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Technology Evaluation Report:

**BIOLOGICAL TREATMENT OF WOOD PRESERVING
SITE GROUNDWATER BY BIOTROL, INC.**

**RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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NOTICE

The information in this document has been funded by the U.S. Environmental Protection Agency under the auspices of the Superfund Innovative Technology Evaluation (SITE) Program under Contract Nos. 68-03-3485 and 68-CO-0048 to Science Applications International Corporation. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

FOREWORD

The Superfund Innovative Technology Evaluation (SITE) program was authorized in the 1986 Superfund amendments. The program is a joint effort between EPA's Office of Research and Development and Office of Solid Waste and Emergency Response. The purpose of the program is to assist the development of hazardous waste treatment technologies necessary to implement new cleanup standards which require greater reliance on permanent remedies. This is accomplished through technology demonstrations designed to provide engineering and cost data on selected technologies.

This project consisted of a demonstration of BioTrol, Inc.'s fixed-film, amended biological treatment process and a careful and extensive analysis of the effectiveness of the system. The study was carried out at the MacGillis and Gibbs Company site in New Brighton, Minnesota, where wood preserving operations have been carried out over several decades using first creosote, later pentachlorophenol, and most recently, chromated copper arsenate. In 1984 the site was added to the National Priorities List as one where soil and groundwater were contaminated with hazardous chemicals. Documentation for the project consists of two reports. The field activities and analytical results of the study are summarized in this Technology Evaluation Report. The companion Applications Analysis Report analyzes the broader applicability and economics of the biological treatment process for the elimination of pentachlorophenol and polynuclear aromatic hydrocarbons from groundwater.

For further information, please contact the Superfund Technology Demonstration Division at the Risk Reduction Engineering Laboratory.

E. Timothy Oppelt, Director
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ABSTRACT

The BioTrol, Inc. Aqueous Treatment System (BATS), a fixed-film, aerobic biological treatment process for contaminated groundwaters and other wastewaters, was evaluated at three different throughput rates, each maintained for 2 weeks to provide steady-state conditions for both operation and sampling.

This report presents a detailed description of the process and the system and provides detailed results of the six weeks of monitoring at the MacGillis and Gibbs Company wood preserving site in New Brighton, MN. Technological effectiveness of the process is assessed on the basis of an extensive analytical program coupled with a quality assurance program. The economics of the process were also assessed.

From the results of the pilot scale demonstration study it is concluded that (a) the fixed film aerobic process is effective at degrading pentachlorophenol, achieving more than 96% removal; (b) effluent concentrations of pentachlorophenol well below 1 ppm are attainable by controlling throughput rate; (c) removal of PCP is largely by mineralization to carbon dioxide, water, and salt; (d) acute toxicity of the groundwater to minnows and water fleas is eliminated, and (e) operating cost is about \$3.45/1000 gal at 5 gpm and would decrease to \$2.43/1000 gal at 30 gpm.

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ABBREVIATIONS AND SYMBOLS

BATS	BioTrol Aqueous Treatment System
BGS	below ground surface
BOD	biochemical oxygen demand (mg oxygen/liter)
BTEX	benzene, toluene, ethyl benzene, and xylenes
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
cfm	cubic feet per minute
COD	chemical oxygen demand (mg oxygen/liter)
EMSL	Environmental Monitoring Systems Laboratory
GC/MS	gas chromatograph/mass spectrometer
gpd	gallons per day
gpm	gallons per minute
HPLC	high pressure liquid chromatography
HSWA	Hazardous and Solid Waste Amendments to RCRA - 1984
kwh	kilowatt-hour
LC(50)	Lethal concentration to 50% of a test species population
Mgd	million gallons per day
mg/L	milligrams per liter
ng/kg	nanograms per kilogram
ng/L	nanograms per liter
NPL	National Priorities List
O/G	oil and grease

ORD	Office of Research and Development
OSHA	Occupational Safety and Health Act/Administration
OSWER	Office of Solid Waste and Emergency Response
PAHs	polynuclear aromatic hydrocarbons
PCP	pentachlorophenol
PEL	Permissible Exposure Limit
POTW	publicly owned treatment works
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act of 1976
RI/FS	Remedial Investigation/Feasibility Study
RREL	Risk Reduction Engineering Laboratory
SARA	Superfund Amendments and Reauthorization Act of 1986
SITE	Superfund Innovative Technology Evaluation
TCPS	tetrachlorophenols
TOC	total organic carbon (mg carbon/liter)
TSS	total suspended solids (mg solids/liter)

CONVERSION FACTORS

	<u>English (US)</u>	x	<u>Factor</u>	=	<u>Metric</u>
Area:	1 ft ²	x	9.2903 x 10 ⁻²	=	m ²
	1 in ²	x	6.4516	=	cm ²
Flow Rate:	1 gal/min	x	6.3090 x 10 ⁻⁵	=	m ³ /s
	1 gal/min	x	6.3090 x 10 ⁻²	=	L/s
	1 Mgal/d	x	43.8126	=	L/s
	1 Mgal/d	x	3.7854 x 10 ³	=	m ³ /d
	1 Mgal/d	x	4.3813 x 10 ⁻²	=	m ³ /s
Length:	1 ft	x	0.3048	=	m
	1 in	x	2.54	=	cm
	1 yd	x	0.9144	=	m
Mass:	1 lb	x	4.5359 x 10 ²	=	g
	1 lb	x	0.4536	=	kg
Volume:	1 ft ³	x	28.3168	=	L
	1 ft ³	x	2.8317 x 10 ⁻²	=	m ³
	1 gal	x	3.7854	=	L
	1 gal	x	3.7854 x 10 ⁻³	=	m ³

ft = foot, ft² = square foot, ft³ = cubic foot

in = inch, in² = square inch

yd = yard

lb = pound

gal = gallon

gal/min (or gpm) = gallons per minute

Mgal/d (or MGD) = million gallons per day

m = meter, m² = square meter, m³ = cubic meter

cm = centimeter, cm² = square centimeter

L = liter

g = gram

kg = kilogram

m³/s = cubic meters per second

L/s = liters/sec

m³/d = cubic meters per day

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Finally, the project could not have been carried out without the tireless efforts of the many SAIC and Radian field and laboratory personnel.

SECTION 1

INTRODUCTION

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), EPA's Office of Solid Waste and Emergency Response (OSWER) and the Office of Research and Development (ORD) established the Superfund Innovative Technology Evaluation (SITE) Program. The goal of this program is to promote and accelerate the development of innovative technologies for consideration in the clean up of Superfund sites across the country.

The SITE Program seeks to meet new federal and state cleanup standards by providing permanent remedies to waste problems, rather than temporary measures. Such methods include destruction, stabilization, and treatment processes that will assure - to the maximum extent possible - that problems will not resurface in the future.

The SITE Program is composed of two major elements: the Demonstration Program and the Emerging Technologies Program. The focus of the Demonstration Program is to provide reliable engineering and cost data based on field tests of selected technologies. The Emerging Technologies Program fosters the investigation and development of technologies now at the laboratory scale. A third component of the SITE Program, the Measurement and Monitoring Technologies Program, assists in the development of innovative technologies to better characterize Superfund sites.

In this case, EPA was able to carry out two demonstration projects and the assessment of a measurement and monitoring methodology at one facility, thereby making maximum use of personnel and resources. Documented in this report are the sampling and analyses results used to evaluate the treatment of contaminated groundwater by a fixed film bioreactor. The other two research efforts, soil washing and an Immunoassay analytical technique for pentachlorophenol, are briefly noted and are documented in separate reports.

PROJECT OBJECTIVES

The major objectives of this SITE Demonstration Project were to:

1. Determine the capability of the BioTrol technology to remove pentachlorophenol (PCP) from groundwater at a wood treatment facility, where a range of other contaminants may be present;
2. Determine the effect of throughput rate (flow) on removal efficiency;
3. Determine the capability of the BioTrol process to remove polynuclear aromatic hydrocarbons from a wastewater contaminated by creosote; and
4. Determine the cost of the treatment and the factors that impact on the cost of the process.

DESCRIPTION OF PROJECT

Biological treatment has a long history of use for a wide variety of municipal and industrial wastewaters. Only recently has it become apparent that even organics thought to be highly resistant to biodegradation, such as the chlorinated phenols used to impart rot resistance to wood, could be degraded biologically under carefully selected conditions.

On the basis of fundamental research over the last several years, BioTrol, Inc. developed an innovative process to carry out such a biological degradation process compactly, efficiently, and economically. The process is carried out aerobically in stages on an inert support matrix. Local soil bacteria already able to resist and even degrade pentachlorophenol are supplemented or "amended" with an inoculum of a pentachlorophenol-specific bacterium to give maximum biodegradation in the first stage, where the concentration of the pentachlorophenol is highest. The staged arrangement of the technology then allows other constituents to be degraded in the latter stages of the reactor, after the "toxic" pentachlorophenol has been reduced.

For the demonstration project, three different throughput rates were examined over the course of about six weeks to evaluate the effect of flow rate on the efficiency of treatment, particularly in terms of pentachlorophenol removal. An extensive sampling and analysis program defined by an EPA Category II Quality Assurance Project Plan (QAPP) was an integral part of the project.

The site selected for the demonstration was a wood preserving facility in New Brighton, Minnesota. Earlier screening of the site as part of a Remedial Investigation/Feasibility Study indicated significant contamination of both soil and groundwater with pentachlorophenol and polynuclear aromatic hydrocarbons as the result of many years of operation with creosote, pentachlorophenol. Currently, chromated copper arsenate (CCA) is used and waste

management is consistent with current regulatory requirements. The site had been added to EPA's National Priorities List in 1984.

This report and the companion Applications Analysis Report document, analyze, and interpret the results of the SITE demonstration project.

PROJECT ORGANIZATION

Through a Cooperative Agreement between EPA and BioTrol, Inc., the developer was responsible for operating its equipment while EPA and its contractor, Science Applications International Corp. (SAIC), located and installed a suitable well to supply the groundwater for the project, prepared the demonstration plan, designed the sampling plan, conducted sampling and analysis, evaluated the data, and prepared the final reports. In addition, EPA's contractor was responsible for pre-demonstration sampling of the groundwater, for managing public information meetings, and for site decontamination.

SECTION 2

PROCESS DESCRIPTION

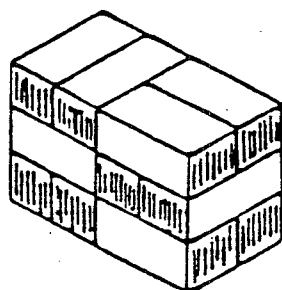
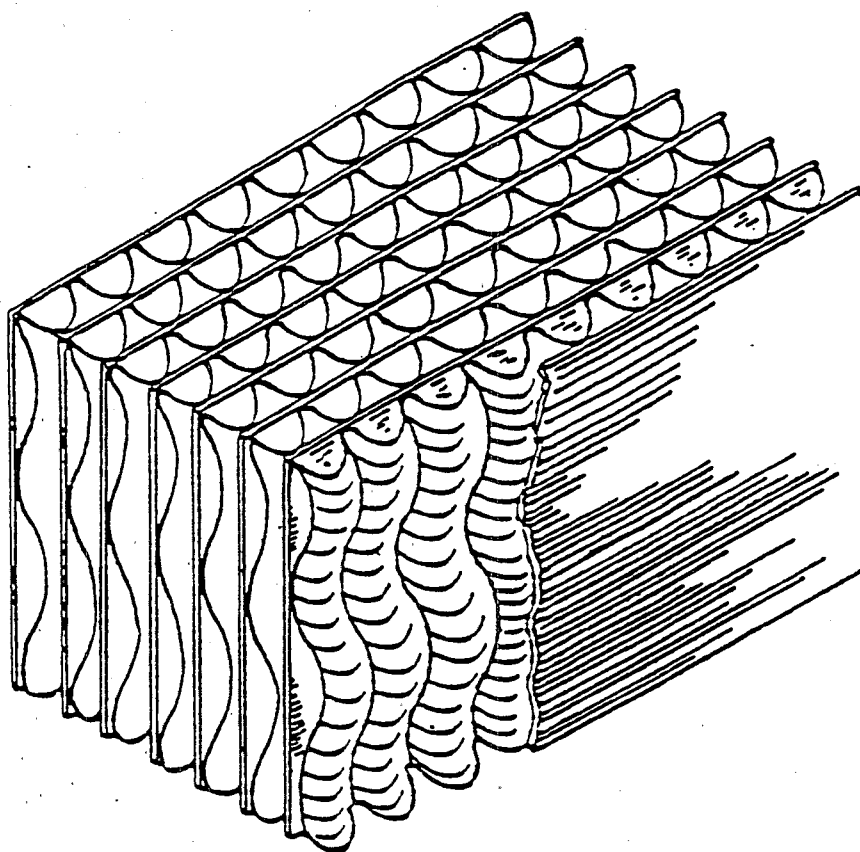
INTRODUCTION

Biological processes have been widely used for many years in the treatment of industrial and municipal wastewaters, with aerobic treatment being the most widely used technology. As industrial products have been developed to provide resistance to degradation by the environment, it has often been assumed that these chemicals also would be resistant to conventional biodegradation. It has now been recognized that such is not the case and, using proper procedures and suitable biological populations, efficient biodegradation of many organic chemicals, including chlorinated aromatics such as pentachlorophenol, can be achieved.

