--	--	--	--	--	--	--	0.002	--
Chlorobenzene	--	--	--	--	0.012	0.0063	0.0411	0.0089	0.0166	0.0528	0.0025	--
Dichlorobenzene	--	0.15	--	0.16	38	--	--	--	--	--	--	<0.001
Alkyl Benzenes	0.005	--	--	0.020	78	--	--	--	--	--	--	--
Toluene	0.038	0.005	--	0.022	0.13	--	0.0028	0.0041	0.0015	0.002	0.0019	--
Ketones	0.037	0.30	1.0	2.2	26	1	2	2	2	1	1	<1.0
Hydrocarbons Total												
n-Alkanes	40	--	--	58	454							
Branched	158	--	0.009	0.11	456							

Note: -- indicates values less than method detection limit

- Aerobic: O_2 + nutrients
- Anaerobic: amended with nutrients
- Sterile anaerobic control: amended with nutrients.

The study was conducted over a 100-day period and triplicate samples were collected after 1, 24, 49, and 100 days of incubation. Samples were analyzed for volatile organic hydrocarbon compounds. Specific details of the biodegradation study experimental design, analytical methods, laboratory quality assurance/quality control procedures, and the raw data obtained from the study are presented in Volume I of this report.

Results from the study, shown in Figure 2, as the ratio of unresolved to resolved hydrocarbons versus time, indicate significant amounts of resolvable hydrocarbons (straight chain, n-alkane compounds) were removed from the soil extracts in the oxygen-and peroxide-treated systems. Results from compound-specific chemical analyses of the microcosm extracts also indicated that chlorobenzene was degraded under aerobic conditions (Figure 3).

The anaerobic microcosms and sterile controls showed essentially no significant aliphatic hydrocarbon degradation over the 100-day period. However, anaerobic degradation of tetrachloroethylene (PCE) (Figure 4) and trichloroethylene (TCE) (Figure 5) occurred within the first 49 days of the study. During the first 24 days, concentrations of trans-1,2-dichloroethylene (trans-1,2-DCE) increased in the anaerobic microcosms, followed by a gradual decrease in trans-1,2-DCE from Day 24 through Day 100 (Figure 6). Decreases in groundwater concentrations of PCE and TCE and increases in trans-1,2-DCE concentrations were also observed during the field demonstration program. The laboratory biodegradation studies, therefore, were a successful tool for determining the treatability of contaminants and predicting what would occur in the field. The field results are discussed in subsequent chapters.

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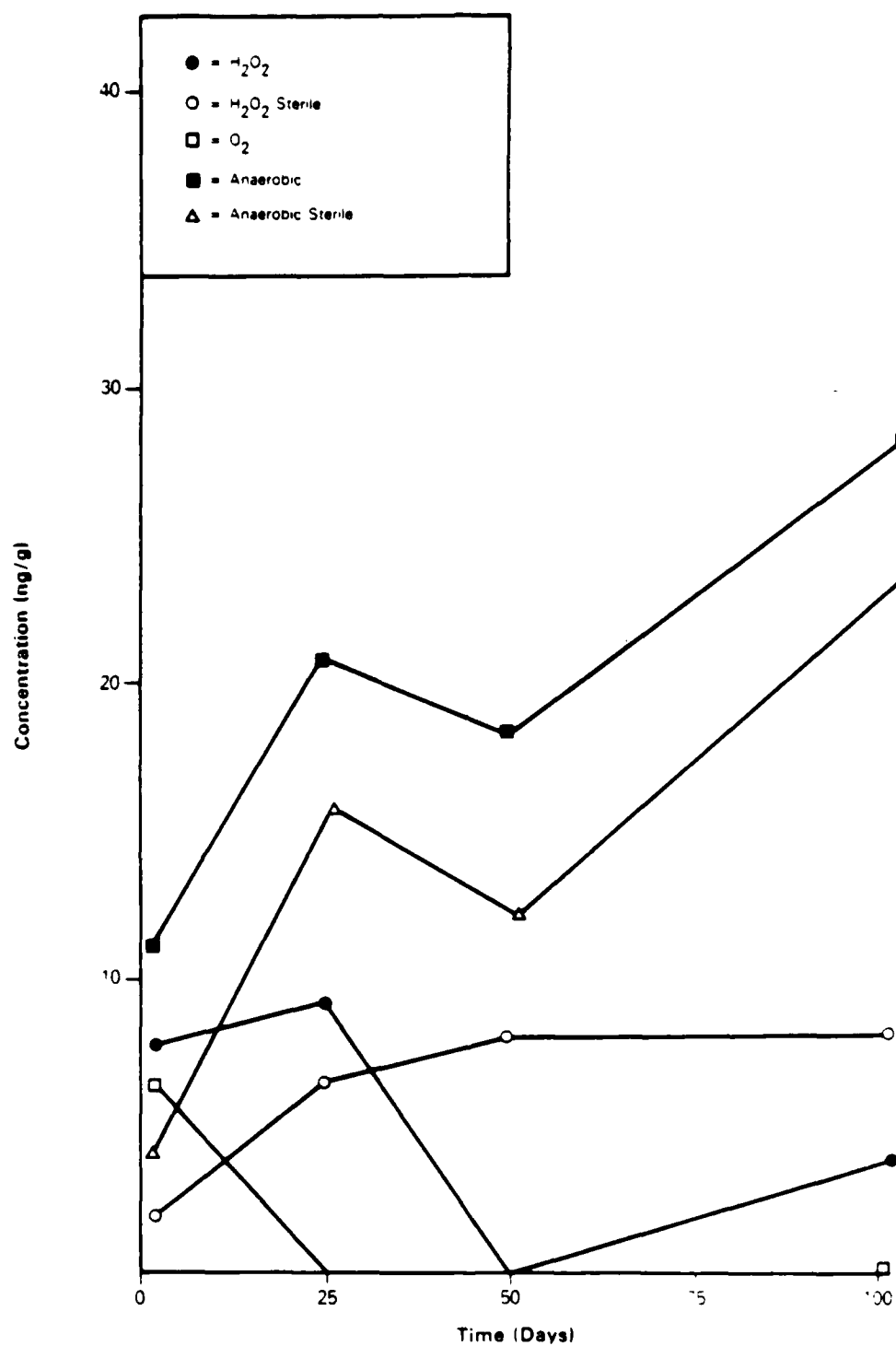
Figure 3. Chlorobenzene Concentration Versus Time

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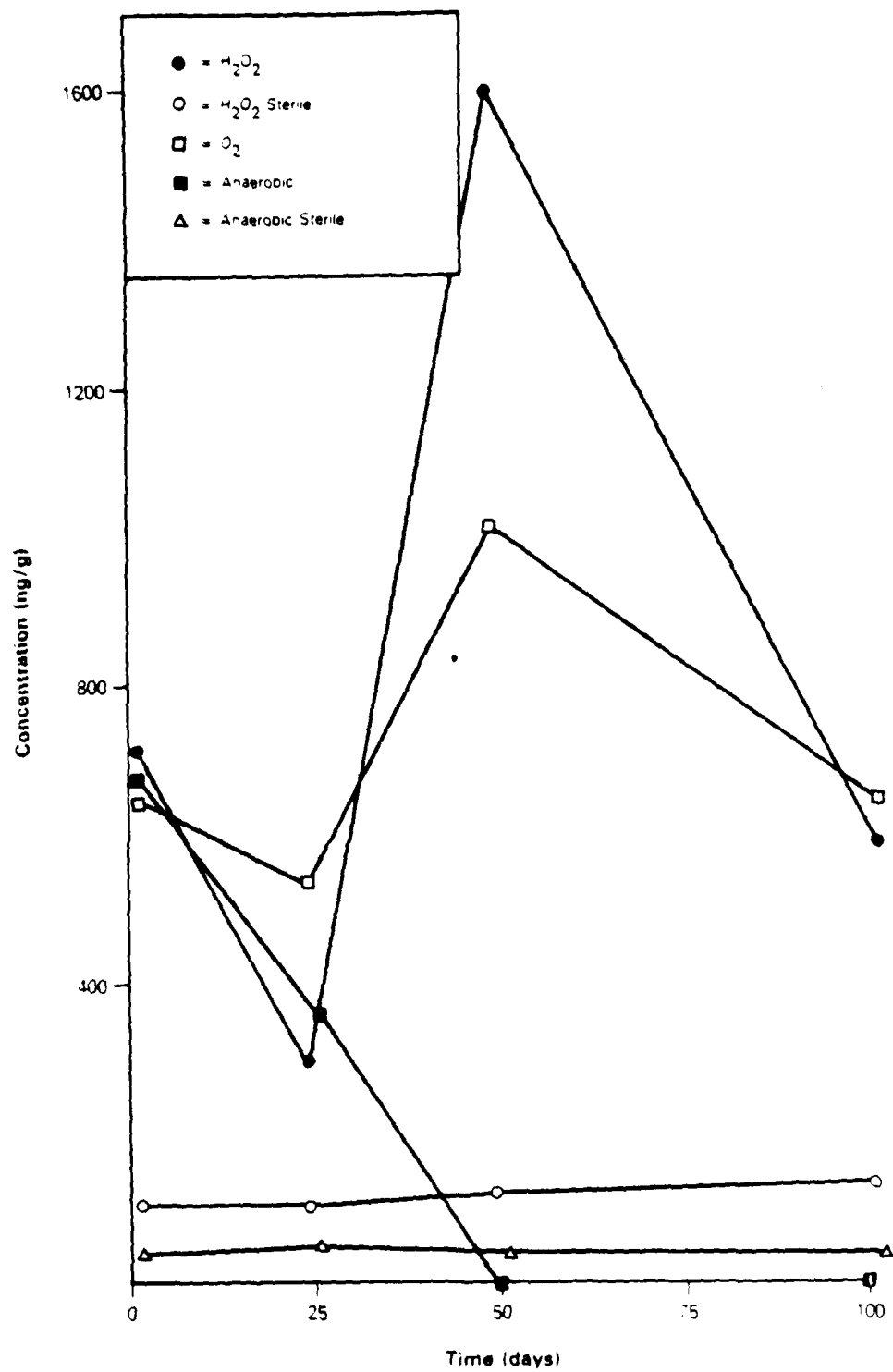
Figure 4. Tetrachloroethene (PCE) Concentration Versus Time

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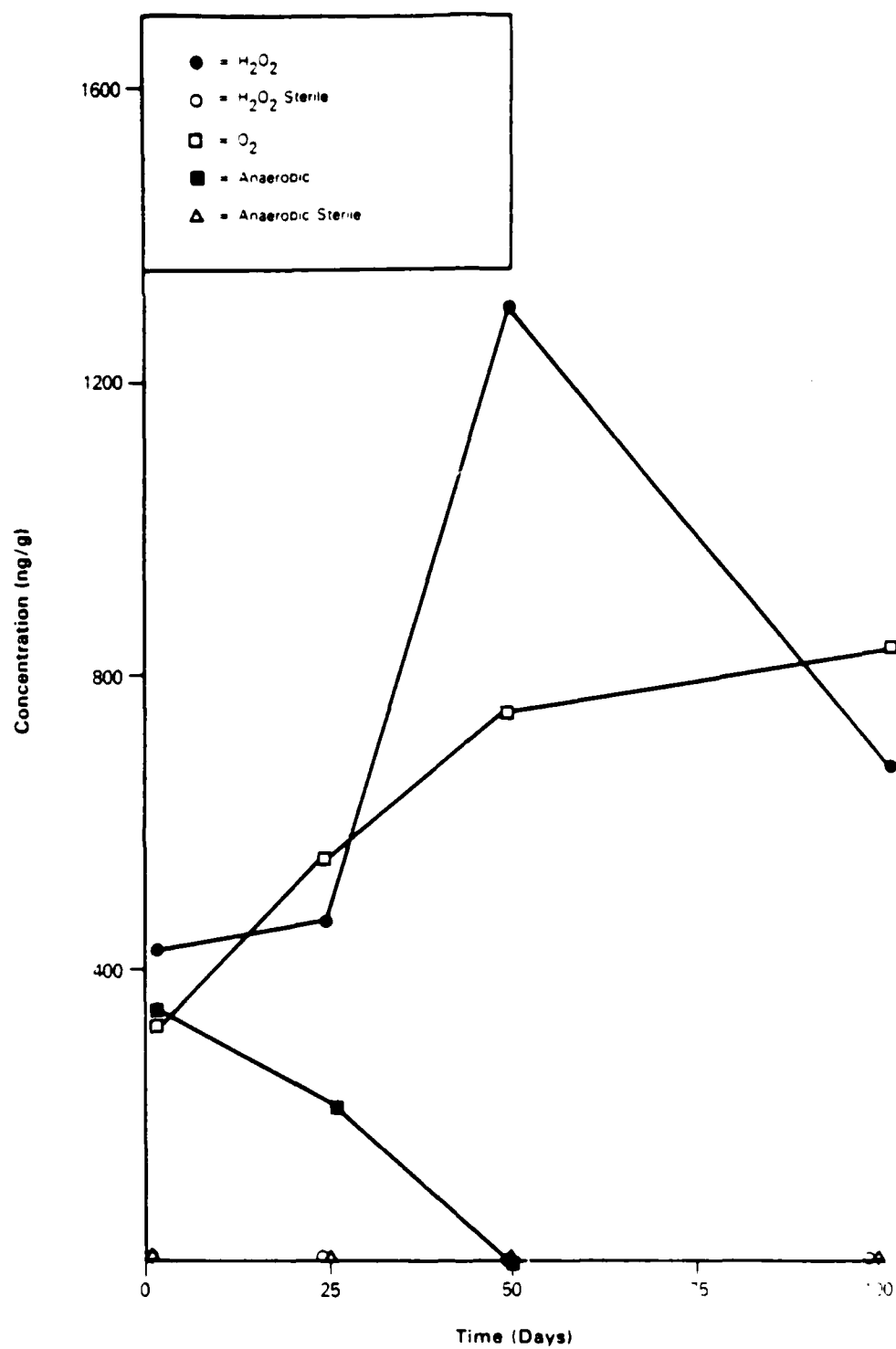
Figure 5. Trichloroethene (TCE) Concentrations Versus Time
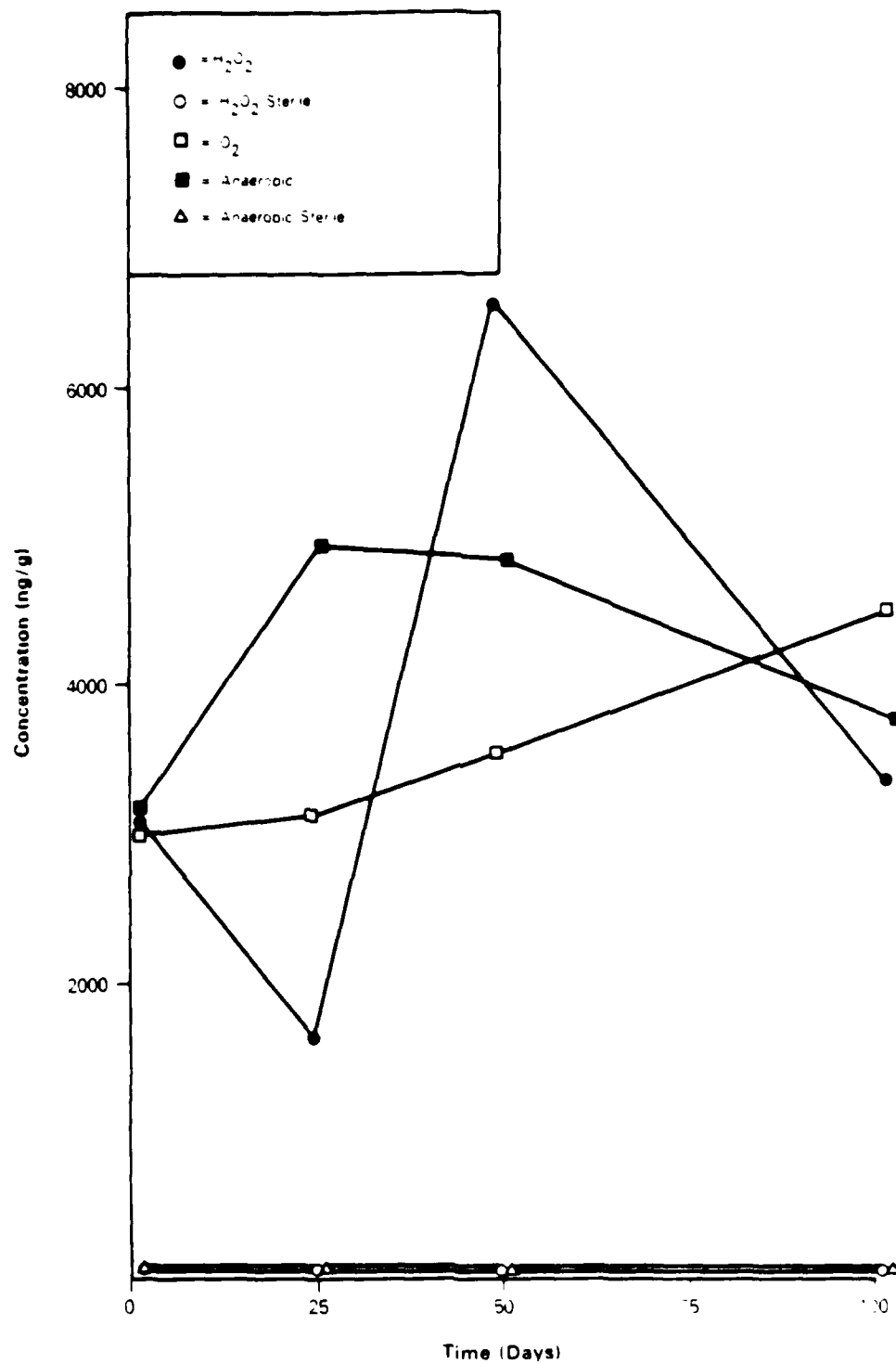
Figure 6.   Trans-1,2 Dichloroethene (Trans-1,2-DCE)
            Concentration Versus Time

21

In general, the results of the laboratory treatability study demonstrated that: (1) in situ microbial populations could degrade the contaminants present in the soil at Kelly AFB; (2) active cultures were developed which demonstrated degradation of aliphatic hydrocarbons (n-alkanes) and aromatic compounds (chlorobenzene) under aerobic conditions and chlorinated hydrocarbons under anaerobic conditions; (3) oxygen treatment and introduction of hydrogen peroxide worked equally well for degradation of petroleum-type compounds; and, (4) biotransformation of PCE and TCE to the lower-molecular weight chlorinated aliphatic compounds, trans-1,2-DCE and 1,1-DCE, occurred under anaerobic conditions. Chlorinated hydrocarbon degradation under anaerobic conditions has been reported previously in the literature (Reference 15).

2. Permeability Studies

Permeability studies were conducted on soil samples collected from the Kelly AFB site to determine the effect of nutrient (Restore® 375K) and hydrogen peroxide (Restore® 105) addition on soil permeability. Triaxial permeameters were used to determine the permeability of two undisturbed soil cores. A solution of nutrients, hydrogen peroxide, and groundwater (collected from the site) was permeated through the soil samples and leachate was collected periodically and analyzed for chloride, phosphate, and hydrogen peroxide concentrations. Details of the sampling methods, analytical procedures, and raw data are given in Volume I of this report.

Results from the permeability studies (Figures 7 and 8) showed chloride breakthrough occurred first, followed by phosphate breakthrough. Phosphate concentrations in the leachate solutions did not exceed 60 to 70 percent of the influent phosphate concentrations. This was attributed to calcium phosphate precipitation in the soil. Similar effects, i.e.,

C/Co

○ Peroxide
△ Phosphate
□ Chloride

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

Groundwater
Only

Groundwater Plus Nutrients and
Peroxide

Permeability (CM/SEC)

5×10^{-6}

1×10^{-6}

5×10^{-7}

Slope = .0 19
r = .0 67

1×10^{-7}

5×10^{-6}

1 0   0 0   1 0   2 0   3 0   4 0

Pore Volume
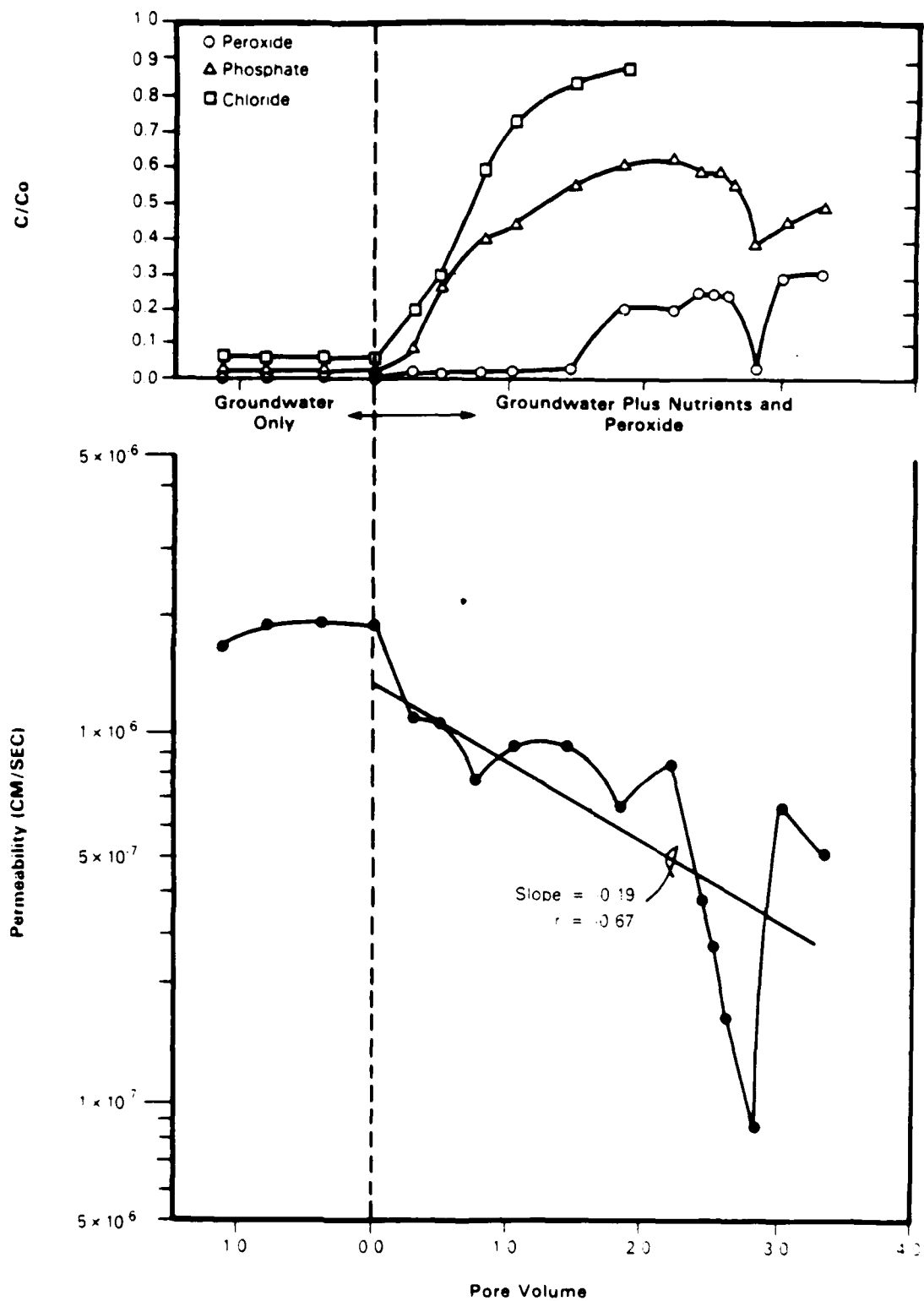
Figure 7.   Permeability and Nutrient Solution Breakthrough
for Soil Sample Number One

23
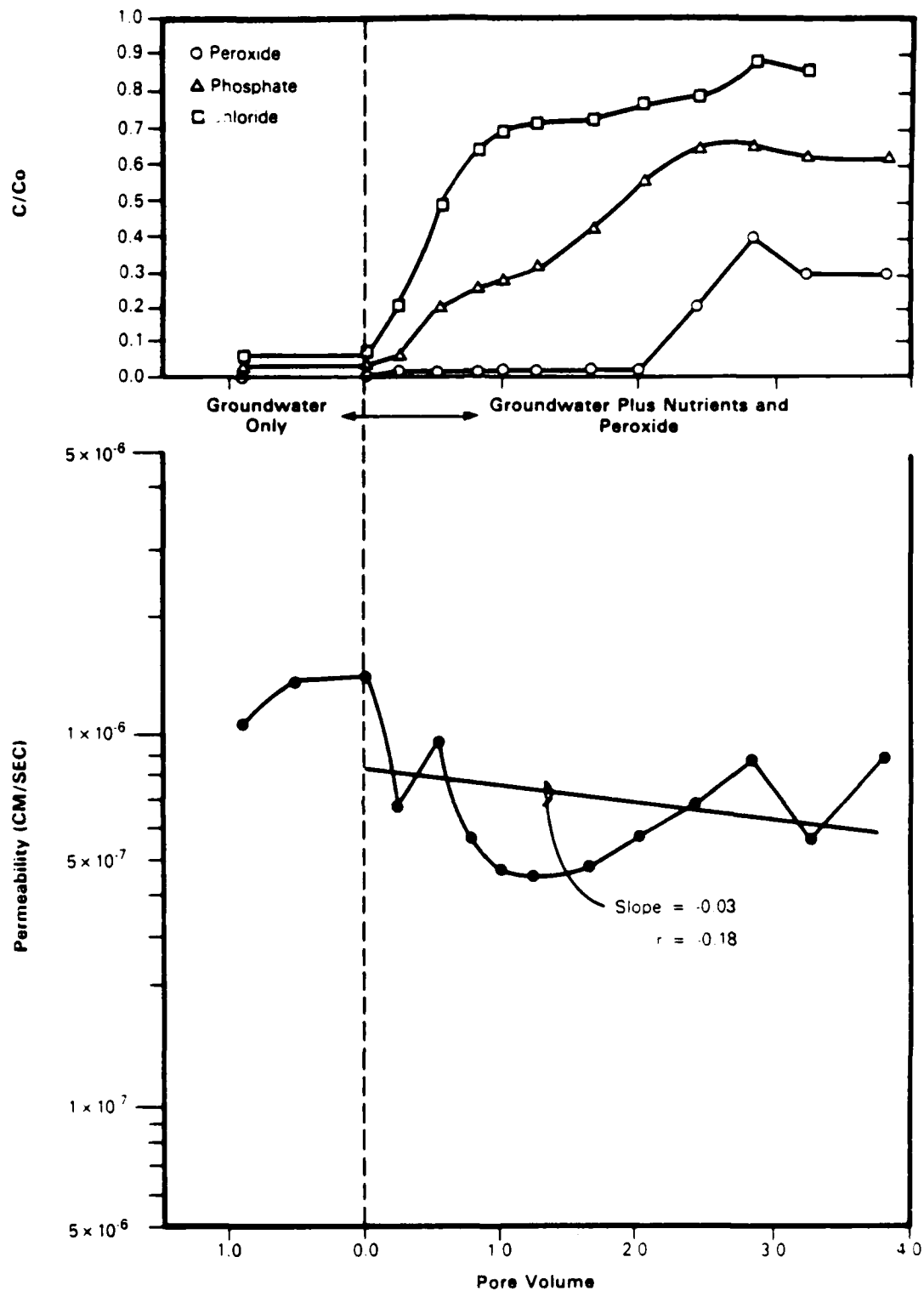
Figure 8.   Permeability and Nutrient Solution Breakthrough
Curves for Soil Sample Number Two

24

initial breakthrough of chloride followed by low phosphate breakthrough, were observed during the field study. Results from these studies also indicated that permeability reduction of the soils occurred following addition of nutrients and hydrogen peroxide. This effect was also observed during the field demonstration project and is discussed in subsequent chapters. The permeability studies also indicated that peroxide breakthrough was slower than that for phosphate, as was observed in the field.

D. DESIGN AND INSTALLATION OF TREATMENT SYSTEM

Many site-specific factors were considered in developing a treatment approach that would best suit the conditions present at the Kelly AFB site. The variable geology at Site E-1 necessitated a system that could be readily adjusted to conform to actual subsurface characteristics within the treatment zone, which would not be known with certainty until system wells were installed and tested. Circulation of groundwater, introduction of nutrients, and introduction of an oxygen source were the necessary conditions for providing adequate microbial activity over a specific area. A major concern was the probable hydrologic communication between the shallow aquifer and nearby Leon Creek. The system was designed to provide a closed circuit operation (containment and recirculation of groundwater within the demonstration area) to prevent contaminants from migrating toward Leon Creek. Due to the constraints of site characteristics and time, the treatment test was performed within a small area of Site E-1 and not for the entire site. The area was chosen because soil in the saturated zone had high concentrations of petroleum hydrocarbons which could be aerobically biodegraded.

After considering several alternatives, it was decided that a series of injection wells surrounded by pumping wells would best provide the closed system necessary for the demonstration. Several well configurations were tested with a two-dimensional geohydrologic model which simulated groundwater flows. The model assumed a homogenous site

and an isotropic aquifer of uniform thickness. The actual conditions at Kelly AFB were more complicated, limiting the models' ability to accurately represent site reaction to various pumping and injection schemes. Even so, the model was useful in determining a site configuration that would keep water levels stable and minimize the effect outside the treatment zone.

The resulting well system configuration, illustrated in Figure 9, was constructed at the Kelly AFB site in April and May 1985. The system consisted of nine pumping wells and four injection wells arranged in a grid pattern within a circular area 60 feet in diameter. It was designed so that each injection well would be surrounded by four equidistant pumping wells 15 feet away. The pumping wells were 4 inches in diameter and the injection wells were 6 inches in diameter. All wells were 30 feet deep and cased with PVC piping. The bottom 15 feet of the casing was slotted. In addition, 2-inch monitoring wells were placed one up-gradient and one downgradient of the demonstration site. Existing Well CC was used as an additional downgradient monitoring well.