To provide the most efficient and cost effective treatment of wastewaters containing such contaminants, BioTrol, Inc. has developed a proprietary process based on amended fixed-film aerobic treatment. Using a multi-stage reactor, an initial biogrowth is developed on an inert support matrix such as corrugated polyvinyl chloride sheets (Figure 1) using indigenous bacteria from a source such as soil at the site. This bacterial population, having been derived from the local soil, is resistant to the toxicity of the local contaminants and may even have a population distribution which favors the destruction of chemicals from the site. After this bacterial source has been allowed to acclimate on the matrix in the presence of nutrients, an inoculum of a Flavobacterium specific to the target chemical, pentachlorophenol, is added. Further acclimation then is allowed to occur in a total recycle mode before the system is ready for once-through treatment of the groundwater.

The design of the BioTrol system allows the development of the largest concentration or population of bacteria capable of degrading pentachlorophenol in the first chamber, where the concentration is highest. As the wastewater flows through the reactor and the pentachlorophenol concentration decreases, other bacteria more suitable to degradation of other contaminants, but perhaps more sensitive to deactivation by pentachlorophenol, have the opportunity to grow and consume those contaminants.

The BATS fixed-film process has a further advantage in that very little sludge is generated and, consequently, sludge management is not a significant factor in operation.



BLOCKS
CROSS-STACKED

FIGURE 1. CORRUGATED POLYVINYL CHLORIDE MEDIA

BioTrol Soil Washing Process

In addition to the BioTrol Aqueous Treatment System (BATS), BioTrol, Inc. also has developed a soil washing process that separates coarser, relatively uncontaminated soil from more heavily contaminated fine material such as clay. PCP contamination of the fines then can be treated by other methods such as biological degradation in a slurry bioreactor. The relatively clean washed soil and even the slurry reactor-treated fines may then be returned to the site. The BATS which is the subject of this report also is employed in the soil washing sequence to treat the washwater used to separate the sand and fine materials. The Soil Washing process is the subject of a separate SITE Demonstration Program at the MacGillis and Gibbs facility and is reported separately.

Field Immunoassay for Pentachlorophenol

While this project was being developed, EPA's Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas was searching for a facility where a new immunoassay method for field monitoring pentachlorophenol in wastewaters could be studied under real-world conditions. The groundwater study at the MacGillis and Gibbs facility offered an ideal environment to evaluate this technique in parallel with the extensive analyses being done as part of the demonstration. Consequently, arrangements were made to have EPA's contractor carry out the field test as part of their assignment.

The immunoassay test, developed by Westinghouse, is based on the inhibition of bacterial enzyme activity when a target chemical, in this case pentachlorophenol, is present. The inhibition is observed by a color change in a reagent matrix and is readily quantified using standards. Only very small samples of material are needed and the results are generated in about an hour. Field experience was needed to learn how well results correlated with the standard GC/MS analysis and larger, laboratory-scale immunoassays; how sensitive the test was with real-world wastewater matrices, and how conveniently and reliably it could be carried out in the field by relatively inexperienced personnel.

Reference is included to make the reader aware of this effort and the potential availability of the method. A report documenting the procedure and results of this study will be available separately.

PROCESS DESCRIPTION

The BioTrol equipment used in this demonstration consists of a single mobile trailer (20 ft. in length) fitted with all the necessary tanks, pumps, etc. (Figure 2). A level area (ideally a concrete apron) about 50 x 50 ft is needed to support the trailer and auxiliary facilities. The capacity of the mobile system is about 5 gpm, depending on the concentration of the pollutants to be

degraded, and its hydraulic capacity is about 10 gpm. Contaminated water is brought to the 100 gallon mixing or conditioning tank where pH is automatically adjusted to slightly above 7.0 by metering in a caustic solution. A solution of nitrogen and phosphorus nutrients (urea plus trisodium phosphate) is also metered into the conditioning tank at a pre-determined rate. For this study a mixture of 2.5 lbs of urea and 5.0 lbs of trisodium phosphate in 50 gal of water was metered in at a rate of 2.5 ml/gal of wastewater. The mixed water passes through a heat exchanger and then a heater which is available to elevate the temperature to about 70°F (21°C), which is considered an optimal temperature for biological treatment.

The influent is then introduced into the base of the first of the 3-celled biological reactor (Figure 3) and moves from cell to cell by means of underflow weirs. In the pilot unit each cell, containing the PVC matrix, has approximately 160 gallon capacity, giving a total system capacity of about 500 gallons. Thus, at 5 gpm the retention time is approximately 1.7 hours; at 3 gpm the retention time would be 2.7 hours and at 1 gpm the retention time would be 8.3 hours. Air is continuously injected to the base of each chamber and distributed by a network of sparger tubes to maintain sufficient dissolved oxygen (DO) to support aerobic conditions for biodegradation (about 5 ppm). The combination of the flow, the air sparging, and the design of the plastic media are such that upward and lateral distribution of the water and the air occur in each chamber. After moving through the three chambers, the effluent exits from the third chamber via an overflow weir.

While the process is claimed to be relatively insensitive to suspended solids and dispersed oil and the mobile trailer is not equipped to remove these contaminants, oil/water separation or solids removal could be added externally if necessary, depending on the quality of the wastewater being treated. Such pretreatment was deemed unnecessary with the MacGillis and Gibbs groundwater.

Similarly, while BioTrol's experience has been that post-treatment such as suspended solids removal or carbon polishing are not usually necessary, EPA made the decision that a small bag filter and a carbon adsorber would be added to the effluent line to assure that the discharge to the Minneapolis Metropolitan POTW would be of high quality. The bag filter was installed in the effluent line leaving the bioreactor and was followed by a 50 cubic foot carbon adsorber (Figure 4). EPA also chose to install a smaller carbon adsorber on the air exhaust line exiting from the bioreactor to assure that no hazardous volatile chemicals were emitted. During the course of the demonstration, analyses were carried out before and after both carbon adsorbers to assess the need for such protective devices.

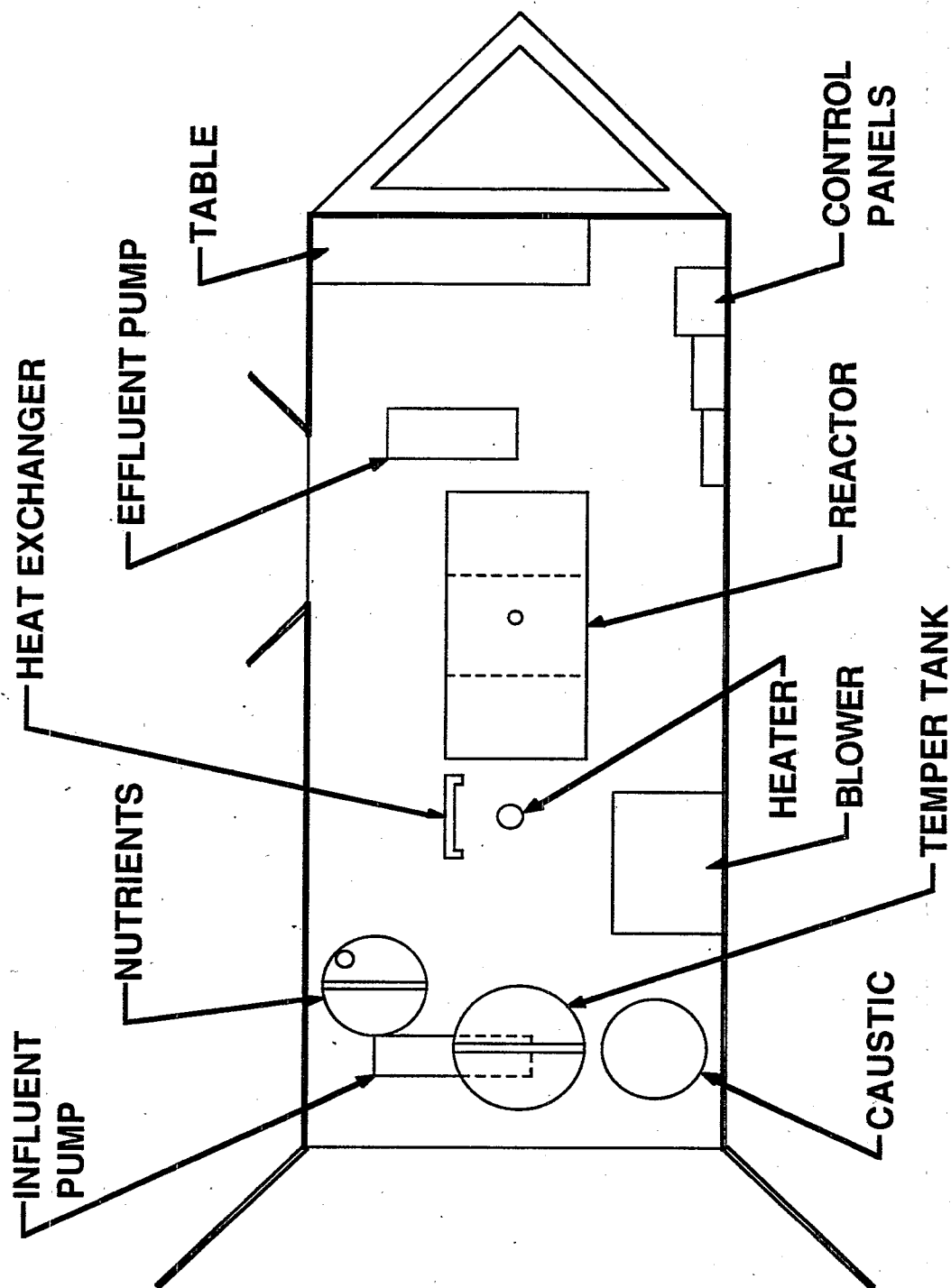


FIGURE 2. BIOTROL, INC. MOBILE AQUEOUS TREATMENT SYSTEM (ATS).

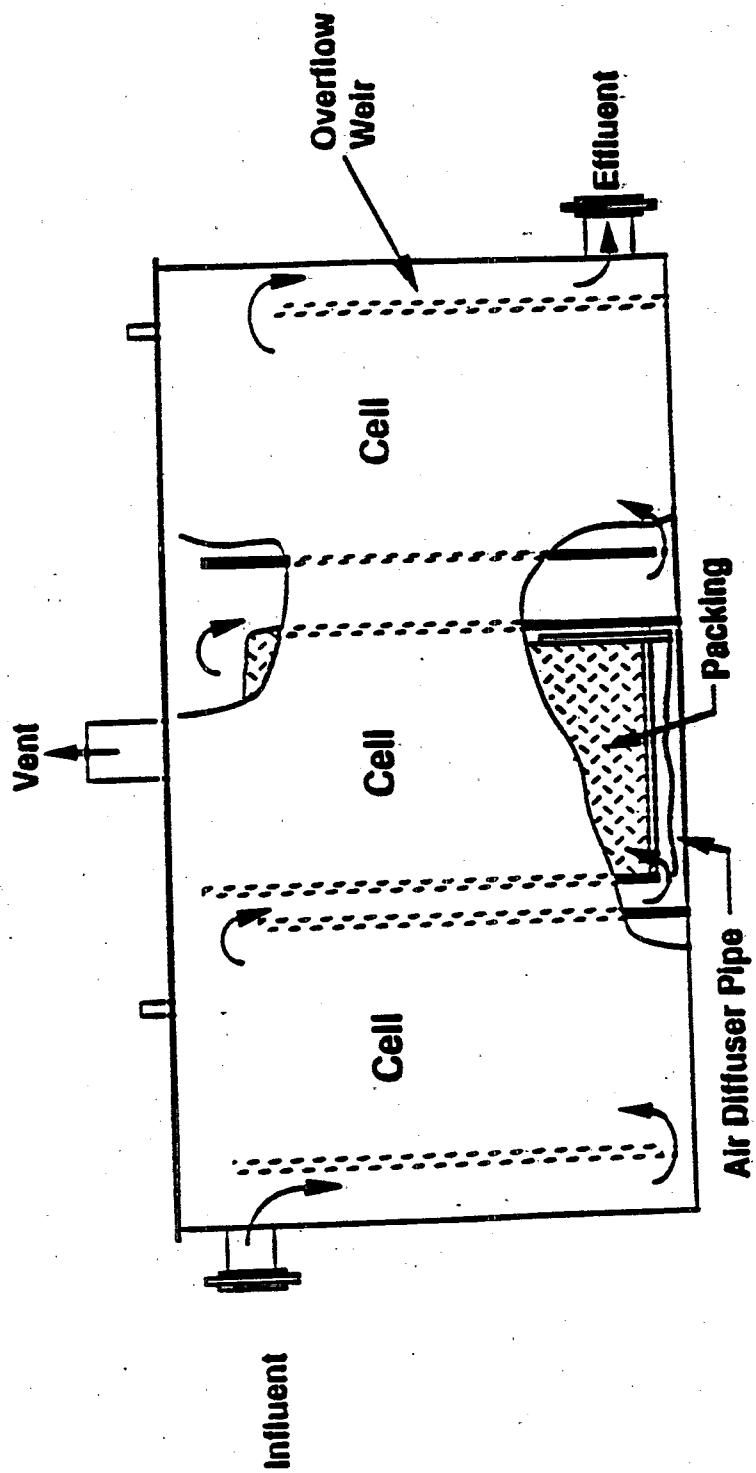


Figure 3. BATS Reactor

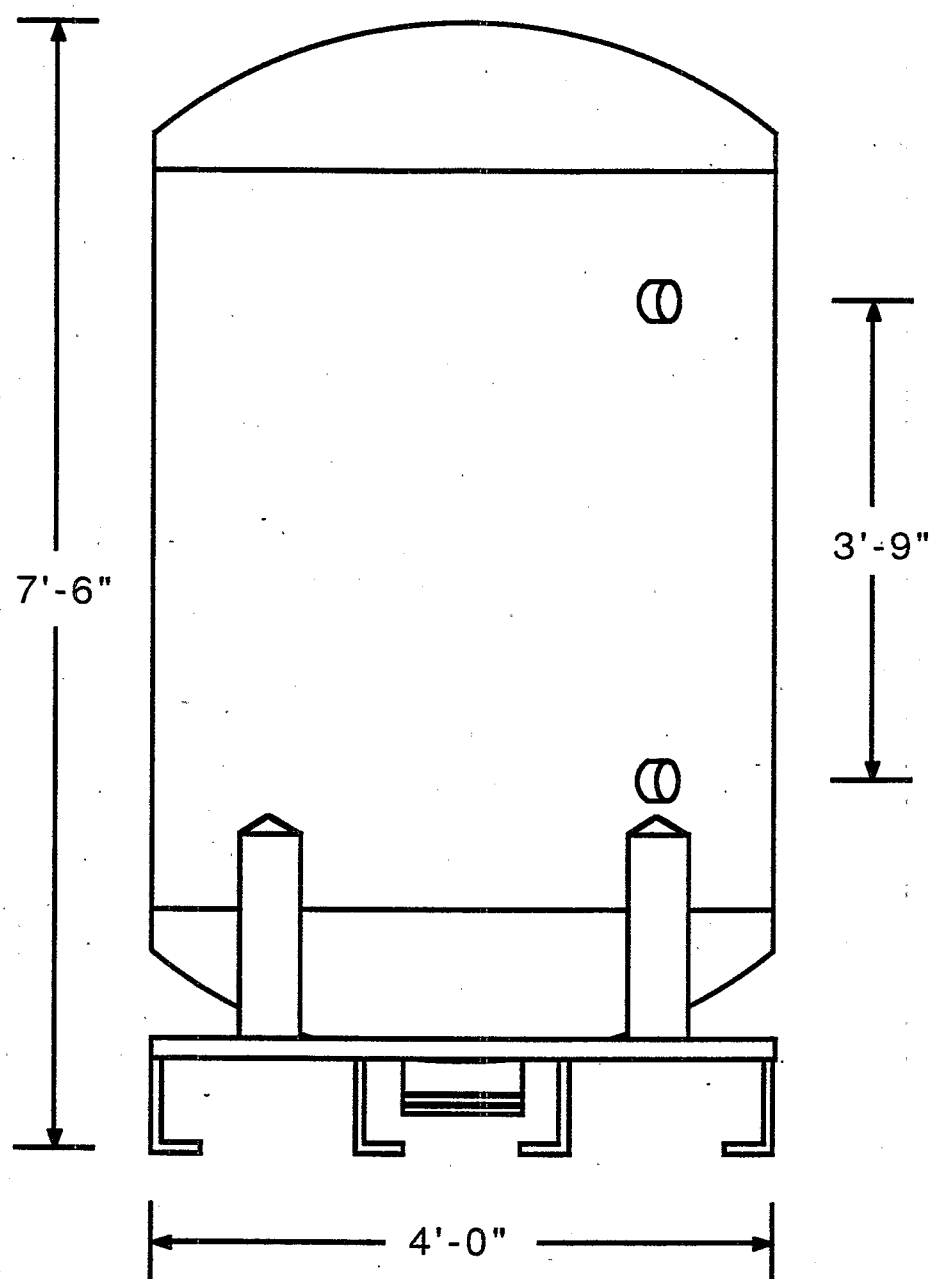


FIGURE 4. CARBON ADSORBER

SITE CHARACTERISTICS

In the demonstration program the mobile pilot scale system required only a level base (ideally a concrete pad); potable water and power for pumps, the heater, lighting, etc. were supplied by the facility operator. If necessary at other sites, potable water could be trucked in and power could be provided by an on-site generator.

The MacGillis and Gibbs Company facility has been used for wood preserving for several decades. Originally creosote was used in the treatment; subsequently, in the 1950's, pentachlorophenol in oil was substituted. Operations were carried out in open troughs, presenting many opportunities for spills and leaks. Treated lumber was stored on the site where further contamination could occur as the result of rain wash-off. In addition, for a period in the 50's, waste pentachlorophenol solution was used for weed control on the site. As shown in Figure 5, the southwestern section of the MacGillis and Gibbs property where disposal has frequently taken place also collects water and forms a pond. There has been suspicion that some of the contamination in this area may be due to run-off from the adjacent Bell Pole property. In the 1970's, MacGillis and Gibbs replaced pentachlorophenol with the chromated copper arsenate process and substituted closed reactors for the open troughs, thus minimizing the opportunities for inadvertent spills and leaks.

The facility originally came to the attention of the EPA as part of an investigation of the neighboring Bell Pole facility where wood treatment was also being carried out. Ultimately, as the result of an RI/FS, it was concluded that the soil and groundwater at both sites was contaminated with pentachlorophenol and lesser concentrations of polynuclear aromatic hydrocarbons. Both sites were placed on EPA's National Priorities List in 1984.

MacGillis and Gibbs has a discharge permit for discharge of its sanitary wastewater to the Minneapolis/St. Paul Treatment Works. An agreement was reached for the POTW to accept treated effluent from the bioreactor on the condition that it contained <2 ppm of PCP.

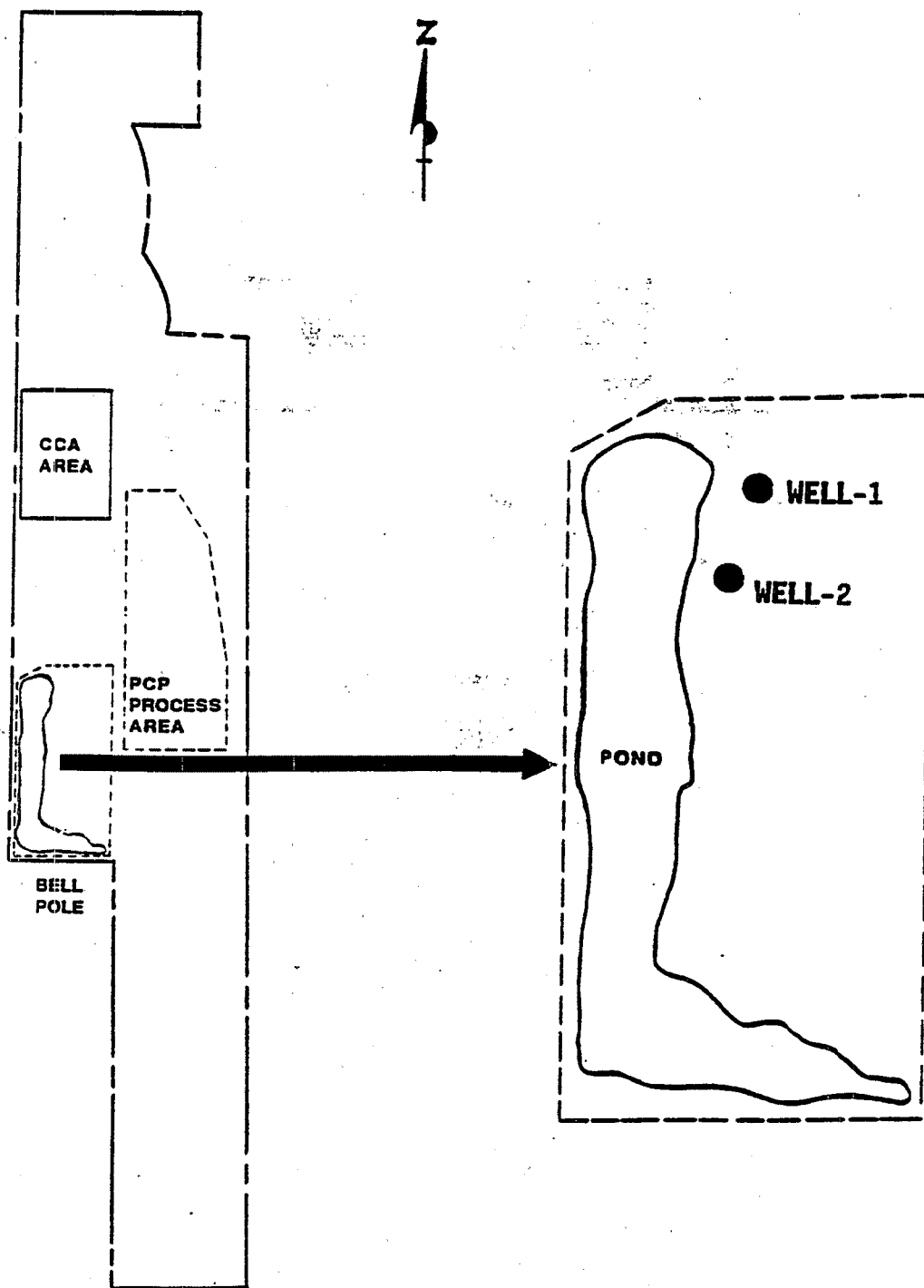


FIGURE 5. MACGILLIS & GIBBS SITE

SECTION 3 FIELD OPERATIONS

PREDEMONSTRATION WELL DRILLING

Before the demonstration project could be initiated or a decision reached as to whether this facility was appropriate for evaluation of the process, it was necessary to establish whether a suitable groundwater was available. Criteria established by the developer were (a) up to 100 ppm of pentachlorophenol; (b) flowrate of at least 5 gpm, and (c) some concentration of polynuclear aromatic hydrocarbons.

Reports by Twin Cities Testing Corp., a Remedial Investigation (RI) contractor, documented soil borings at the site which strongly suggested that suitable groundwater was present in the vicinity of the disposal area and pond in the southwestern portion of the site. Several of these borings had been found to contain very high levels of PCP and PAHs, but some had also indicated high concentrations of oil. Based on these reports, a 4-inch well (#1) was drilled by a contractor in what appeared to be an attractive area, as shown in Figure 5. The well was drilled to a depth of 45 ft. and screened from approximately 30 ft to 45 ft. Samples were taken at 5 foot intervals as the well was drilled and rapidly analyzed (24-hour turnaround) using BioTrol's High Pressure Liquid Chromatography (HPLC) method so that the operation could be terminated if the well proved to be unsuitable in PCP analysis.

The results of the initial analyses (Table 1) showed considerably less PCP than anticipated; while not quantified, PAH concentrations also appeared to be quite low.

TABLE 1. PCP CONCENTRATIONS IN WELL #1 BOREHOLE

depth (ft)	PCP conc. (ppm)
10	12.1
15	19.6
20	18.
25	13.4
30	29.2
35	31.4
40	45.7

Based on these initial results, and to minimize the risks associated with relying on a single well for the demonstration project, a second well was then drilled approximately 65 feet north of Well #1, in an area where pentachlorophenol contamination also was expected to be high. Starting at about 10 feet, considerable contamination with an oil-like material was observed in this well and groundwater was not detected in the borehole even down to 20 feet. A static water level of 11 feet below ground surface (BGS) was observed after operations had been left for the weekend and a floating liquid layer was also clearly evident. Drilling was continued to a depth of 46 feet where clay-like material was encountered. Evidence of oil was observed at several different depths.

Two groundwater samples were analyzed from Well #2, believed to be representative of 15 ft BGS and 45 ft BGS. Pentachlorophenol concentrations at these depths were 97.8 and 5.7 ppm, respectively; only traces of PAHs were detected in the 45 ft sample.

Each well was then developed using a surge block and submersible pump, continuing the pumping until the water was turbidity-free and field measurements of pH, temperature, and conductivity had stabilized to within 10%. A sample of Well #1 was then taken using a Teflon bailer and submitted for extensive analyses. The results of those analyses are shown in Table 2.

TABLE 2. ANALYSES OF WELL #1 GROUNDWATER AFTER DEVELOPMENT

Constituent	Concentration	Units

Volatile Organics		
methylene chloride	5*, 5*	ppb
toluene	6, 5*	ppb
Semivolatile Organics		
pentachlorophenol	15, 13	ppm
2-methyl phenol	20, 23	ppb
4-methyl phenol	20, 24	ppb
2,4-dimethyl phenol	32, 33	ppb
naphthalene	86, 90	ppb
2-methyl naphthalene	50, 52	ppb
Metals		
lead	8	ppb
zinc	280	ppb
Total Phenolics	0.859, 0.706	ppm
TOC	51	ppm
Oil/Grease	14, 10	ppm
Chloride	23, 30#	ppm
Dioxins	All <detection limits	

* Below detection limit

Two different methods used

Development of the wells was followed by a three-day (69 hour) pump test of Well #1 to establish flow rate and allow for additional PCP monitoring. During the test approximately 17,500 gallons of water were pumped to storage tanks, equating to a flow rate of about 4.3 gpm. Samples were taken approximately every 10 hours from a tap in the line leading from the well to the storage tanks and analyzed by BioTrcl (Table 3), using the HPLC method for PCP. It should be noted that samples taken from both wells after development, but before Well #1 was pump-tested, were found to contain only 11.2 ppm (Well #1) and 8.1 ppm (Well #2) PCP using EPA Method 8270.