Although biodegradation of contaminants takes place underground, groundwater circulation, groundwater and chemical storage facilities, and chemical addition equipment were installed on the surface. Each pumping well was equipped with a durable, 1/2 horsepower, submersible pump which was selected to be able to run continuously for the life of the project. A pump capable of operating continuously for a long time at the extremely low flow rates required at this site could not be found. Therefore, it was necessary to pump water from each well at a much higher rate than needed and return the unused portion to the well. This was achieved with a dual-valve system located above the well casing. Figure 10 illustrates a typical pumping well. The release valve was set to allow the desired amount of flow into the system; the check valve provided the necessary back pressure on the pump and allowed the overflow to pass into the overflow line and return to the well. Each pump was individually controlled by dedicated electrodes that sensed high and low water levels in the well. When the level of water in the well dropped

26
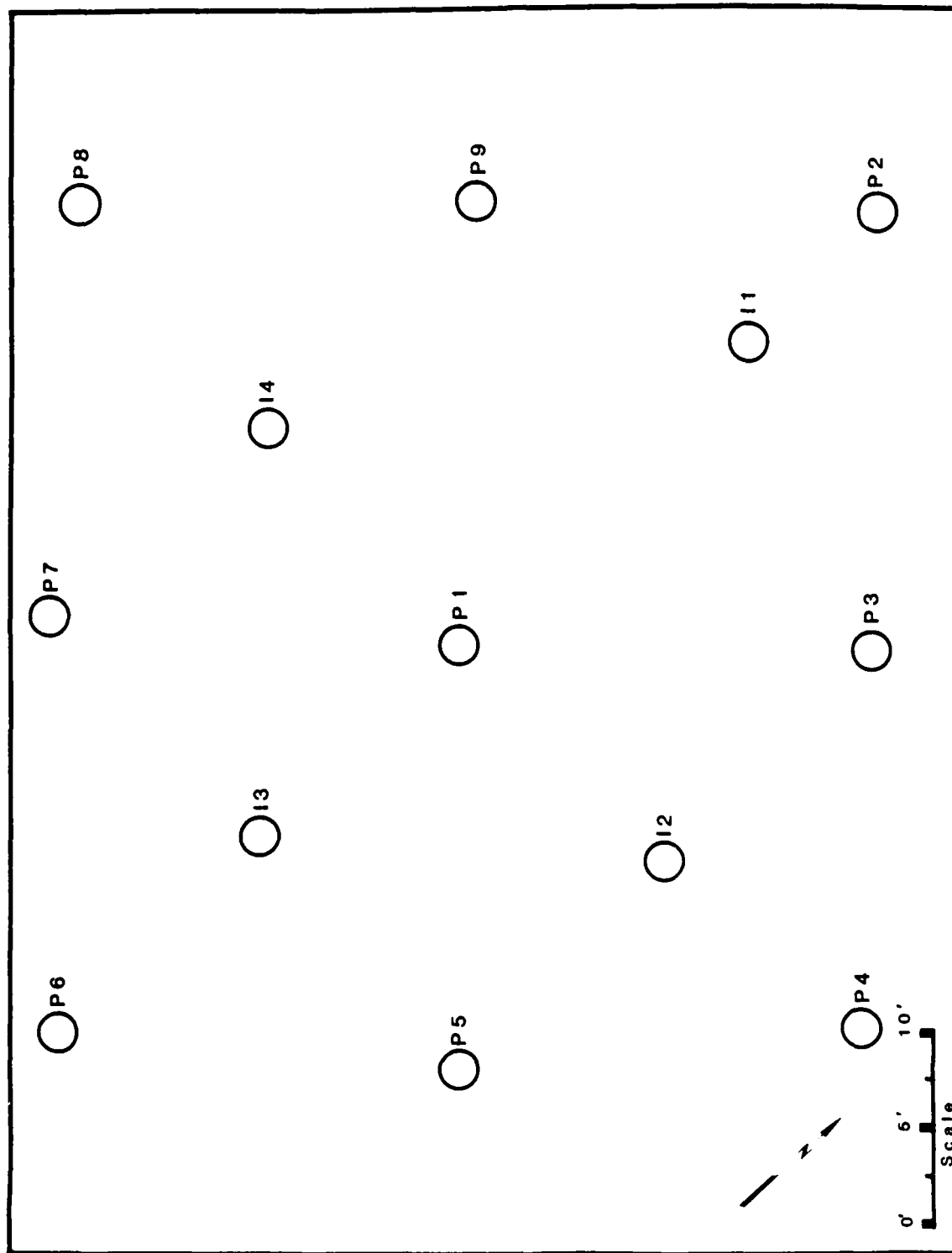
Figure 9. System Well Configuration
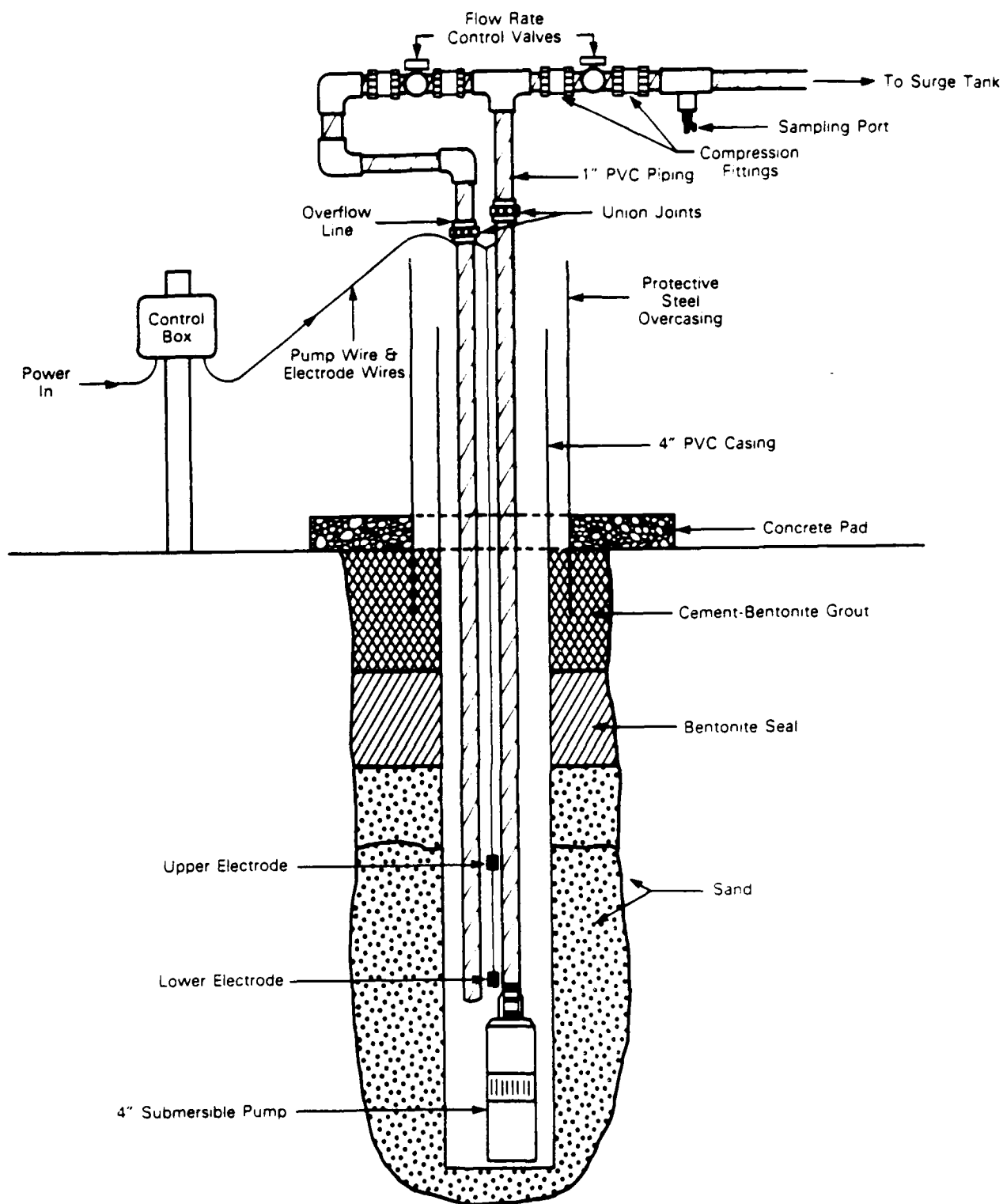
Figure 10. Cross Section of a Typical Pumping Well

(Not to Scale)

below a safe level for pump operation (0.5 foot above the intake), the pump shut off automatically. After the well recharged, the pump began operating once again.

Once groundwater entered the system, it flowed by gravity to a central surge tank. A valve at the bottom of the surge tank released water at a controlled rate into a feed pipe in which the nutrient and hydrogen peroxide solutions were also introduced. This combined flow then passed through a section of baffled pipe to facilitate mixing before it entered a distribution box which divided the flow among the four injection wells. Flow in three of the four lines to the injection wells was controlled by valves, while the fourth line remained unobstructed to prevent a backup of water in the distribution box. The system configuration is illustrated in Figure 11.

Choice of materials was a major consideration in system design. All materials chosen were first determined to be nonreactive with contaminants known to be present at Site E-1 or the treatment chemicals. PVC was chosen for all piping, valves, and fittings. All connections were heat-welded to avoid the use of glues, which could have introduced unwanted organic chemicals to the system. Pumps and electrodes were constructed of stainless steel. Other plastics that came in contact with groundwater included insulation for pump electrical wiring. No detectable adverse effects were found to result from the materials chosen for constructing the treatment system.

Key:

● Injection Wells
○ Pumping Wells
⊙ Monitoring Wells
— Pumping Lines
--- Injection Lines
A Distribution Box
B Surge Tank

Drainage

P6 P7 P8
I3 I4
M2
P5 A P1 B P9
M1
I2 I1
P4 P3 P2
Electrical Line
Circuit Box

Site Office Trailer

Storage Yard

N
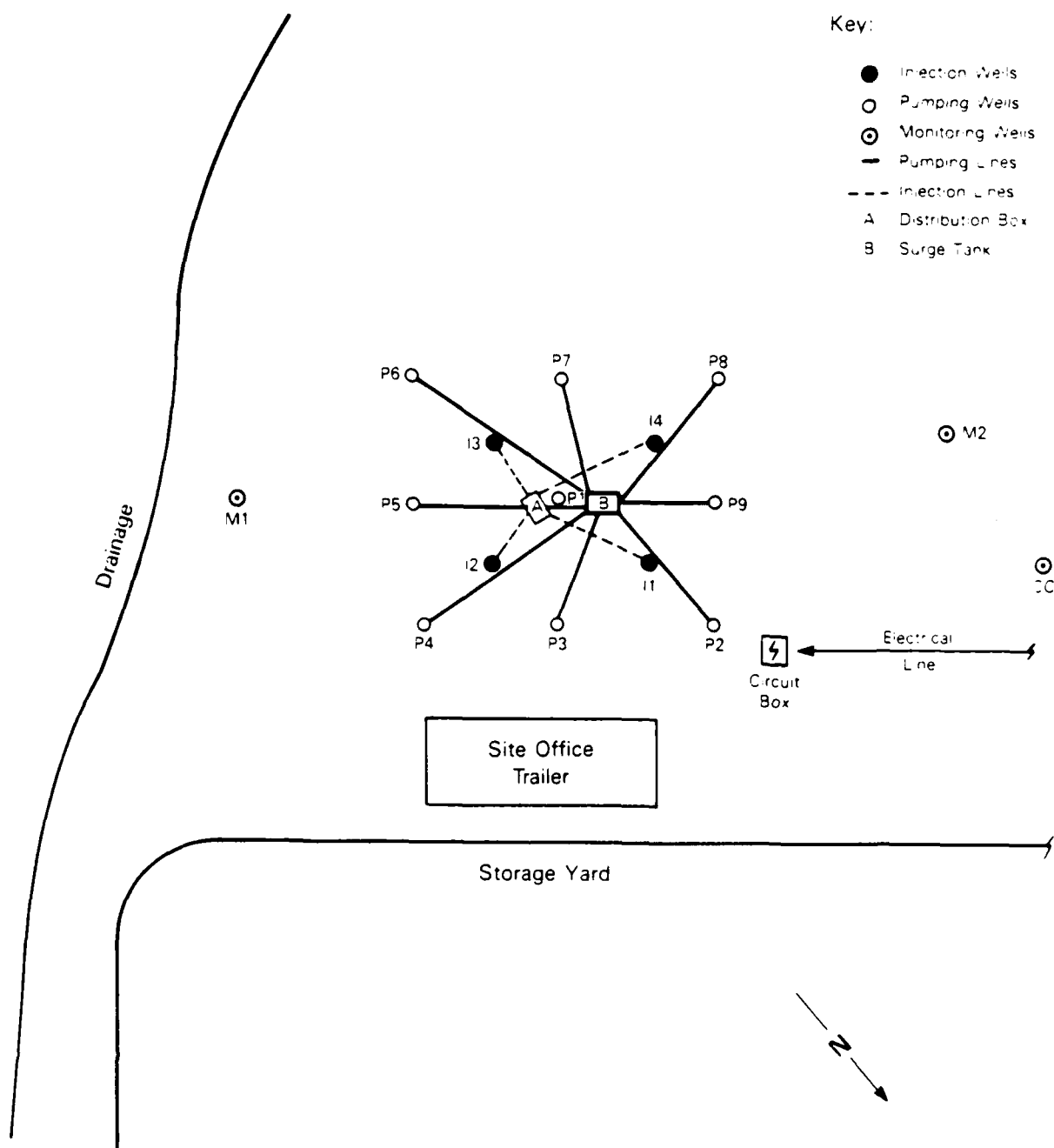
Figure 11.   Plan View of System Configuration

(Not to Scale)

30

SECTION III

TEST PROCEDURES

A. DESCRIPTION OF FIELD OPERATING PROCEDURES

For most system operations, one field technician was responsible for
all onsite activities. A field operations manual was developed by SAIC
to ensure that proper procedures were followed at all times. The field
technician (engineer or geologist) was responsible for mechanical opera-
tion of the system and the sampling and analysis program. The following
sections discuss the details of these activities.

1. System Operation

System operation activities included operation and maintenance
of all pumps, piping, and electrical controls as well as mixing nutrient
and peroxide solutions for gravity injection. Because of insufficient
injection capacity, pumps were operated on a rotational basis. Usually four
pumps were operating at any one time, along with pumping well P1, which was
a very poor producer. The flow rate from each operating pump was recorded
as were rates to each injection well. Nutrient and peroxide flow rates were
set at the specified level and allowed to run while groundwater was being
circulated. Concentrated nutrient solution was only introduced at a
few gallons per day and stopped completely in late October 1985. Peroxide
was injected during the entire period of pump operation, with the exception
of the first 2 weeks and several weeks in November 1985.

A daily log sheet was completed each day. This form reported
flow rates, water levels, and other important operating characteristics.
These data were summarized weekly in a report to the project manager.
Maintenance of injection wells required periodic redevelopment which

31

included air surging and hand bailing to clean well screens and remove fines and precipitate.

2. Sampling Schedule and Procedures

A detailed sampling and analysis program was followed throughout the operation of the treatment system. Groundwater and soils analyses were performed both onsite and in offsite laboratories for a number of physical, chemical, and biological parameters. Table 2 lists these parameters and indicates the frequency of analysis for each one.

The field technician was responsible for collecting all of the samples and performing all of the onsite analyses. Laboratory samples were placed on ice and mailed by overnight air freight to the designated laboratory. Strict adherence to site-specific QA/QC and health and safety procedures were followed during all sampling activities. These procedures are addressed in subsequent sections of this report.

Sampling for tests performed onsite was normally performed in the morning so that analyses could be performed the same day. Samples from pumping wells were taken from the sampling ports located near the release valves of each well (see Figure 10). Samples of groundwater from injection and monitoring wells were obtained with a PVC bailer. Soil samples were obtained using a standard, thin-walled sampling tube (Shelby-tube). The samples were split once and placed into: (1) two 750 mL jars for total phosphates, inorganic orthophosphate, hydrocarbons, and priority pollutants, and (2) four small, sterile glass jars for microbe counts. Soil sampling locations are shown in Figure 12.

Great care was taken to ensure sterile sampling conditions and to prevent cross-contamination of samples. The decontamination procedures followed are discussed in Section III-B.

TABLE 2. GROUNDWATER MONITORING SCHEDULE

Parameter	Sampling Frequency		
	Extraction Wells	Injection Wells	Monitoring Wells
Temperature	2/Week	2/Week	Weekly
Conductivity	2/Week	2/Week	Weekly
pH	2/Week	2/Week	Weekly
Dissolved Oxygen	2/Week	2/Week	Weekly
Carbon Dioxide	2/Week	2/Week	Weekly
Ammonia	2/Week	Weekly	Monthly
Phosphate	2/Week	Weekly	Monthly
Chloride	2/Week	Weekly	Monthly
Hydrogen Peroxide	Weekly	Weekly	Monthly
Nitrate	2/Month	2/Month	Monthly
Sulfate	2/Month	2/Month	Monthly
Acidity	2/Month	2/Month	Monthly
Alkalinity	2/Month	2/Month	Monthly
Total Hardness	2/Month	2/Month	Monthly
Chromium	Monthly	---	Monthly
Lead	Monthly	---	Monthly
Oil and Grease	Monthly	Monthly	Monthly
Total Hydrocarbons (Alkanes)	Quarterly Analysis of 10 Wells		
Priority Pollutants (Volatile Organics and Metals)	Quarterly Analysis of 10 Wells		
Microbial Plate Counts	Monthly	Monthly	Monthly
Groundwater Elevations	Daily	Daily	Daily
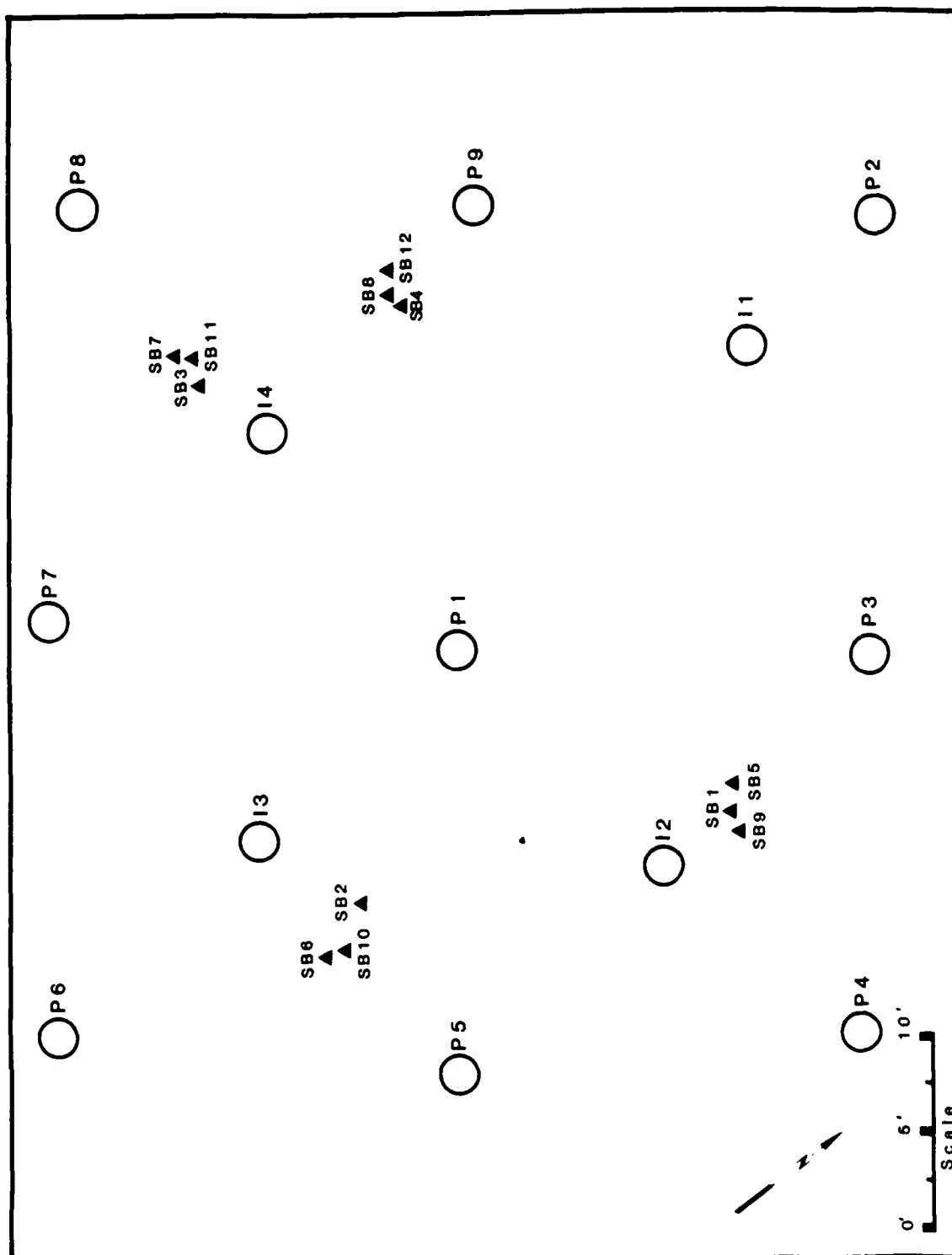
Figure 12.   System Well Configuration Showing Soil Sampling Locations

B. DESCRIPTION OF ANALYTICAL PROCEDURES

Soil and groundwater samples were collected periodically during the field demonstration project to evaluate system performance and treatment effectiveness. A quality assurance project plan was developed by SAIC to ensure that proper analytical procedures were followed both in the laboratory and in the field. Details regarding QA/QC procedures are discussed in subsequent sections of this report. The sampling frequencies for chemical and microbiological analyses are given in Table 2. The following sections discuss the procedures used for both laboratory and field analyses.

1. Microbiological Enumeration

Soil and groundwater samples were collected and sent to contracted laboratories for enumeration of total bacteria and hydrocarbon utilizing bacteria. FMC/Aquifer Remediation Systems laboratory performed the analyses on samples collected from April 1985 through October 1985. No soil or groundwater samples were collected for microbial analyses during November 1985. Microbial samples collected from December 1985 through February 1986 were analyzed by Biosystems, Inc.

The enumeration methods used by each lab consisted of plating groundwater or soil solutions on nutrient agar media to determine total bacteria colonies. The enumeration of hydrocarbon-degrading bacteria was conducted by incubating the inoculated basal mineral salts agar plates in dessicator jars supplemented with gasoline. Dilution series plates were used for all samples to obtain 20-300 colonies per plate. Duplicate enumeration analyses were performed on selected soil and groundwater samples as part of the QA/QC procedures. Specific media compositions and procedures utilized by each contract laboratory are presented in Volume III (Appendix E).

2. Laboratory Chemical Analyses

Groundwater and soil samples were collected throughout the
field demonstration project and sent to contracted laboratories for
chemical analyses. Chemical analyses on samples collected during
April and May 1985 were performed by Aqualab, Inc. All subsequent
chemical analyses were conducted by Environmental Research Group
(ERG). Chemical analyses performed on soil samples included priority
pollutant volatile and metal compounds, total hydrocarbons (alkanes),
oil and grease, total organic carbon, total inorganic carbon, total
phosphorus, and inorganic orthophosphate. Groundwater samples were
analyzed for chemical parameters which included priority pollutant
volatile and metal compounds, total hydrocarbons (alkanes), oil and
grease, total organic carbon, and total inorganic carbon. Field QA/
QC samples included field blanks, bailer washes and duplicates. Con-
tract laboratories performed in-house QA/QC procedures including dupli-
cates and matrix spike additions. QA/QC procedures are discussed in
detail in later sections of this report.

Analytical procedures used for chemical analyses of soils and
groundwater are listed below.

Soils
Priority Pollutant Analysis
    Volatile organics   EPA Method 8240
    Metals   EPA 600/4-79-020
Total Hydrocarbons (alkanes)   Nonstandard
                                        (See Volume III, Appendix D)
Oil and Grease   Extraction/EPA 413.2
Total Organic Carbon   EPA Method 9060
Total Inorganic Carbon   EPA Method 9060
Total Phosphorus   ASTM 424
Inorganic Orthophosphate   ASTM 424

Groundwater

Priority Pollutant Analysis

Volatile Organics	EPA Method 624
Metals	EPA 600/4-79-020
Total Hydrocarbons (alkanes)	Nonstandard
	(See Volume III, Appendix D)
Oil and Grease	EPA Method 413.2
Total Organic Carbon	EPA Method 415.1
Total Inorganic Carbon	EPA Method 415.1

All chemical analyses were performed in accordance with the standard chemical methods listed.

3. Field Chemical Analyses

Soil samples were collected at the Kelly AFB site on a quarterly basis and a split from each sample was kept onsite for field test analyses. Soil analyses were performed by the field technician (engineer or geologist) for the following parameters: pH, calcium, iron, magnesium, manganese, ammonium, nitrate, nitrite, phosphorus, and sulfate. Analyses were performed using a Simplex Soil Testing Kit (Reference 18). Instructions and chemicals for conducting the field analyses were provided with the field test kit. These analyses were performed to obtain estimates of the parameter concentrations for use in system operation decision-making and were not intended to replace analyses performed by contract laboratories.

Groundwater was monitored onsite for the following parameters: pH, temperature, conductivity, dissolved oxygen, carbon dioxide, ammonium, phosphate, chloride, hydrogen peroxide, alkalinity, acidity, total hardness, nitrate, sulfate, lead, and chromium.

At the time of collection, groundwater samples were split once. One split was immediately analyzed for dissolved oxygen, temperature,

37

pH, and conductivity by placing probes from the oxygen analyzer and temperature/pH/conductivity meters in the beakered sample.

The remaining sample was temporarily stored in an ice chest until all groundwater samples had been collected and splits from each had been analyzed with the portable meters.

The instruments used for measurements onsite included an Engineering Systems model OXAN oxygen analyzer and a Cambridge Scientific model 301353 combination conductivity/temperature/pH meter. Both instruments were calibrated routinely in the field - the oxygen analyzer before each use and the Cambridge instrument weekly. Standard buffered solutions of 4, 7, and 10 pH, and 1,413 umhos were utilized to calibrate field instruments for pH and conductivity measurement. Standard solutions were not reused but discarded after each use.

Field lab analyses were performed onsite using LaMotte test kits (Reference 19). Each kit contained specific instructions which were straightforward and easy to follow. Chloride analyses were performed in accordance with procedures guidelined by FMC Aquifer Remediation Systems during its involvement with the demonstration project (June - September 1985). Also, because the detection limit for hydrogen peroxide with the LaMotte kit (code 3515) was relatively high, FMC's method for this test was used when a lower detection limit was needed.

Backup analytical methods were provided for many of the chemical parameters. This allowed the field technician to cross-check questionable results, as well as provide a means of analysis for a given parameter if reagent supplies ran low, became weak or contaminated, or otherwise unusable. The field technician noted any changes in the test methods used.

QA/QC procedures on field chemical analyses included analyzing duplicate samples on a routine basis and analyzing selected standard solutions with the field test kits. Standard solutions were provided by Raba Kistner Laboratories of San Antonio and included the following parameters: chloride, ammonium, phosphate, lead, and chromium. Field QA/QC procedures are discussed in subsequent sections.

C. SITE HEALTH AND SAFETY PLAN

A detailed health and safety plan was developed to establish site-specific procedures and was followed for all activities at the Kelly AFB site. Specific protection levels were established for the following site activities:

- Routine system operation
- Groundwater sampling
- Handling of hydrogen peroxide
- Drilling and soil sampling
- Test kit operation.

Protective equipment was maintained onsite to provide EPA Level "C" protection for at least three persons. In addition, the following safety measures were taken:

- First aid kit was made available in an onsite trailer
- Fire extinguisher was provided in the trailer
- Eye and body wash kits were made available onsite
- CAUTION and NO SMOKING signs were posted to indicate fire and electrical hazards
- Flagging was used to mark trip and overhead hazards
- Emergency phone numbers were posted in the trailer
- First aid and laboratory safety charts were posted in the trailer.

D. SITE MITIGATION PLAN

A detailed site mitigation plan was developed to establish proce-
dures for monitoring contaminant migration from the treatment area and
develop a course of action for mitigation in the event that significant
contaminant migration was discovered. Monitoring well CC was designated
to monitor contaminant migration. Each new set of results was compared
with historical values to determine if unacceptable levels of any con-
taminant were threatening to reach Leon Creek.

In the event that high levels of contaminants were found in Well CC,
SAIC would report this information to EG & G and the Air Force. A joint
decision by the Air Force, EG & G, and SAIC would then be made as to
whether mitigative action was justified. Immediate action would have
consisted of pumping the entire system at capacity to try to draw ground-
water away from Leon Creek. Several system modifications were suggested
to permit the system to operate at a higher pumping rate for a longer time
period than planned for in the system design. More permanent mitigative
measures were suggested in the mitigation plan including barrier walls
and an onsite treatment system. These methods were cost-prohibitive and
were to be implemented only as a last resort.

E. SYSTEM SHUTDOWN

The final day of system operation at Kelly AFB was February 17, 1986.
The system was then completely disassembled. All wells were left intact
and locked. The circuit box and electrical outlets were also left on-
site but power was turned off. All other project-related items were
removed from the site.

SECTION IV

SYSTEM PERFORMANCE

A. STARTUP

System construction was completed in mid-May 1985. Following construction, pumping tests were performed to determine transmissivity values for all nine pumping wells. Using the data collected from these tests, each pump was set to a rate determined from the pumping tests to result in steady-state yield. Pumping rates were highly variable because of the heterogeneity of the test site, and the total flow from all nine wells was only slightly more than 1 gallon per minute because of low yield of the shallow aquifer. This flow was originally distributed equally among the four injection wells. However, each of the injection wells exhibited different permeabilities and the flows were adjusted to the maximum that could be accepted by each well. Groundwater was circulated through the system for several days prior to the introduction of nutrients so that flow rates could be readjusted and any other problems with the system could be worked out. Several pumps had to be removed during this testing period to be cleaned, because of fines remaining in the wells after development.

Nutrient introduction began on June 7 and was performed for several weeks before hydrogen peroxide injection began on June 26. The initial plan was to begin hydrogen peroxide concentrations at 100 ppm in the groundwater injection flow. Concentrations were then to be increased by 100 ppm every 2 weeks to achieve a final total concentration of 500 ppm in the injected groundwater. Due to the steadily decreasing flow rates, however, much higher levels were actually introduced. This is discussed more thoroughly in Section IV-B.

41

Initially, a system was set up to introduce both the nutrients and peroxide in a single solution. Set volumes of each solution were mixed together with water in a 30-gallon drum to achieve the desired concentrations. A small chemical feed pump was then used to transfer the solution at a set rate into the groundwater circulation flow. After approximately 3 weeks, the system was altered so that nutrients and peroxide were controlled by separate feed pumps. This change was made so that the nutrient solution could be injected at a higher concentration over a shorter time to control precipitation. This problem is further discussed in Section IV-C.

B. SCHEDULE OF CHANGES OF OPERATING PARAMETERS

Table 3 provides a weekly summary of the major changes made or incurred in the operation of the well system with regard to: average chemical concentrations of injection well fluids, the oxygen source as hydrogen peroxide (H_2O_2), and nutrients (the inert parameter as chloride, Cl; the nitrogen source as NH_3; the phosphorous source as PO_4); groundwater circulation volumes and rates; and other parameters such as well workover frequency, days of peroxide and nutrient injection, soil and groundwater sampling for microbial and priority pollutant analysis, and field staffing level.

A total of 52,267 gallons of groundwater were circulated over a period of 259 days, from June 5, 1985 to February 18, 1986. Based on a 60-foot diameter of the well area, a 10-foot vertical aquifer thickness, 20 percent porosity and a grain density of 162 lbs/ft^3, this volume of circulated groundwater corresponds to a displacement of 1.25 pore volumes. This nominal geometry of the well pattern contains 1850 tons of soil and 42,300 gallons of groundwater.

Nutrient addition to the groundwater was in effect from June 7, 1985 to November 7, 1985. Following November 7, 1985, residual

TABLE 3. SUMMARY OF SYSTEM OPERATING PARAMETER CHANGES

Week Ending Date	Total Weeks	Weekly Average of Injection Well Chemical Concentrations (ppm)				Groundwater Circulation			Well Workovers in Week	Days H2O2 Used	Days Nutrient Used	Days of System Operation	# of Field Staff	Microbial Sampling	Priority Pollutant Sampling
		H2O2	Cl	NH3	PO4	Weekly Gallons	Average Rate(gpd)	Cumulative Gallons							
06/07/85	0.4	0	43	0	0	4,320	1,440	4,320	0	0	0	3	2	GW	.
06/14/85	1.4	0	520	107	118	8,590	1,227	12,910	0	0	7	7	2	.	.
06/21/85	2.4	0	2446	261	267	3,663	523	16,573	0	0	7	7	1	.	.
06/28/85	3.4	4625	4200	1192	531	2,649	378	19,222	0	3	7	7	2	GW	.
07/05/85	4.4	388	2688	256	967	1,410	201	20,632	4	7	5	7	1	.	.
07/12/85	5.4	0	2971	2000	3500	680	97	21,312	6	6	7	7	1	.	.
07/19/85	6.4	8000	5500	2000	2500	2,800	400	24,112	5	7	7	7	1	GW	.
07/26/85	7.4	10000	5000	2000	2500	1,660	238	25,772	3	7	7	7	2	.	.
08/02/85	8.4	5000	5000	2000	2125	1,672	239	27,444	1	7	6	7	1	.	.
08/09/85	9.4	500	2012	2038	2458	2,188	313	29,632	0	7	7	7	2	Soil & GW	Soil & GW
08/16/85	10.4	148	5800	2000	5000	2,757	394	32,389	1	7	7	7	1	GW	.
08/23/85	11.4	NA	NA	NA	NA	1,690	241	34,079	0	7	5	7	1	.	.
08/30/85	12.4	420	3800	1781	3688	730	122	34,809	1	7	5	6	1	GW	.
09/06/85	13.4	438	1550	113	60	800	114	35,609	1	7	7	7	2	.	.
09/13/85	14.4	500	NA	131	38	770	155	36,379	2	7	5	5	1	.	.
09/20/85	15.4	50	150	26	0	960	160	37,339	1	7	6	6	2	GW	.
09/27/85	16.4	NA	NA	NA	NA	516	86	37,855	0	7	5	6	1	.	.
10/04/85	17.4	66	525	143	83	828	118	38,683	0	7	1	7	1	GW	.
10/11/85	18.4	4	NA	233	438	820	117	39,503	0	5	3	7	1	.	.
10/18/85	19.4	213	1525	469	0	700	100	40,203	1	7	6	7	2	GW	.
10/25/85	20.4	600	475	119	0	834	119	41,037	0	7	7	7	2	GW	.
11/01/85	21.4	250	3019	1975	325	423	60	41,460	0	7	6	7	1	.	.
11/08/85	22.4	2	440	56	18	418	60	41,878	0	5	5	7	1	.	.
11/15/85	23.4	6	345	400	525	652	93	42,530	1	0	3	7	3	.	.
11/22/85	24.4	0	76	7	NA	1,262	180	43,792	0	0	0	7	3	.	.
11/29/85	25.4	0	34	2	NA	907	130	44,699	0	0	0	7	2	.	.
12/06/85	26.4	0	51	39	NA	1,146	164	45,845	0	0	0	7	2	Soil & GW	Soil & GW
12/13/85	27.4	165	126	10	NA	995	142	46,840	0	7	0	7	2	.	.
12/20/85	28.4	190	129	13	5	805	115	47,645	1	7	0	7	1	.	.
12/27/85	29.4	141	119	13	<1	516	74	48,161	0	7	0	7	1	.	.
01/03/86	30.4	201	179	36	11	468	67	48,629	1	7	0	7	1	.	.
01/10/86	31.4	286	156	14	NA	511	73	49,140	0	7	0	7	2	.	.
01/17/86	32.4	636	96	114	NA	597	85	49,737	0	7	0	7	2	.	.
01/24/86	33.4	525	89	13	NA	526	75	50,263	1	7	0	7	1	GW	.
01/31/86	34.4	200	81	8	0	685	98	50,948	0	7	0	7	2	.	.
02/07/86	35.4	191	87	5	0	735	105	51,683	0	7	0	7	1	.	.
02/14/86	36.4	NA	87	5	0	584	83	52,267	0	7	0	7	1	.	.
02/21/86	37.4	103	90	5	<1	0	0	52,267	0	3	11	3	2	Soil & GW	Soil & GW

nutrient in the groundwater obtained from the production wells provided the only source of nutrient for the injection wells. During the period of nutrient addition to the groundwater (June 7, 1985 to November 7, 1985) average nutrient chemical concentrations based on bulk chemical addition were:

- 812 ppm NH_4 as nitrogen source
- 1598 ppm PO_4 as phosphorous source
- 1598 ppm Cl as inert.