TABLE 3. ANALYTICAL RESULTS ON GROUNDWATER DURING PUMP TEST

Test duration hours	PCP Conc.* (ppm)	PAH conc. (ppb)

0.3	46.8	--
13	45	--
25	45.8	--
34	46	145
47	45.8	--
57	46	--
69	46.2	295

* by HPLC

Slug tests were also carried out on both wells using a Hermit data logger to provide additional flow rate data. Analysis of the data indicated flow rates of 28 gpm and 3 gpm for Well #1 and Well #2, respectively.

On the basis of the foregoing data, a decision was made to proceed with the demonstration project using the groundwater from Well #1 as the feed water to the BioTrol system. The well was cased and protected as shown in Figure 6.

FIELD OPERATIONS

Once the well had been selected and constructed, a 1 inch PVC line running some 800 feet to the pilot BATS unit was installed. The line was buried where it traversed railroad tracks and a road to avoid accidental rupture and interruption of operations. A submersible pump was used to withdraw the groundwater.

In anticipation of start-up, BioTrol personnel acclimated the bioreactor to the groundwater contaminants, first with closed loop recycle of the water from the well development and pump test, which had been stored in tanks adjacent to the reactor trailer. Acclimation consisted of introducing air, nutrients, and a slurry of soil from the site to supply indigenous bacteria. After about one week of closed loop operation with this water source, the flavobacterium specific to pentachlorophenol was introduced to the conditioning tank and acclimation was continued. Delays in start-up of the demonstration phase of the program made it necessary for BioTrol to continue operation for several weeks, ultimately using the groundwater directly from the well. In effect, this placed the system in steady state operation even before the demonstration was initiated.

A separate trailer was brought on-site for contractor personnel to use in preparing samples and related documentation (and in which to carry out the immunoassay tests for EPA-EMSL/Las Vegas). Composite samplers were installed adjacent to the reactor trailer to collect 22-hour samples from the influent, each cell of the bioreactor, and the effluent. Procedures were reviewed to assure that all sampling could be carried out as planned. The bag filter and the carbon adsorbers for the effluent and for the combined exhaust from the cover over the bioreactor were connected.

On July 24, 1989 the project was officially initiated at an initial flow rate of 1 gpm. Nutrient solution was continuously added to the conditioning tank and pH was adjusted to about 7.3 by the addition of 50% caustic solution. Some problems were initially encountered due to foaming in the bioreactor, but this soon subsided. Both composite and grab samples were collected as scheduled over the course of two weeks of operation at this flow

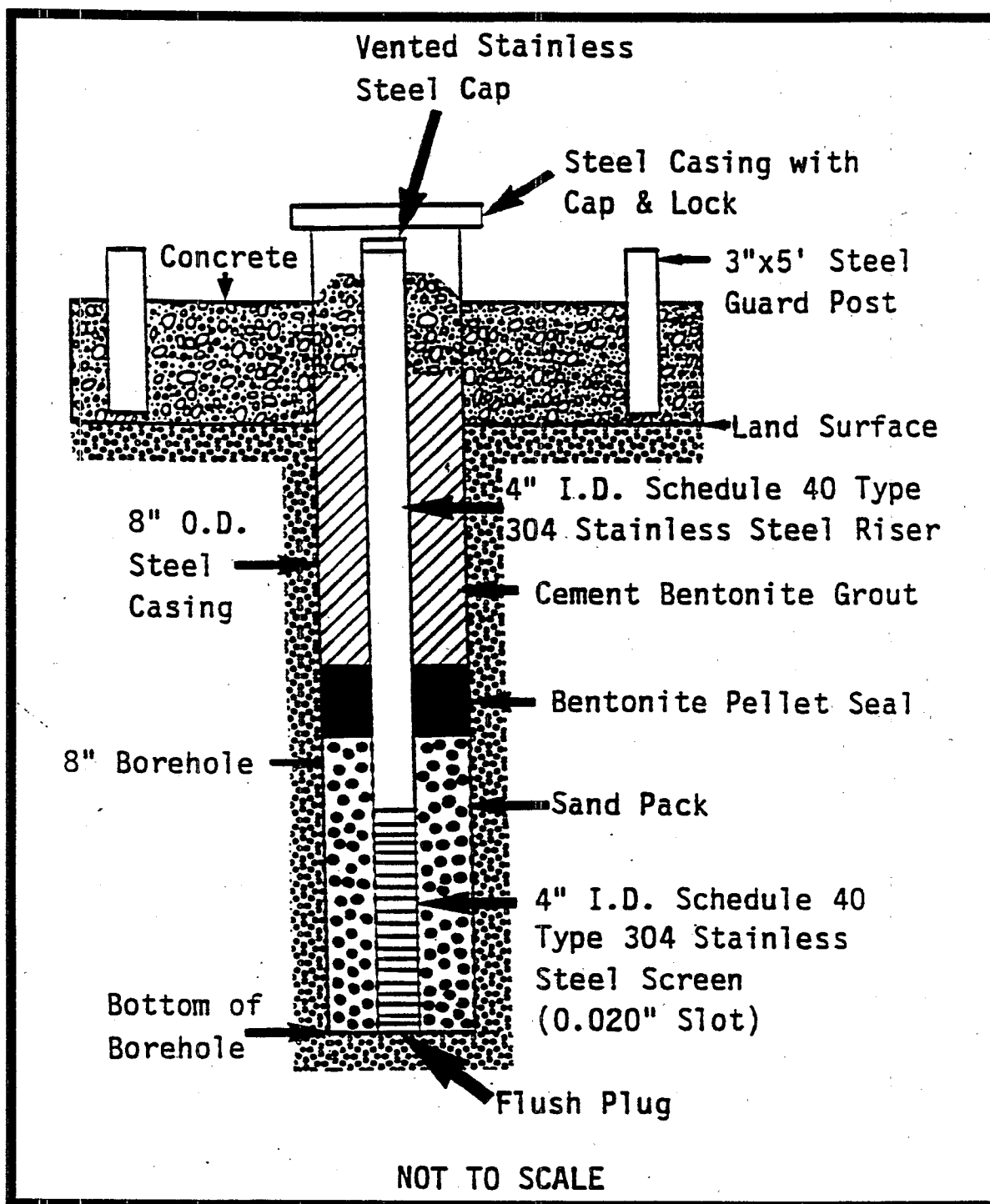


FIGURE 6. WELL CONSTRUCTION

rate. System parameters (temperature, pH, dissolved oxygen, and flow rate) were measured to assure that the system was operating within planned parameters. The summary of the system data for the entire project is presented in Table 4.

After two weeks of operation at 1 gpm, the flow rate was increased to 3 gpm on August 6, 1989 by changing the discharge pump rate. One 24-hour period was allowed for equilibration and return to steady state before sampling was restarted. Operation was again continued for two weeks, to August 19, 1989.

On August 20, 1989, flow was again increased, to 5 gpm, and sample collection resumed after one day of equilibration.

On September 1, 1989, the demonstration phase was completed. Because of the long delay in receiving analytical results for key parameters, it was not feasible to review data as a means of deciding whether any segment of the project needed to be repeated.

Because the demonstration project took place during the summer months, it was unnecessary to use the heater in the system.

[Originally, plans for the project had called for "spiking" of the groundwater with a much higher concentration of PCP to determine the impact of such shock loading. However, all parties agreed that (a) such shock loading was not reasonable to expect from a groundwater, and (b) dilution of such a spiked feedwater with effluent or potable water would be a viable means of preventing shock loading. In addition, plans called for the unit to be used in the immediate future for treatment of wastewaters from the soil washing study. If successful, the shock loading experiment would have deactivated the biological growth and necessitated re-acclimation. Since this was not desirable, the spiking segment of the study was not undertaken.]

Normally, the system would have been decommissioned after completion of the demonstration project; however, plans called for the unit to be used for treating process waters from the soil washing demonstration. It was left in a "stand-by" mode, operating at a low flow rate on groundwater, until the second project was operational. When that project was completed, the BATS was drained, electrical and water hook-ups disconnected, and the PVC matrix removed and discarded. Wastes that were collected during the project included sludge, analytical wastes such as cleaning solvents, and contaminated protective gear. Liquids and solids were stored, segregated, in 55 gal drums for off-site disposal as hazardous wastes. The carbon from both adsorbers was removed to be thermally regenerated.

TABLE 4. SYSTEM FIELD MEASUREMENTS
pH

DAY OF RUN	SAMPLE NUMBER	PROCESS FLOW (MGD)	pH (s.u.)							
			SAMPLING POINT							
			#02 INFLUENT		#03 MID POINT 1		#04 MID POINT 2		#05 EFFLUENT	
			FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB
1	ST1-A-01	0.75	7.4	7.9	8.4	8.5	8.4	8.3	8.3	8.4
2	ST1-A-02	0.95	7.6	7.6	8.3	8.5	8.3	8.4	8.2	8.4
3	ST1-A-03	1.25	7.6	7.6	8.0	8.3	8.3	8.3	8.4	8.2
4	ST1-A-04	NA	7.6	7.6	8.3	8.4	8.3	8.4	8.3	8.4
5	ST1-A-05	NA	7.6	6.9	8.4	8.3	8.3	8.2	8.4	8.3
6	ST1-A-06	0.97	6.9	7.9	8.0	8.1	8.0	8.1	8.0	8.2
7	ST1-A-07	0.92	7.9	7.7	8.2	8.1	8.4	8.2	8.1	8.3
8	ST1-A-08	0.96	7.4	7.6	8.0	8.0	8.0	8.2	8.1	8.4
9	ST1-A-09	0.88	7.7	7.9	8.0	8.2	8.1	8.3	8.3	8.4
10	ST1-A-10	0.87	7.3	7.5	8.2	8.2	8.3	8.4	8.4	8.4
11	ST1-A-11	1.1	7.8	7.4	8.0	8.2	8.2	8.4	8.3	8.4
12	ST1-A-12	1.24	7.3	7.5	7.8	7.8	8.5	8.1	8.3	8.2
1	ST1-B-01	2.74	8.3	7.1	7.8	8.5	8.0	7.8	8.1	8.1
2	ST1-B-02	2.98	7.0	7.9	7.5	7.7	7.7	7.9	7.9	7.9
3	ST1-B-03	2.71	7.8	8.2	7.9	7.8	7.8	7.8	7.8	8.0
4	ST1-B-04	3.15	7.4	7.3	7.8	7.7	7.7	7.9	7.9	8.0
5	ST1-B-05	3.04	8.0	7.9	7.7	7.7	7.8	8.0	7.9	7.9
6	ST1-B-06	2.88	7.4	7.6	7.8	7.8	7.9	7.9	7.9	8.0
7	ST1-B-07	2.97	7.7	8.0	7.8	7.9	7.9	7.9	7.9	7.9
8	ST1-B-08	3.04	8.0	8.7	8.0	7.7	8.0	7.8	8.1	7.8
9	ST1-B-09	3.04	8.4	7.1	7.8	7.6	7.9	7.6	7.9	7.6
10	ST1-B-10	2.81	8.3	8.7	7.7	7.8	7.8	7.8	7.8	7.9
11	ST1-B-11	2.99	7.7	7.6	7.7	7.8	7.8	7.8	7.9	7.8
12	ST1-B-12	3.24	7.3	8.7	7.7	7.9	7.7	7.9	7.9	8.0
1	ST1-C-01	NA	7.1	NA	7.5	NA	7.5	NA	7.6	NA
2	ST1-C-02	NA	7.5	7.2	7.6	7.8	7.9	7.8	7.7	7.7
3	ST1-C-03	4.96	7.6	7.5	7.7	7.6	7.7	7.7	7.7	7.8
4	ST1-C-04	5.24	7.3	8.0	7.6	7.9	7.6	7.8	7.7	8.0
5	ST1-C-05	5.17	8.0	7.5	7.7	7.7	7.7	7.7	7.7	7.8
6	ST1-C-06	5.21	7.4	7.1	7.8	7.2	7.8	7.2	7.7	7.3
7	ST1-C-07	5.05	7.5	7.0	7.8	7.4	7.5	7.4	8.0	7.4
8	ST1-C-08	5.04	7.0	6.9	7.2	7.3	7.1	7.3	7.4	7.5
9	ST1-C-09	5.21	7.1	6.8	7.0	7.2	7.0	7.2	7.2	7.2
10	ST1-C-10	4.84	7.3	7.7	7.8	7.7	7.7	7.7	7.3	7.7
11	ST1-C-11	4.97	7.3	7.4	7.7	7.7	7.7	7.7	7.7	7.8
12	ST1-C-12	5.06	7.3	7.1	7.7	7.7	7.8	7.7	7.8	7.8

TABLE 4. SYSTEM OPERATING PARAMETERS (cont'd)
Dissolved Oxygen

DAY OF RUN	SAMPLE NUMBER	PROCESS FLOW (MGD)	Dissolved Oxygen (mg/l)							
			SAMPLING POINT							
			#02 INFLUENT		#03 MID POINT 1		#04 MID POINT 2		#05 EFFLUENT	
			FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB
1	ST1-A-01	0.75	9.7	3.8	9.6	3.5	9.6	3.6	9.8	3.5
2	ST1-A-02	0.95	3.8	4.3	3.5	4.4	3.5	4.4	3.2	4.7
3	ST1-A-03	1.25	3.7	NA	3.6	NA	3.3	NA	3.8	NA
4	ST1-A-04	NA	NA	NA	5.2	NA	5.86	NA	5.28	NA
5	ST1-A-05	NA	6.56	NA	6.7	NA	6.64	NA	7.3	NA
6	ST1-A-06	0.97	5.8	NA	6.48	NA	6.62	NA	0.42	NA
7	ST1-A-07	0.92	6.12	4.82	6.85	5.93	7.17	8.16	6.79	6.17
8	ST1-A-08	0.96	6.7	7.7	8.7	6.5	8.7	7.4	8.1	7.7
9	ST1-A-09	0.88	3.6	5.64	5.9	6.11	5.6	6.52	7.1	6.37
10	ST1-A-10	0.87	5.4	4.12	6.2	6.88	6.03	5.92	6.5	5.86
11	ST1-A-11	1.1	4.73	5.04	5.15	5.76	5.75	5.99	5.96	5.89
12	ST1-A-12	1.24	4.15	5.48	5.58	6.14	5.75	6.63	5.42	6.21
1	ST1-B-01	2.74	7.4	3.26	6.85	6.83	7.63	6.03	7.26	6.8
2	ST1-B-02	2.98	3.8	4.24	6.37	6.45	5.5	6.58	4.75	6.1
3	ST1-B-03	2.71	4.24	3.82	5.87	6.08	5.92	6.58	4.85	5.34
4	ST1-B-04	3.15	5.3	4.65	6.56	6.48	6.54	6.52	6.35	4.95
5	ST1-B-05	3.04	3.62	4.23	6.22	5.78	6.11	6.42	5.72	4.74
6	ST1-B-06	2.88	5.17	4.77	6.84	5.92	6.49	6.43	6.6	6.33
7	ST1-B-07	2.97	6.16	5.45	5.94	5.81	6.11	5.85	5.81	6.23
8	ST1-B-08	3.04	5.23	6.8	6.07	5.06	6.56	6.23	6.02	6.06
9	ST1-B-09	3.04	6.11	5.26	3.22	4.96	5.93	5.75	5.67	5.26
10	ST1-B-10	2.81	5.32	5.32	4.86	5.51	5.22	5.24	2.0	5.51
11	ST1-B-11	2.99	4.09	5.81	5.6	5.52	6.04	5.31	4.88	5.62
12	ST1-B-12	3.24	4.85	6.4	5.27	4.37	5.5	5.07	5.81	5.24
1	ST1-C-01	NA	6.46	NA	5.95	NA	6.1	NA	5.83	NA
2	ST1-C-02	NA	5.54	5.85	5.8	5.92	5.57	6.1	5.92	5.62
3	ST1-C-03	4.96	5.8	5.12	5.68	5.17	5.81	5.31	5.06	5.79
4	ST1-C-04	5.24	4.35	6.4	5.65	5.35	5.3	5.2	5.65	6.41
5	ST1-C-05	5.17	5.92	5.96	5.54	4.9	5.49	4.62	5.92	5.8
6	ST1-C-06	5.21	3.94	6.31	4.53	5.76	4.44	5.74	3.61	6.19
7	ST1-C-07	5.05	5.84	6.03	5.6	6.21	6.29	5.39	5.88	6.11
8	ST1-C-08	5.04	5.05	5.16	5.9	5.81	5.52	5.47	5.96	6.32
9	ST1-C-09	5.21	5.23	4.95	5.31	6.0	5.07	5.38	5.64	6.1
10	ST1-C-10	4.84	5.49	5.33	5.75	5.77	5.1	5.12	5.89	6.13
11	ST1-C-11	4.97	6.03	5.77	5.97	6.17	5.47	5.04	6.03	6.31
12	ST1-C-12	5.06	6.41	5.33	6.56	6.57	6.16	5.78	6.2	5.58

TABLE 4. SYSTEM FIELD MEASUREMENTS (cont'd)
Temperature

DAY OF RUN	SAMPLE NUMBER	PROCESS FLOW (MGD)	Temperature (oF)							
			SAMPLING POINT							
			#02 INFLUENT		#03 MID POINT 1		#04 MID POINT 2		#05 EFFLUENT	
			FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB	FIRST GRAB	SECOND GRAB
1	ST1-A-01	0.75	23	22	23	24	24	24	24	24
2	ST1-A-02	0.95	30	25	29	26	29	27	31	27
3	ST1-A-03	1.25	28	26	28	26	28	26	29	27
4	ST1-A-04	NA	26	27	26	27	26	27	27	27
5	ST1-A-05	NA	29	20	27	25	27	25	27	23
6	ST1-A-06	0.97	21	17	25	20	25	20	25	21
7	ST1-A-07	0.92	23	18	21	21	20	20	21	20
8	ST1-A-08	0.96	23	23	23	21	23	22	23	22
9	ST1-A-09	0.88	25	21	24	24	24	24	25	24
10	ST1-A-10	0.87	27	22	25	24	25	25	24	23
11	ST1-A-11	1.1	25	22	25	25	25	24	26	25
12	ST1-A-12	1.24	20	17	27	23	26	23	27	24
1	ST1-B-01	2.74	14	12	19	18	19	19	19	20
2	ST1-B-02	2.98	17	15	19	20	19	21	19	19
3	ST1-B-03	2.71	20	16	22	20	21.5	19	24	19
4	ST1-B-04	3.15	20	14	19	19	19	20	21	20
5	ST1-B-05	3.04	20	16	20	19.5	22	19.5	22	20
6	ST1-B-06	2.88	19.5	18	20	19	20	19	23	19
7	ST1-B-07	2.97	17	13	20	19	19	19	21	19.5
8	ST1-B-08	3.04	16	12	19	19	19	19	19	19
9	ST1-B-09	3.04	13	11	18	23	18	22	20	23
10	ST1-B-10	2.81	14	14	23	23	23	23	23	23
11	ST1-B-11	2.99	19	17	22	23	22	23	22	23
12	ST1-B-12	3.24	16	14	22.5	23	22.5	22	23	22
1	ST1-C-01	NA	18	NA	20	NA	20	NA	20	NA
2	ST1-C-02	NA	19	19	21	22	20	22	21	21
3	ST1-C-03	4.96	14	11	20	19	20	19	20	20
4	ST1-C-04	5.24	17	12	25	19	25	21	25	19
5	ST1-C-05	5.17	14	12	20.5	20	20.5	20	21.5	19
6	ST1-C-06	5.21	15	14	21	20	21	21	22	21
7	ST1-C-07	5.05	13	14	21	20	21	19	20	19
8	ST1-C-08	5.04	15	12	21	21	21	21	21	21
9	ST1-C-09	5.21	14	14	22	21	24	21	24	21
10	ST1-C-10	4.84	16	12	20	21	21	21	21	19
11	ST1-C-11	4.97	15	16	21	21	20	21	20	21
12	ST1-C-12	5.06	16	14	22	21	22	22	22	22

SECTION 4

SAMPLING AND ANALYSIS PROGRAM

The Demonstration Test Plan for this project, dated July 1989, is part of the Appendices to this report. The Plan provides a detailed discussion of the overall sampling and analytical procedures and methods discussed in this section. The Plan also references the procedures used in the Predemonstration well drilling effort and the HPLC method developed by BioTrol for PCP analysis.

In essence, the sampling and analysis plans developed in anticipation of the study were adhered to during the investigation. Composite samples of the influent, effluent, and midpoints of the reactor were decreased from 24-hour samples to 22-hour samples to allow equipment to be prepared for the next cycle within the same 24-hour period. Because of access problems, it was necessary to use a stainless steel beaker to withdraw certain grab samples from the reactor cells.

The one area where serious sampling problems were encountered was the sludge in the bag filter. The nature and amount of the sludge was such that the original plan could not be adhered to. To obtain any sample it became necessary to remove the bag and manually separate solids from the layers of the fabric. Even with that technique, only a small amount of sludge could be collected. These difficulties should be considered when reviewing the sludge analysis data.

Air monitoring was carried out in accordance with the EPA Modified Method 5 (MM5), although it was necessary to provide additional air by fan to obtain flow against the resistance of the carbon canister and to insure isokinetic sampling. The simultaneous 3-point sampling could not be achieved because of the narrow chimney exiting the bioreactor cover. Instead, 3 samples were taken on consecutive days. Organic vapors were adsorbed on XAD resin traps for subsequent analysis by standard methods. The procedure is discussed in more depth in the Demonstration Test Plan and the Quality Assurance Project Plan.

The sampling schedule, sample type, and analytical methods for all tests are summarized in Table 5 as originally developed for the the Quality Assurance Project Plan and the Demonstration Test Plan. Sampling points are as shown on the schematic of the BATS in Figure 7.

TABLE 5. ANALYTICAL SAMPLING SCHEDULE AND METHODS

medium	parameter	frequency	method	
WATER	PCP	daily	846	3510/8270
	Sol PAHs/PCP	3/wk	"	"
	Volatiles	1/wk	846	8240
	Semi-volatiles	1/wk	846	3510/8270
	Dioxins/furans	1/wk	846	8280
	Metals	1/wk		
	Be, Cd, Cr, Cu,		846	3005/6010
	Ni, Ag, Zn		"	"
	Sb		846	3005/7041
	As		846	7060
	Hg		846	7470
	Pb		846	3020/7421
	Se		846	7740
	Th		846	3020/7841
	Chloride	daily	846	9252
	TOC	daily	846	9060
	Total Phenolics	1/wk	846	9065
	Oil/grease	3/wk	846	9070
	Alkalinity	1/wk	SM 403	
	Residue	3/wk	SM 209	
	Ammonia	3/wk	EPA 350.1	
	Nitrate/nitrite	3/wk	EPA 353.1	
	Phosphate	3/wk	SM 424	
	Biotoxicity	1/wk		

SLUDGE*				
	PCP/PAHs	1/wk	846	3550/8270
	Semi-volatiles	1/wk	846	3550/8270
	Dioxins/furans	1/wk	846	8280
	Metals	1/wk		
	Be, Cd, Cr, Cu,		846	3050/6010
	Pb, Ni, Ag, Zn		"	"
	Sb		846	3050/7041
	As		846	3050/7060
	Hg		846	7471
	Se		846	3050/7740
	Th		846	3050/7841
	Total Phenolics	1/wk	846	9065
	Residue	1/wk	SM 209	

AIR	PAHs/PCP	1/2wk	846	0010(collect)
				3510/3540/8270

* As noted in report, difficulties were encountered in obtaining sufficient sample for analyses.

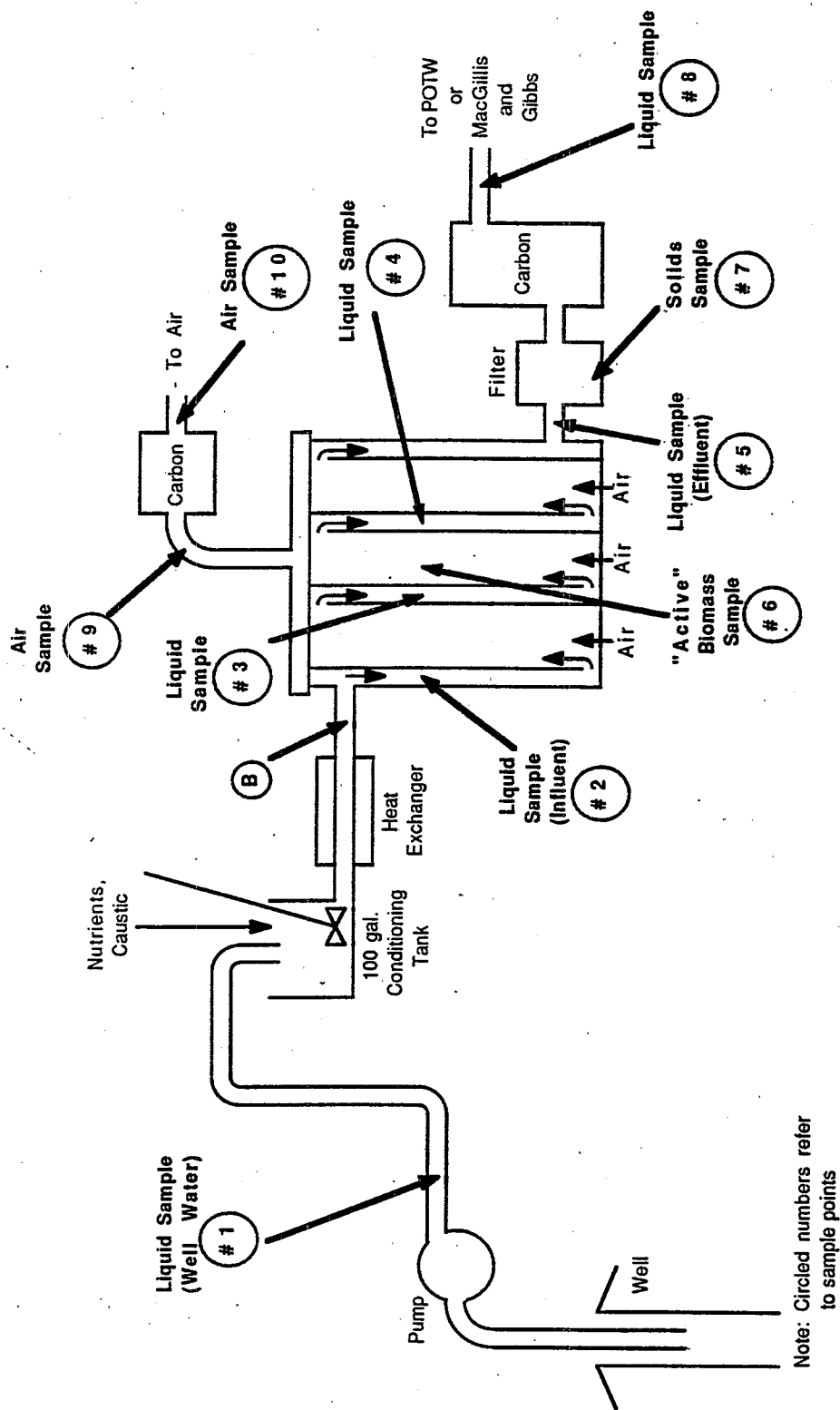


Figure 7. BATS with Sampling Points Shown

As noted earlier, significant differences were observed between results of the BioTrol HPLC method and the EPA Standard Method (8270) for PCP during the predemonstration well drilling. While the cause of the difference remains unclear, it may be attributable to the fact that the samples for GC/MS were collected while the groundwater was standing in the well. In any case, recognition of the differences led to a small study which confirmed that the two methods were comparable, at least down to 1 ppm of PCP.