The chloride (Cl) is used as a chemical tracer to analyze well pattern chemical effects as initial groundwater background levels averaged less than 40 ppm.

The total quantity of hydrogen peroxide added to the injection wells during the field operation was 299 pounds. Based on a nominal well pattern groundwater volume of 42,300 gallons, a soil mass of 1850 tons, and an average hydrocarbon contaminant oxygen demand of 3 parts oxygen per part contaminant, a maximum reduction of 133 ppm hydrocarbon in the groundwater or 12.8 ppm hydrocarbon concentration in the soil would have been possible. Hydrogen peroxide (H_2O_2) addition to the circulated groundwater was in effect from June 21, 1985 to November 7, 1985, and from December 6, 1985 to February 14, 1986. The average H_2O_2 concentration added to the groundwater during the first time period was 1328 ppm, and 355 ppm H_2O_2 was added during the second time period. It must be emphasized that this concentration represents what was placed in the injection wells. No estimate could be made of the actual concentration entering the formation from the injection well or the speed with which the hydrogen peroxide decomposed to water and oxygen once in the injection well or in the formation.

The volume of the saturated zone within the test area is used as a baseline to judge the potential for peroxide to react with hydrocarbons. It is recognized that hydrocarbons may not have been uniformly distributed

44

over this nominal volume, and certainly were not of uniform concentration where they did exist. However, using this nominal volume and the peroxide mass injected in conjunction with a hydrocarbon demand of 3 parts oxygen per part of contaminant, it is shown that less than 13 ppm of hydrocarbon would have been affected over the time of the field test. This level is an order of magnitude lower than the reported hydrocarbon concentrations. This indicates that only sufficient peroxide was injected to have impacted localized pockets of hydrocarbon, either in the saturated zone, or above it in a comparable 60-foot diameter. However, sufficient peroxide was present to have impacted contaminants in the water, as the total quantity of injected peroxide was sufficient to reduce contaminant concentrations by 133 ppm in the groundwater.

Following the initiation of nutrient and peroxide addition in June 1985, a significant reduction in the groundwater circulation rate occurred which could not be restored by mechanical cleaning of the wells. A 93 percent reduction in the groundwater circulation rate was observed in the first 5 weeks of operation. Less than a 21 percent restoration of the initial circulation rate was achieved by subsequent changes in peroxide and nutrient concentrations and 30 mechanical well workovers.

System operation covered the period between June 5, 1985 and February 18, 1986, 259 days of 24 hours per day and 7 days per week operation. System downtime was 5 days, less than 2 percent of the total time. The field operations staff averaged between one and two persons per day.

C. MAJOR OPERATING PROBLEMS

From the time the first test wells were drilled, it was clear that low transmissivity and high variability at the site would cause operational difficulties. The first significant problem arose during well construction. While flushing the drilling mud out of Injection Well I2, muddy water began

45

to flow out of completed Pumping Wells P4 and P5. These wells required redevelopment. This occurrence suggested the presence of underground channeling in that area of the site. However, subsequent results did not substantiate this assumption. In addition, low permeability made well development difficult.

Pumping rates for most of the wells were even less than the low values originally anticipated. These low pumping rates created a problem with the temperature of the groundwater in the pumping wells. Due to the small volume of groundwater actually removed from the well, the temperature of the water was increased by the heat generated by the pump. As a result, the groundwater temperature in some wells temporarily reached as high as 100°F.

In addition to the low pumping rates, injection rates were also found to be much lower than expected. Several of the wells repeatedly overflowed and the rates had to be reduced. This created a situation in which more water was being pumped into the surge tank than could be placed in the injection wells. To solve this problem and the problem of elevated water temperature, the pumping operation was switched to a cycling mode. Alternate pumps were operated for a given time period and then shut off for an equal period. This reduced the total flow into the surge tank and allowed the pumps a period of downtime which controlled the temperature of the water in the well.

After several days of nutrient addition, a considerable drop in the injection rate was noticed. A thick, white precipitate was also observed in the distribution box. Jar tests were performed to determine if nutrient precipitation was occurring which may have resulted in clogging of the well screens. Results from the jar tests confirmed that precipitation of nutrients was occurring and showed that precipitation in the distribution box could be eliminated by increasing the concentration of nutrients added to the groundwater. This was attributed to chelating agents present in the nutrient solution. Nutrient

addition was also switched to a batch mode over a 3-hour period, rather than continuous addition during system operation, to maintain the over-all nutrient loading. These changes in the initial design of system operation eliminated any precipitation in the distribution box. However, injection rates did not substantially increase. The injection wells were then manually cleaned, using a large diameter pipe brush. This removed a large amount of precipitate from each of the wells and re-sulted in increased injection rates.

After a short period of system operation, however, injection rates decreased further. It was believed that precipitation of nutrients had occurred in the formation and resulted in the clogging of pore spaces. Upon regular cleaning of injection wells, precipitate continued to be present. Finally, nutrient injection was suspended in late October 1985 to monitor the effects on system performance.

D. WELL PATTERN FLOW EFFECTS

This section discusses system performance with regard to groundwater circulation rates and fluid communication between wells.

1. Analysis of Changes in Groundwater Circulation Rates

The average weekly groundwater circulation rate is plotted as a function of weeks of operation in Figure 13. The cross-hatched areas correspond to periods of declining circulation rates and the shaded areas correspond to periods of increasing circulation rates. Table 4 lists the changes in the circulation rates over the 14 periods, average chemical concentrations of injection well fluid, and mechanical work-overs of the wells.

The largest change in the circulation rate, a decline of 93 per-cent, occurred in Periods 2 and 3, corresponding with the first addition of nutrient and peroxide to the groundwater. The subsequent action, including

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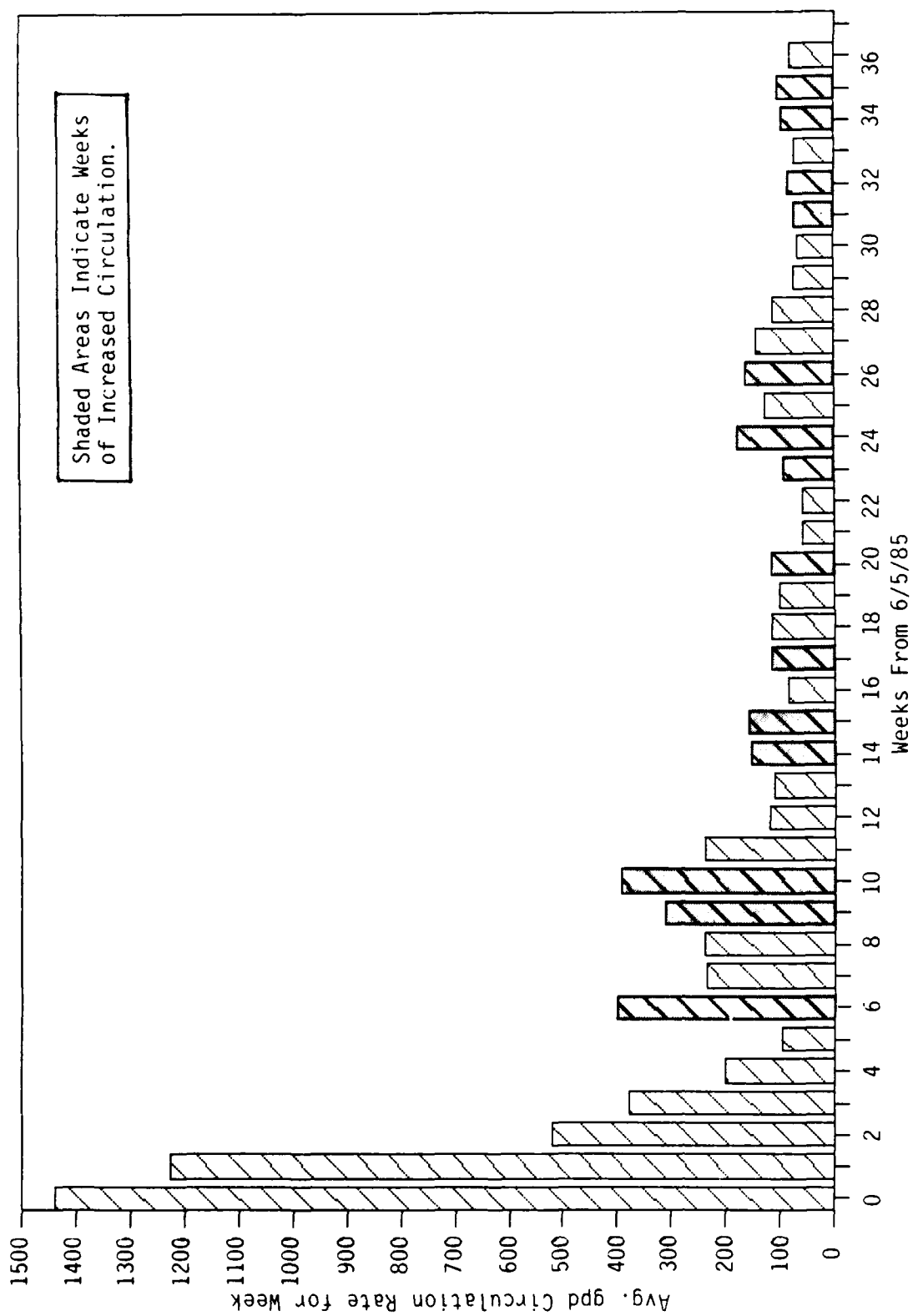
Figure 13. Weekly Average Groundwater Circulation

TABLE 4. SUMMARY OF SYSTEM OPERATION CHANGES

	Time Interval	Comments	Change In Circulation Rate GPD	Average Injection Well Chemical Concentration (ppm)				Number of Well Workovers
				H_2O_2	CI	NH_4	PO_4	
1	Day 0 to 3	• No H_2O_2 or nutrient injection	Base 0	0	43	0	0	0
2	Day 4 to 18	• No H_2O_2 injection • Intermediate level nutrient • No well workovers	-917	0	2360	184	193	0
3	Day 19 to 40	• Intermediate H_2O_2 level • Intermediate nutrient level • High well workover level	-426	2507	3286	1149	1666	10
4	Day 41 to 48	• High H_2O_2 level injection • High nutrient level injection • Intermediate well workover level	+303	8000	5500	2000	2500	5
5	Day 49 to 63	• High H_2O_2 level injection • High nutrient level injection • Intermediate well workover level	-161	7500	5000	2000	2313	4
6	Day 63 to 77	• Low H_2O_2 level • Intermediate nutrient level • Low well workover level	+155	324	3906	2019	3729	1
7	Day 78 to 99	• Low H_2O_2 level • Intermediate nutrient level • Low well workover level	-280	429	2675	947	1874	2
8	Day 100 to 114	• Low H_2O_2 level • Low nutrient level • Low well workover level	+ 46	275	150	79	19	3
9	Day 114 to 121	• No chemical data injection • No well workover	- 74	-	-	-	-	0
10	Day 121 to 149	• Low H_2O_2 level • Low nutrient level • Low well workover level	+ 33	221	842	241	261	1
11	Day 150 to 164	• Low H_2O_2 level • Intermediate nutrient level • No well workover	- 59	126	1730	1016	172	0
12	Day 165 to 179	• No H_2O_2 injection • No nutrient injection • Low well workover level	+104	1.5	127	112	525	1
13	Day 180 to 215	• Low H_2O_2 level • No nutrient injection • Low well workover level	- 91	197	142	17	24	2
14	Day 216 to 259	• Low H_2O_2 level • No nutrient injection • Low well workover level	+ 10	388	88	29	0	1

49

mechanical cleaning of the wells, resulted in more than a 21 percent restoration of the initial groundwater circulation rate (Period 4). It is likely that addition of both hydrogen peroxide and nutrient contributed to the permeability decrease. Two likely mechanisms contributed to this reduction. The first is peroxide decomposition to water and free oxygen gas that can reduce permeability due to gas blockage of soil pores. The second is the exchange of ammonium ions in the nutrient with calcium in the soil resulting in precipitation of calcium phosphate which blocks soil pores. As a result of the reduction in permeability during Periods 1, 2, and 3, over 40 percent of the groundwater circulation occurred during 15 percent of the operating time.

The highest restoration of circulation rate occurred during Period 4 when both peroxide and nutrient concentrations were increased over the levels used in Period 3. Five well workovers also occurred in this period. The nutrient solution contained a chemical additive (chelating agent) to minimize precipitation. Increasing the nutrient concentration in the distribution tank forced the white precipitate back into solution since higher levels of the additive (chelating agent) were also present. However, the response in the well pattern area to increased nutrient concentration could have actually caused further precipitation; the higher nutrient concentration increased the ammonia level which could have promoted additional release of calcium from the soil. In the distribution box the calcium concentration is limited as there are no calcium exchanging clays. Another approach would have been to add the stabilizer separately so that the stabilizer concentration could have increased without increasing the nutrient concentration.

Additional evidence of the impact of hydrogen peroxide injection on permeability is obtained by comparing circulation rates for Periods 12 and 13. During Period 12 no peroxide or nutrient was added to the groundwater and the circulation rate increased by 104 gallons per day. During Period 13 peroxide was added, nutrient was not added, and the circulation rate declined by 91 gallons per day.

The circulating groundwater serves as the transport mechanism to supply chemicals (oxygen, nutrients) to the contaminants. The rate of chemical supply is proportional to the product of the groundwater circulation rate and the concentration of oxygen and nutrient in the injection fluid. In a system where the key chemical reagents (peroxide and nutrient) also reduce permeability, an optimum concentration of reagents may exist where the rate of supply is maximized. Below this optimum concentration the circulation rate is higher but the rate of chemical supply is limited by chemical concentration. Above the optimum concentration, low circulation rate limits the rate of chemical supply. Column treatability testing of representative soils is one method of identifying levels of optimum chemical concentrations.

2. Fluid Communication in Well Pattern

Fluid communication, based on chloride breakthrough, was achieved in all pumping wells. The level of this communication varied considerably between the nine pumping wells and did not correlate with initial permeability. The chloride ion is used as a fluid tracer because concentration levels in the nutrient were two orders of magnitude higher than background levels.

Background chloride levels in the groundwater were less than 70 ppm and averaged 45 ppm for all wells. Chloride monitoring in pumping and monitoring wells revealed the following:

● Fluid communication was achieved between the injection wells and all pumping wells, indicating that the opportunity existed for oxygen and nutrient to interact with contaminants throughout the entire well pattern.
● The level of this fluid communication was highly variable, as follows: high for Wells P9, P1, P2 (rating 4); medium for Wells P3 and P5 (rating 3); low for Wells P6, P7, P8, M2 (rating 2); and very low for Wells P4, M1, CC (rating 1) (see Table 5 for a summary of ratings).

51

TABLE 5. SUMMARY OF RELATIVE WELL PATTERN CHEMICAL RESPONSES

Well	Initial Permeability	Chemical or Tracer (Cl) Communication	Nutrient (NH_3PO_4) Communication	Initial CO_2 Production	Hardness Communication
#P-9	High (4)	High (4)	High (4)	High (4)	Low (2)
#P-8	High (4)	Low (2)	Med (3)	Med (3)	Low (2)
#P-7	Med (3)	Low (2)	None (0)	Med (3)	Med (3)
#P-6	Med (3)	Low (2)	None (0)	Med (3)	High (4)
#P-5	Med (3)	Med (3)	Med (3)	Med (3)	Low (2)
#P-4	Med (3)	Very Low (1)	None (0)	Med (3)	Low (2)
#P-3	Low (2)	Med (3)	None (0)	Med (3)	Med (3)
#P-2	Very Low (1)	High (4)	Med (3)	Med (3)	High (4)
#P-1	Low (2)	High (4)	Low (2)	Med (3)	High (4)
#M-1	---	Very Low (1)	---	Very Low (1)	None (0)
#CC	---	Very Low (1)	---	High (4)	Very Low (1)
#M-2	---	Low (2)	---	Med (3)	None (0)

52

● Comparable levels of chloride tracer were obtained in Wells
P9 (highest initial permeability) and P2 (lowest initial
permeability). Figures 14 and 15 indicate the locations of
relative levels of initial permeability and fluid communica-
tion. Comparison of these data indicates a negative overall
correlation (high permeability-low communication), highlight-
ed by a plot of relative ratings (see plot below). Factors
such as well placement relative to groundwater flow direction
and the presence of clay lenses may influence interwell fluid
communication to a greater extent than well permeability.
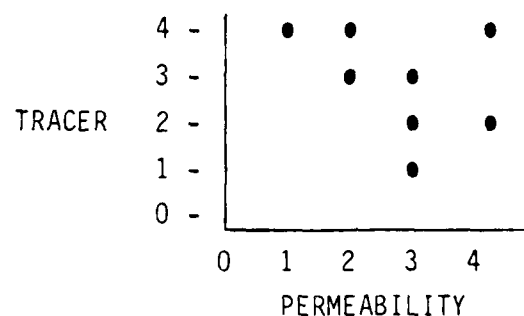
● The chloride levels in the downgradient monitoring well M2
are not in the high and medium levels of communication. This
indicates that natural groundwater flow did not interfere to
a high degree with the circulation of well pattern fluids.
Further evidence of this is the sustaining high levels of
chloride in Wells P1, P2, P3, P5, P9 after day 160 (November
8, 1985) when nutrient containing chloride was not added to
the injection fluid. A strong groundwater effect would have
resulted in a rapidly declining chloride level following day
160.

As a means of evaluating the impact of various changes in operat-
ing parameters on fluid communication, pumping wells with high and

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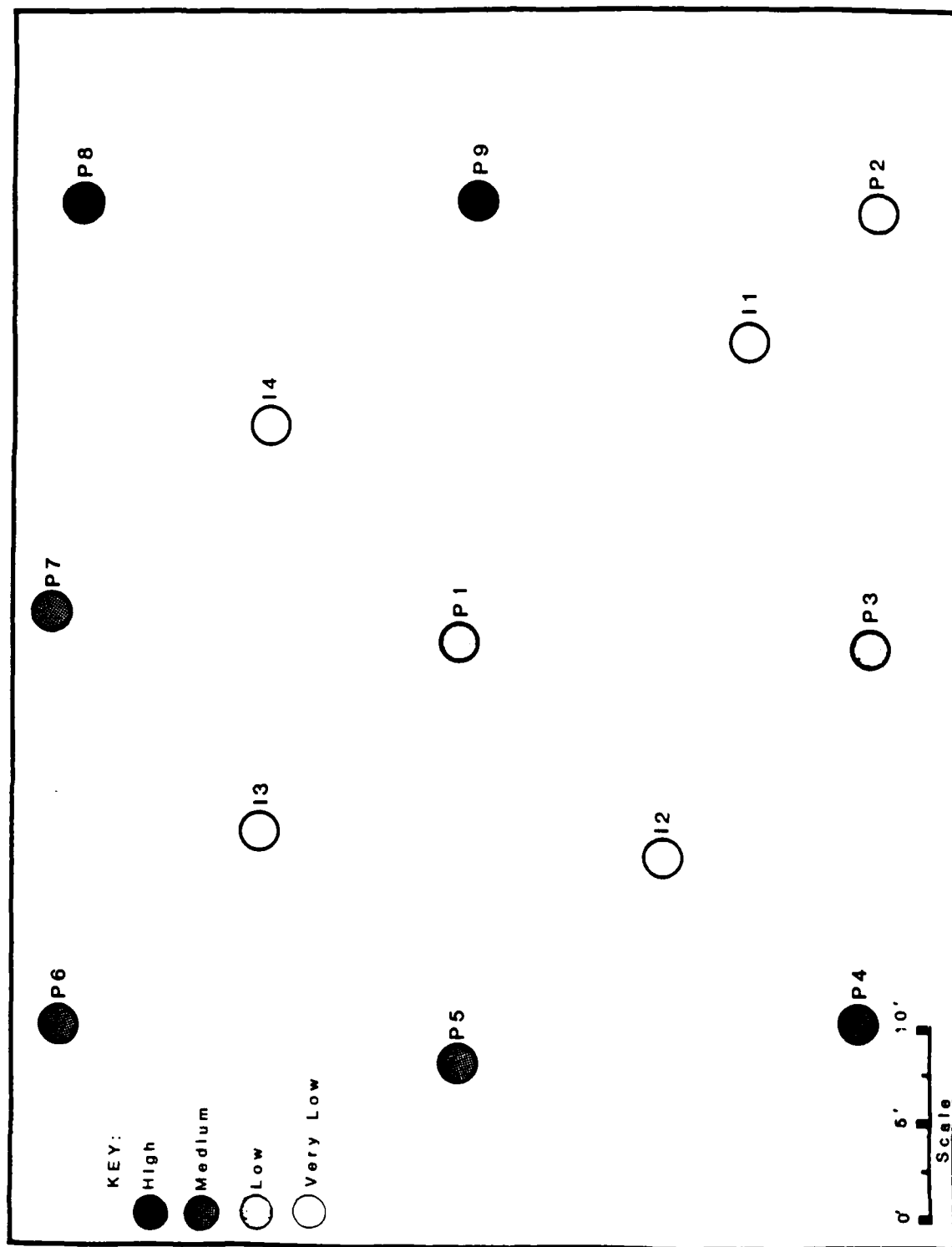
Figure 14.   Initial Permeability of Production Wells
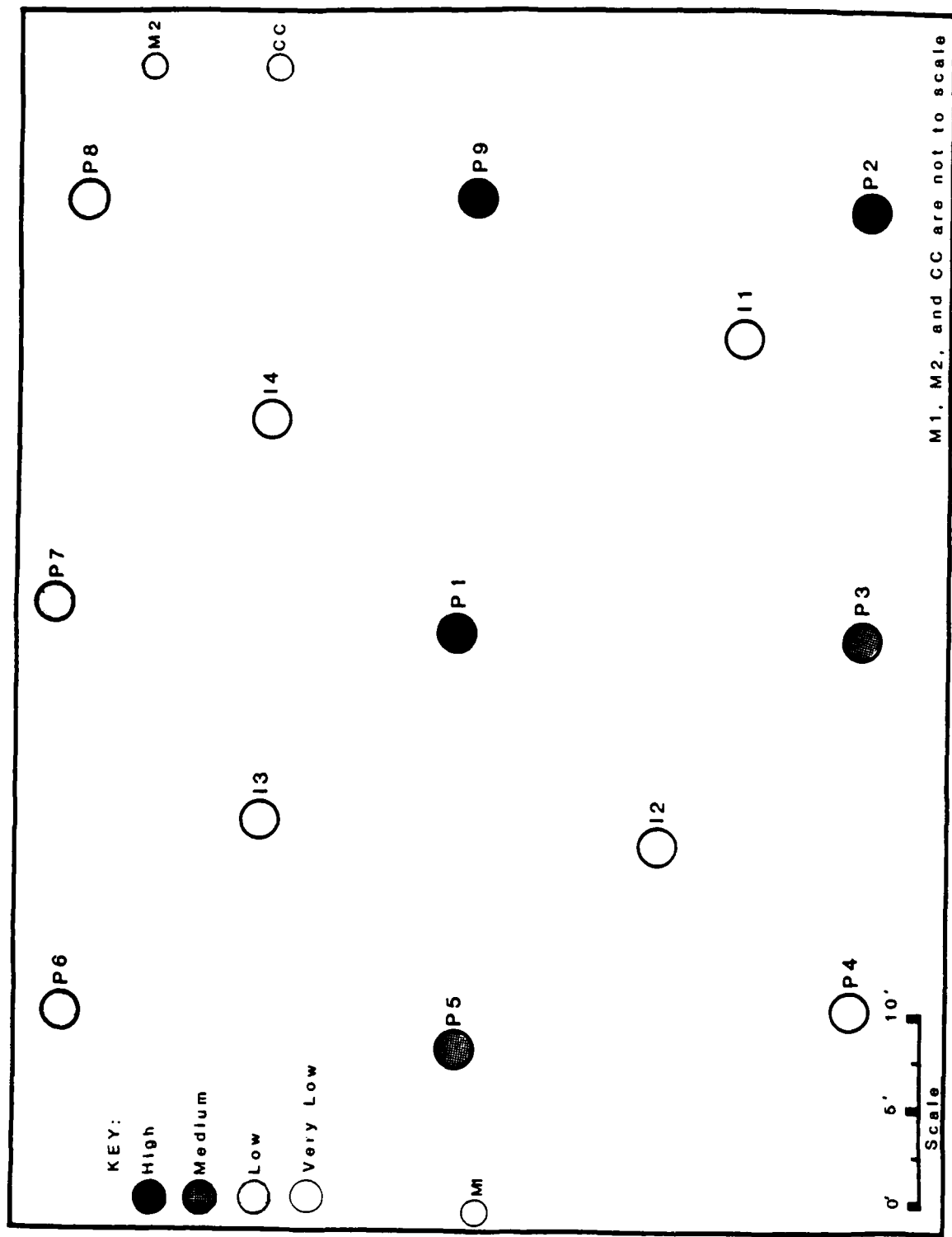
Figure 15. Chemical Tracer Breakthrough

KEY:
High
Medium
Low
Very Low

M1, M2, and CC are not to scale

55

medium communication (P1, P2, P3, P5, P9) and low and very low communication (P4, P6, P7, P8) were grouped in two sets, and the weekly average chloride levels for each set plotted as a function of time in Figure 16. The following can be noted.

- Injection well density in the vicinity of a pumping well varies considerably throughout the well pattern. Expressing density as the number of injection wells that are approximately the same distance from a pumping well; P1 is density 4; Wells P3, P5, P7, P9 are density 2; and Wells P2, P4, P6, P8 are density 1. On this basis, Well Set P1, P3, P5, P7, P9 would be expected to have higher chloride levels than Well Set P2, P4, P6, P8 since the former "see" less background groundwater. Wells P2 and P7 are the exceptions to this correlation.

- The peaks and valleys of the two sets correlate up to Day 180. Following Day 180, Well Set P4, P6, P7, P8 was pumped at a 60 percent higher rate than Well Set P1, P2, P3, P5, P9 in an attempt to draw high chloride to these well areas. This did not occur. In fact, until Day 248, Well Set P4, P6, P7, P8 produced essentially background groundwater. This suggests that a flow barrier may have initially existed or was formed during peroxide and nutrient injection between well pairs.

- Before Day 180 (termination of nutrient injection) the two highest peaks in both well sets occurred between Days 75 and 90 and between Days 135 and 145. Reference to Figure 13 does not indicate a considerable difference in the behavior of the groundwater circulation rate in these two periods. These peaks are most likely a result of flow dispersion of high injected chloride levels before Day 75 over an area larger than the nominal area of the well pattern.

- Based on a materials inventory supplied by FMC Aquifer Remediation Systems, 500 pounds of chloride were added to the ground-

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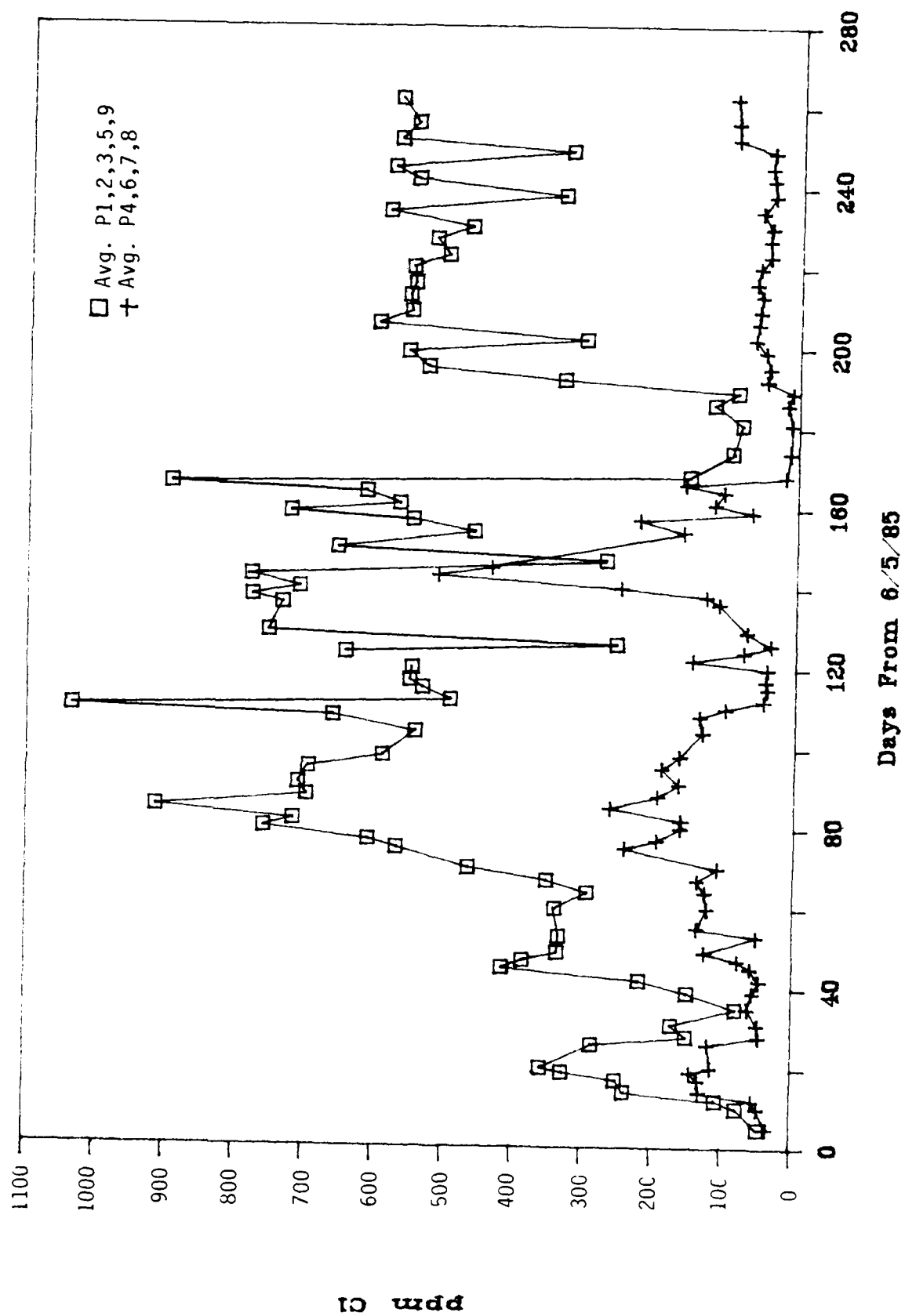
Figure 16.   Comparison of Average Chloride Concentrations

water with the nutrient from Day 3 to Day 64. During this
same time interval 37,558 gallons of groundwater were cir-
culated. If the chloride had been added at a uniform con-
centration, this would be equivalent to 1598 ppm chloride.
When compared with the individual peaks of 1500 ppm in Wells
P9, P1, P2, and 750 ppm in P5, indications are that a con-
siderable portion of the soil volume between these wells and
the injection wells was contacted by circulating groundwater.

E. WELL PATTERN CHEMICAL EFFECTS

This section discusses relative chemical effects observed at the
pumping and monitoring wells resulting from interaction of hydrogen
peroxide and nutrient with groundwater, soil, and contaminants. Chemi-
cal inventories of materials added to the circulating groundwater are
listed in Table 6. Major findings are summarized below.

- Most of the nutrient was taken up by the soil or precipitated in
  the groundwater. This uptake varied considerably over the well
  pattern area.
- Ammonia loss was less than phosphate. Ammonia breakthrough
  occurred in 5 of the 9 pumping wells; phosphate appeared in
  only 2 of the 9 pumping wells.
- Levels of dissolved carbon dioxide measured in the pumping
  wells may indicate considerable oxidation of organics by hydrogen
  peroxide.
- Well locations associated with low initial permeability appear
  to correlate with areas of higher initial levels of ion-exchang-
  ing clay.

1. Nutrient (Ammonia and Phosphate) Communication

To assess the relative magnitude of nutrient communication in
the well pattern, ratios of ammonia to chloride (NH_3/Cl) and phosphate to

58

TABLE 6. MATERIALS INVENTORY OF CHEMICALS ADDED TO GROUNDWATER

Dates	Days From 5 Jun 85	Chloride (pounds Cl)	Nitrogen (pounds NH$_4$)	Phosphoros (pounds PO$_4$)	Hydrogen Peroxide (pounds H$_2$O$_2$)	Groundwater Circulated (gallons)
5 Jun 85- 7 Nov 85	1 - 156	500	254	500	280	41,878[3]
8 Nov 85- 5 Dec 85	157 - 184	0	0	0	0	3,967
6 Dec 85- 18 Feb 86	185 - 259	0	0	0	19	6,422

1. Inventory supplied by Aquifer Remediation Systems (ARS), a subsidiary of FMC (ARS provided hydrogen peroxide and nutrient as part of a technical services support contract):

2. During this time period, 35 percent technical grade hydrogen peroxide was purchased by SAIC directly from Accron Chemical. The hydrogen peroxide inventory was obtained from SAIC daily logs.

3. 37,588 gallons during nutrient addition; 25,305 gallons during peroxide addition.

chloride (PO_4/Cl) are plotted as a function of time for representative wells where ammonia and phosphate breakthrough occurred (see Figures 17 and 18). Although free ammonia (NH_3) was not injected into the groundwater, NH_3 is used to report nitrogen (N) levels added as ammonium ion (NH_4^+) in the nutrient. Based on chemical inventory provided by FMC Aquifer Remediation Systems (Table 6), the respective ratios in the nutrient supply are 0.48 and 1.0. Since chloride is an inert ion, it is used as a marker to judge chemical interaction of the NH_3 and PO_4 with the soil and groundwater. The important findings are presented below.