The HPLC data became much more important during the demonstration when it was found that GC/MS results for PCP in the composite influent samples were considerably lower than the values (also GC/MS) obtained for grab samples of the well water. Process monitoring samples taken by BioTrol just ahead of the bioreactor (Sampling point "B" in Figure 7) -- and also ahead of the influent sampling point (sampling point #2 in Figure 7) -- were analyzed using the HPLC method and consistently gave higher values in agreement with the well water. These data suggested that some other factor was contributing to the inconsistency of the influent character (sampling point #2). Ultimately, it was concluded that backmixing under the weir separating each bioreactor cell from the preceding cell was diluting the samples taken at sample points 2, 3 and 4, leading to lower PCP results on samples taken at those points. While decreases across the bioreactor could still be measured using either the HPLC results or the well water data, these findings precluded any consideration of changes from one chamber to the next for PCP or other pollutants.

Acute biomonitoring with two different species was used as the ultimate test of the benefit of the biotreatment. The procedure consisted of determining the LD(50) for sand fleas and fresh water minnows when various amounts of the groundwater, influent, and effluent was added to the test water.

SECTION 5

DEMONSTRATION RESULTS

INTRODUCTION

The goal of this demonstration project was to study the effectiveness of the BATS at removing relatively high concentrations of PCP and PAHs from wood treating wastewaters. Upon consideration of the BioTrol process and the groundwater available for testing, it was determined that the key variable that could be tested was flow rate. At a constant concentration, this allowed the capacity of the system in terms of pentachlorophenol concentration and removal to be studied. To avoid shock loading and the need for re-acclimation, it was further determined that this could best be accomplished by incrementally increasing the flow and allowing the system to stabilize at each flow so that analytical results of "steady state" operation could be obtained. Based on the capacity of the system (pumps, tanks, etc.) three experimental stages, each of two-week duration, at 1 gpm, 3 gpm and 5 gpm, were selected.

Using sampling and analytical methods as described in Section 5 and in the Appendices to this report, an extensive data base was collected. These data allowed the system to be evaluated in terms of (a) removal of PCP and other organics; (b) the ultimate fate of the PCP; (c) the effect of other contaminants such as oil/grease and metals on this and, potentially other applications of the BATS; and (d) the need to be concerned about air emissions and disposal of carbon, from either a health or an environmental perspective.

RESULTS

Extensive analyses using standard methods for sampling and analyses were carried out over the course of the study. The following sections discuss the individual parameters and present essentially all of the analytical results. As noted earlier, it appears that a backmixing or reverse flow phenomenon was occurring throughout the study, with partially treated water passing back under the underflow weir separating each cell of the bioreactor. This was detected in the PCP analyses of influent to the system where two methods and two different sampling points were fortuitously used. The data supporting this backmixing hypothesis are presented in the section on pentachlorophenol. From that data, it must be assumed

that analyses at the intermediate sampling points in the bioreactor (points #3 and #4 in Figure 7) are similarly affected while the data for the groundwater and the effluent are unaffected. Consequently, the most reliable assessments of changes in parameters are considered to be those based on differences between the groundwater and the effluent, at least at the lower flow rates where the backmixing seemed to have had its greatest impact.

System Parameters

Nitrogen, as nitrate, nitrite, and ammonia; and phosphorus, as phosphate, were monitored throughout the course of the investigation. No unusual effects were observed; the presence of residual nutrients in the effluents suggests that reaction (biodegradation) was not inhibited by insufficient nutrients. The results are presented in tabular form for the three flow rates in Table 6 (nitrate/nitrite), Table 7 (ammonia), and Table 8 (phosphate).

Similarly, dissolved oxygen was measured in each chamber of the reactor twice daily over the course of the study and found to remain between 5 and 6 ppm. There was a slight increase in the dissolved oxygen as the water passed through the system and was aerated by the air sparger system. The incoming groundwater contained <1.0 ppm dissolved oxygen. This data was presented earlier in Table 4.

Some variation in temperature was observed throughout the project, as summarized in Table 9; complete data were presented earlier in Table 4. First, the temperature of the influent to the bioreactor was lower in the 3 gpm (14-17°C) and the 5 gpm (14-21°C) experiments than in the 1 gpm study (22-25°C). This probably was partially due to a decrease in the temperature of the groundwater over the course of the program (11-16°C), and possibly partially due to the heat exchanger returning insufficient heat to the incoming groundwater from the effluent to maintain a constant temperature for all three runs. Since the study was carried out in the summer, the heater which is a part of the BATS was not brought into operation. As would be expected, there was a slight temperature increase as the wastewater passed through the system, i.e., the effluent temperature was slightly higher than the influent temperature in all three study segments.

TABLE 6. NITRATE/NITRITE ANALYTICAL RESULTS
NO₂/NO₃ (mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT				
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT
1	7/24/89	ST1-A-01	<0.100	0.370			8.100
2	7/25/89	ST1-A-02					
3	7/26/89	ST1-A-03		0.091			7.700
4	7/27/89	ST1-A-04					
5	7/28/89	ST1-A-05		0.680			9.900
6	7/29/89	ST1-A-06					
7	7/31/89	ST1-A-07		0.095			1.800
8	8/01/89	ST1-A-08	0.120				
9	8/02/89	ST1-A-09		0.620			5.600
10	8/03/89	ST1-A-10					
11	8/04/89	ST1-A-11		0.230			8.500
12	8/05/89	ST1-A-12					
AVERAGE			0.11	0.35			6.93
SD(n-1)			0.01	0.26			1.19
1	8/07/89	ST1-B-01	0.054	0.120			3.400
2	8/08/89	ST1-B-02					
3	8/09/89	ST1-B-03		0.320			3.600
4	8/10/89	ST1-B-04					
5	8/11/89	ST1-B-05		0.120			2.700
6	8/12/89	ST1-B-06					
7	8/14/89	ST1-B-07		NA			4.000
8	8/15/89	ST1-B-08	0.094				
9	8/16/89	ST1-B-09		0.280			1.700
10	8/17/89	ST1-B-10					
11	8/18/89	ST1-B-11		0.025			2.500
12	8/19/89	ST1-B-12					
AVERAGE			0.07	0.17			2.98
SD(n-1)			0.03	0.12			0.35
1	8/21/89	ST1-C-01	0.160	1.200			0.025
2	8/22/89	ST1-C-02					
3	8/23/89	ST1-C-03		0.200			0.670
4	8/24/89	ST1-C-04					
5	8/25/89	ST1-C-05		0.340			0.370
6	8/26/89	ST1-C-06					
7	8/27/89	ST1-C-07					
8	8/28/89	ST1-C-08	<0.020	0.400			0.620
9	8/29/89	ST1-C-09					
10	8/30/89	ST1-C-10		0.240			
11	8/31/89	ST1-C-11		0.200			0.500
12	9/01/89	ST1-C-12					
AVERAGE			0.09	0.43			0.44
SD(n-1)			0.10	0.39			0.10

* - Not included in Calculation of Averages or Standard Deviations.

TABLE 7. AMMONIA ANALYTICAL RESULTS
NH₄ (mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT				
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT
1	7/24/89	ST1-A-01		12.00			14.00
2	7/25/89	ST1-A-02					
3	7/26/89	ST1-A-03		3.10			3.00
4	7/27/89	ST1-A-04					
5	7/28/89	ST1-A-05	0.06	1.40			0.54
6	7/29/89	ST1-A-06					
7	7/31/89	ST1-A-07		3.60			2.70
8	8/01/89	ST1-A-08					
9	8/02/89	ST1-A-09		4.70			2.10
10	8/03/89	ST1-A-10	<0.04				
11	8/04/89	ST1-A-11		2.80			0.83
12	8/05/89	ST1-A-12					
AVERAGE			0.05	4.60			3.86
SD(n-1)			0.02	3.78			2.10
1	8/07/89	ST1-B-01		0.45			0.37
2	8/08/89	ST1-B-02					
3	8/09/89	ST1-B-03		1.20			0.36
4	8/10/89	ST1-B-04	0.67				
5	8/11/89	ST1-B-05		1.50			0.38
6	8/12/89	ST1-B-06					
7	8/14/89	ST1-B-07		NA			1.07
8	8/15/89	ST1-B-08					
9	8/16/89	ST1-B-09		2.10			2.30
10	8/17/89	ST1-B-10	0.41				
11	8/18/89	ST1-B-11		2.20			1.30
12	8/19/89	ST1-B-12					
AVERAGE			0.54	1.49			0.96
SD(n-1)			0.18	0.71			0.32
1	8/21/89	ST1-C-01		0.24			1.30
2	8/22/89	ST1-C-02	0.40				
3	8/23/89	ST1-C-03		0.64			1.40
4	8/24/89	ST1-C-04					
5	8/25/89	ST1-C-05		0.56			1.80
6	8/26/89	ST1-C-06					
7	8/27/89	ST1-C-07					
8	8/28/89	ST1-C-08		0.83			2.40
9	8/29/89	ST1-C-09					
10	8/30/89	ST1-C-10		0.80			4.00
11	8/31/89	ST1-C-11	0.44	0.68			3.10
12	9/01/89	ST1-C-12					
AVERAGE			0.42	0.63			2.33
SD(n-1)			0.03	0.21			0.44

* - Not included in Calculation of Averages or Standard Deviations

TABLE 8. PHOSPHATE ANALYTICAL RESULTS
PO₄ (mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT					
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT	#14 DUPLICATE
1.0	7/24/89	ST1-A-01		2.4			2.3	
2.0	7/25/89	ST1-A-02						
3.0	7/26/89	ST1-A-03		2.4			3.2	
4.0	7/27/89	ST1-A-04						
5.0	7/28/89	ST1-A-05	2.4	0.4			2.7	
6.0	7/29/89	ST1-A-06						
7.0	7/31/89	ST1-A-07		1.5			1.3	
8.0	8/01/89	ST1-A-08						
9.0	8/02/89	ST1-A-09		2.2			3.0	
10.0	8/03/89	ST1-A-10	0.4					
11.0	8/04/89	ST1-A-11		3.3			0.1	
12.0	8/05/89	ST1-A-12						
AVERAGE			1.4	2.0			2.1	
SD(n-1)			1.4	1.0			0.5	
1.0	8/07/89	ST1-B-01		0.4			1.4	
2.0	8/08/89	ST1-B-02						
3.0	8/09/89	ST1-B-03		2.0			2.0	
4.0	8/10/89	ST1-B-04	0.3					
5.0	8/11/89	ST1-B-05		1.0			1.0	
6.0	8/12/89	ST1-B-06						
7.0	8/14/89	ST1-B-07					3.4	
8.0	8/15/89	ST1-B-08						
9.0	8/16/89	ST1-B-09		1.2			0.8	
10.0	8/17/89	ST1-B-10	0.2					
11.0	8/18/89	ST1-B-11		1.0			0.6	
12.0	8/19/89	ST1-B-12						
AVERAGE			0.2	1.1			1.5	
SD(n-1)			0.1	0.6			0.4	
1.0	8/21/89	ST1-C-01	1.4	1.5			1.5	
2.0	8/22/89	ST1-C-02						
3.0	8/23/89	ST1-C-03		1.3			0.8	
4.0	8/24/89	ST1-C-04						
5.0	8/25/89	ST1-C-05		1.2			0.5	
6.0	8/26/89	ST1-C-06		0.2				
7.0	8/27/89	ST1-C-07						
8.0	8/28/89	ST1-C-08		1.2			0.6	
9.0	8/29/89	ST1-C-09						
10.0	8/30/89	ST1-C-10					2.8	
11.0	8/31/89	ST1-C-11	0.2	1.4			0.6	
12.0	9/01/89	ST1-C-12						
AVERAGE			0.8	1.1			1.1	
SD(n-1)			0.8	0.5			0.4	

* - Not included in Calculation of Averages or Standard Deviations

TABLE 9. TEMPERATURE ACROSS BIOTROL SYSTEM

Flow gpm	Temperature (°C, avg)				
	gdwater #1	influent #2	midpt #3	midpt #4	effluent #5
1	21	23.4	24.6	24.5	24.8
3	11	15.7	20.4	20.4	20.9
5	13	14.6	20.8	21.0	20.9

While the developer's specifications called for a pH of about 7.3 in the tempering (conditioning) tank, the pH measured in the three chambers of the bioreactor usually was somewhat higher, particularly at the two lower flows and, at least at the 1 gpm flow, appeared to increase across the system. The pH of the groundwater drawn from the well was consistently in the range of 6.7-6.9 standard units (Table 4).