- Ammonia breakthrough occurred in five (P_1, P_2, P_5, P_8, P_9) of the pumping wells and phosphate in two (P_8, P_9) of the pumping wells. No substantial levels of nutrient were measured in the monitoring wells. This result, in combination with the previous finding that chloride breakthrough occurred in all pumping and monitoring wells, indicates substantial ammonia and phosphate uptake by the soil and/or precipitation in the soil.

- Ammonia saturation was approached only in Well P9 for the time interval Day 95 to 185 (September 8, 1985 to December 7, 1985). During this period, considerable loss of phosphate continued. During the last 30 days of this period, no nutrient was added to the injected groundwater.

- Based on the maximum values of the NH_3/Cl ratio observed for each well, relative ratings of nutrient communication are: Well P9 high (Rating 4); Wells P2, P5, P8 medium (Rating 3); Well P1 low (Rating 2); Wells P3, P4, P6, P7 none (Rating 0). Figure 19 shows the location in the well pattern area of these relative ratings. Comparison with Figure 20 does not show a correlation between nutrient and fluid communication, indicating considerable variability of nutrient uptake by soil throughout the well pattern.

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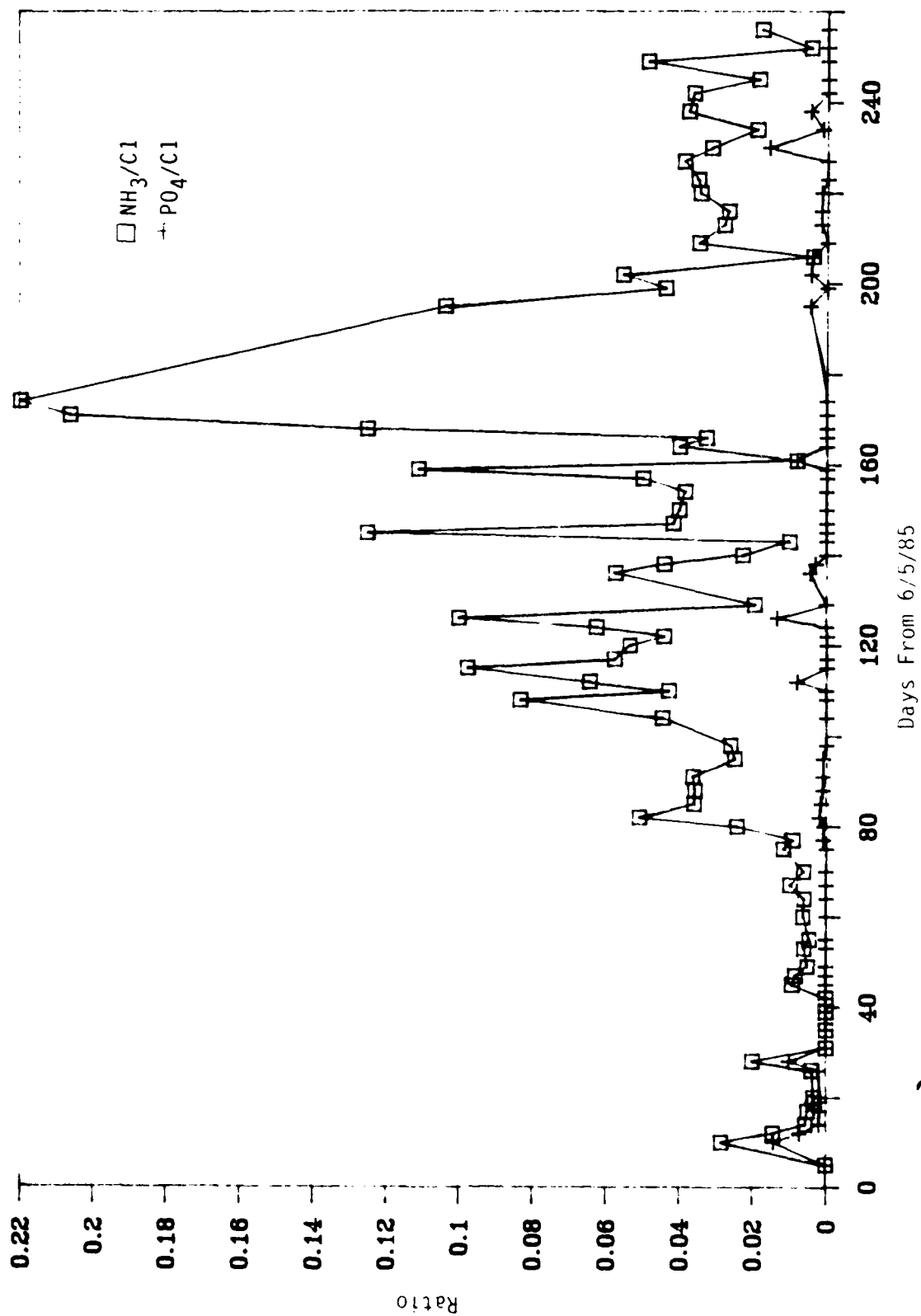
Figure 17. Ammonia and Phosphate Ratios for Well P5
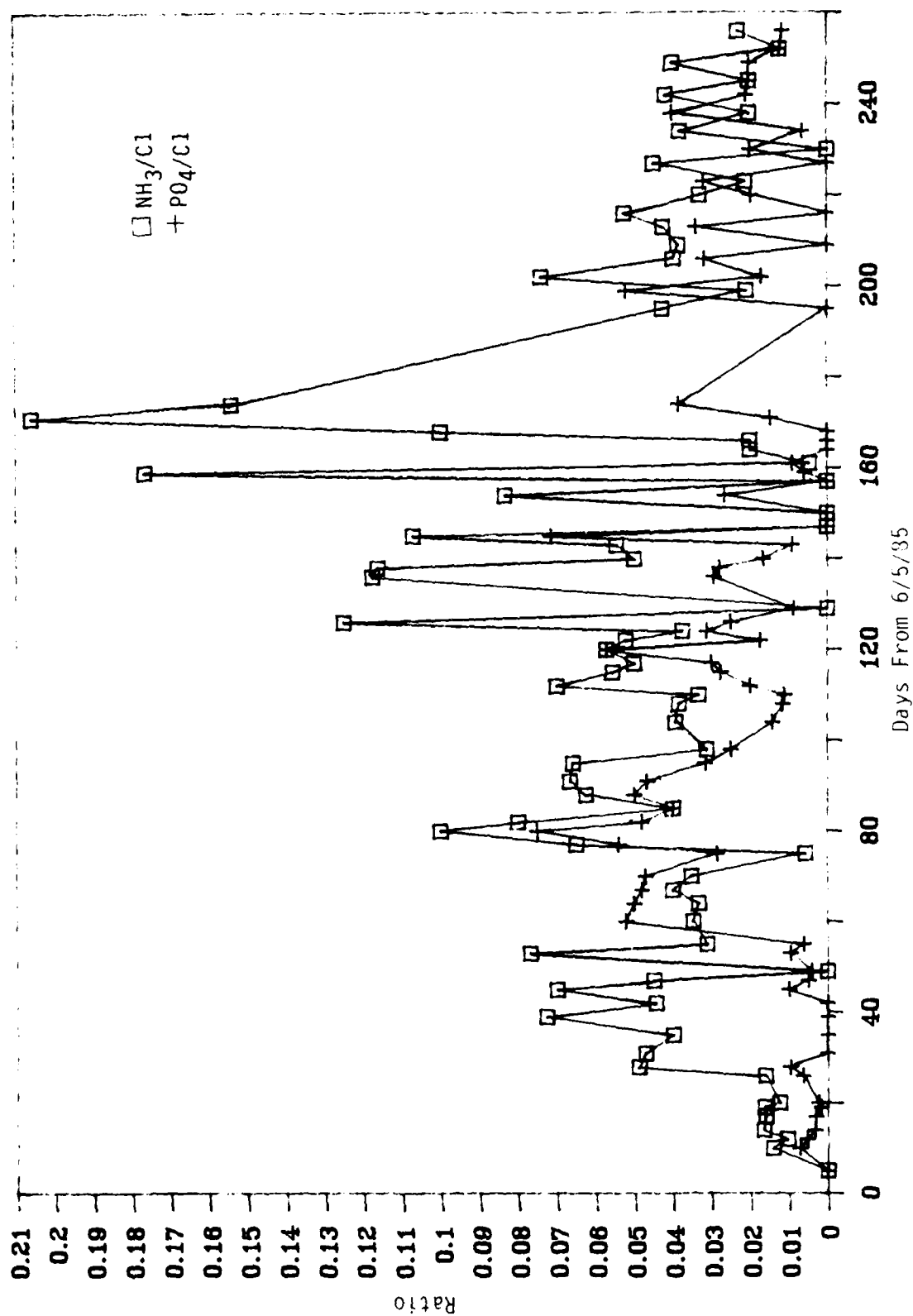
Figure 18. Ammonia and Phosphate Ratios for Well P8
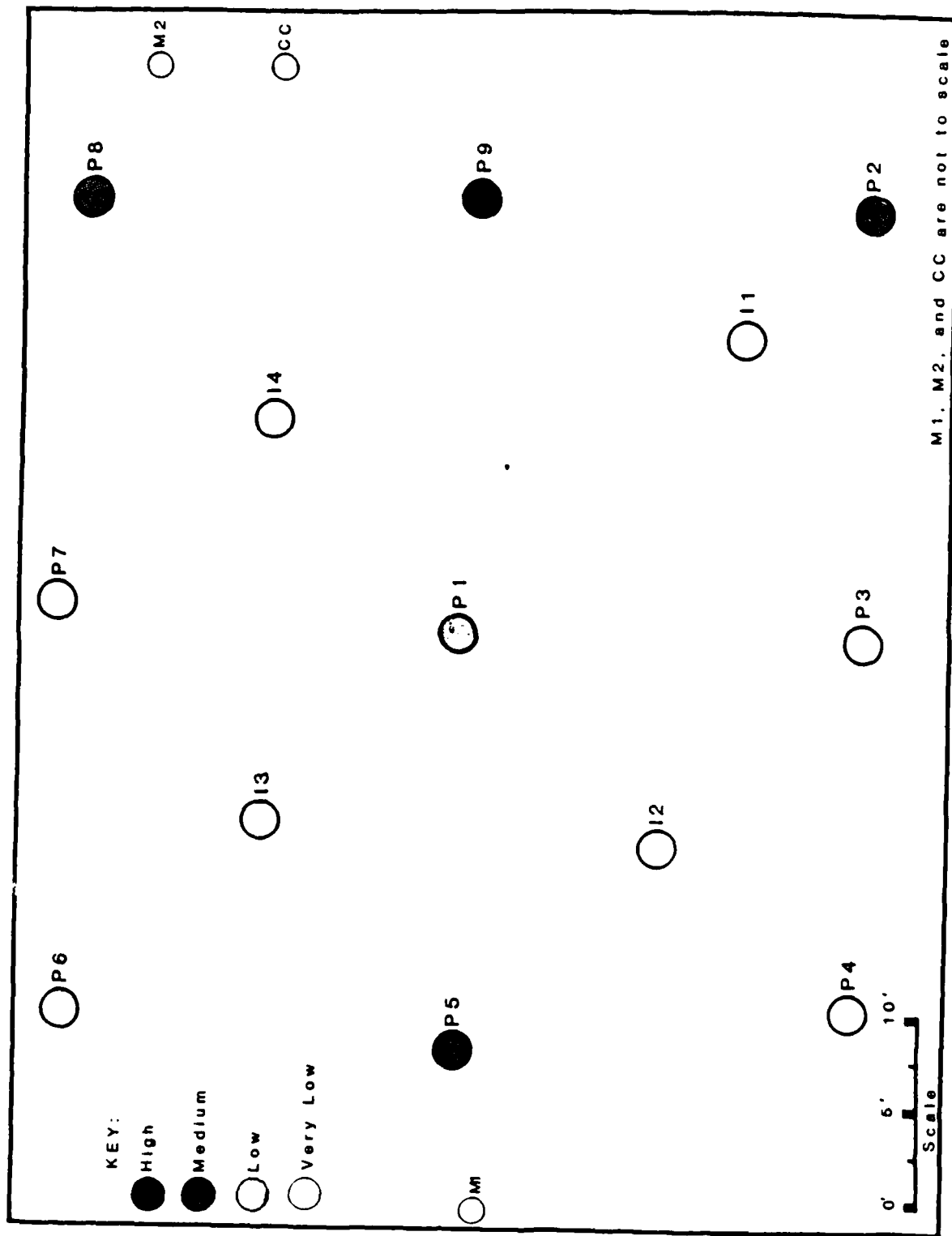
Figure 19. Nutrient Breakthrough
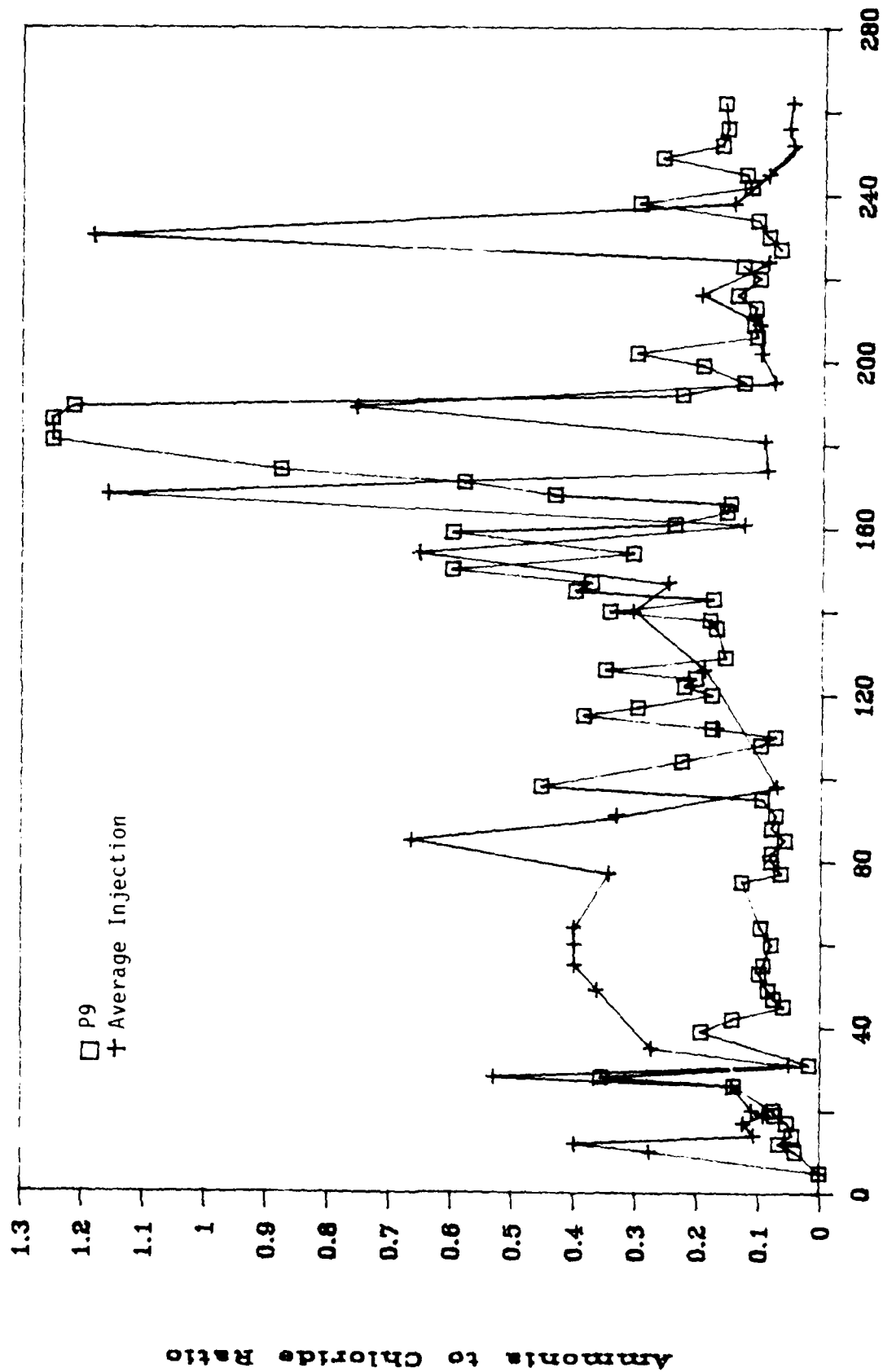
Figure 20. Ammonia to Chloride Ratios for Well P9 and Average of Injection Wells

64

Calcium-exchanging clays present in the soil could account for
a substantial loss of both ammonia and phosphate from groundwater, re-
sulting in a reduction in the soil permeability. The calcium ion exchanges
with ammonium ion (NH_4^+) in the nutrient (nitrogen source, expressed as
ammonia). The calcium ion then reacts with nutrient phosphate to pre-
cipitate calcium phosphate. This precipitate can reduce permeability
by clogging pores in the soil. This reaction would proceed until all
the calcium-exchanging clays were saturated with ammonium ion. This
mechanism is discussed in the following paragraphs.

- The net loss of phosphate relative to ammonia is 1.85 parts
  PO_4 per part NH_3 according to the following reaction equations:

  $$Ca\text{-}clay + 2NH_4^+ \longrightarrow (NH_4)_2 \text{-} clay + Ca^{++}$$

  $$Ca^{++} + (2/3) PO_4 \longrightarrow 1/3 (Ca)_3 (PO_4)_2 \downarrow \text{ precipitate}$$
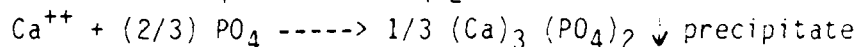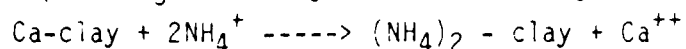
  The ratio in the nutrient was 2.08 (see Table 6). Since this
  ratio is larger than the 1.85 ratio associated with precipita-
  tion, phosphate breakthrough comparable to NH_3 would have been
  expected. This did not occur, indicating that a considerable
  portion of the phosphorous in the nutrient was not supplied
  in a stabilized form. Calcium initially in the groundwater
  could also precipitate phosphate.

- The cation ion exchange capacity (CEC) for a Kelly AFB soil
  sample, reported in Table F-6 of Volume I is 41.3 milliequiv-
  alents per liter of soils of calcium and magnesium (primarily
  calcium). Based on this value, an equivalent ammonia uptake
  at saturation of 270 ppm (based on soil) would be expected.
  This translates to 988 pounds of ammonia for a well pattern
  60 feet in diameter, 10 feet thick, and with 20 percent
  porosity. Based on the materials inventory for NH_4 in Table
  6, only 240 pounds of NH_3 were added to the groundwater, 24
  percent of the saturation value. The fact that on the average
  only 24 percent of the potential ammonia uptake was supplied,
  that only one well, P9, at one point approached saturation, and
  that not all wells of high fluid communication had high

65

ammonia breakthrough indicates a highly variable exchange
capacity throughout the well pattern.

● The concentration of ammonia in the injection fluid is likely
to affect the amount of ammonia uptake. Well P9 had the
highest breakthrough of nutrient. The ammonia-to-chloride
ratio (averaged on a weekly basis) is plotted as a function
of time in Figure 20 for both P9 and the average of injec-
tion wells. The two ratios show correlation except for weeks
4.5 through 13.5. In this time period, the highest concentra-
tion of nutrient was added to the groundwater. The flat or
slightly declining response in P9 fluid in this time interval
suggests an increase in uptake of ammonia by the soil at a
higher injection concentration.

2. Hardness Changes in Circulated Groundwater

The hardness of the circulated groundwater should provide a rela-
tive marker of those areas of high ion exchange sites since hardness is a
measure of dissolved calcium and magnesium (Figure 21). Relative ratings
of hardness are: Wells P1, P2, P6 high (Rating 4); Wells P3, P7 medium
(Rating 3); Wells P4, P5, P8, P9 low (Rating 2); Wells M2 and CC, very
low (Rating 1); and Well M1 none (Rating 0). These are summarized by
well location in Figure 22. Comparison of initial well permeability and
hardness ratings indicate a negative correlation. This suggests that
high levels of ion exchanging clay could be a contributing factor to low
initial permeability. For future tests, CEC capacity measured on soil
samples obtained during site investigation, as well as petrographic
examination of the soil for clay, could be used to provide an initial
mapping of permeability. Consideration also should be given to the
possibility that high clay content could concentrate contamination.

66
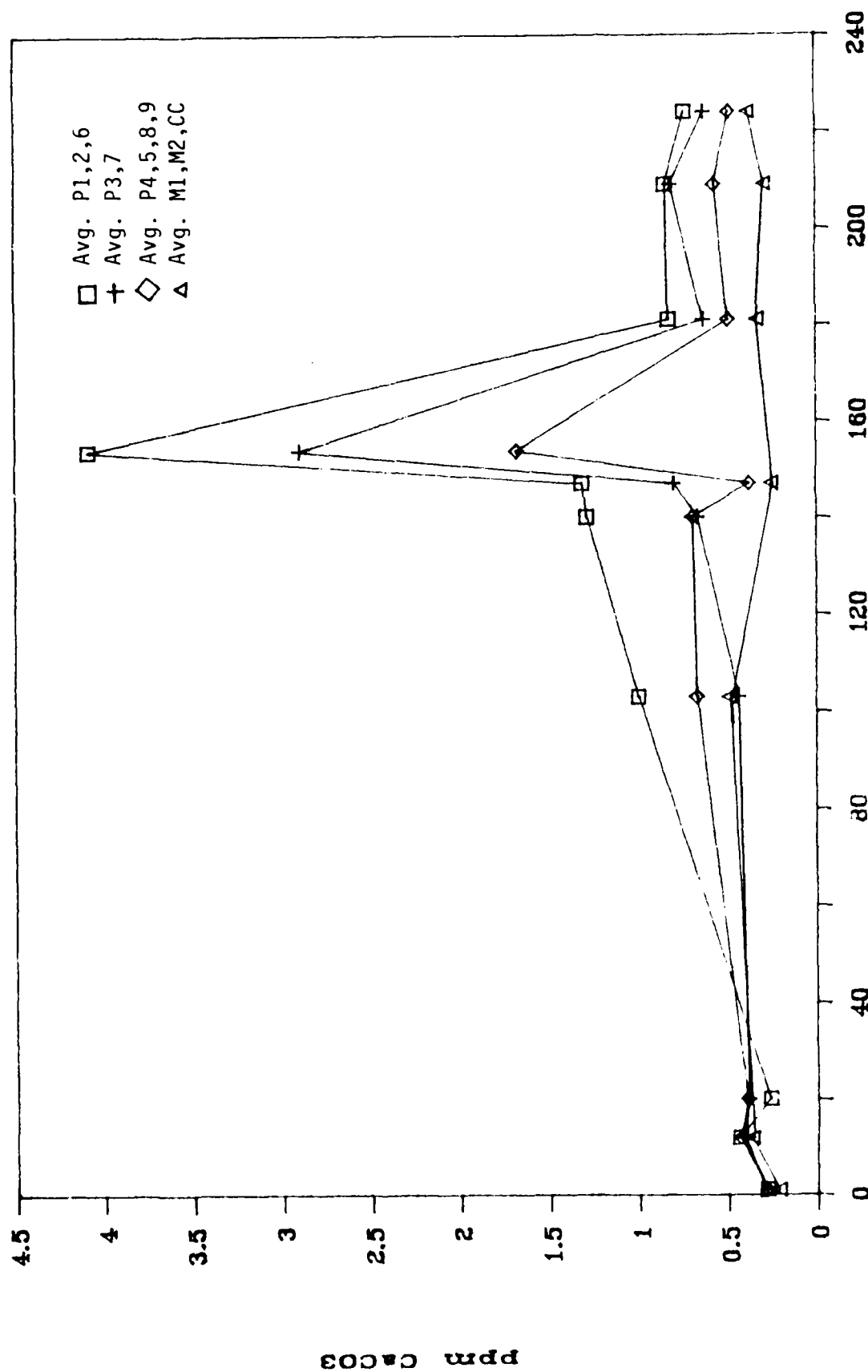
Figure 21. Comparison of Average Hardness Levels in Pumping and Monitoring Wells

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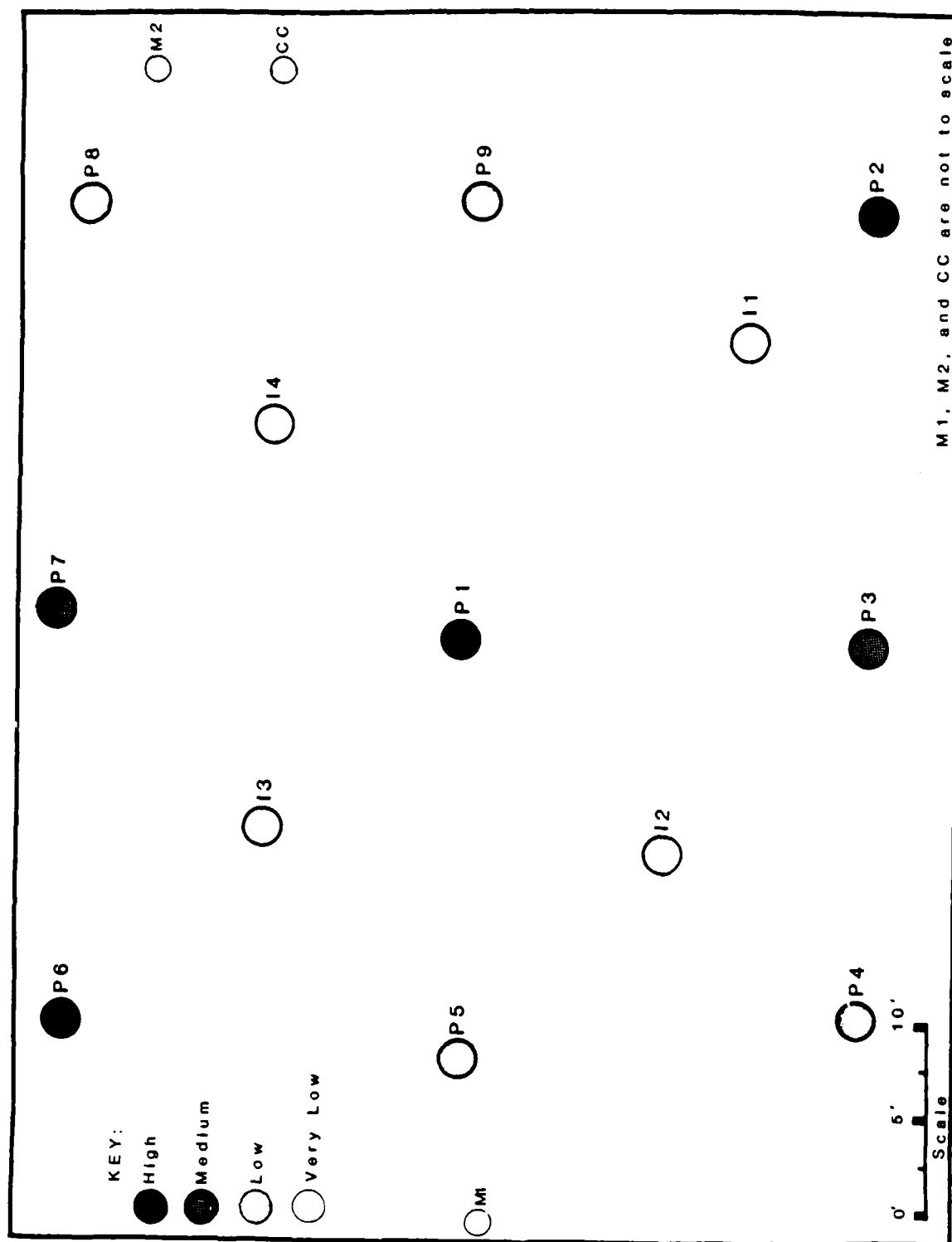
Figure 22. Hardness Breakthrough

```
4 -      •    •    •
3 -           •    •
HARDNESS  2 -         •  •   •
1 -
0 -
   0  1  2  3  4
      PERMEABILITY
```
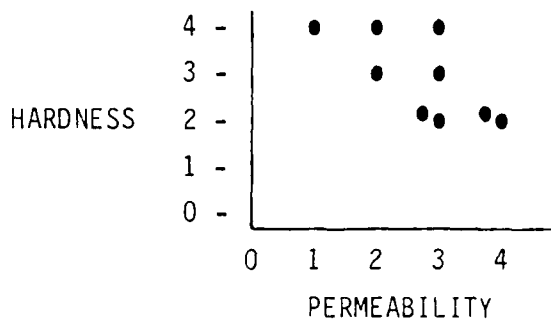
Considerable quantities of white precipitate, identified as calcium phosphate, were observed in the distribution tank. This resulted from calcium-enriched groundwater mixing with nutrient phosphate in the mixing tank. Indications of this effect are noted in a decline in hardness levels of the injection well groundwater after Day 60 (see Figure 23).

Prior to Day 60 the hardness levels rose from an initial low background level. One explanation is that the calcium exchanged from the soil exceeded that amount of phosphate available to precipitate the calcium. This excess calcium appeared as an initial increase in hardness. As the test progressed, phosphate concentrations in the injection wells were increased to a maximum level of 3729 ppm between Days 59 and 73 (Table 4, time interval 5). The combination of increased calcium from the pumping wells and increased phosphate addition could have resulted in phosphate precipitation in the mixing tank which would reduce the hardness of the injection water. Large reductions were then made in the quantities of ammonia and phosphate added to the injection wells (see Table 4). This would reduce the source for calcium generation and the source for calcium precipitation. The hardness would be expected to return to background levels (250 ppm).

3. Carbon Dioxide (CO_2) Production

Field measurements of carbon dioxide (CO_2) dissolved in circulating groundwater were obtained after November 13, 1985 using a La-

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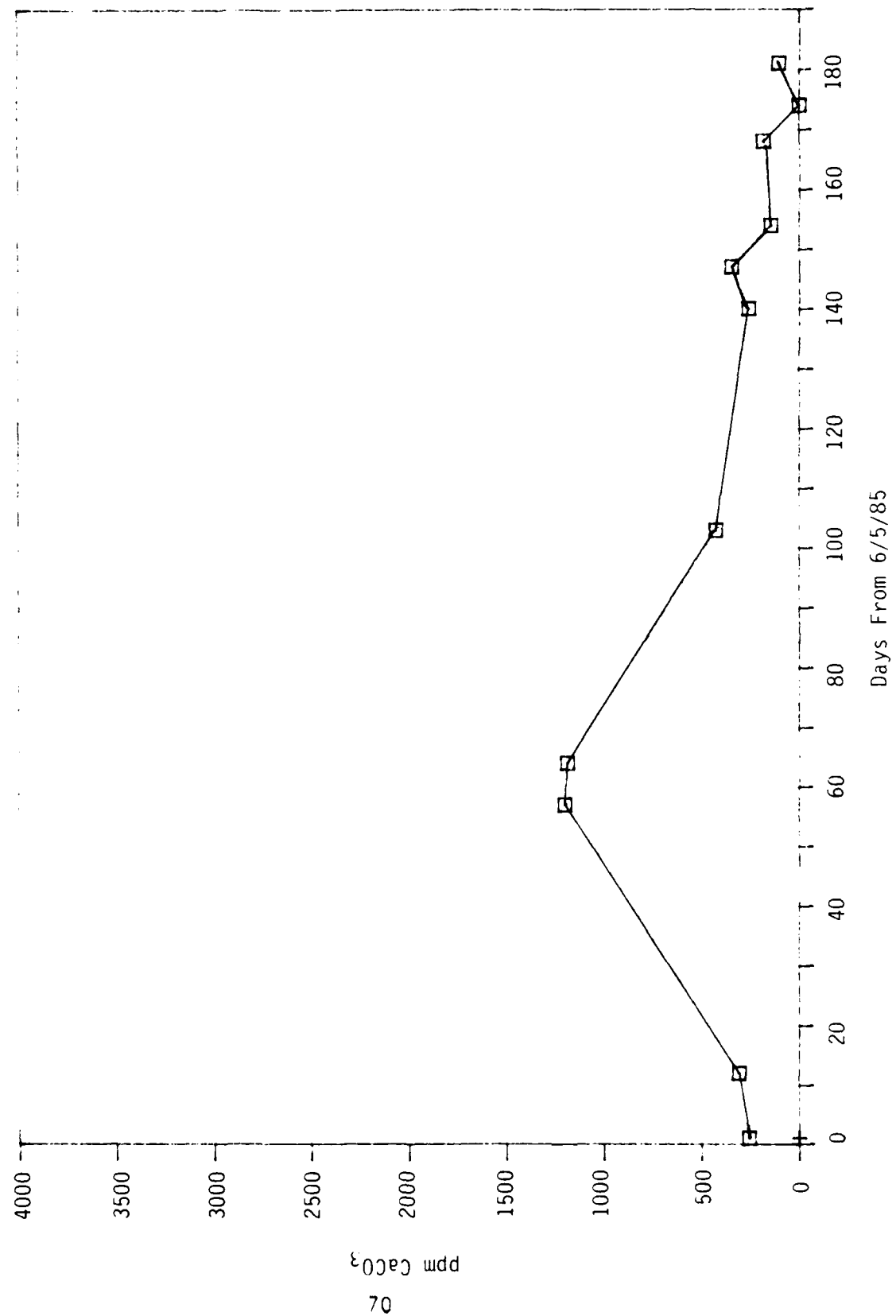
Figure 23. Average Hardness Levels for Injection Wells

70

Motte field test kit. Figures 24 and 25 plot CO_2 levels versus time in pumping, monitoring, and injection wells.