Initial oil and grease (O/G) concentrations of approximately 50 ppm were reduced by passage through the system to <10 ppm (Table 10). While the design of the bioreactor cells is such that formation of an oil layer at the underflow weirs might have been expected, a significant amount of oil was observed only occasionally during the 1 gpm portion of the study. At these influent oil levels, there is no reason to expect the oil to adversely affect the bioreaction; considerably higher levels are tolerated well in conventional activated sludge systems. The complete data for oil and grease are presented in Table 11.

TABLE 10. AVERAGE TSS AND OIL ACROSS THE BIOTROL SYSTEM

Flow gpm	groundwater		influent		effluent	
	TSS	O/G	TSS	O/G	TSS	O/G
	mg/L		mg/L		mg/L	
1	2.5±.07	54.5± 2.1	29.6±9.4	57.5±10.7	53.6± 6.6	6.0±0.4
3	13 ±12.7	61.0± 1.4	24.2±17.6	37.8±14.9	26.3±11.1	6.0±1.3
5	1.5± 0.7	47.5±10.6	15.7±8.9	50.8±10.5	22.5± 9.5	8.0±2.4

Total suspended solids (TSS) levels in the incoming well water were quite low (<5 ppm) and increased somewhat (to 54 ppm at 1 gpm, 26 ppm at 3 gpm, and 18 ppm at 5 gpm) over the course of the study (summarized in Table 10, full data in Table 12). At these incoming levels, suspended solids would not be expected to interfere with the reaction. In the effluent the suspended solids probably contains biomass sloughed from the PVC matrix. Even suspended solids levels of 54 ppm, as observed in the 1 gpm portion of the study, do not represent a significant mechanism for removal of

TABLE 11. OIL AND GREASE ANALYTICAL RESULTS
(mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT					
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT	#14 DUPLICATE
1	7/24/89	ST1-A-01		8 *	<5	5 *	<5	
2	7/25/89	ST1-A-02						
3	7/26/89	ST1-A-03		47	<5	5	8	
4	7/27/89	ST1-A-04						
5	7/28/89	ST1-A-05	56	53	5	5	7	
6	7/29/89	ST1-A-06						
7	7/31/89	ST1-A-07		58	<5	5	<5	
8	8/01/89	ST1-A-08						
9	8/02/89	ST1-A-09		371 *	48 *	20 *	21 *	19 (EFF) *
10	8/03/89	ST1-A-10	53					
11	8/04/89	ST1-A-11		72	20 *	5	<5	
12	8/05/89	ST1-A-12						
AVERAGE			54.5	57.5	5.0	5.0	6.0	
SD(n-1)			2.1	10.7	0.0	0.0	0.4	
1	8/07/89	ST1-B-01		57	7	<5	<5	57 (INF)
2	8/08/89	ST1-B-02						
3	8/09/89	ST1-B-03		15	14	6	6	
4	8/10/89	ST1-B-04	60					
5	8/11/89	ST1-B-05		31	9	<5	<5	
6	8/12/89	ST1-B-06						
7	8/14/89	ST1-B-07		33	9	5	8	
8	8/15/89	ST1-B-08						
9	8/16/89	ST1-B-09		50	13	<5	<5	
10	8/17/89	ST1-B-10	62					
11	8/18/89	ST1-B-11		41	12	8	7	5 (EFF)
12	8/19/89	ST1-B-12						
AVERAGE			61.0	37.8	10.7	5.7	6.0	
SD(n-1)			1.4	14.9	2.7	1.2	1.3	
1	8/21/89	ST1-C-01		58	12	<5	<5	
2	8/22/89	ST1-C-02	55					
3	8/23/89	ST1-C-03		59	14	19	11	
4	8/24/89	ST1-C-04						
5	8/25/89	ST1-C-05		37	32 *	12	9	
6	8/26/89	ST1-C-06						
7	8/27/89	ST1-C-07						
8	8/28/89	ST1-C-08		58	10	11	10	
9	8/29/89	ST1-C-09						
10	8/30/89	ST1-C-10		42	18	15	7	
11	8/31/89	ST1-C-11	40	NA *	15	10	6	40 (INF)
12	9/01/89	ST1-C-12						
AVERAGE			47.5	50.8	13.8	12.0	8.0	
SD(n-1)			10.6	10.5	3.0	4.7	2.4	

* - Not Included in Calculation of Average or Standard Deviation

TABLE 12. TSS ANALYTICAL RESULTS
(mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT					
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT	#14 DUPLICATE
1	7/24/89	ST1-A-01		29	26	35	23	
2	7/25/89	ST1-A-02						
3	7/26/89	ST1-A-03		38	48	47	67	
4	7/27/89	ST1-A-04						
5	7/28/89	ST1-A-05	3	39	53	52	64	
6	7/29/89	ST1-A-06						
7	7/31/89	ST1-A-07		4 *	4 *	4 *	4 *	
8	8/01/89	ST1-A-08						
9	8/02/89	ST1-A-09		26	46	54	54	52 (EFF)
10	8/03/89	ST1-A-10	2					
11	8/04/89	ST1-A-11		16	50	69	60	
12	8/05/89	ST1-A-12						
AVERAGE SD(n-1)			2.5 0.7	29.6 9.4	44.6 2.7	51.4 3.6	53.6 6.6	
1	8/07/89	ST1-B-01		10	10	10	8	14 (INF)
2	8/08/89	ST1-B-02						
3	8/09/89	ST1-B-03		54	84	72	56	
4	8/10/89	ST1-B-04	22					
5	8/11/89	ST1-B-05		23	22	16	12	
6	8/12/89	ST1-B-06						
7	8/14/89	ST1-B-07		NA	20	14	67	
8	8/15/89	ST1-B-08						
9	8/16/89	ST1-B-09		22	18	94	11	
10	8/17/89	ST1-B-10	4					
11	8/18/89	ST1-B-11		12	8	6	4	6 (EFF)
12	8/19/89	ST1-B-12						
AVERAGE SD(n-1)			13.00 12.73	24.20 17.64	27.00 7.78	35.33 12.05	26.33 11.09	
1	8/21/89	ST1-C-01		27	34	31	32	
2	8/22/89	ST1-C-02	2					
3	8/23/89	ST1-C-03		8	12	12	14	
4	8/24/89	ST1-C-04						
5	8/25/89	ST1-C-05		6	11	10	8	
6	8/26/89	ST1-C-06						
7	8/27/89	ST1-C-07						
8	8/28/89	ST1-C-08		13	8	8	6	
9	8/29/89	ST1-C-09						
10	8/30/89	ST1-C-10		26	50	36	66	
11	8/31/89	ST1-C-11	<1	14	12	9	9	11 (INF)
12	9/01/89	ST1-C-12						
AVERAGE SD(n-1)			1.50 0.71	15.67 8.91	21.17 4.67	17.67 4.01	22.50 9.52	

* - Not included in Calculation of Averages or Standard Deviations

organic pollutants. For example, at a 51 ppm increase in suspended solids and a PCP concentration of 34 ppm, this would account for only 0.00025 lbs of PCP over the course of the 12 days of operation at 1 gpm. With total PCP removal during that period of 5.97 lbs, the amount in the sludge is negligible. The volatile suspended solids (VSS) represent approximately 45% of the total suspended solids, possibly increasing slightly (to ~50%) at the highest flow rate (Table 13).

Pentachlorophenol Removal

With the receipt of the PCP analytical data generated by SW-846, Method 8270, it became clear that the results were not as anticipated. Influent PCP values (point #2 in Figure 7) were significantly lower than the concentrations leaving the well (point #1), as summarized in Table 14. Grab samples taken by BioTrol from a "T" just before the influent chamber (point B on Figure 7) and analyzed by BioTrol's HPLC method agreed well with the well samples (point #1). In addition, the groundwater (point #1) and influent (point #2) PCP values approached agreement as the flow rate was increased each two weeks. Within limits discussed later, free chloride and Total Organic Carbon (TOC) data at the various sampling points also supported these observations.

TABLE 14. AVERAGE PENTACHLOROPHENOL REMOVAL BY BIOTROL SYSTEM

Flow (gpm)	PCP (#1) gdwtr	PCP (#2) infl.	PCP (#5) effl.	Removal [------(%)-----]	
				gdw/eff	infl/effl
1	42.0±7.1*	6.9±3.4	0.13±.25	99.8	98.1
3	34.5±7.8*	19.0±5.8	0.34±.15	98.5	98.2
5	27.5±0.7*	24.2±6.8	0.99±.49	96.4	95.9

* The gradual decrease in groundwater concentration may be a result of well drawdown over the 6 weeks of operation.

At first it was thought that the difference might have been due to foaming during the extractions for the analytical procedure (SW-846 Methods 3510/8270). While that problem did persist throughout the study and did affect the recovery achievable for the samples, it became clear that it was not the cause of the differences between the well or BioTrol's samples and the influent chamber samples.

Other possible explanations for the anomalous results were considered, including absorption of PCP on the walls of the bioreactor, separation of a PCP-in-oil layer, and backmixing under the underflow weirs separating the chambers. Calculations indicated that the amount of an absorbed film of PCP or a PCP-in-oil layer

Table 13. VSS/TSS ANALYTICAL RESULTS
(mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT				
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT
1	7/24/89	ST1-A-01		8/29	11/26	16/35	10/23
2	7/25/89	ST1-A-02					
3	7/26/89	ST1-A-03		16/38	17/48	20/47	29/67
4	7/27/89	ST1-A-04					
5	7/28/89	ST1-A-05	2/3	16/39	20/53	19/52	25/64
6	7/29/89	ST1-A-06					
7	7/31/89	ST1-A-07		2/4	2/4	1/4	1/4
8	8/01/89	ST1-A-08					
9	8/02/89	ST1-A-09		10/26	18/46	21/54	20/54
10	8/03/89	ST1-A-10	1/2				
11	8/04/89	ST1-A-11		7/16	21/50	26/69	22/60
12	8/05/89	ST1-A-12					
AVERAGE V/T			0.58	0.40	0.41	0.38	0.37
SD(n-1)			0.12	0.07	0.02	0.03	0.04
1	8/07/89	ST1-B-01		4/10	4/8	4/10	2/8
2	8/08/89	ST1-B-02					
3	8/09/89	ST1-B-03		27/54	38/84	32/72	27/56
4	8/10/89	ST1-B-04	4/22				
5	8/11/89	ST1-B-05		11/23	10/22	8/16	6/12
6	8/12/89	ST1-B-06					
7	8/14/89	ST1-B-07			12/20	8/14	33/67
8	8/15/89	ST1-B-08					
9	8/16/89	ST1-B-09		8/22	8/18	51/94	5/11
10	8/17/89	ST1-B-10	3/4				
11	8/18/89	ST1-B-11		6/12	5/8	3/6	4/4
12	8/19/89	ST1-B-12					
AVERAGE V/T			0.47	0.45	0.51	0.49	0.53
SD(n-1)			0.40	0.06	0.02	0.02	0.13
1	8/21/89	ST1-C-01		16/34	14/31	16/32	1/2
2	8/22/89	ST1-C-02	<1/2				
3	8/23/89	ST1-C-03		6/8 *	6/12 *	6/12 *	8/14 *
4	8/24/89	ST1-C-04					
5	8/25/89	ST1-C-05		3/6	6/11	6/10	4/8
6	8/26/89	ST1-C-06					
7	8/27/89	ST1-C-07					
8	8/28/89	ST1-C-08		4/13	4/8	4/8	3/6
9	8/29/89	ST1-C-09					
10	8/30/89	ST1-C-10			22/50	18/36	32/66
11	8/31/89	ST1-C-11	<1	6/14	6/12	6/9	5/9
12	9/01/89	ST1-C-12					
AVERAGE V/T			0.75	0.49	0.49	0.54	0.52
SD(n-1)			0.35	0.16	0.01	0.03	0.02

* - Not Included in Calculation of Average

needed to explain the differences were simply not present. Consequently, backmixing appeared to be the best explanation for the observed differences. And, as flow through the system was increased each two weeks, the impact of the backmixing decreased, explaining the gradual improvement in agreement between well water data, BioTrol process monitoring data by the HPLC method, and influent data.

On the assumption that the "real" concentration of PCP in the influent was about 45 ppm in the 1 gpm study but was measured at about 7 ppm, it was estimated that approximately 5 gallons was "leaking" back through the system for every gallon introduced in the first two weeks. At higher flows, the effect of backmixing would be expected to be less.

Because the influent sampling problem was only discovered when samples had been analyzed, an additional QA study was carried out to compare BioTrol's HPLC method for determining PCP concentrations with EPA's Standard Method (SW-846, Method 8270). This investigation, reported in the Quality Assurance Review Appendix to this report, confirms that the two methods are comparable when extraction efficiency in Method 3370/8270 is taken into consideration.

On the basis of this additional information, it was concluded that concentrations of PCP in the well water were better representations of the concentrations entering the first cell of the bioreactor than the influent samples. Because of the backmixing phenomenon, the analytical data from the intermediate sampling points in the bioreactor (points #3 and #4) were used only to confirm that gradual reduction in PCP (and other parameters) was taking place in the expected direction. PCP analytical results for all sampling points are presented in Table 15. Removal efficiencies have been based on well water and effluent data (both by Method 8270) instead of the influent samples.

It remains clear that the BioTrol Aqueous Treatment System does effectively remove PCP from the groundwater as it moves through the system. Effluent concentrations of PCP after treatment (but before carbon polishing) averaged 0.13 ppm at the 1 gpm flow rate and increased to approximately 0.99 ppm at the 5 gpm flow rate. Thus, depending on the level of PCP required in the effluent, effluent quality can be adjusted by adjusting the flow rate. Using the well water data as the influent concentrations and the observed effluent concentrations for PCP, the system achieves an average of 96.4% PCP removal at the 5 gpm flow rate and this increases to 99+% at the lower flow rates.