The lowest CO_2 levels before Day 220 were detected in Well M1 and the injection wells. M1 was the upgradient monitoring well, thus, the initial CO_2 levels most likely corresponded to background groundwater levels resulting from calcite solubility. The injection well groundwater has been recirculated and thus exposed to the atmosphere. In this process, dissolved CO_2 escapes to the atmosphere and reduces the CO_2 level in the liquid phase. This effect was demonstrated by controlled tests and is discussed in Section IV-J.

Prior to Day 180, with the exception of Well M1, CO_2 levels in pumping and monitoring wells ranged from 100 to 200 ppm. This was five to 10 times higher than the CO_2 levels in the injection wells, which indicates a net gain of CO_2 as groundwater is circulated in the well pattern.

A net increase of 100 ppm CO_2 cannot be attributed to calcite solubility in water, which is 7 ppm, or to oxidation of organics based on the solubility of atmospheric oxygen which is 9 ppm. This increase occurred during the production of 35,694 gallons of groundwater and is equivalent to a removal of 29.7 pounds of CO_2 from the subsurface environment. A discussion of the most likely sources of this CO_2 follows.

Reaction of oxygen with organic carbon is a potential source of CO_2, resulting in a consumption of 21.6 pounds of oxygen, which is equivalent to 15.5 percent usage of the oxygen contained in the injected hydrogen peroxide. At a usage factor of 3 parts oxygen per part organic, this would result in a 2 ppm reduction in soil contaminants or a 21 ppm reduction in groundwater contaminants. As will be discussed in Part G of this section, the latter (21 ppm groundwater) is comparable to the maximum level of 23.9 ppm volatile priority pollutants concentration measured in Well CC in June 1984.

71
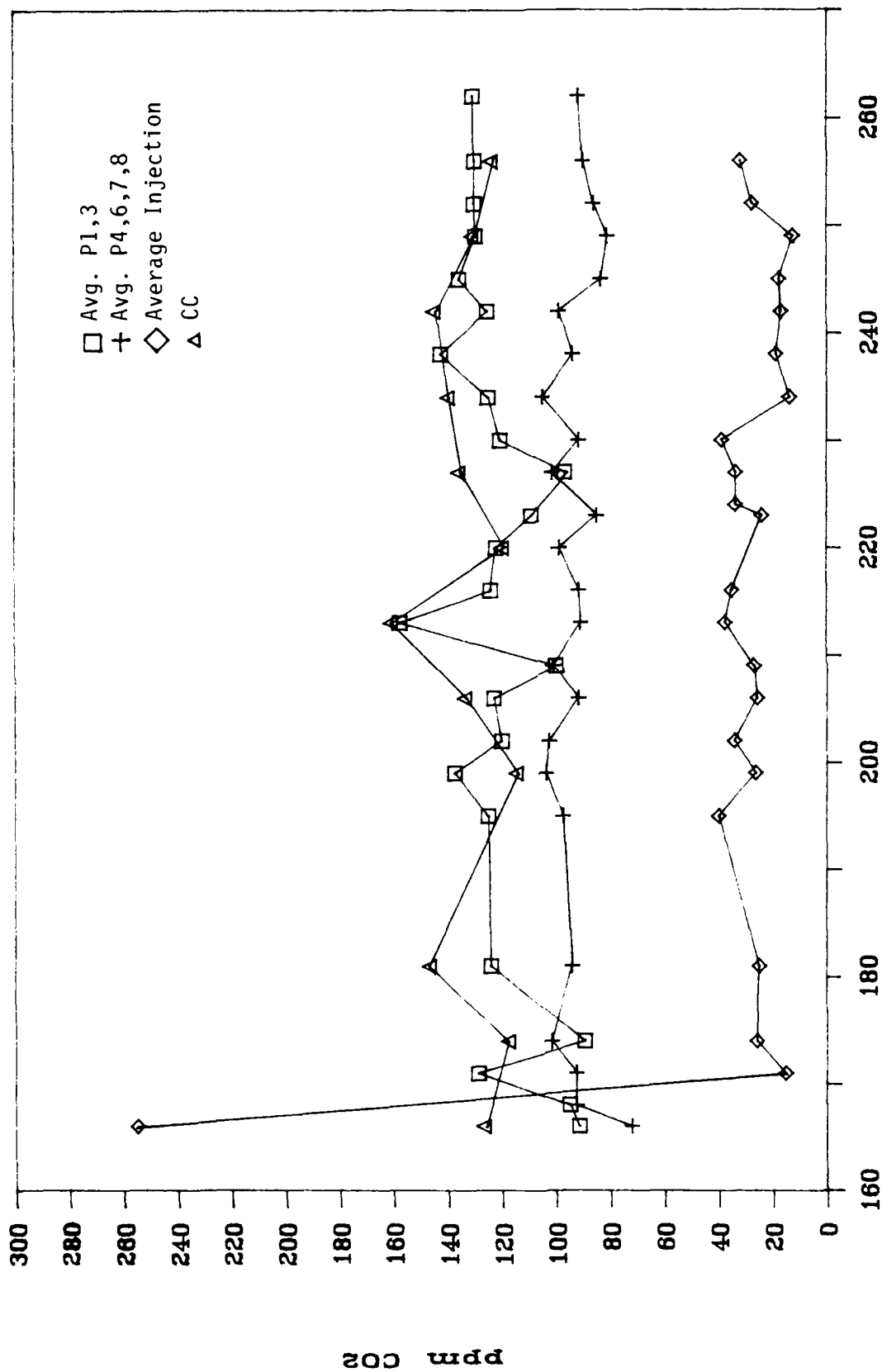
Figure 24. Comparison of Average CO_2 Levels
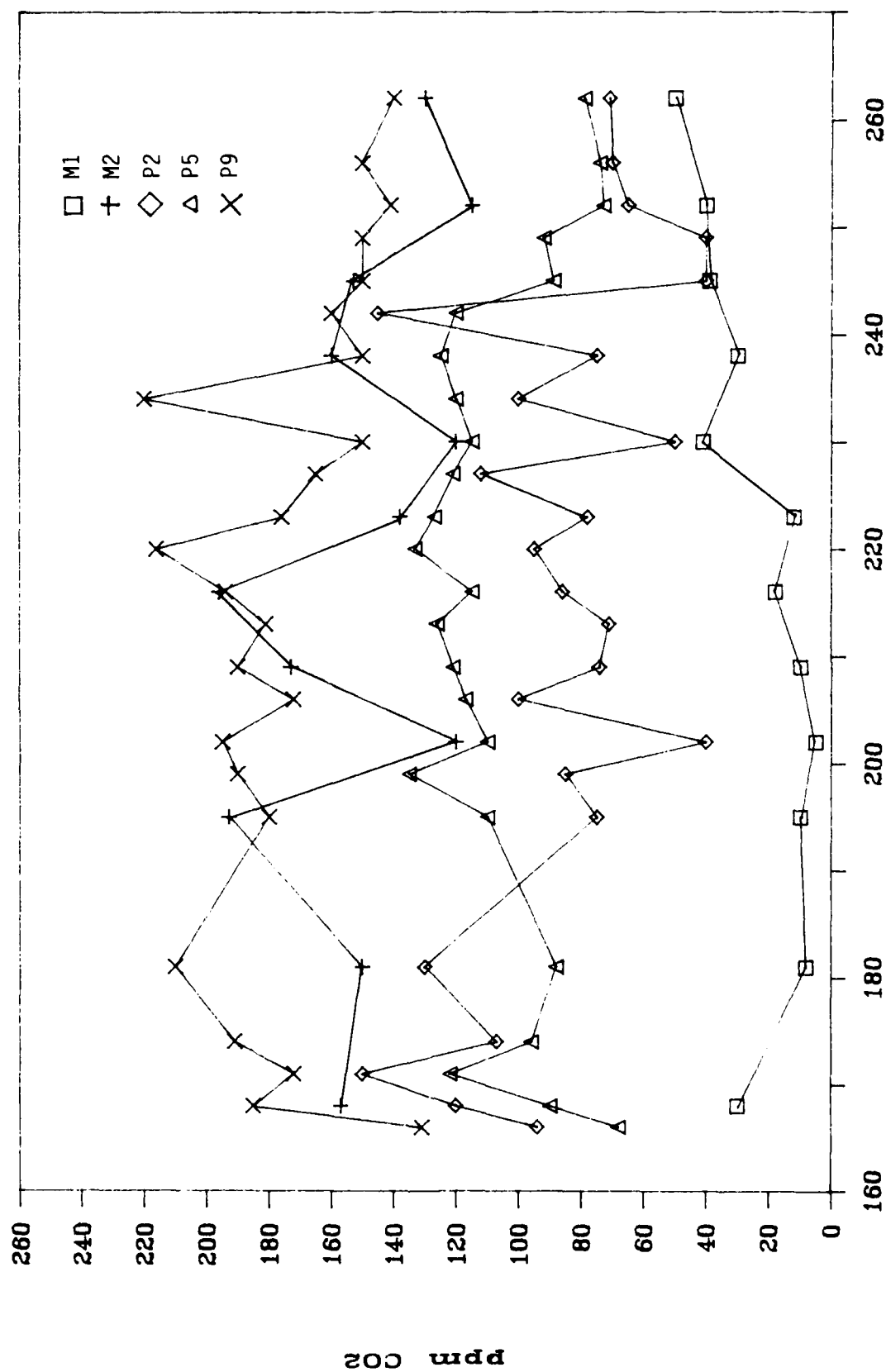
Figure 25. CO_2 Concentrations in Wells M1, M2, P2, P5, and P9

73

Reaction of acid with calcite ($CaCO_3$) minerals in the soil is also a possible source of CO_2. This reaction requires in situ generation of acid, since the calcite is attacked by acid to produce CO_2 according to the following: $2H^+ + CaCO_3 \longrightarrow Ca^{+2} + CO_2 + H_2O$. The quantity of CO_2 produced would require a solution with an initial pH of less than 2.5. As will be shown in Section V-D.1, groundwater from pumping wells was considerably lower in pH than the groundwater in the injection wells, which indicates in situ acid generation. One mechanism by which this acid could be generated is the oxidation of NH_4, a constituent of the nutrient, according to the following reaction: $NH^+_4 + 2O_2 \longrightarrow NO^-_3 + 2H^+ + H_2O$. This reaction would consume 43.2 pounds of oxygen to produce enough acid to generate 29.7 pounds of CO_2, which is equivalent to 31 percent use of injected peroxide. A net consumption of 11.4 pounds of NH_4^+ would result, which is a small fraction of the injected NH_4^+. This reaction would also result in the production of 41.9 pounds of nitrate (NO_3^-), which represents an increase in concentration of 141 ppm in the groundwater. No consistent increase in nitrate is observed in the pumping wells. To maintain this reaction mechanism for CO_2 generation another reaction must occur to remove nitrate. This denitrification can result by interaction of organic carbon with nitrate according to the following equation: 5/4 organic carbon + $NO_3^- \longrightarrow 1/2 N_2 + 5/4 HCO_3^- + 1/4 H^+ + 1/2 H_2O$. This would consume 34 ppm of organic carbon in the groundwater or 3.3 ppm on the soil.

Another potential source of CO_2 is associated with the shift in carbonate equilibrium resulting from the pH reduction in the groundwater. As the pH of the groundwater drops from 7 to 6.5 or 6, CO_2 increases as the dominant form of carbonate. Just prior to the start of CO_2 measurements, the pH measurements in the high level CO_2 wells (Injection Wells and M1) were approximately 7. It is likely that carbonate equilibrium plays an important role. Several acids were, or could have been, produced. These include nitrate (oxidation of ammonia), fatty acids (biosurfactants), and carbon dioxide (biodegradation or chemical oxidation).

Another mechanism that could produce acid in situ is the reaction of oxygen with trace quantities of sulfides, such as pyrite (FeS_2), according to the following: $FeS_2 + 3.75\ O_2 + 2H_2O \longrightarrow 2SO_4^{-2} + 4H^+ + FeOOH$ and/or $+ 1/2\ Fe_2O_3$. This reaction would consume 40.2 pounds of oxygen (29 percent of the injected peroxide), resulting in a 65 ppm rise in sulfate (SO_4^{-2}) in the groundwater, and form hematite (Fe_2O_3) and/or goethite (FeOOH). Sulfate increases were observed in the pumping wells, although not consistently at a 65 ppm level. In addition, both hematite and goethite were identified as principal constituents of the sediment produced in Well P7 (Volume III, Appendix A). The significance of this reaction is that it does not result in any reduction in organics.

Based on the previous discussion, the quantity of CO_2 produced from the pumping wells would account for no more than 31 percent of the injected peroxide. The remaining 69 percent of the oxygen could have reacted in one of the following ways.

- The oxygen could have vented vertically in an unproductive manner. A 10-foot water table applies an absolute pressure of 1.3 atmospheres to the groundwater in the soil. At this pressure, oxygen has a solubility of equivalent to 89 ppm H_2O_2. Based on an average H_2O_2 injection concentration of 1000 ppm, 91 percent of the oxygen content is not soluble when peroxide decomposes.
- Reactions outside of the area of the pumping wells could have occurred.
- Reactions could have occurred with nonorganics such as metals.
- Incomplete oxidation may have resulted.

Initial ratings (prior to Day 180) of CO_2 levels in the pumping and monitoring wells are: Wells P9, M2 high (Rating 4); Wells P1, P2, P3, P4, P5, P6, P7, P8, M2, CC medium (Rating 3); Well M1 very low (Rating 1). Figure 26 indicates relative ratings by well location.
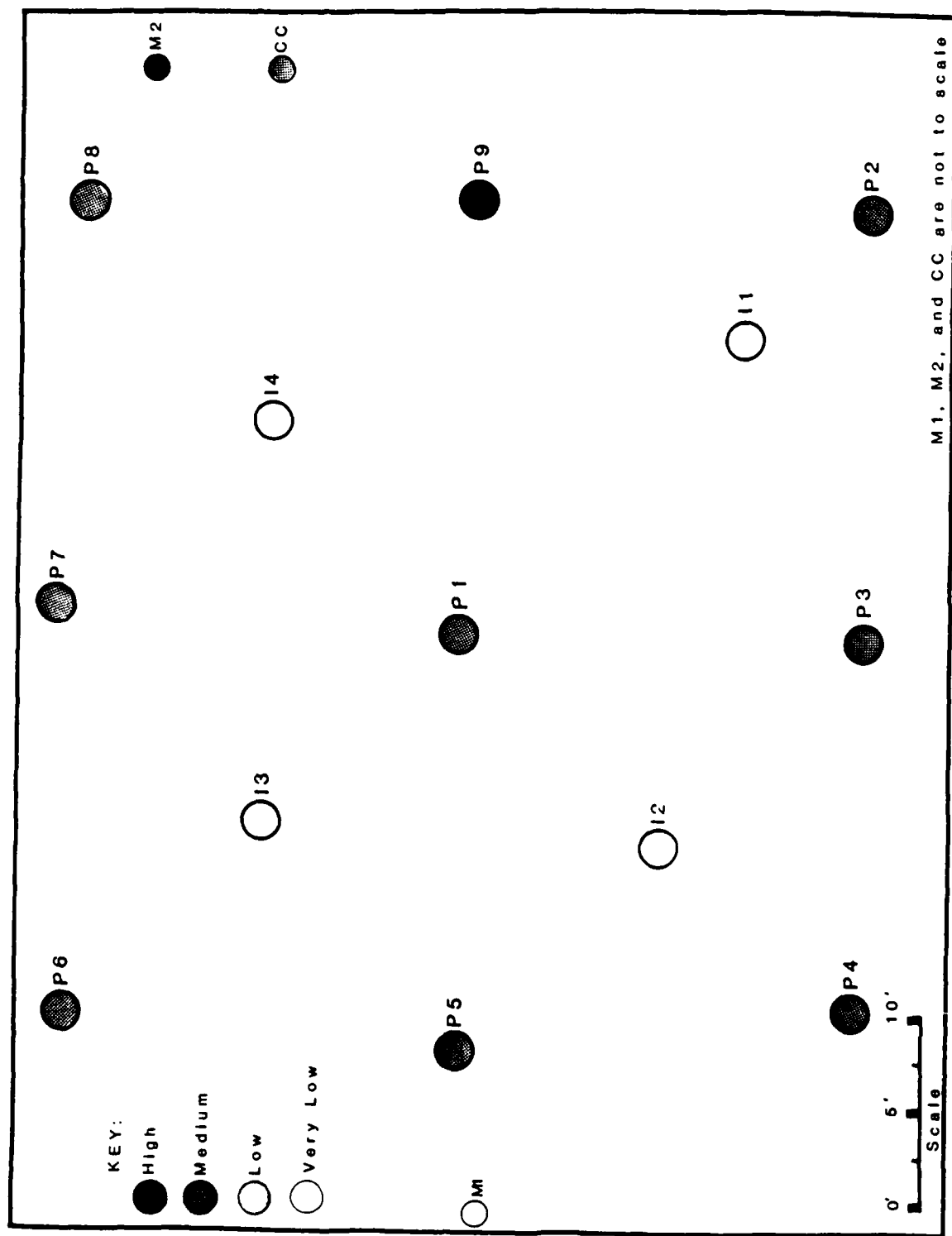
Figure 26.   Carbon Dioxide Breakthrough

Variations in CO_2 levels between pumping wells are considerably less than variations in chemical and nutrient communication. A possible explanation is that peroxide decomposes in the soil to free oxygen gas and water. This mixture reduces flow in the higher permeability zones relative to the lower permeability zones which results in a flow smoothing. Free gas can also "finger" through the groundwater and reach contaminated areas prior to the arrival of large quantities of injected liquid.

The "fingering" of gas refers to an instability that results in two-phase flow (References 20, 21). Gas, having a lower viscosity than water (a higher mobility), will tend to move more rapidly under an applied pressure differential than the water. Gas aphrons are produced under special conditions to overcome this instability. In the oil industry, nitrogen and carbon dioxide gas are injected into oil reservoirs to displace oil. Special conditions must be used to prevent that gas from fingering through the reservoir fluid instead of displacing it.

It may be possible to use dispersions of oxygen gas bubbles and liquid to achieve a higher average level of contaminant reduction within a well pattern area of variable permeability.

Wells P2, P5, P9, and M2 show a declining trend in CO_2 with time, while Wells P1, P3, P4, P6, P7, P8, and CC show a more uniform production trend. Since hydrogen peroxide, averaging 355 ppm, was added to the injection fluid from Day 185 to 257, a substantial portion of the CO_2 reduction in the first set of wells is probably associated with depletion of contaminants. Peroxide breakthrough was observed in Wells P1, P2, and P3 after day 234 (20 ppm in P1, 10 ppm in P2, and 40 ppm in P3).

4. Metals Changes in the Soil

Assessment of changes in soil metal values are based on the data listed in Table 7, which correspond to soil borings and groundwater

77

TABLE 7.   SUMMARY OF COMPARISONS OF SOIL METAL CHANGES DURING SYSTEM OPERATION

Analysis Conducted By	Sample Date	Locations	Antimony A	Antimony B	Arsenic A	Arsenic B	Cadmium A	Cadmium B	Chromium A	Chromium B	Copper A	Copper B
Aqualab	04/22/85 to 04/26/85	P1, P3, P9 12, 13, 14	170	71-249	4.4	2.4-6.3	5.1	1.9-9.3	116	9.3-233	6.3	5.6-8
ERG	07/30/85 to 08/02/85	SB1, SB2, SB3, SB4	<13	ND-50	1.8	ND-4.9	0.02	ND-0.08	398	180-880	7.4	<4-15
ERG	12/03/85 to 12/04/85	SB5, SB6, SB7, SB8	<25	<25	3.3	0.4-4.9	<2	<2	1268	57-5800	12.6	8-16
USBM	02/19/86	(1) SB9, SB10, SB11, SB12	175	128-210	<10	<10	<12	<10-20	2620	1600-3800	<148	<100-200
		(2)	259	177-360	<10	<10	<10	<10	620	320-840	<115	<100-150
		(3) -20 mesh	70	64-73	<4	<4	<6	<6	550	266-810	53	<36-92
USBM	12/04/85	SB7 (3)	270	270	<10	<10	<10	<10	290	290	<100	<100
USBM		(3)	68	68	<3	<3	<3	<3	73	73	<25	<25
USBM	12/11/85	P7	450	450	200	200	<10	<10	110	110	--	--

(1) - 200 mesh
(2) + 200/-14 mesh
(3) Average of sample assuming no metals in +14 mesh
A - Average
B - Range
Soil sampling location shown in figure 12
All concentrations in ppm
(--) Indicates analyses not performed

For SB9   24.7% minus 14 mesh
For SB10 34.4% minus 14 mesh
For SB11 48.0% minus 14 mesh
For SB12 33.8% minus 14 mesh

TABLE 7. SUMMARY OF COMPARISONS OF SOIL METAL CHANGES DURING SYSTEM OPERATION (Concluded)

Analysis Conducted By	Sample Date	Locations	Lead		Nickel		Silver		Thallium		Zinc	
			A	B	A	B	A	B	A	B	A	B
Aqualab	04/22/85 to 04/26/85	P1, P3, P9 12, 13, 14	56	30-88	25	17-33	8.6	5-13.6	36	25-59	90	21-249
ERG	07/30/85 to 08/02/85	SB1, SB2, SB3, SB4	ND	ND	<12	<10-14	<1	ND-4	<20	<20	45	23-60
ERG	12/03/85 to 12/04/85	SB5, SB6, SB7, SB8	37	13-92	8.1	5.5-12	<4	<4-5.2	<10	<10	263	20-1200
USBM	02/18/86	SB9, SB10, SB11, SB12 (1)	<100	<100	<100	<100	--	--	<100	<100	140	90-200
		(2)	<100	<100	<100	<100	--	--	<100	<100	80	50-150
		(3) -20 mesh	<40	<40	<40	<40	--	--	<40	<40	49	23-108
USBM	12/04/85	SB7	<100	<100	<100	<100	--	--	<100	<100	180	180
		mesh (3)	<25	<25	<25	<25	--	--	<25	<25	45	45
USBM	12/11/85	P7	180	180	--	--	--	--	<100	<100	1200	1200

(1) - 200 mesh
(2) + 200/-14 mesh
(3) Average of sample assuming no metals in +14 mesh
A - Average
B - Range
Soil sampling location shown in Figure 12
All concentrations in ppm
(--) indicates analyses not performed

For SB9   24.7% minus 14 mesh
For SB10 34.4% minus 14 mesh
For SB11 48.0% minus 14 mesh
For SB12 33.8% minus 14 mesh

79

samples obtained from the well pattern area before, during, and following peroxide/nutrient addition to the groundwater. In addition, a sediment sample obtained from a flow line at production well P7 was analyzed for heavy metals. Chemical analyses of the samples were performed by the three laboratories listed below:

- SAIC's La Jolla, California laboratory analyzed the microcosm samples (Table 7).

- Aqualab analyzed the soil samples collected in April 1985.

- TMA/ERG (formerly ERG) Ann Arbor, Michigan, analyzed the soil samples collected in July and December 1985.

- Analysis of metals by TMA/ERG for the February 1986 sampling are not shown because an error in the method of analysis was identified which invalidated the measurements.

- Duplicate samples from the February 1986 sampling were sent to the U.S. Bureau of Mines (USBM) Twin Cities Research Center for metals and petrographic analysis. Results for individual sampling locations are provided in Table 8, averages and ranges are shown in Table 7 for comparison with previous sampling times. The USBM separated the fine grain material from the bulk of the soil on which the chemical analyses were conducted [Rows (1) and (2) in the tables]. Row (3) is a calculated bulk average which assumes no metals are present in the +14 mesh size.

Although anomalies exist, specifically between the TMA/ERG and USBM analysis, indications are that metals appear to be mobilized from the soil. A specific mechanism of mobilization and transport has not been identified.

TABLE 8. SUMMARY OF U.S. BUREAU OF MINES METALS ANALYSIS OF KELLY SOIL SAMPLES

Sample Date	Location		Concentrations in ppm								
			Antimony	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Thallium	Zinc
12/4/85	SB7	-20 mesh	270	<10	<10	290	<100	<100	<100	<100	180
		(3)	67.5	<3	<3	73	<25	<25	<25	<25	45
12/11/85	P7		450	200	<10	110	--	180	--	<100	1200
2/13/86	SB9	(1)	210	<10	<10	2100	220	110	<100	<100	150
		(2)	360	<10	<10	320	150	<100	<100	<100	150
		(3)	73	<2	<2	266	44	<25	<25	<25	37
2/18/86	SB10	(1)	128	<10	<10	1600	140	<100	<100	<100	90
		(2)	250	<10	<10	490	100	<100	<100	<100	50
		(3)	64	<3	<3	343	40	<30	<30	<34	23
2/18/86	SB11 A&B	(1)	176	<10	20	3000	130	<100	<100	<100	200
		(2)	177	<10	<10	820	100	<100	<100	<100	70
		(3)	71	<4	<6	779	92	<40	<40	<40	108
2/18/86	SB12	(1)	186	<10	<10	3800	<100	<100	<100	<100	120
		(2)	247	<10	<10	840	110	<100	<100	<100	50
		(3)	73	<3	<3	810	<36	<34	<34	<34	29

(1) -200 mesh
(2) +200/-14 mesh
(3) Average for sample assuming no metals in +14 mesh
(--) Indicates analyses not performed

81

Table 9 summarizes the results of trace metals analysis corresponding to the laboratory microcosm study. Note the following:

- The shaded numbers refer to antimony concentrations in the water (50 ppb level) and soil (50 ppm level) prior to treatment. The circled numbers correspond to water (5 ppb level) and soil (<0.5 ppm level) concentrations after 49 days of treatment with hydrogen peroxide.

- The treatment resulted in a 100 to 1 reduction of antimony in the soil, but no subsequent rise in antimony in the water phase occurred. This effect parallels the field results.

- A possible explanation for this is that the antimony was mobilized as a fine particle in the water phase, and the water phase following treatment was decanted from the soil and filtered prior to chemical analysis. If this occurred, then no antimony increase would be measured in the water phase following treatment as was observed.

Metals changes in the soil before and during the system operation are summarized in Table 7. Column A is the average of multiple samples, Column B represents the range. Samples taken from April 22, 1985 to April 26, 1985 were collected before nutrient and peroxide injection. A summary discussion of the data follows.

Changes in metal concentrations corresponding to the Aqualab and ERG analyses indicate the following:

- Antimony reductions are the largest and most consistent with increasing time. These reductions correlate with the laboratory microcosm studies.

- Cadmium, nickel, silver, and thallium also show reductions with time.

82
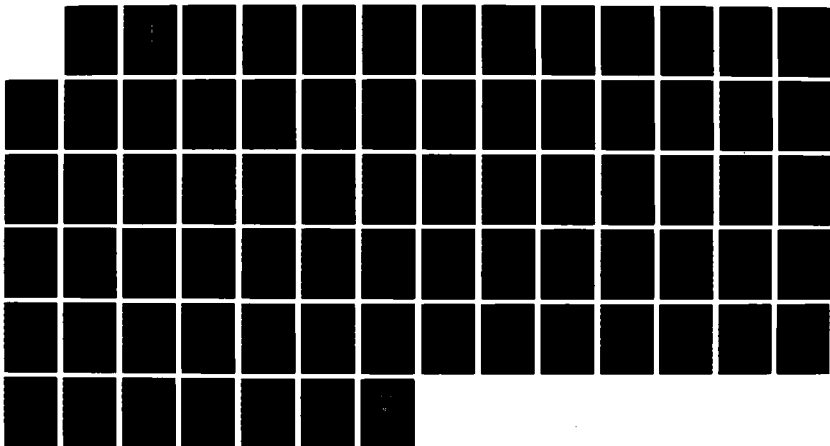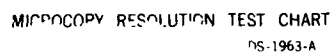
MICROCOPY RESOLUTION TEST CHART

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TABLE 9. SELECTED TRACE METAL CONCENTRATIONS IN WATER AND SOILS
BEFORE AND ON DAY 49 OF THE LABORATORY STUDY

	Water (ppb)					Soil (ppm)					
	Well[1] AA	Well[1] BB	Well[1] CC	49-H[2]	49-O[3]	BH-1[4]	BH-2[4]	BH-3[4]	BH-4[4]	BH-5[4]	49-H5
Silver	<10	<10	70	0.11	0.10	5.8	4.3	4.6	4.6	4.3	1.3
Cadmium	20	<10	<10	0.38	0.59	5.4	4.0	4.4	5.1	4.7	4.3
Chromium	40	60	20	20.5	24.4	141	58.3	252	67.3	70.1	71.1
Lead	110	120	170	4.03	8.3	51.3	34.3	40.0	42.3	48.8	66.1
Antimony	<50	<50		<5	<5						<0.5

1 Groundwater sampled July 1984 and analyzed by independent laboratory.
2 Water from Day 49 hydrogen peroxide-amended microcosm.
3 Water from Day 49 oxygen-amended microcosm.
4 Soil sampled July 1984 and analyzed by independent laboratory.
5 Soil from Day 49 hydrogen peroxide-amended microcosm.

83

- Arsenic, chromium, copper, lead, and zinc changes do not
  indicate a consistent change with time and may reflect varia-
  tions in initial metals distribution over the wellfield area.

Comparison of USBM analyses of samples obtained at the end of the
field test with ERG analyses of prior samples indicates the following:

- Antimony and cadmium levels are not considerably different
  than the 04/22/85 to 04/26/85 levels present before peroxide
  and nutrient were added to the groundwater.
- Copper, chromium, and zinc appear to be concentrated in the smaller
  size soil grains at concentrations that exceed the initial
  average measured on the soil prior to field testing.
- The above are based on the measurements obtained on the lower
  sized fraction of the soil, in which higher concentrations of
  metals might be expected (Rows (1) and (2) in Table 7). If
  it is assumed that no metals are contained in the +14 mesh
  size fraction (Row (3) Table 7), reduced concentrations of
  antimony are indicated.

The USBM analysis of the sediment obtained from Well P7 indicates
significant levels of antimony, arsenic, chromium, lead, and zinc. The
concentration of these metals in the sediment, except for chromium, is
much higher than in the soil. The USBM also conducted a petrographic
(microscopic) analysis of both the soil and sediment and observed that
similar clay and calcite mineral particle sizes and shapes were identified
in both the soil and sediment. This result, in combination with the pre-
sence of metals in the sediments, suggests that circulating groundwater
appears to entrain soil particles which may contain metals and transport
them to the pumping wells. This process could be enhanced by surface
active chemicals initially present in the soil or formed by biodegradation
of organics.

84

The USBM petrographic analysis also identified significant variations between the oxidation states of iron minerals in the soil and P7 sediment. Iron in the soil is principally ferrous, while iron in the sediment is ferric. Three possible effects can be associated with this finding: (1) groundwater entrains and transports ferric minerals, (2) hydrogen peroxide oxidizes soil ferrous material which precipitates at a high pH as ferric compounds, which are then transported by the groundwater, and (3) ferrous iron contained in the groundwater, when contacted with air on the surface, is oxidized and precipitates at a high pH as a ferric compound such as ferric hydroxide which was detected by the USBM to be present in the surface sediments. The second effect will impact peroxide consumption by soil.

Oxidation of metals by hydrogen peroxide is one possible method of initiating metals mobilization. The groundwater pH is too high to maintain oxidized metals in solution and they would likely precipitate as oxides which could then be transported by the circulating flow. The initial oxidation state of the metals was not measured. Had the metals initially existed in a reduced state the oxidation process could consume a considerable fraction of the oxygen content of the peroxide and would not then be available for aerobic interaction with organic contaminants. Based on the concentration of the metals (excluding chromium) contained in the soil prior to peroxide and nutrient addition, it is estimated that the oxygen demand is equivalent to 20 ppm hydrocarbon in the soil or 208 ppm in water (see table below). The following discussion presents a calculation of the maximum possible oxygen demand by metals oxidation. These calculations are based on the average values given in Table 8.

Metal	Reaction	ppm Metal	ppm O_2 Demand
Sb	Sb --> Sb_2O_3	170	33.5 (White)
As	As --> As_4O_6	4.3	1.4
Cd	Cd --> CdO	5.1	0.7
Cu	Cu --> Cu_2O	6.3	0.8

85

Metal	Reaction	ppm Metal	ppm O_2 Demand
Pb	Pb --> PbO	56.3	8.5 (Yellow to Brown)
Ni	Ni --> NiO_2	24.7	13.5 (Black)
Ag	Ag --> Ag_2O	8.6	0.6 (Brown)
Tl	Tl --> TlOH	36.3	2.8
Zn	Zn --> ZnO	90.2	<u>22.1</u> (White)
		Total	83.9 ppm relative to soil

This translates to 650 pounds of peroxide addition to a 60-foot diameter, 10-foot thick, and 20 percent porous treatment volume. The antimony (Sb) oxygen demand is 40 percent of the total. A total of 299 pounds of peroxide were used during system operation. This calculation illustrates the impact of reduced metals on soil oxygen demand and the need to assess the initial oxidation state of metals present in the soil, including the fraction of iron that is ferrous.

The sediment contained considerable quantities above 100 ppm of antimony, arsenic, chromium, lead, and zinc, which were all present in the soil before system operation. The USBM data, listed in Table 7, indicate that these metals are associated with the smaller soil particles which have a large surface to volume ratio. Mobilization rates of the metals by chemical or biological reaction, or by physical erosion by circulating groundwater, are expected to be higher for particles of high surface to volume ratios.

5. In Situ Acid Generation

The pH measurements of the groundwater indicate that the in situ treatment generates small quantities of acid, which most likely is the end result of biodegradation reactions that lower pH and/or air oxidation of pumping well groundwater.

86

A summary of pH variations is shown in Table 10. The lowest pH value measured in all wells prior to addition of peroxide and nutrients was 6.4. The groundwater in pumping wells shows a higher incidence of pH values less than 6.4 than those in injection wells. Well M1 (up-gradient) has a lower incidence than M2 and CC which are the downgradient monitoring wells. A survey of the data also shows the period of lowest pH (pH 6) occurred from September 12, 1985 to November 4, 1985.

6. Monitoring Groundwater Nitrate (NO_3)

Nitrate can be produced by oxidation of NH_4^+ in the presence of nitrifying bacteria. A 50 ppm increase in NO_3 would produce sufficient acid to reduce the pH to 2.8. This reaction would also consume 110 ppm H_2O_2. The low frequency of NO_3 concentrations above background and the fact that the elevated levels in Well P4 occurred prior to the time of maximum acid generation indicates that either this reaction was not a dominant factor in the process or both nitrate and acid were rapidly consumed by organics and calcite.

7. Monitoring Groundwater Sulfate (SO_4)

Table 11 summarizes the groundwater sulfate concentration measure-ments. The largest sulfate value measured in groundwater prior to peroxide and nutrient addition was 65 ppm. The top portion of the table lists those wells in which sulfate concentrations above background were measured by increasing frequency of occurrence. The bottom portion of the table lists average background sulfate concentrations and average sulfate con-centrations during treatment for various well groupings.

The concentration of sulfate in Well P2 is consistently above back-ground, suggesting that a small quantity of sulfate production is occurring in situ. Potential sources are oxidation of trace sulfides, such as pyrite, which would also produce acid, and/or increased solubility of any anhydrite

TABLE 10. SUMMARY OF pH VARIATIONS

Days	Time Frame	Average pH Values				
		I Wells	P Wells	M_1 Well	M_2 Well	CC Well
	Before Treatment 05/23/85	7.2	>7	7.2	7.2	No Data
17	06/17/85	6.8	7.1	7.2	6.7	6.7
19 to 55	06/19/85 to 07/25/85	6.9	6.3	6.8	6.4	6.6
60 to 95	07/30/85 to 09/03/85	7.0	6.8	6.9	6.6	6.9
98 to 157	09/06/85 to 11/04/85	6.9	6.0	6.9	5.9	6.1
161 to 189	11/08/85 to 12/06/85	7.6	6.9	7.4	6.9	6.9
192 to 223	12/09/85 to 01/09/86	7.1	7.1	7.0	7.0	7.0
224 to 262	01/10/86 to 02/17/86	7.7	6.8	7.2	6.7	6.8

TABLE 11. AVERAGE SULFATE CONCENTRATIONS IN GROUNDWATER

Occurrences of SO_4 > 65 ppm	Well Number
0 out of 26 data points	P1, P7, M1
1-to-3 out of 26 data points	P4, P6, P8, P9, I1, I2, I3, I4, CC
6-to-8 out of 26 data points	P3, P5, M2
21 out of 26 data points	P2

Well Units	Average SO_4 Concentration During Treatment ppm	Average Baseline SO_4 Concentration Prior to Treatment ppm
P1, P7	14	20
P4, P6, P8, P9	34	35
P3, P5	57	58
P2	84	65
Average of Production Wells	47	44
Average of Injection Wells	72	43
M1	15	35
M2	56	65
CC	32	NA

NA - Data not available

that may be present due to the increase in ionic strength of the groundwater by nutrient chloride.

F. WELL PATTERN MICROBIOLOGICAL EFFECTS

Groundwater and soils were periodically sampled to obtain measurements of total and hydrocarbon utilizing bacteria counts. Ranges and averages are summarized in Table 12. To identify major deviations from background (counts prior to nutrient and peroxide addition), average values for injection and pumping wells and soils are plotted versus time (see Figures 27 through 29). Monitoring well data for M1 and M2 are plotted separately (Figures 30 and 31), providing an upgradient versus downgradient comparison.

The largest deviation from background, a reduction in cell counts, occurs in the injection wells after Day 40 (July 15, 1985). Referring to Table 3, the highest injected peroxide levels (>5000 ppm) and nutrient concentrations were associated with the time period July 12, 1985 through August 2, 1985. However, subsequent reductions in concentrations of nutrient and peroxide did not restore microbial counts. Since no consistent trend in count reduction was noted for the pumping well groundwater after Day 40, and since this groundwater is transported directly to the injection wells, it is not likely that a chemical produced from the soil, by itself, has a negative impact on the bacteria counts in the injection wells. Two separate mechanisms may have contributed to the decline in counts. First, the decline may be associated with chemical attack by excess peroxide. Second, an entrapment of microbes on the precipitate (most likely calcium phosphate) that formed in the injection well may have occurred.

The soil microbe counts, especially the hydrocarbon-utilizing microbes, decline with time. This suggests that the circulating groundwater may strip these microbes from the soil. This could explain why no consistent

90

TABLE 12. SUMMARY OF RANGES AND AVERAGES OF BACTERIA COUNTS

Date	Days From 6/5	Groundwater cell count x 10^{-5}/ml										Soil cell count x 10^{-5}/gm	
		Injection Wells		Pumping Wells		Monitoring Wells							
						Total			Hydrocarbon				
		Total	Hydrocarbon	Total	Hydrocarbon	CC	M2	M1	M2	M1	CC	Total	Hydrocarbon
05/15	-20	0.7-5.8 (3.7)	0.7-1.9 (1.3)	0.4-29 (14.7)	0.07-8.7 (3.5)	-	1.9	17	0.2	4.9	-	0.43-100 (29.3)	0.18-110 (24.8)
06/06	1	No Data (No Data)	0.8 (0.8)	0.4-31 (7.2)	0.04-1.3 (0.5)	-	1	0.4	0.7	0.2	-		
06/25	20	No Data (No Data)	No Data (No Data)	0.6-3.2 (1.6)	0.002-0.16 (0.07)	-	1.3	38	0.34	0.8	-		
07/15	40	5-160 (50)	2.8-130 (36)	3.8-22 (12)	0.015-8.8 (2.8)	-	11	22	2	2.9	-		
07/31	56	0.017-0.39 (0.3)	0.001-0.34 (0.09)	0.083-4.1 (1.4)	0.005-0.25 (0.07)	-	1.3	14	0.87	2.5	-	0.04-120 (57.9)	0.12-8.5 (5.7)
08/14	70	0.001 (0.001)	0.001 (0.001)	0.85-3.7 (2.3)	0.12-2.1 (1.1)	-	22	25	11	0.68	-		
08/29	85	0.001 (0.001)	0.001 (0.001)	2.8-20 (7.4)	0.2-2.3 (0.82)	0.25	15	16	16	1.4	.01		
09/17	104	0.001 (0.001)	0.001 (0.001)	1.7-23 (4.9)	0.012-9.2 (1.4)	1.7	19	36	4.1	4.2	0.42		
10/08	125	0.001 (0.001)	0.001 (0.001)	2.2-12 (6.0)	0.024-18 (2.5)	-	2.3	6.7	0.91	7.5	-		
10/25	142	0.001 (0.001)	0.001 (0.001)	0.66-21 (7.1)	0.035-9.8 (3.1)	1.3	5.3	21	2.5	0.33	0.36		
12/04	182	0.076-0.24 (0.17)	0.035-0.069 (0.056)	0.068-1.28 (0.43)	0.0002-0.048 (0.012)	-	.03	.18	.024	.055	-	.0026 to 0.82 (.34)	0 to .00923 (.0054)
01/16	225	.001-26.0 (0.68)	(.006-1.52) (.050)	(1.28-14.4) (4.1)	(.002-1.52) (0.50)	.56	1.1	42	.22	.44	.18	(.51)	
02/17	257	0-.0032 (.014)	0.0006-.0016 (.0074)	0.24-17 (2.2)	0.042-9.4 (1.0)	0.68	0.69	3.5	.16	5.8	.20		(.28)

Numbers in parentheses represent averages.

91
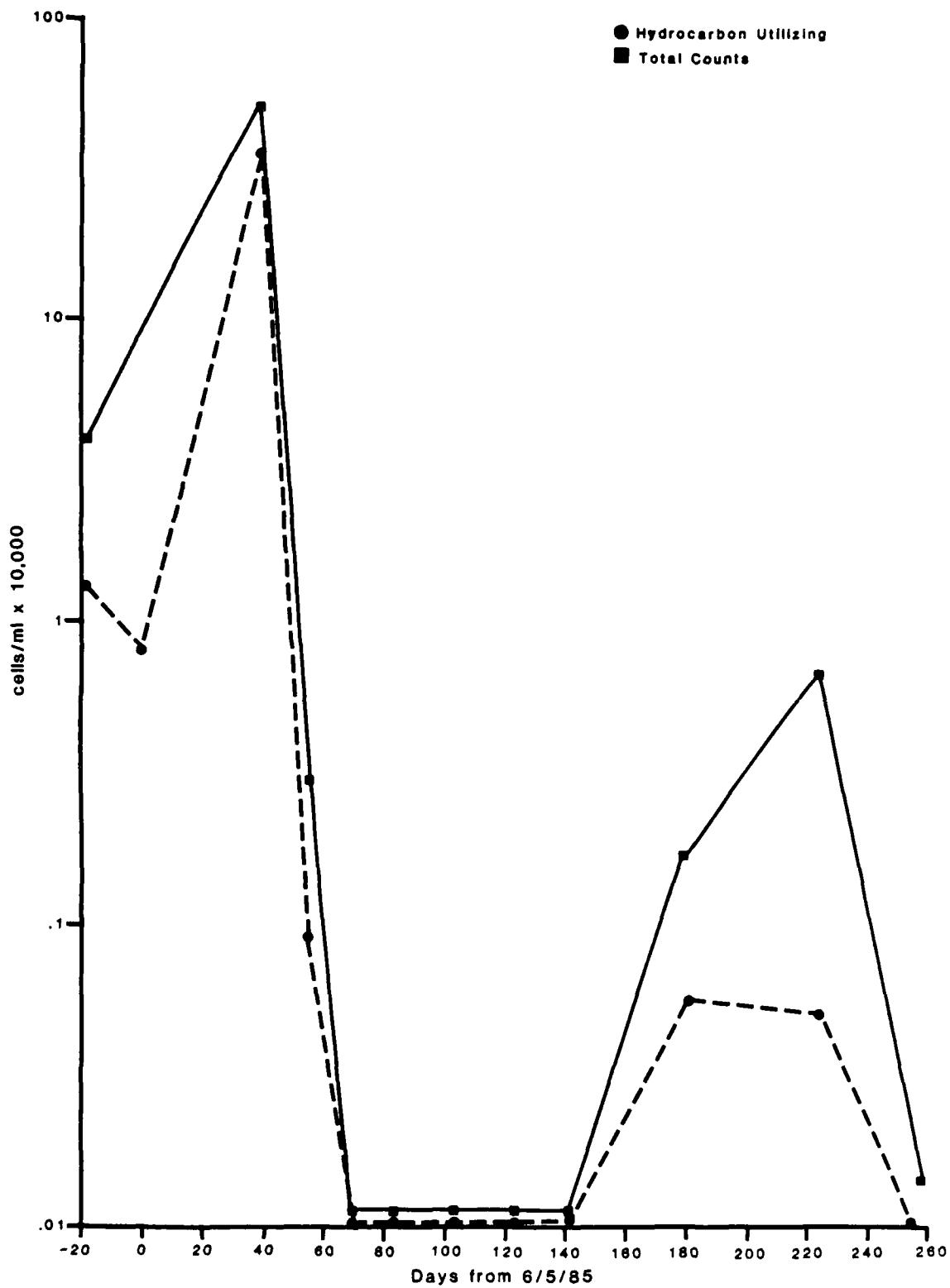
Figure 27. Average of Bacteria Counts for Injection Wells
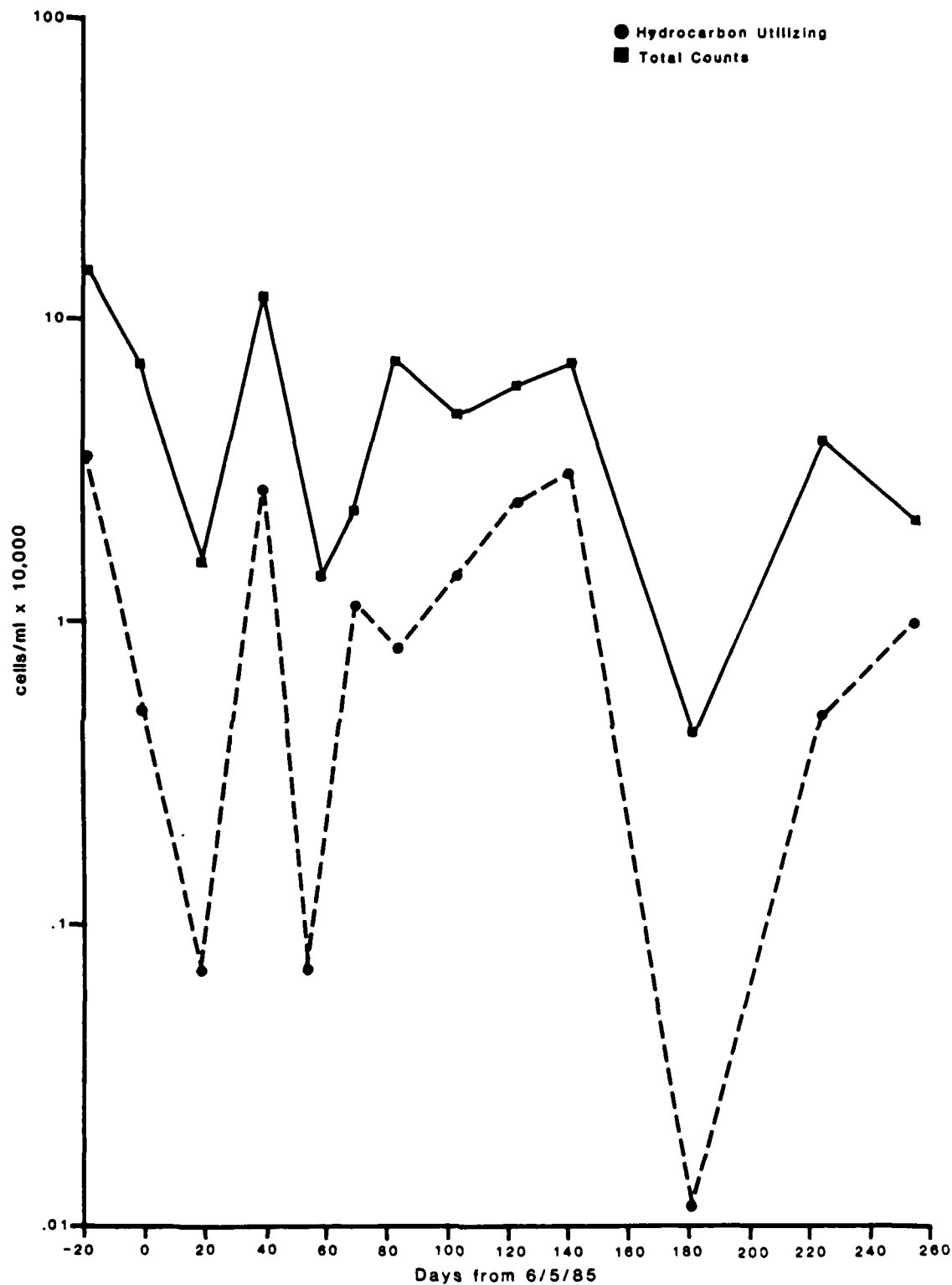
Figure 28. Average of Bacteria Counts for Pumping Wells

93
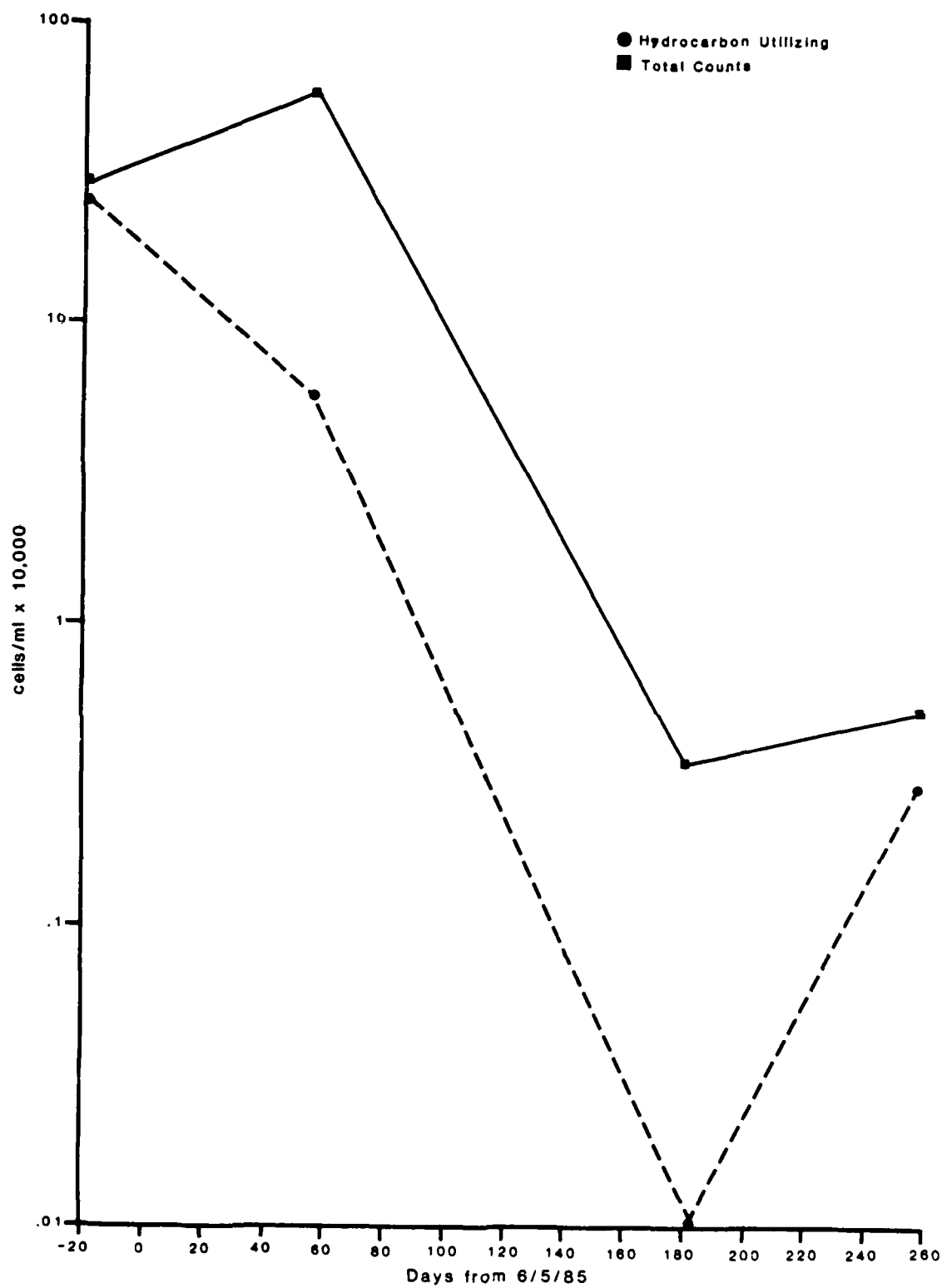
Figure 29.   Bacteria Counts for Soil

94
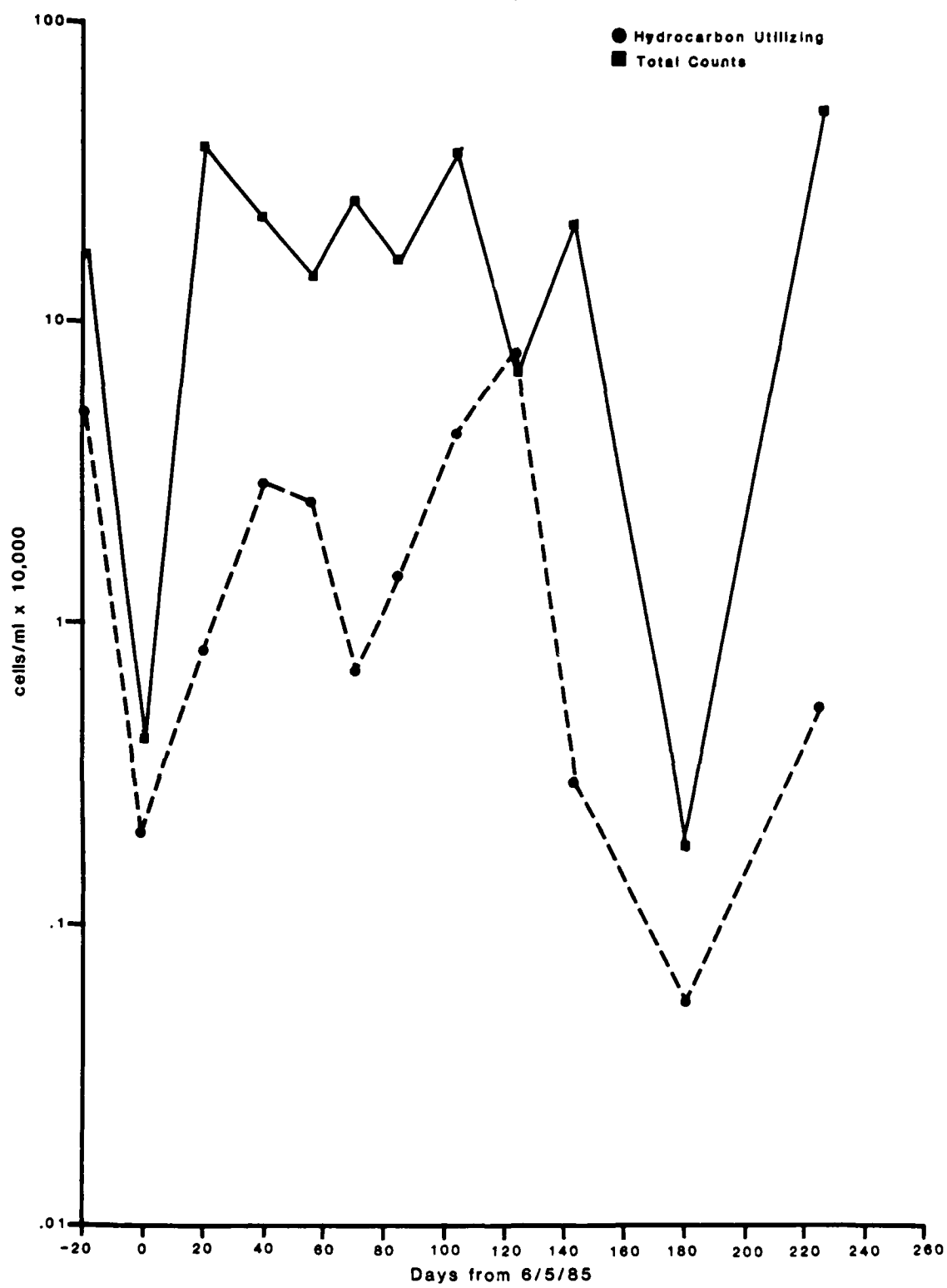
Figure 30. Bacteria Counts for Well M1

95
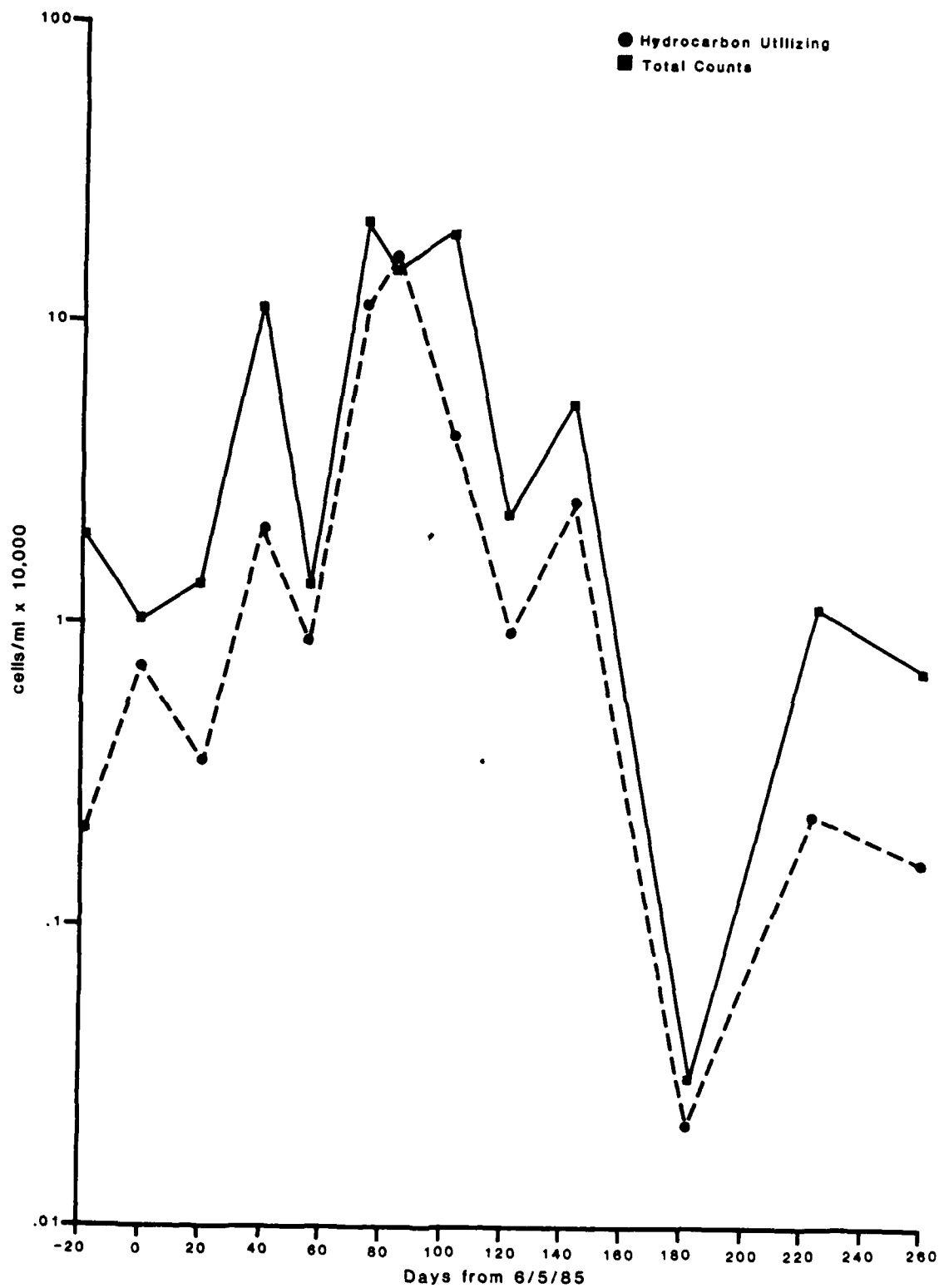
Figure 31.   Bacteria Counts for Well M2

96

declining trend in pumping well microbe counts is observed while the injection well microbe counts are considerably below background.

Finally, substantial microbe count changes for each plot are assumed to occur where counts are outside the background range (counts for Days -20 and 0, June 5, 1985). An increase in counts is observed in Well M2 before Day 145 (October 27, 1985). No particular chemical or process effect appears to correlate with this observation.

G. WELL PATTERN ORGANIC CONTAMINANT CHANGES

The initial state (before June 5, 1985) of the contaminants within the well pattern area (soils and groundwater) is highly variable. Concentrations of volatile organics in groundwater varied more than two orders of magnitude in the wells within the treatment area. Total VOCs in the pumping wells averaged 8.4 ppm before treatment. The key factors associated with these data which affect the evaluation of changes during treatment are discussed in this section.

Most of the mass of the organics per unit well pattern volume is in the soil, in excess of 200 ppm for the soil versus less than 3 ppm for the groundwater. Each unit volume of well pattern area, at 20 percent porosity, will contain 10.4 times as much mass in the soil as in the groundwater at the same ppm level. This is important for the following three reasons:

- Based on the addition of 299 pounds of hydrogen peroxide and a usage of 3 parts of oxygen per part of contaminant, less than a 13 ppm change in the organic concentration in the soil could be expected by peroxide activity. Since the variability of the initial soil organic concentration exceeded this by orders of magnitude, no change in total soil organic content was measured.
- If the principal source of the organics in the groundwater is the soil, then it is not likely that any change in the groundwater

concentrations would be observed since the large soil reservoir of mass would resupply the groundwater.

● If considerable changes in soil or groundwater organic concentrations are observed where most of the source is in the soil, then the effect of the peroxide/nutrient mixture is to mobilize these materials and transport them from one location to another. One mechanism by which this may occur is through the formation of biosurfactants, which have been observed to mobilize hydrocarbons in enhanced oil recovery (Reference 22).

Total hydrocarbon and oil and grease concentrations in the soil are listed in Table 13. Variations in both measurements over the initial 200 ppm levels indicate both considerable localized increase and reduction in total hydrocarbon and increases in oil and grease. Since these changes exceed the level of chemical reactivity of the hydrogen peroxide, the peroxide/nutrient addition to the groundwater may have resulted in mobilization of and redeposition of these materials within the well pattern indirectly by formation of an intermediate chemical such as a surfactant (Reference 22).

Total hydrocarbons concentrations in the groundwater are listed in Table 14. Although variations between sampling points are large, a comparison of samples collected August 8, 1985 and September 12, 1985 with those collected December 5, 1985 and February 17, 1986 indicates a qualitative reduction in the groundwater organic level.

Table 15 lists groundwater oil and grease concentrations before and during treatment. No considerable change with treatment is observed.

Table 16 lists well pattern groundwater concentrations of volatile priority pollutants prior to and at three sampling times during treatment. The major observations are summarized below.

98

TABLE 13.   CONCENTRATIONS OF TOTAL HYDROCARBONS AND OIL AND GREASE IN SOIL

| Date | Day | Hydrocarbon Concentration (ppm) in Soil | | | |
| | | Samples Taken Above 25' BGS | | Samples Taken Below 25' BGS | |
		GC-FID	O&G	GC-FID	O&G
6/84	Back-ground	221	---	---	---
4/85	Back-ground	---	180-535	---	140-195
8/85	69	---	---	ND (0.05)-0.071	---
12/85	188	ND (50)-1000	ND (200)-1300	ND (50)	800

Treatment began June 1985
BGS - Below ground surface

99

TABLE 14.   TOTAL HYDROCARBONS IN GROUNDWATER, GC SCAN (ppm)

Sample ID	8/8/85	9/12/85	12/5/85	2/17/86
P1	ND (0.05)	-	ND (0.05)	ND (0.05)
P2	ND (0.05)	-	ND (0.05)	-
P3	-	-	-	-
P4	6.80	49.0	ND (0.05)	0.36
P5	-	-	-	0.31
P6	ND (0.05)	-	ND (0.05)	0.076
P7	-	-	ND (0.05)	-
P8	ND (0.05)	280.0	ND (0.05)	0.20
P9	0.580	ND (0.05)	ND (0.05)	0.37
I1	0.150	ND (0.05)	-	-
I2	-	-	ND (0.05)	-
I3	1.40	1.70	ND (0.05)	ND (0.05)
I4	730.0	ND (0.05)	ND (0.05)	ND (0.05)
M1	-	ND (0.05)	-	-
M2	4700.0	18.0	ND (0.05)	ND (2.4)
CC	-	ND (0.05)	ND (0.05)	3.8
Blank	-	15.0	ND (0.05)	0.055
Bailer Wash	-	ND (0.05)	ND (0.05)	0.061

- Well was not sampled
ND(#) - Not Detected (detection limit)

TABLE 15. OIL AND GREASE IN GROUNDWATER (ppm)

Sample ID	5/23/85*	12/5/85	1/16/86	2/17/86
P1	1	<1	<1	2
P2	2	2	2	<1
P3	<1	<1	2	ND(1)
P4	2	2	<1	<1
P5	<1	<1	2	ND(1)
P6	2	<1	1	1
P7	<1	4	<1	2
P8	1	2	2	ND(1)
P9	1	2	<1	<1
I1	<1	1	<1	ND(1)
I2	<1	4	<1	<1
I3	1	<1	<1	<1
I4	3	<1	<1	<1
M1	<1	2	2	1
M2	3	<1	<1	<1
CC	-	4	1	<1
Blank	-	1	ND(1)	ND(1)
Bailer Wash	-	2	ND(1)	ND(0.001)

* Different Laboratory
- Well was not sampled
ND(#) - Not Detected (detection limit)

TABLE 16.   SUMMARY OF GROUNDWATER TCE, PCE, AND TRANS-1,2-DCE
CHANGES DURING TREATMENT

Priority Pollutant	Date	Average All Production Wells (ppm)	I4	M2	CC
TCE	05/23/85 (Before Treatment)	2.3	No Data	No Data	No Data
(Decrease)	08/08/85	1.7	No Data	No Data	No Data
	12/05/85	0.69	0.21	5.5	0.099
	02/17/86	0.47	.009	7.1	9.4
PCE	05/23/85 (Before Treatment)	1.7	No Data	No Data	No Data
(Decrease)	08/08/85	1.8	No Data	No Data	No Data
	12/05/85	0.74	0.21	1.0	0.11
	02/17/86	0.46	0.023	10	0.10
Trans-1,2 DCE	05/23/85 (Before Treatment)	0.027	No Data	No Data	No Data
(Increase)	08/08/85	2.4	No Data	No Data	No Data
	12/05/85	0.76	0.4	1.0	.009
	02/17/86	1.4	0.026	2.0	2.9
Vinyl Chloride (No Change)	05/23/85 (Before Treatment)	0.26	No Data	No Data	No Data
	08/08/85	0.32	No Data	No Data	No Data
	12/05/85	0.11	No Data	ND (1.0)	ND (.001)
	02/17/86	0.23	No Data	0.14	0.61
Chlorobenzene (Initial Rise No Net Increase)	05/23/85 (Before Treatment)	0.021	No Data	No Data	No Data
	08/08/85	0.049	No Data	No Data	No Data
	12/05/85	0.095	No Data	1.0	.001
	02/17/86	0.029	No Data	.1	0.1
Methylene Chloride (Increase)	05/23/85 (Before Treatment)	<0.005	No Data	No Data	No Data
	08/08/85	<0.026	No Data	No Data	No Data
	12/05/85	0.30	0.059	ND (1.0)	ND (0.001)
	02/17/86	0.12	ND (0.015)	27.0	2.8

No Data - Sample not analyzed for this parameter
ND (#) - Not Detected (detection limit)
< - detected at a value less than that shown

- PCE and TCE, the two compounds with initial concentrations in excess of 1.5 ppm, show a reduction in concentration during treatment. Both of these chemicals showed anaerobic reduction during the treatability studies. Since hydrogen peroxide break-through did not occur, except to a minimal level at the end of treatment, a considerable portion of the well pattern may have been in an anaerobic state during nutrient addition. The possibility of chemical oxidation should also be considered for the long residence times associated with this operation.
- Trans-1,2-DCE and methylene chloride concentrations showed a net increase.
- Vinyl chloride and chlorobenzene concentrations did not show a net increase.

Table 17 lists well pattern soil concentrations of volatile priority pollutants prior to and at three sampling times during treatment. Major observations are summarized below.

- Essentially only small quantities of PCE and TCE are measured in the soil in comparison to the groundwater levels.
- The methylene chloride levels in the soil for August 1985 and December 1985 (0.055 ppm and 0.23 ppm), although comparable in concentration to the groundwater concentrations (<0.026 ppm and 0.30 ppm), are 10.4 times higher per unit volume of well pattern in the soil than the groundwater (Table 15).

It appears that a higher activity of volatile priority pollutants occurred on the downgradient side of the well pattern area. This is illustrated by the data in Table 18 and indicates that pollutants are either being transported and concentrated downgradient or that higher initial concentrations existed downgradient, as evidenced by the 5 to 1 variation in initial values between the average concentration of all pumping wells (4.6 ppm) and the concentration in Monitoring Well CC (23.9 ppm).

103

TABLE 17.   VOLATILE PRIORITY POLLUTANT CONCENTRATIONS IN SOIL

Date	Sampling Location	PCE Average (ppm)	TCE Average (ppm)	Methylene Chloride Average (ppm)
4/85* (Before Treatment)	I2, I3, I4	<0.5	<0.5	<1.0
8/85	SB1, SB2, SB3, SB4	ND (0.001)	ND (0.001)	0.055
12/85	SB5, SB6, SB7, SB8	ND (0.01)	ND (0.01)	0.23
02/86†	SB9, SB10, SB11, SB12	<0.00043	ND (0.00012)	<0.0032

* Conducted at Aqua Lab.
† EPA 601 instead of EPA 624.

104

TABLE 18. TOTAL CONCENTRATION OF VOLATILE PRIORITY POLLUTANTS
IN GROUNDWATER (ppm)

DOWNGRADIENT
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Date	P Average	P8	P9	M2	CC
05/23/85	4.6	8.0	8.9	No Data	23.9 (6/84 data)
08/08/85	6.2	3.9	6.2	No Data	No Data
12/05/85	2.7	1.4	9.7	13.1	0.22
02/17/86	2.8	5.3	5.0	46.5	29.9

H. MECHANICAL AND ELECTRICAL EQUIPMENT

The various equipment and materials used in the demonstration system were selected to provide durability and performance without interfering with experimental results. Throughout the course of the demonstration, there were very few equipment or material-related problems. The few problems that did occur were minor.

Once the pumps were installed, they all operated throughout the life of the project without any mechanical problems. The pumps used did present a potential problem due to excessive heat generation caused by the extremely low pumping rates. Efforts to locate a pump that would operate at such low rates and still be durable enough to run continuously were unsuccessful. For future systems, it would be beneficial to order custom-made pumps to meet the necessary specifications. The pump casings were made of stainless steel which did not present a contamination or reaction problem. Upon completion of the demonstration, some rust was discovered but was not sufficient to have hampered system performance.

Electrical controls used to control pump operation performed as designed throughout the life of the project. The discharge and re-circulation piping and pump electrical wiring present in the pumping wells often made it difficult to use water level probes and precluded the use of a bailer for removal of samples or a probe-type monitoring device for collecting pH, dissolved oxygen, temperature and conductivity data.

The PVC and plastic materials used in all piping, joints, and valves proved adequate. All piping and heat-welded joints performed well under normal system operation. Several joints cracked in a single occurrence when valves were improperly adjusted, resulting in increased back pressure on the pumps. The PVC pipe installed near joints which had been welded tended to become more brittle and were subject to cracking when subjected to severe stress. The clear sections of PVC pipe placed in the system to monitor flow from the pumping wells were more brittle than the normal

106

Schedule 80 PVC used in most of the system. The PVC pipe located aboveground and exposed to a great deal of sunlight faded slightly and also became more brittle. No failure was recorded due to this occurrence and it was not believed to present a major problem. The PVC ball valves used throughout the system were extremely functional but did not deliver the degree of accuracy anticipated and had to be adjusted regularly. With higher flows, this may not have been a problem.

The metering pumps used to introduce nutrients and peroxide were very effective and allowed close control over the low volumes of injected solution. The electrical timers installed later in the demonstration period allowed for effective operation of the system overnight. Float valves installed on the injection wells were not effective in preventing overflow due to the very small infiltration rates. The valves did not provide a complete seal and allowed a small flow to continue into the well. This flow was sufficient to continue to flood the well. A valve providing a better seal, however, would have prevented the problem of well flooding.

I. MITIGATION RESPONSE

Throughout the operation of the system, Well CC was monitored closely for variations from historical concentrations of contaminants. In two instances, some concern was given to elevated levels of contaminants in Well CC. In the December 5, 1985 sampling round, the concentration for chromium was considerably higher (3.3 ppm) in Well CC than in the other wells sampled. A historical search showed similarly high levels for chromium in Well CC. Analyses were repeated to verify the result. The value for the second analysis was much higher (14 ppm) and cast some doubt on the validity of either number. A letter of explanation was requested from the laboratory which detailed several possible explanations for the wide variance of values. The second instance of concern involved the relatively high level of total inorganic carbon in Well CC in the December 5, 1985 sampling round. Unfortunately, no earlier data are available because

107

total inorganic carbon testing had not been performed. In both cases, evidence was insufficient to show that these levels of contaminants were a result of system operation; therefore, mitigative response was not recommended. Later sampling did not show concentrations as high.

The monitoring wells were used to monitor any changes that may have occurred outside the treatment area that could be attributed to the treatment operations. However, these wells were located within the contaminated zone and should not have been expected to have lower levels of contamination than wells located within the treatment area. Because of the peninsula shape of the site, it was not possible to locate monitoring wells beyond the contaminated area. Leon Creek and surrounding land were not Air Force property.

J. SAMPLING AND ANALYSIS

The Groundwater Monitoring Schedule followed at Kelly AFB is shown in Table 2. In general, as implemented, sampling and analysis at Kelly AFB provided useful results. The test kits proved to be economical and accurate enough to monitor system performance. The use of test kits allowed for quick results which could be implemented in adjusting system operations if necessary. The test kits, however, are subject to human error and interpretation. Different operators performed the tests during the span of the field program and, as a result, some procedures and interpretations of results were not uniform. Also the test kits are subject to interference by other chemical compounds in the groundwater.

It was possible that the high CO_2 levels shown in using the test kits could have been the result of other ions. A number of tests were conducted to ensure that the reported CO_2 values were the result of CO_2 gas. In the first test, one sample of Well P9 water was analyzed over a 3 day period, leaving the sample exposed to the atmosphere. Over the 3 day period, the measured CO_2 levels declined to a nondetect-

able level, indicating that CO_2 was being released to the atmosphere. The results of this experiment are given below as follows:

Date	ppm CO_2 By Field Kit Analysis
01/30/86	185
01/31/86	42
02/01/86	ND

In the second test, samples of fluid from the distribution box were analyzed for CO_2 before and after H_2O_2 addition. No difference in the CO_2 levels was observed, both were 59 ppm. Prior data indicated that injection solution CO_2 levels were two to three times lower than the produced fluid levels. This test demonstrated that peroxide addition did not affect the CO_2 level and that the most likely explanation for the reduction of CO_2 levels between produced and injected solutions was the exposure of these solutions to the atmosphere.

A third series of tests was performed on P9 produced water to further demonstrate that CO_2 was the chemical species being measured by the field test kit analysis. Two groups of samples of P9 water were monitored for CO_2 over a three day period (see results given below). In both cases, duplicate samples were used. Samples 1 and 2 were left exposed to air and demonstrate continual decline in CO_2 levels. Samples 3 and 4 were sealed in a bottle and not exposed to the atmosphere until the analyses were performed. Samples taken and sealed on February 7 and analyzed on February 8 and February 9 showed no decline in reported CO_2. Results are as follows:

	Exposed to Atmosphere		Sealed Samples	
Date	Sample #1	Sample #2	Sample #3	Sample #4
02/07/86	144 ppm	143 ppm	150 ppm	151 ppm
02/08/86	40 ppm	36 ppm	160 ppm	156 ppm
02/09/86	5 ppm	6 ppm	150 ppm	158 ppm

These tests indicated that CO_2 levels measured by field test kit analysis reflect the presence of dissolved CO_2 in the groundwater. However, the source of the CO_2 remains to be identified as biodegradation or shifts in carbonate equilibrium.

The laboratory analyses performed provided sufficient data on the parameters of concern at the site. Because of the high cost of these analyses only selected wells were sampled. Therefore, the data generated did not always provide a complete overview of results due to the highly variable nature of the site. This situation is discussed at length in Section VI. One major inconsistency in the laboratory results is the reporting of total hydrocarbons. The first samples were sent to Aqualab Inc., in Austin, Texas which reported oil and grease as total hydrocarbons. Subsequent samples were sent to ERG in Ann Arbor, Michigan which reported total hydrocarbons using a GC scan. These two numbers cannot be correlated because the GC hydrocarbon scan quantifies lower molecular weight hydrocarbons which will volatilize during the oil and grease extraction procedures. Although later samples were collected for both GC total hydrocarbons and oil and grease, the lack of baseline data severely limits conclusions that can be made about degradation of these compounds.

Future _in situ_ field projects should consider more frequent hydrocarbon analyses to monitor changes in organic levels and biodegradation results. Onsite GC equipment could be rented and analyses performed weekly or monthly depending on the size of the field project.

K. HEALTH AND SAFETY

The Health and Safety Plan developed for the field operations at Kelly AFB was detailed enough to provide guidelines for safe practices during all site activities. These procedures were strictly followed by all field personnel. As a result, there were no field accidents reported during the extent of field operations.

Adherence to health and safety procedures did not hinder effective site operation in any way. Visitors to the site and any subcontractor personnel were required to take necessary precautions detailed in the Health and Safety Plan. Upon leaving the site at the conclusion of the field activities, SAIC personnel were careful to ensure that all potential hazards were removed.

SECTION V

PROJECT QA/QC

A. QA/QC PLAN

A detailed Quality Assurance/Quality Control Plan was developed by
SAIC and approved by the funding agencies for all aspects of the demon-
stration at Kelly AFB. The major points of this plan as performed at
Kelly AFB are summarized in this section.

B. SAMPLING PROCEDURES

Bailer decontamination was performed before sampling each well.
This decontamination procedure involved scrubbing the bailer with
Alconox® detergent followed by complete rinsing with distilled water.
The drawstring was replaced between sampling of each well and sterile
gloves were worn by sampling personnel at all times. Before sample
collection, each well was purged of up to five times its saturated zone
volume. Field blanks and bailer washes were taken as necessary.

All equipment used in soil sample collection was steam-cleaned
prior to contact with the subsurface. Sterile gloves and containers
were used and gloves were replaced between each sample.

Accurate records were maintained throughout the sampling procedure
to document the sampling environment, sample characteristics, and other
pertinent information. Each sample was identified by a label showing
its specific characteristics. Samples being sent to laboratories were
shipped immediately by overnight courier in coolers with sufficient
blue ice to maintain a temperature of approximately 4°C during ship-
ment. All samples were sent to approved laboratory facilities and

were accompanied by chain-of-custody documents to ensure accuracy of reporting.

C. TESTING PROCEDURES

Onsite testing was performed by both meters and chemical test kits. The accuracy of these procedures was assessed regularly, using a number of methods. All meters were calibrated weekly using standard solutions. Spare meters were also used to verify these readings on a regular basis. Selected test kit results were checked by analyzing standard solutions provided by a local analytical laboratory. These checks showed test kit results to be within at least 20 percent of standard solution values.

Upon collection of groundwater samples, readings were taken immediately for dissolved oxygen, pH, temperature, and conductivity. The remaining sample was placed on ice until analytical laboratory analysis were performed. EPA standard laboratory methods were used, as discussed in Section III.B. At least one replicate, field blank, and bailer wash were analyzed for each round of sampling.

D. SYSTEM AND PERFORMANCE AUDITS

. A complete audit was performed in November 1985. This audit reviewed both field and office operations. The following items were addressed:

- Data recording practices
- Test kit analysis schedule
- Data analysis techniques
- Quality control
- Data management
- Reporting audits
- Data validation

- Sampling techniques
- Field meter performance.

E. PREVENTIVE MAINTENANCE AND ENGINEERING QUALITY CONTROL

The field operators performed regular assessments of system operation which included the following items:

- Inspection of all welds and joints for leaks
- Inspection of all wiring for proper connections, exposed or worn wiring, and possible overloading of circuits
- Inspection of pumps for proper operation
- Inspection of pump controls for proper operation
- Regular calibration of all valves to provide accurate measurement of flow
- Regular maintenance and calibration of all meters and measurement instruments.

All technical work performed on this project was subject to SAIC's peer review process. A peer review committee consisting of senior level employees from a variety of disciplines worked closely with the QA officer to review engineering performance. These activities helped to ensure the highest level of engineering quality in all aspects of the project.

SECTION VI

IMPLEMENTATION AND COST OF IN SITU TREATMENT

A. GENERAL CONSIDERATIONS FOR IMPLEMENTING IN SITU BIODEGRADATION

This section describes the activities involved in the design and operation of an in situ treatment system using the same general approach as in the Kelly AFB demonstration. The reader should be aware that other methods of groundwater circulation and treatment are also available. These methods include infiltration trenches or troughs and conventional land farming techniques. This generic plan will discuss only groundwater pumping and injection via wells.

1. Site Characterization

Characterizing a hazardous waste site is one of the most complex activities in any remedial action. The site characterization requirements for in situ treatment are even more extensive than for most other remedial alternatives. Figure 32 outlines the site characterization process associated with in situ treatment, presents the associated tasks, and lists the data that can be expected from these tasks. All or most of this data will be necessary before an in situ treatment system can be designed. Activities associated with the generally prescribed approach for characterizing DOD or CERCLA sites are identified on Figure 32 above the dotted line. The activities more specific to in situ treatment are listed below the dotted line. Major differences from those activities normally performed during a remedial investigation are groundwater and soil treatability studies. The next section discusses the types of treatability studies that may be performed and when they would be appropriate.
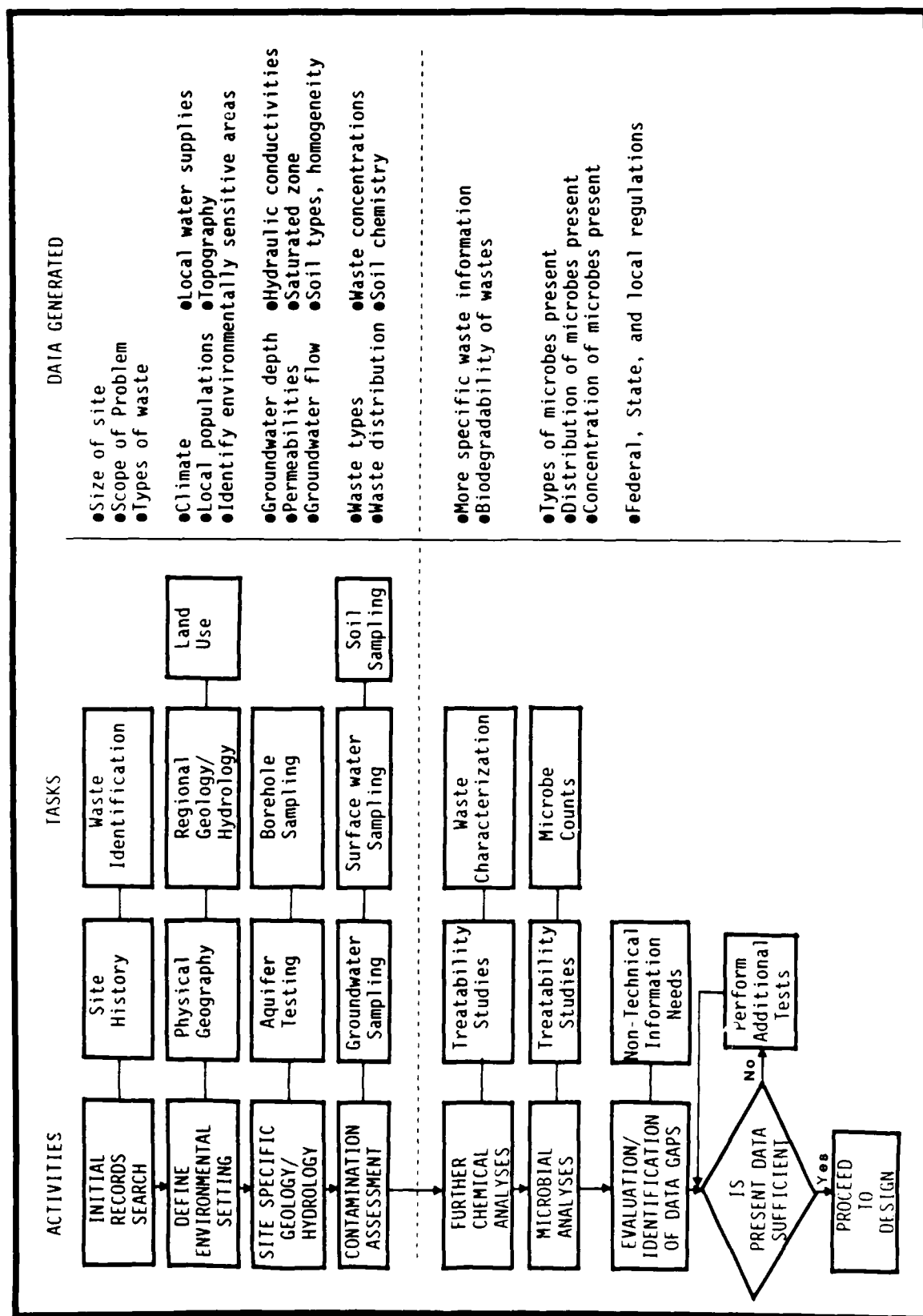
Figure 32. Site Characterization for In Situ Treatment

2. Soil and Groundwater Treatability Studies

Treatability studies are normally conducted following site
characterization and contaminant assessment and include chemical and
microbiological studies of both soil and groundwater from a waste site.
Treatability studies for in situ treatment are designed to provide ad-
ditional data on waste characteristics and the biodegradability of the
contaminants present, identify and quantify the microbial population
present in the subsurface, and evaluate potential chemical effects of
in situ treatment on soil and groundwater characteristics. The studies
are conducted with soil and groundwater from the waste site and are
designed to reflect various aspects of the proposed treatment approach.

a. Contaminant Biodegradation Studies

Biodegradation studies are conducted with soil and ground-
water from the site and provide information concerning waste charac-
teristics including the biodegradability of the contaminants. Informa-
tion can also be obtained from these studies to determine if toxic
intermediate metabolites or oxidation/reduction products will be formed
that may interfere with in situ treatment success.

Biodegradation studies can range from sophisticated micro-
cosm studies to simple microbial plate counts, depending on the type of
information required from the study. Full-scale microcosm studies are
useful when the groundwater and soil contain a wide variety of organic
and inorganic contaminants and the chemical interactions between the
soil and groundwater and the treatment solutions are uncertain. Micro-
cosm studies may also be warranted when the contaminated soil and ground-
water have not been fully characterized with respect to contaminants
present, or when sufficient information is unavailable on the treata-
bility of particular contaminants. These studies are useful in deter-
mining whether nutrient addition is warranted and, if so, what formula-
tion would be best suited to the microbial populations present. Full-

117

scale microcosm studies may not be necessary when only a few contaminants are present in the soils and groundwater or when existing data supports the biodegradability of particular compounds of concern.

Simpler biodegradation studies can be conducted by performing microbial spread plate counts using the contaminated groundwater as the sole carbon source for aerobic bacteria. Incubation of the plates is followed by cell counts to determine if the subsurface microbial populations are able to use the contaminants. These studies provide only general but often useful information regarding potential treatability of the contaminated soil and groundwater.

Contaminant biodegradation studies can be designed to evaluate both aerobic and anaerobic treatment approaches. Both oxygen and hydrogen peroxide treatment can be evaluated in aerobic microcosms. In addition, various nutrient formulations can be tested to determine tne necessity and/or type of nutrients for biodegradation. Microcosm studies conducted over extended periods of time can provide data on biodegradation rates which, when combined with specific site characteristics such as hydraulic conductivity and soil permeabilities, are important to determining the feasibility of in situ biological treatment. The treatability program can be quite diverse but should be designed to help refine the proposed treatment approach.

b. Microbiological Investigations

The design of microbiological investigations can be quite varied and also depends on existing microbial data available on the site and the type of additional information required. Typically, microbial studies consist of direct and/or viable cell counts performed using dilution-spread plate procedures. These studies are relatively inexpensive to perform and are useful for determining if an adequate microbial population exists for conducting in situ biological treatment of the contaminants present. 'n addition, data on the types of microbes

113

present and their distribution can be obtained. Microbiological studies can also provide information regarding general biodegradability of the contaminants, as discussed above with regard to treatability studies.

c. Soil Tests

Soil column tests are also conducted with soil and ground-water collected from the site. These studies are important for evaluating soil permeability and the chemical reactions which may occur between the soil and groundwater and the proposed in situ treatment solutions (oxygen source and nutrients, if necessary).

Soil column studies are usually conducted with permeameters; groundwater and treatment solutions are passed through the soil, and leachate solutions are collected and analyzed. Various treatment solutions can be permeated through several permeameters to optimize treatment solutions with respect to soil and groundwater chemical effects. Mineralogical and petrological studies may also be performed to gain a greater knowledge of physical and chemical properties of soils.

Results can be obtained from these studies which will accurately reflect problems and conditions which may arise during field implementation. These data include breakthrough curves of treatment solution constituents, information on exchange reactions between the soils and treatment solutions, and the effects of treatment solutions on soil permeability. Each of these factors are important to in situ treatment success and should be considered before final system design and implementation.

3. Design of the Well and Chemical Systems

The design of a pumping and injection treatment system requires a great deal of site-specific information. These information needs were presented as "Data Generated" on Figure 32. This section discusses

119

how the data can be used in making design decisions and describes some alternatives available in designing an in situ system using pumping and injection wells.

a. Well Design

The size, number, and spacing of pumping and injection wells will depend largely on site-specific characteristics. The spacing of wells will be largely dependent on the permeability of soils and pumping rates. Wells in less permeable soils will generally need to be closer together in order to effect treatment in a reasonable period of time. The size of the well will also be affected by soil permeabilities as larger diameter wells will allow for higher rates of pumping and injec-tion. The ratio of pumping to injection wells should be maintained so that no excess groundwater is generated. The cost of removing large amounts of hazardous wastewater would greatly negate the cost-efficiency of in situ treatment. The spacing of wells can be varied over a site to compensate for subsurface variabilities.

In sizing of wells, attention should be paid to the amount of space that will be needed for the pump, piping, and electrical equip-ment such as water level sensors. In addition, enough room should re-main for the use of a bailer and monitoring devices.

b. Transport and Mixing System

Many options are available for the mixing of nutrients and peroxide with the groundwater. The most desirable is an in-line system whereby nutrients and peroxide are added directly into the transport lines between pumping and injection wells. This system, however, is only practical at sites with very high pumping and injection capacities. In such cases, flow regulation into injection wells is unnecessary and overflow of the wells is not a problem. At low flow rates, it is necessary to monitor pumping and injection volumes very closely. It

120

then becomes more difficult to continuously monitor flow rates and chemical concentrations to ensure that too much flow or too high a chemical concentration is not entering the injection wells.

For low flow rates, a batch-type mixing sy.,tem will probably be most feasible. A large central mixing tank will allow nutrients and peroxide to be added to desired concentrations before being transported to the injection wells at regulated flows. Tanks should be protected against overflow and provide a sampling point to analyze circulating groundwater.

The size and location of a central mixing system will depend largely on the flow rate, size of the site, and site topography. For large sites, more than one mixing system may be necessary. Gravity is generally the best method of groundwater transport. The pumps in the pumping wells may provide enough pressure to transport water to the central mixing tank in cases where the topography prohibits gravity flow. Also, the head on the mixing or distribution tank may provide sufficient pressure to transport water to the injection wells.

c. Treatment Chemicals

Selection of nutrient and oxygen sources will be important to system design. Precipitation was a major problem at the Kelly AFB demonstration site. It is important to quantify this problem prior to system operation and take measures to prevent it from adversely affecting the system. It may be necessary to weigh the advantages of adding nutrients against the potential for precipitation. Enhanced biodegradation may be possible at some sites without the addition of nutrients.

Hydrogen peroxide proved to be an effective supplier of oxygen and requires little special equipment. Other methods of oxygenation such as forced air do require additional mechanical equipment which require additional maintenance.

121

d. Equipment and Material Selection

Durability is the primary factor to consider in selecting materials and equipment to use in an in situ treatment system. The system will be operating continuously and place a great deal of stress on pumps and piping. System downtime will cause delayed treatment and added expense. It is also important that all materials be non-reactive and noninterfering. This requires complete knowledge of how all materials will react with the contaminants onsite and proposed treatment chemicals. If this is unknown, simple laboratory scale studies can be performed.

Pumps and electrical controls will be subject to the most stress. All metal surfaces should be corrosion-free and pump housings must be durable enough to prevent any leaking of oil. The pump itself need not have a variable flow capacity as the flow can be controlled by valves at the surface. The pump should be rated within the full range of expected pumping rates to avoid unnecessary stress on the pump. Valves and flow meters should be sensitive enough to accurately measure the smallest flow anticipated for the well.

e. Operational Characteristics

The system will be operated continuously for a long time and as high a degree of automation as feasible should be implemented. Automatic devices in the pumping wells should turn off the pump when the water level is too low. Similar devices should be incorporated into the injection wells and mixing tanks to prevent overflow. Timers can be incorporated to cycle pumps, if necessary. More complex systems at very large sites could be designed to regulate flow and adjust pumping rates automatically. Although this would be expensive, the cost could probably be recovered in reduced operating expenses.

Another operational consideration is the provision for sampling and monitoring, as these operations are integral to any _in situ_ treatment system. As mentioned in the Well Design Section, wells should be designed large enough so that samples may be retrieved. In addition, a great deal of onsite analysis may be performed to monitor system performance. An onsite GC unit would allow for more frequent sampling and more samples at a lower cost than an offsite laboratory. It also provides results in a much more timely manner to allow for operational monitoring. A facility suitable for this purpose will be necessary, as well as an area for decontaminating field equipment and disposing of laboratory wastes. Sampling soil is more difficult and more expensive than sampling groundwater. Analyzing soils is also more expensive. It is, therefore, probable that soils will be sampled much less frequently and groundwater results will be relied upon to provide information on performance of the system. The most logical soil sampling schedule would be to do widespread sampling at the very beginning and end of treatment and very little, if any, during treatment.

4. Construction of the System

Construction will always begin with well installation and wells need to be installed properly. A poorly developed well will be of little use to the treatment system due to reduced pumping rates. Fines left in pumping wells could cause pump damage and mud and silt at the bottom of the well could cause pump clogging and cloud groundwater samples. Pumps should not be placed in the wells until as much of this material as possible is removed.

Pumps, piping, and electrical equipment placed in the wells should be constructed so that removal can be performed easily without disrupting the entire system. Glues should be avoided whenever possible to reduce the possibility of chemical interference. Welding, threaded joints, or compression fittings can all be used with good results.

A central electrical circuit board with individual controls for each pump should be located within close proxim:ty to the site for emergency shutdowns. The electrical lines should be buried underground to prevent accidents and disruption of power.

5. Startup and Operation

Once construction is complete, groundwater should be circulated for a few weeks without introduction of treatment chemicals. This should provide sufficient time to adjust pumping and injection rates and remove all residual fines from pumping wells. When pumping and injection rates are known, it is then simple to calculate the desired nutrient and peroxide concentrations. This initial period also provides a shake-down of the system so that any operational problems may be resolved before treatment is commenced.

The first few weeks of treatment should be monitored carefully to determine system performance. Results of frequent onsite testing will be useful in determining chemical transport and guide decisions as to the concentrations of treatment chemicals and/or the rates of pumping and injection. Once the system is operating effectively, the frequency of onsite sampling and analysis can be reduced to a reason-able level to provide long-term performance analysis. Onsite analysis is not expensive or difficult but it can be very time-consuming. Field staffing should be scheduled according to the quantity of tests to be performed. Normal operation and maintenance of a treatment facility should rarely require more than one individual, however, relevant health and safety regulations require more than one person to be present during activities at a hazardous waste site.

B. BREAKDOWN OF COSTS AT KELLY

The actual costs of performing the demonstration at Kelly AFB are presented in this section. The costs presented are approximate and

do not include profit or general and administrative costs. The costs have been broken down to reflect specific tasks.

1. Initial Field Characterization and Laboratory Studies

Labor (3376 hours)	=	$111,000 (fully loaded)
Soil Borings	=	25,000
Laboratory Studies	=	100,000
Permeability Studies	=	23,000
Travel and Other Direct Costs	=	21,750
Consultants	=	18,000
Total Costs	=	$298,750

2. Pumping Characterization (January 1985)

Labor (240 hours)	=	$ 10,000
Drilling (Three test wells)	=	12,000
Travel and Other Direct Costs	=	3,000
Total Costs	=	$ 25,000

3. System Design

Labor (1000 hours)	=	$ 44,000
Other Direct Costs	=	5,000
Consultants	=	2,235
Total Costs	=	$ 51,235

4. System Construction and Startup

Labor (800 hours)	=	$ 24,000
Travel and Expenses	=	10,000
Drilling (13 Wells)	=	33,000
Electrical	=	4,000
Piping	=	2,200
Pumps/Controls	=	4,000
Tools/Misc. Supplies	=	1,500
Total Costs	=	$ 78,700

5. System Operation, Sampling, and Analysis

Labor (2150 hours)	=	$ 55,000
Travel and Expenses	=	32,000
Onsite Trailer Rental (10 months)	=	2,000
Onsite Assistance and Treatment Chemicals	=	36,000
Sampling and Onsite Analyses	=	6,300
Maintenance	=	550
Misc. Field Supplies	=	1,725
Soil Sampling	=	4,850
Health and Safety Equipment	=	800
Chemical Analyses (56 groundwater samples, 19 soil samples)	=	$ 50,000

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          Biological Analyses  =     4,000
          (30 groundwater
          samples, 10 soil
          samples)
          Shipping             =     3,350


          Total Costs          = $196,575
```

6. Office and Administrative Costs

```
          Labor (4670 hours)   = $150,000
          Word Processing      =     1,600
          Graphics and Xerox   =     4,500
          Computer Use         =     1,000
          Temporaries          =     5,000
          Phone                =    10,000


          Total Costs          = $171,100


        Sum of all Costs = $821,360
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C. COST ESTIMATION FOR IN SITU BIODEGRADATION

Table 19 presents a list of variables that can be used in estimating the cost of performing in situ treatment. Four worksheets are presented in Figure 33 which provide a simple method of cost estimating using these variables. The worksheets assume a continuous site of relative homogeneity and uniform thickness of contamination. All costs are ultimately converted to dollars per ton as an end result so that in situ costs can be compared to costs of other alternatives such as removal. The cost categories considered in the worksheets correspond to those activities discussed in the generic site plan, specifically: site characterization, system design, system construction, and system operation. Variables used on the worksheets are described in Table 19.

TABLE 19.   DESCRIPTION OF VARIABLES USED
            ON COST ESTIMATION WORKSHEETS

A   area to be treated (acres)

C_a total analytical cost per sample (includes metals, priority
        pollutants, and total hydrocarbons)

C_{cs} concentration of contamination in soil (ppm)

C_{cw} concentration of contamination in groundwater (ppm)

C_d cost of installing wells (per foot of well)

C_l field operation labor costs (per employee per day)

C_n cost of nutrients (per ton)

C_p cost of peroxide (per ton)

D   depth of wells (feet)

D_f fluid density (pounds per cubic foot)

D_s soil particle density (pounds per cubic foot)

E   fraction of all wells sampled during a single sampling event

H   thickness of contaminated zone (feet)

L   total number of laboratory sampling events

M   total mass of contaminated soil (tons)

M_p concentration of hydrogen peroxide at introduction to groundwater

N   total number of wells

N_a number of wells per acre

N_i number of injection wells

N_p number of pumping wells

N_{pv} number of pore volumes circulated during treatment

P   porosity of soil (fraction)

PV   pore volume of contaminated zone (gallons)

Q   total circulation rate (gallons per day)

Q_i flow into individual injection wells (gpd)

S   average number of field personnel

S_f frequency of laboratory sampling events (days between events)

S_p number of laboratory sampling events per PV displacement

S_w number of wells sampled per event

128

TABLE 19. DESCRIPTION OF VARIABLES USED
ON COST ESTIMATION WORKSHEETS (Continued)

t time for one pore volume displacement (days)

T total time required to achieve cleanup (days)

U_n nutrient use per unit mass of contaminant (lb of nutrient per lb contaminant)

U_p peroxide use per unit mass of contaminant (lb of peroxide per lb contaminant)

U_{tn} total nutrient required (pounds)

U_{tp} total peroxide required (pounds)

Worksheet 1. Site Characterization

(1) Records Search: #people x #days x rate = $ _____ .

(2) Define Environmental Setting: #people x #days x rate = $ _____ .

Assessment of site specific geology and waste characterization:
- Well drilling: #wells x #feet x cost per foot = $ _____ .
- Field labor: #persons x #days x rate = $ _____ .
- Travel: (#days ÷ 10) x #persons x air fare = $ _____ .
- Expenses: (auto + per diem + daily expenses) x #persons x #days = $ _____ .
- Petrological and/or mineralogical assessments: #soil samples x cost = $ _____ .
- Metals Analyses: #wells x cost of analysis = $ _____ .
- Priority Poll. Analyses: #wells x cost of analysis = $ _____ .
- Hydrocarbons Analyses: #wells x cost of analysis = $ _____ .
- Microbes Analyses: #wells x cost of analysis = $ _____ .
- Analysis of Results: #people x #days x rate = $ _____ .
- Other Direct Costs: estimate = $ _____ .

(3) Total = $ _____ .

Treatability Studies:
- Permeability Testing: #tests x rate = $ _____ .
- Degradation Tests: #tests x rate = $ _____ .
- Analysis of Results: #people x #days x rate = $ _____ .
- Other Direct Costs: estimate = $ _____ .

(4) Total = $ _____ .

   ** Site Characterization Cost Per Ton = [(1) + (2) + (3) + (4)] ÷ M =
      $ _____ .

Figure 33. Cost Estimation Worksheets

Worksheet 2.   Operating Characteristics

Site Characteristics

A = area of site = _____ acres.

D_s = particle density = _____ lb/ft^3.

D_f = fluid density = _____ lb/ft^3.

P = porosity of soil = _____.

H = thickness of contaminated zone = _____ ft.

M = total mass of contaminated soil = [A] [H] [D_s] [1-P] [21.78] = _____ tons.

PV = pore volume = [A] [H] [P] [325,872] = _____ gallons.

C_{cs} = concentration of contamination in soil = _____ ppm.

C_{cw} = concentration of contamination in groundwater = _____ ppm.

Design Parameters

N_a = number of wells per acre = _____.

N = number of wells = Na x A = _____.

N_p = number of pumping wells = _____.

N_i = number of injection wells = _____.

D = depth of wells = _____.

Q_i = flow per injection well = _____ gpd.

Q = total circulation rate = Q_i x N_i = _____ gpd.

M_p = concentration of peroxide = _____ ppm.

S_p = sampling events per pore volume displacement = _____.

E = fraction of wells sampled per event = _____.

U_n = nutrient use per unit mass of contaminant = _____ lb/lb.

U_p = peroxide use per unit mass of contaminant = _____ lb/lb.

S_w = number of wells sampled per event = NAS_pE = _____.

Figure 33.   Cost Estimation Worksheets (Continued)

Operation Parameters

T = time to achieve cleanup = $\dfrac{325,800 \ [C_{cs} \ D_s \ (1-P) \ + \ C_{cw} \ D_f \ P] \ U_p \ H \ A}{Q \ M_p \ D_f}$ =

_____ days.

t = time for 1 PV displacement = PV/Q = _____ days.

N_{pv} = # pore volumes circulated during treatment = T/t = _____

U_{tp} = total peroxide used* = $U_p[(C_{cs})(M \times 2000)(10^{-6}) \ + \ (C_{cw})(PV \times D_f)(10^{-6})/$

(7.48)] = _____ lbs.

U_{tn} = total nutrient used = $U_n[(C_{cs})(M \times 2000)(10^{-6}) \ + \ (C_{cw})(PV \times D_f)(10^{-6})/$

(7.48)] = _____ lbs.

S_f = sampling frequency = t/sp = every _____ days.

L = total # sampling events = T/S_f = _____.

S = average # of field personnel = $N/40$ = _____.

Unit Cost Parameters

C_d = cost of drilling = $ _____ per foot.

C_n = cost of nutrients = $ _____ per ton.

C_p = cost of peroxide = $ _____ per ton.

C_a = analytical costs = $ _____ per sample.

C_l = (S) (daily rate + travel + expenses) = $ _____ per day.

C_s = cost of system shutdown = $ _____ per foot of well.

Note: The numbers generated here are used on Worksheets 3 and 4.

*U_{tp} assumes all contaminants are aerobically degradable.

Figure 33. Cost Estimation Worksheets (Continued)

Worksheet 3.   Design and Construction Costs

Design Costs:
    #people x #days x rate = $ _____.
    Other direct costs = $ _____.

(1) Total = $_____.

(2) Well Installation: N x D x C_d = $ _____.

Field Labor:
    (10 man days/well) x N x C_l = $_____.
    Other Direct Costs: estimate = $ _____.

(3) Total = $ _____.

Construction Materials and Supplies:
    ● pumps: cost x N_p = $ _____.
    ● piping: cost x total feet = $ _____.
    ● controls/electrical: cost x N_p = $ _____.
    ● flow valves + meters: cost x N_p = $ _____.
    ● mix tank: # x cost = $ _____.
    ● distribution tank: # x cost = $ _____.
    ● tools: estimate = $ _____.
    ● misc. supplies: estimate = $ _____.
    ● chemical feed system: # x cost = $ _____.

(4) Total = $ _____.

    ** Construction Cost Per Ton = [(1) + (2) + (3) + (4)] ÷ M =
       $ _____.

Figure 33.   Cost Estimation Worksheets (Continued)

133

Worksheet 4.   System Operation and Shutdown

Chemical Costs: Peroxide: $U_{tp} \times C_p$ = \$ _____.

Nutrients: $U_{tn} \times C_n$ = \$ _____.

(1) Total = \$ _____.

Laboratory Costs:

Total Analytical Costs: $L \times C_a \times S_w$ = \$_____.

or:

Priority Pollutants: $L \times cost \times S_w$ = \$ _____.

Metals: $L \times cost \times S_w$ = \$ _____.

Hydrocarbons: $L \times cost \times S_w$ = \$ _____.

Microbes: $L \times cost \times S_w$ = \$ _____.

(2) Total = \$ _____.

Costs of System Operation:

Field Operation, Sampling, and Analysis Labor: $T \times C_l$ = \$_____.

Other Direct Costs: estimate ≈ \$ _____.

Maintenance: 5% of construction costs annually = \$ _____.

(3) Total = \$ _____.

On Site Analysis:

GC Rental or Purchase: cost over life of project = \$ _____.

Weekly Test Kit Analyses: #tests $\times$ N $\times$ T/7 $\times$ cost = \$_____.

Sampling Supplies: estimate (small cost) = \$ _____.

(4) Total = \$_____.

System Shutdown:

(5) Cost of removal and grouting of wells = $N \times D \times C_s$ = \$_____.

** Operating Cost Per Ton = [(1) + (2) + (3) + (4)]/M = \$ _____.

Total Cost Per Ton = \$ _____.

Figure 33.   Cost Estimation Worksheets (Concluded)

Worksheet 1 calculates the costs of performing site characterization. All of these costs are not specific to the performance of in situ treatment and the required activities will vary from site to site. This worksheet will provide the user with a method of developing a general overview of potential costs of performing a site characterization.

Worksheets 2, 3, and 4 are directed specifically at the performance of in situ treatment. Worksheet 2 is used for developing all variables that will be used in calculating costs of treatment. This worksheet is divided into four categories: (1) site characteristics, (2) design parameters, (3) operation parameters, and (4) unit cost parameters. The site characteristics information will be generated as a result of site characterization activities. Design parameters will be established by using data gained through site characterization and treatability studies. Operation parameters can then be calculated as shown. The unit costs of the major treatment components are estimated and applied to the specific operation parameters for the site. Using this information, design and construction costs are calculated in Worksheet 3 and system operation and shutdown costs are calculated in Worksheet 4.

D. SENSITIVITY ANALYSIS FOR CONSTRUCTION AND OPERATING COSTS

Using the worksheets presented in Figure 33, a cost sensitivity analysis was performed to determine how the cost of in situ treatment to other treatment was affected by changing various parameters. This sensitivity analysis is useful in comparing the cost of in situ treatment to other technologies. Sensitivity analyses of this type should be performed for future applications of in situ treatment in order to develop the most efficient design possible. The analysis only deals with construction and operating costs. It is assumed that site characterization and design costs will not fluctuate greatly between sites and are therefore not considered. These costs are also not unique to in situ treatment and would bias the total cost of treatment.

The sensitivity of cost for performing _in situ_ will depend on design
parameters as well as site parameters. Design parameters are the variables
in the cost of treatment dependent upon the design of the system. The
most important of these will be the spacing and number of wells installed.
For the cost model, wells are considered by number per acre (N). The
relationship between spacing and number of wells per acre is as follows:

- 10 foot spacing ----> 400 wells per acre
- 15 foot spacing ----> 200 wells per acre
- 20 foot spacing ----> 100 wells per acre
- 50 foot spacing ----> 50 wells per acre.

Increasing the number of wells will increase the total circulation rate
and reduces the time for treatment. This will act to reduce the duration
of operating costs, however, more wells also means increased construction
and unit operating costs. Increasing the number of wells may require the
number of sampling events per pore volume and the fraction of wells to be
sampled (E) to be decreased to a reasonable value. The circulation rate
may or may not be a design function. If transmissivity of soils is high,
some latitude may exist in determining the flows to be used. In many
cases, such as at Kelly AFB, soil conditions will be the major factor in
determining flows. Other design variables of importance include the
concentration of hydrogen peroxide (M_p), the well depth (D), and analytical
and labor costs (C_a, C_l). However, there is much less control over these
factors. Peroxide concentrations will be chosen to be the highest feasible
values at the given site. The depth of wells will be largely determined
by site conditions. Analytical and labor costs can be minimized through
efficient operation but will still be determined greatly by the size of
the site.

Site variables are those cost variables solely dependant on site
specific conditions. These include both rate and mass variables. Rate
variables include soil permeability which determines flow (Q) and nutrient
and peroxide use (U_n and U_p). The value assumed for U_n may be an upper limit

136

for nutrient use and was based on initial recommendations from Aquifer Remediation Systems for the Kelly AFB site. Although this value may be an upper limit, the cost of nutrients has a small impact on the economic evaluation of in situ treatment. Mass variables include contaminant concentrations (C_{cs} and C_{cw}), densities (D_s and D_f), porosity (P), and the extent of contamination (H and A). The most important of these variables will be the flow potential and the extent of contamination.

The cost sensitivity analysis presented in this section is an attempt at showing the relationships between the variables involved in in situ treatment and their relative importance. It does not necessarily present realistic costs of performing in situ treatment at a particular site and it does not represent the costs and site conditions experienced at Kelly AFB.

The analysis was performed by first developing a baseline site situation. This baseline situation is presented as a completed "Worksheet 2" and presented in Figure 34. Ten scenarios were then developed by adjusting the values for number of wells (N), flow (Q_i), area (A), thickness of contaminated zone (H), well depth (D), contaminant concentrations (C_{cw} and C_{cs}), analytical costs (C_a), peroxide use (U_p), and field labor required (S). The costs of these ten scenarios and the cost of the baseline situation are presented in Table 20.

This analysis provides a number of observations regarding the cost of performing in situ treatment. The affect of each variable change presented in Table 20 is discussed in the following paragraphs.

Scenario #1. Reducing the number of wells by half saves a great deal of money by reducing the construction and shutdown costs. Though the time for treatment is doubled, laboratory costs went down due to fewer wells to sample. This would probably be offset somewhat by increasing the percentage of wells sampled when spaced further apart. Labor costs went up, but were partially offset by the need for fewer personnel and smaller maintenance costs.

137

Worksheet 2.   Operating Characteristics

Site Characteristics

A = area of site = _____1_____ acre.

D_s = particle density = ___170___ lb/ft^3.

D_f = fluid density = ___62___ lb/ft^3.

P = porosity of soil = ___0.2___ .

H = thickness of contaminated zone = ___10___ ft.

M = total mass of contaminated soil = [A] [H] [D_s] [1-P] [21.78] = _29,621_ tons.

PV = pore volume = [A] [H] [P] [325,872] = _651,744_ gallons.

C_{cs} = concentration of contamination in soil = ___100___ ppm.

C_{cw} = concentration of contamination in groundwater = ___10___ ppm.

Design Parameters

N_a = number of wells per acre = ___200___ .

N = number of wells = Na x A = ___200___ .

N_p = number of pumping wells = ___150___ .

N_i = number of injection wells = ___50___ .

D = depth of wells = ___30___ .

Q_i = flow per injection well = ___250___ gpd.

Q = total circulation rate = Q_i x N_i = _12,500_ gpd.

M_p = concentration of peroxide = ___500___ ppm.

S_p = sampling events per pore volume displacement = ___1___ .

E = fraction of wells sampled per event = ___0.5___ .

U_n = nutrient use per unit mass of contaminant = ___5___ lb/lb.*

U_p = peroxide use per unit mass of contaminant = ___5___ lb/lb.

S_w = number of wells sampled per event = NAS_pE = ___100___ .

*Upper limits for nutrient use based on initial recommendation for
 Kelly AFB site.

Figure 34.   Characteristics of Baseline Scenario for
Cost Sensitivity Analysis

Worksheet 2.   Operating Characteristics (Continued)

Operation Parameters

T = time to achieve cleanup = $\dfrac{325,800\ [C_{cs}\ D_s\ (1-P) + C_{cw}\ D_f\ P]\ U_p\ H\ A}{Q\ M_p\ D_f}$ =

   577 days.

t = time for 1 PV displacement = PV/Q = _____52_____ days.

N_{pv} = # pore volumes circulated during treatment = T/t = ____11____

U_{tp} = total peroxide used* = $U_p[(C_{cs})(M \times 2000)(10^{-6}) + (C_{cw})(PV \times D_f)(10^{-6})/$
   $(7.48)]$ = _29,891_ lbs.

U_{tn} = total nutrient used = $U_n[(C_{cs})(M \times 2000)(10^{-6}) + (C_{cw})(PV \times D_f)(10^{-6})/$
   $(7.48)]$ = _29,891_ lbs.

S_f = sampling frequency = t/sp = every ____52____ days.

L = total # sampling events = T/S_f = ____11____ .

S = average # of field personnel = N/40 = ____5____ .

Unit Cost Parameters

C_d = cost of drilling = $ _100_ per foot.

C_n = cost of nutrients = $ _1000_ per ton.

C_p = cost of peroxide = $ _1000_ per ton.

C_a = analytical costs = $ _500_ per sample.

C_l = (S) (daily rate + travel + expenses) = $ _400_ per day.

C_s = cost of system shutdown = $ _30_ per foot of well.

Note: The numbers generated here are used on Worksheets 3 and 4.
*U_{tp} assumes all contaminants are aerobically degradable.

Figure 34.   Characteristics of Baseline Scenario for
Cost Sensitivity Analysis (Concluded)

TABLE 20. SUMMARY OF COST SENSITIVITY ANALYSIS RESULTS

Scenario #	Changes from Baseline Values	Time to Affect Treatment (Days)	Construction Costs	Operation, Maintenance, and Shutdown Costs	Total Costs (Excluding Site Characterization)
Baseline		577	$1,700,000 $57.39/ton	$2,064,899 $69.71/ton	$3,764,899 $127.10/ton
1	Number of Wells per acre (N_a) from 200 to 100	1154	$850,000 $28.70/ton	$1,930,726 $65.18/ton	$2,780,726 $93.88/ton
2	Flow per injection Well (Q_i) from 250to750gpd	192	$1,700,000 $57.39/ton	$1,194,894 $40.34/ton	$2,894,894 $97.73/ton
3	Depth of Wells (D) from 30 to 60 feet	577	$2,300,000 $77.65/ton	$2,292,329 $77.39/ton	$4,592,329 $155.04/ton
4	Site Area (A) from 1 to 2 acres	577	$3,400,000 $57.39/ton	$4,129,798 $69.71/ton	$7,529,798 $127.10/ton
5	Thickness of Contaminated Zone(H) from 10to20 feet	1154	$1,700,000 $28.70/ton	$3,399,798 $57.39/ton	$5,099,798 $86.08/ton
6	Cost of Laboratory Analysis(C_a) from $500 to $250 per sample	577	$1,700,000 $28.70/ton	$1,789,899 $60.43/ton	$3,489,899 $117.82/ton
7	Peroxide Use (U_p) from 5 to 10 lb/lb	1154	$1,700,000 $57.39/ton	$3,934,852 $132.84/ton	$5,634,852 $190.23/ton
8	Contamination Concentration in Soil (C_{as}) from 100 to 10 ppm	62	$1,700,000 $57.39/ton	$374,345 $12.64/ton	$2,074,345 $70.03/ton
9	Contamination Concentration in Water (C_{cw}) from 10 to 100 ppm	624	$1,700,000 $57.39/ton	$2,223,450 $75.06/ton	$3,923,450 $132.46/ton
10	Number of Field Personnel from 1 per 40 to 1 per 60 wells	577	$1,700,000 $57.39/ton	$1,603,245 $54.13/ton	$3,303,245 $111.52/ton

Scenario #2. Increasing the circulation rate (Q) will greatly reduce operating costs by reducing the time required for treatment. This reduces labor costs and maintenance requirements. Laboratory analysis costs did not change but were assumed to occur much more frequently.

Scenario #3. Increasing the depth of wells will act to increase capital costs, maintenance costs, and shutdown costs. Time required to perform sampling procedures will also increase slightly but should not have a major impact on costs.

Scenario #4. Doubling the site area will exactly double all costs but will not affect unit cost or time to affect treatment.

Scenario #5. Doubling the thickness of the contaminated zone greatly increases the total volume of waste to be treated. Time to affect treatment is doubled, as are costs for chemicals, operation, and onsite analyses. Laboratory costs are not increased but are assumed to occur less frequently as time to displace a single pore volume is doubled.

Scenario #6. Reducing laboratory costs by half greatly reduces operating costs. The $500 per sample cost level was assumed to include priority pollutants, metals, and total hydrocarbons. If all of these analyses were not required, a lower cost could be assumed.

Scenario #7. Increasing the peroxide demand will greatly increase operating costs by increasing the time required for treatment. Actual costs for the peroxide are small in comparison with increases in costs for labor and laboratory sampling.

Scenarios #8 and #9. Fluctuations in the levels of contamination will affect the total costs of treatment, mainly through changes in time required for treatment. Treatment chemical costs vary slightly but the main impacts result from labor and laboratory costs.

Scenario #10. Reducing the number of personnel required at the site will have a major impact on costs. However, many factors will determine the minimum number of personnel feasible for a site. The level of onsite analyses, the number of wells requiring sampling, the degree of automation, 24-hour operation, and relevant health and safety standards will all affect staffing needs.

Overall it can be seen that performing in situ treatment is a highly labor-intensive activity. This is due primarily to the high degree of monitoring necessary to evaluate peformance and modify operation. This analysis has shown that many variations in costs are possible, but in general the costs for monitoring the system are much greater than construction and operation. The costs of treatment chemicals are smaller and variations do not have a major impact on the total cost of treatment.

SECTION VII

SUMMARY OF OBSERVATIONS

This section provides a summary of the major observations made during the operation of the system at Kelly AFB.

- The installed system circulated groundwater with very few mechanical problems and very little down time.

- Initial addition of nutrients and hydrogen peroxide to the system resulted in an almost immediate permeability reduction from about 1×10^{-4} cm/sec to 1×10^{-5} cm/sec and a calcium phosphate precipitate was found in all injection wells.

- The high levels of nutrients and hydrogen peroxide added during treatment may have caused effects, such as permeability reductions and calcium phosphate precipitation, that otherwise may not have been observed if lower levels had been used.

- During the demonstration, the sum of TCE and PCE levels in site groundwater decreased from 4.0 ppm to 0.96 ppm, while DCE concentrations increased from 0.3 ppm to 1.4 ppm.

- Carbon dioxide concentrations in the system groundwater were of a magnitude greater than the presumed background levels at the site and were equivalent to as much as 30 percent of the peroxide oxygen supplied to the system.

- Mobilization of heavy metals (Sb, As, Cd, Pb, Ag, Zn, Tl) from the soils is indicated by the data, but metals were not detected in the groundwater.

- Heavy metals were found at the surface as sediments in several pumping well discharge lines.

- Chemical communication between injection and production wells was of sufficient strength to indicate that circulation rate counters natural groundwater flow.

- Large uptake of ammonia and phosphate by the soil is indicated; data indicate a higher uptake of phosphate than ammonia.
- Correlation of similarities between laboratory and field tests included: (1) permeability reduction, (2) heavy metals mobilization from soil, (3) phosphate lag of chloride breakthrough, (4) peroxide lag of phosphate breakthrough, (5) PCE and TCE decline, and (6) DCE increase.
- Reduction in soil microbial counts over the life of the demonstration was observed.
- No reduction in production fluid microbial counts was observed.
- Reduction in injection fluid microbial counts was observed, even at reduced levels of peroxide addition and at no peroxide addition.

SECTION VIII

CONCLUSIONS

A. DEGRADATION RESULTS

Analysis of results indicates that the treatment system implemented
at Kelly AFB, Texas successfully enhanced in situ degradation of organic
contaminants. Biological degradation was the most likely method of con-
taminant reduction as evidenced by the following:

- Degradation of chlorinated aliphatics was measured and followed
  known pathways for anaerobic biodegradation.

- Aerobic biodegradation of petroleum hydrocarbons was indicated,
  but could not be quantified since the small amount of degradation
  possible was much less than natural variations in hydrocarbon
  concentrations.

- Evidence indicated that contaminants were degraded by both aerobic
  and anaerobic mechanisms within the same treatment zone. This
  indicates that in situ treatment may be considered for use at
  sites with both aerobically and anaerobically degradable wastes.

B. SITE CHARACTERISTICS

The hydraulic conductivity of a site plays a major role in the
effective implementation of in situ treatment. It dictates the time
required to complete treatment and, therefore, will greatly affect the
total cost of treatment. The field test at Kelly AFB, however, showed
that distribution of chemicals and enhancement of biodegredation are
technically achievable even in low permeability aquifers. Hydraulic
conductivity values at Kelly AFB were as low as 0.11 feet per day. In

145

situ treatment is achievable, therefore, at the many hazardous waste sites located in shallow surface aquifers of low permeability.

C. TREATMENT CHEMICALS

Injection of chemicals to the subsurface can result in many chemical reactions other than those intended to enhance biodegredation. Some of these reactions can adversely affect the effectiveness and efficiency of in situ treatment. Reactions causing precipitation can clog infiltration wells and the aquifer itself. The reaction between the injected nutrient phosphate and the soil mineral calcium caused precipitation at Kelly AFB. Changes in pH and Eh induced by biodegradation and reoxygenation can cause dissolution and precipitation of iron. Injected nutrients and peroxide can react with other inorganic and organic chemicals. Even if these reactions do not result in a precipitate, they will reduce the amount of chemicals available to enhance biodegredation.

Another result of chemical reactions due to in situ treatment is the potential for mobilization of heavy metals. The metals may then be transported as very fine particles, which, if not controlled, can present the threat of spreading contamination. This could preclude the usefulness of in situ bioreclamation of sites which are contaminated with a mixture of organics and heavy metals. However, with proper control of transport and with appropriate removal of heavy metals from circulating groundwater, mobilization of heavy metals could prove beneficial in that they could be removed from the waste site and disposed of properly. Some of the effects observed at the Kelly AFB site may have been due to the high levels of chemicals (nutrients and hydrogen peroxide) added during the treatment process. These effects may not occur if reduced levels of chemicals are added.

D. COST OF IN SITU TREATMENT

Costs for treating all of Site E-1 at Kelly AFB were calculated using the worksheets in Section VI. These costs were calculated to be

146

approximately $100 per ton of contaminated soil or $4,800,000. The costs
of excavation and removal of this entire volume of soil were calculated
at $5,787,000 (based on historical costs at Kelly AFB: $18 per cubic yard
for excavation and loading; $55 per cubic yard for transportation; and $138
per cubic yard for disposal).

By calculating costs for in situ treatment, it is seen that the
largest cost items are for field labor and laboratory analysis. By
increasing the level of automation and decreasing the amount of laboratory
testing through suitable onsite facilities some savings will be realized.
However, increasing the amount of onsite analyses will increase the
staff requirements which may offset a significant portion of the savings.
Reducing the number and frequency of analyses performed will result in
the greatest cost savings but limit monitoring of system performance.

Even using conservative estimates, however, in situ treatment is cost
competitive with removal and provides a more desirable approach to site
cleanup.

E. SAMPLING AND ANALYSIS

Reducing the level of sampling and analysis to reduce costs may
present some difficulties in providing full treatment. It was demon-
strated at Kelly AFB that treatment activity over a site can be highly
variable, even over very small areas. Under such conditions it is neces-
sary to provide a very extensive sampling and analysis program to determine
the effectiveness of treatment and adjust the operation of the system
accordingly. Until much more is known about the specific mechanisms of
in situ treatment, extensive analysis will continue to be warranted
especially for future research efforts. Such efforts may warrant the use
of more complex equipment on site such as a GC/MS unit. This will help
to offset some of the high cost of chemical analyses. For future full-
scale effort, the cost of an onsite GC/MS and operator will probably not
be warranted.

147

SECTION IX

RECOMMENDATIONS

A. REQUIREMENTS FOR FULL-SCALE IN SITU BIODEGRADATION

   Full-scale application of in situ biodegradation will probably re-
quire significantly longer periods of operation than at Kelly AFB in
order to achieve cleanup. Most cleanups will probably take between 2
and 5 years depending on the complexity and quantity of wastes. Some
sites may require even longer than 5 years. After only 8 months
of operation, the PVC pipe used for the test at Kelly AFB had begun to
weather and was subject to cracking under stress. For operations lasting
several years, more durable construction materials would be recommended.
In addition, large, long-term operations may require large surge and/or
onsite storage capacities and should be highly automated to allow greater
operational control and flexibility and reduce the amount of field labor
necessary.

   Sampling and analytical procedures will also play an important role
in the operation of full-scale treatment. Analytical costs may make up
as much as 25 percent of total costs for future applications of this
technology. Before operation begins, a cost-benefit analysis will need
to be performed to determine whether onsite or offsite analysis will
be used. The outcome of this analysis will be primarily determined by
the frequency of analysis required. The frequency of sampling and analysis
will probably be less for full-scale applications than for research pro-
jects and a full-time, onsite laboratory may not be required. For large
sites, however, a single sampling event may involve hundreds of samples.
In addition to onsite and contract laboratory options, laboratory equip-
ment may be rented during sampling events with a chemist assigned to the
site on an as-needed basis. Analyses performed in an onsite laboratory

148

not approved by EPA will probably require periodic confirmation at an approved, contract laboratory.

The required frequency and completeness of groundwater and soil sampling will be highly site-specific. Sampling efforts will be most intense during startup of the system and as treatment nears completion. Many options exist for handling performance of these analyses. Future research programs will define the most efficient and effective means of providing adequate sampling and analysis for full-scale applications of in situ biodegradation.

B. GENERIC COST MODEL

The cost model presented in Section VI was developed as a result of experience gained at Kelly AFB. It is intended to provide an approximate cost for in situ treatment for comparison with other alternatives at any site. Using the model at future sites will provide information that can be used to refine the model to provide greater accuracy and flexibility for a wide variety of conditions. It is recommended, therefore, that the model be used for future research programs and improvements made to provide a simple, accurate means of calculating the cost of full-scale applications.

C. FUTURE TESTS/RESEARCH NEEDS

The test at Kelly AFB evaluated only one specific means of accomplishing in situ treatment. Several problems were identified and numerous questions were raised concerning various aspects of in situ treatment. These problems and questions will need to be addressed in future research efforts before in situ biodegradation can be used effectively at complex waste sites. This section discusses the major issues requiring further study.

149

1. Alternate Injection/Extraction Systems

The groundwater circulation system used at Kelly AFB is only
one method of delivering nutrients and oxygen to the subsurface. Other
methods for reinjection of groundwater include forced injection wells
and infiltration galleries. There may also be opportunities for less
conventional methods such as surface ponding to provide water infiltra-
tion and treatment of contamination close to the ground surface. Small-
scale tests similar to that performed at Kelly AFB would be useful in
determining the applicability of these and other potential methods.

Through numerous tests and research, it should be possible to
develop an optimum groundwater circulation system for a given site. Such
a system would take full advantage of site characteristics and system
geometry to provide the most efficient means of providing nutrient and
peroxide distribution throughout the desired area.

2. Nutrient Selection

An optimum nutrient formulation will provide sufficient nutrients
to enhance growth of microorganisms without adversely affecting soil
permeability. The development of nutrient formulations will be highly
site-specific depending on soil chemistry and the microbes present at
the site. A number of different chemical formulations of nutrients
should be tested against various common soil types to develop guidelines
for nutrient selection under various site conditions.

It will still be necessary to perform site-specific tests with
nutrient formulations to develop the nutrient composition and flow
rate necessary to achieve optimal loading with minimal negative
impacts. In cases where sufficient nutrients may be present in the
soil, introduction of additional nutrients may not provide sufficient
benefit and should be avoided.

3. Use of Hydrogen Peroxide

The use of hydrogen peroxide as an oxygen source should be studied further at sites with mixed chemical wastes. Evidence at Kelly AFB suggested that, in addition to aerobic biodegredation, anaerobic biodegradation and chemical oxidation were also taking place. Tests should be performed to determine if, indeed, all three of these mechanisms are working in the presence of hydrogen peroxide and how to best control the introduction of hydrogen peroxide to provide optimal treatment of wastes degraded by all three mechanisms.

4. Metals Mobilization

The mechanism and chemical factors that control the mobilization and disposition of heavy metals during _in situ_ treatment need to be determined. Data from Kelly AFB indicated that fine particle transport, possibly facilitated by surfactants, may have been responsible for metals mobilization. Changes in Eh and pH also may have played a major role. In addition, the high concentrations of nutrients and hydrogen peroxide added may facilitate transport of the colloidal particles. Additional study is required to develop ways of controlling this mobilization to either leave the metals in place or remove them from the subsurface for treatment and disposal.

5. Precipitation and Clogging

The mechanisms controlling precipitate formation and soil clogging during _in situ_ treatment should be identified so that steps can be taken to avoid the problem at future applications. The precipitate identified at Kelly AFB was calcium phosphate resulting from chemical interactions with the soil. Other possible sources of clogging included biomass, air (oxygen) blocking due to hydrogen peroxide degradation, and mobilization and deposition of fine particles. Iron precipitation might have caused serious clogging problems if the flow rate through the system had been higher. Composition of soils, mineralogy, and soil pH should be

151

studied to determine the effects on precipitation both with and without
the use of nutrients and oxygen.

6. Carbon Dioxide Monitoring

The accuracy of using carbon dioxide measurements as an indica-
tion of biological degradation should be studied at future sites. It is
necessary to quantify the relationship between production of carbon
dioxide due to biological degradation, chemical degradation, and carbo-
nate equilibrium. If successful, carbon dioxide monitoring could be used
as an inexpensive means of quantifying biodegradation during the operation
of in situ treatment systems.

7. Soil Column Testing

It is recommended that column permeability tests using site-spe-
cific contaminated soils and groundwater be used to quantify how specific
sites will react to in situ treatment. At Kelly AFB, these tests, in
combination with laboratory microcosm treatability studies, showed the
same effects as observed in the field operation: significant permeability
reduction; mobilization of metals from the soil; reductions in TCE and
PCE levels, and an increase in DCE concentrations; a lag in phosphate
transport relative to chloride; and a lag in peroxide transport relative
to phosphate. In future applications of in situ treatment the data
previously obtained with microcosm tests could be obtained during column
testing. These studies would constitute engineering design data for
proposed field tests.

It is recommended that future studies be conducted in two
phases. The first phase would address the technical issue of identify-
ing nutrient and peroxide concentrations that maximize the rate of supply

152

(circulation rate x concentration) of each. The second phase, using optimum nutrient and peroxide concentrations would be for obtaining measurements of changes in the organic and metal concentrations in the column with time and changes within the column from a reducing to an oxidizing environment.

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