TABLE 15. PENTACHLOROPHENOL ANALYTICAL RESULTS
PCP (ug/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT					
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT	% removal 02-05/02
1	7/24/89	ST1-A-01	47000	680	11	50	16	97.6
2	7/25/89	ST1-A-02		7000	1200	230	880	87.4
3	7/26/89	ST1-A-03		6900	1500	340	140	98.0
4	7/27/89	ST1-A-04		3000	400	140	140	95.3
5	7/28/89	ST1-A-05		7200	400	100	88	98.8
6	7/29/89	ST1-A-06		13000	1300	410	<5000	---
7	7/31/89	ST1-A-07	37000	7600	17	160	<50	99.3
8	8/01/89	ST1-A-08		6600	200	11	5	99.9
9	8/02/89	ST1-A-09		12000	85	8	5	100.0
10	8/03/89	ST1-A-10		8900	150	<50	8	99.9
11	8/04/89	ST1-A-11		4200	530	<50	<50	98.8
12	8/05/89	ST1-A-12		6100	690	17	50	99.2
AVERAGE SD(n-1)			42000.0 7071.1	6931.7 3434.0	540.3 524.4	130.5 133.3	130.2 253.5	98.1 3.7
1	8/07/89	ST1-B-01	40000	8800	2600	210	82	99.1
2	8/08/89	ST1-B-02		24000	4700	1000	810	96.6
3	8/09/89	ST1-B-03		NA	4800	160	190	---
4	8/10/89	ST1-B-04		21000	NA	1200	NA	---
5	8/11/89	ST1-B-05		19000	2900	490	320	98.3
6	8/12/89	ST1-B-06		21000	3900	570	430	98.0
7	8/14/89	ST1-B-07	29000	NA	5500	900	200	---
8	8/15/89	ST1-B-08		24000	6800	1400	1000	95.8
9	8/16/89	ST1-B-09		22000	10000	1500	<50	99.8
10	8/17/89	ST1-B-10		10000	4300	740	390	96.1
11	8/18/89	ST1-B-11		25000	3700	370	230	99.1
12	8/19/89	ST1-B-12		15000	7400	190	78	99.5
AVERAGE SD(n-1)			34500.0 7778.2	18980.0 5812.2	5145.5 728.1	727.5 191.8	343.6 147.9	98.2 0.9
1	8/21/89	ST1-C-01	27000	15000	4900	3500	3100	79.3
2	8/22/89	ST1-C-02		21000	6700	3200	1200	94.3
3	8/23/89	ST1-C-03		NA	NA	NA	NA	---
4	8/24/89	ST1-C-04		15000	10000	4000	910	93.9
5	8/25/89	ST1-C-05		19000	8100	1200	890	95.3
6	8/26/89	ST1-C-06		23000	6000	1600	1100	95.2
7	8/27/89	ST1-C-07	28000	35000	5300	870	<50	99.9
8	8/28/89	ST1-C-08		23000	2600	3200	140	99.4
9	8/29/89	ST1-C-09		28000	4100	8600	300	98.9
10	8/30/89	ST1-C-10		28000	3700	3900	330	98.8
11	8/31/89	ST1-C-11		25000	6900	5500	140	99.4
12	9/01/89	ST1-C-12		34000	12000	10000	2700	92.1
AVERAGE SD(n-1)			27500.0 707.1	24181.8 6720.4	6390.9 926.9	4142.7 1112.3	987.3 487.4	95.9 4.0

* - Not included in Calculation of Averages or Standard Deviations

The data are presented in terms of pentachlorophenol mass removal in Table 16. Based on the calculated mass of pentachlorophenol introduced to the system over each two week experimental period, and assuming that all pentachlorophenol is lost by biological degradation, mass removals of >95% are consistently achievable.

TABLE 16. MASS REMOVAL OF PENTACHLOROPHENOL

Week	Flow (gpm)	Total PCP In (lbs)* (#1)	Total PCP Out (lbs) (#5)	Removal (%)
1	0.98	3.32	.178	94.6
2	1.0	2.65	.002	99.9
3	2.92	8.39	.077	99.1
4	3.02	6.29	.075	98.8
5	5.14	9.99	.533	94.7
6	5.03	10.13	.221	97.8

* Based on well water (#1) analyses

Comparison of analytical results for total PCP in as-is samples and soluble PCP in samples that had been filtered to remove any suspended solids confirmed that very little if any of the PCP in the as-is samples was absorbed on the filterable solids (Table 17). There were, however, measurable concentrations of PCP in the sludge samples (see Table 21). Considering the small amount of sludge exiting the bioreactor, this is not a significant contributor to the removal of PCP from the system, as discussed earlier. Similarly, the low concentration of oil in the effluent (<10 ppm) strongly argues against loss of PCP by extraction into that phase.

Analyses of the air exhausted from the bioreactor also confirmed that no detectable quantities of pentachlorophenol were lost by this route.

Mineralization. Chloride and TOC monitoring of the influent and effluent produced results that are consistent with an assumption that the bulk of the pentachlorophenol is mineralized, but indicate that other contributors to chloride and TOC are present. The expected reaction would be:

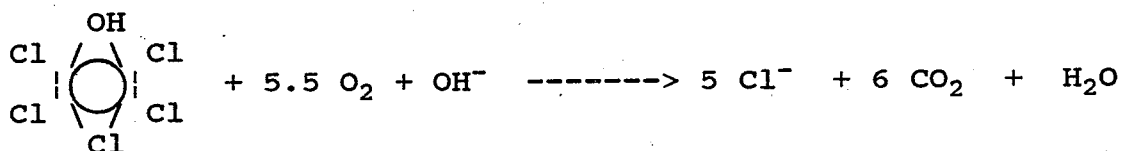


TABLE 17. SOLUBLE PCP/TOTAL PCP ANALYTICAL DATA
PCP (ug/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT				
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT
1	7/24/89	ST1-A-01	39000/47000	690/680	<50/11	6/50	11/16
2	7/25/89	ST1-A-02		—/7000	—/1200	—/230	—/880
3	7/26/89	ST1-A-03		5200/6900	810/1500	350/340	120/140
4	7/27/89	ST1-A-04		—/3000	—/400	—/140	—/140
5	7/28/89	ST1-A-05		—/7200	—/400	—/100	—/88
6	7/29/89	ST1-A-06		15000/13000	1800/1300	710/410	—/ <5000
7	7/31/89	ST1-A-07		5200/7600	13/17	66/160	11/ <50
8	8/01/89	ST1-A-08	41000/37000	—/6600	—/200	—/11	—/5
9	8/02/89	ST1-A-09		11000/12000	96/85	4/8	4/5
10	8/03/89	ST1-A-10		—/8900	—/150	—/ <50	—/8
11	8/04/89	ST1-A-11		—/4200	—/530	—/ <50	—/ <50
12	8/05/89	ST1-A-12		8800/6100	460/690	<50/17	9/50
AVERAGE PCP(tot) SD(n-1)			42000.0 7071.1	6931.7 3434.0	540.3 524.4	130.5 133.3	130.2 253.5
1	8/07/89	ST1-B-01	42000/40000	15000/8800	3200/2600	240/210	77/82
2	8/08/89	ST1-B-02		—/24000	—/4700	—/1000	—/810
3	8/09/89	ST1-B-03		NA	490/4800	540/160	580/190
4	8/10/89	ST1-B-04		—/21000	NA	—/1200	NA
5	8/11/89	ST1-B-05		—/19000	—/2900	—/490	—/320
6	8/12/89	ST1-B-06		21000/21000	3600/3900	640/570	350/430
7	8/14/89	ST1-B-07		NA	4200/5500	830/900	330/200
8	8/15/89	ST1-B-08	29000/29000	—/24000	—/6800	—/1400	—/1000
9	8/16/89	ST1-B-09		22000/22000	8900/10000	1400/1500	1600/ <50
10	8/17/89	ST1-B-10		—/10000	—/4300	—/740	—/390
11	8/18/89	ST1-B-11		—/25000	—/3700	—/370	—/230
12	8/19/89	ST1-B-12		22000/15000	6100/7400	190/190	100/78
AVERAGE PCP(tot) SD(n-1)			34500.0 7778.2	18980.0 5812.2	5145.5 728.1	727.5 191.8	343.6 147.9
1	8/21/89	ST1-C-01	29000/21000	13000/15000	4400/4900	3200/3500	3000/3100
2	8/22/89	ST1-C-02		—/21000	—/6700	—/3200	—/1200
3	8/23/89	ST1-C-03		NA	NA	NA	NA
4	8/24/89	ST1-C-04		—/15000	—/10000	—/4000	—/910
5	8/25/89	ST1-C-05		—/19000	—/8100	—/1200	—/890
6	8/26/89	ST1-C-06		27000/23000	7400/6000	2200/1600	810/1100
7	8/27/89	ST1-C-07		—/35000	—/5300	—/870	—/ <50
8	8/28/89	ST1-C-08	29000/28000	21000/23000	5000/2600	3100/3200	230/140
9	8/29/89	ST1-C-09		—/28000	—/4100	—/8600	—/300
10	8/30/89	ST1-C-10		28000/28000	3100/3700	3600/3900	230/330
11	8/31/89	ST1-C-11		—/25000	—/6900	—/5500	—/140
12	9/01/89	ST1-C-12		32000/34000	10000/12000	9100/10000	3600/2700
AVERAGE PCP(tot) SD(n-1)			27500.0 707.1	24181.8 6720.4	6390.9 926.9	4142.7 1112.3	987.3 487.4

* - Not included in Calculation of Averages or Standard Deviations

or perhaps

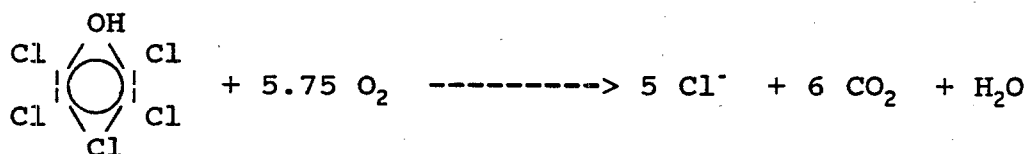


Table 18 summarizes the observed and expected changes in chloride and TOC calculated on the basis of the observed decrease in pentachlorophenol, again using the PCP values for the groundwater rather than the influent. Chloride and TOC values were selected for the same days. The actual analytical data are reported in Table 19 (chloride) and Table 20 (TOC).

TABLE 18. COMPARISON OF CHLORIDE & TOC CHANGES WITH PCP REMOVAL

Flow (gpm)	PCP change	INCREASE IN		DECREASE IN	
		Cl(fd)	Cl(calc) (mg/L)	TOC(fd)	TOC(calc)
1	-41.9	+40.2	+27.9	-25.5	-11.3
3	-34.1	+37.2	+22.7	-31.5	- 9.2
5	-26.5	+27.2	+17.6	-21.0	- 7.0

fd = found (effluent - groundwater)

calc = calculated from change in PCP, as 5Cl/PCP & 6C/PCP

The concentrations of mono-, di-, and trichlorophenols (by SW846 Method 8270) all were below the detection limits in the semivolatile scans of the groundwater, influent, and effluent but the detection limits were often quite high since pentachlorophenol was the primary "target" of the analyses. It is reported that manufactured pentachlorophenol may have contained as much as 20% by weight of tetrachlorophenols (TCPs). If, for example, the original PCP concentration in the groundwater, 42 ppm, were accompanied by 20% by weight as tetrachlorophenols (which were not target analytes), this would mean that 8.4 ppm of TCPs were present. If these tetrachlorophenol isomers degrade as efficiently as PCP, the 8.4 ppm would contribute 5.1 ppm of chloride. And if one also assumed that all of the less chlorinated isomers (mono-, di-, and trichlorophenols) in the semivolatile scan were present at just below their detection limits in the original sample, they could contribute an additional 6.4 ppm of chloride. Table 21 presents calculated chloride yields on the basis of these assumptions for the groundwater sample during the 1 gpm study. [Subsequent review of two archived scans of groundwater indicated TCP contents of about 4% and 10% of the PCP measured.] Other chlorinated phenol species that are not reported as part of the semi-volatile scan also could be present.

TABLE 19. CHLORIDE ANALYTICAL RESULTS
Cl (mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT					
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT	#14 DUPLICATE
1	7/24/89	ST1-A-01		58	53	58	58	
2	7/25/89	ST1-A-02		48	58	68	53	
3	7/28/89	ST1-A-03		56	53	63	58	
4	7/27/89	ST1-A-04		48	63	82	34	
5	7/28/89	ST1-A-05	14	53	63	58	63	48 (INF)
6	7/29/89	ST1-A-06		46	58	58	63	
7	7/31/89	ST1-A-07		48	53	58	58	
8	8/01/89	ST1-A-08		48	53	58	53	
9	8/02/89	ST1-A-09		44 *	53 *	9.7 *	100 *	53 (EFF)
10	8/03/89	ST1-A-10	19	53 *	58	63	58	
11	8/04/89	ST1-A-11		53	58	63	63	
12	8/05/89	ST1-A-12		48	58	53	63	
AVERAGE			16.50	50.82	57.09	62.00	56.73	
SD(n-1)			3.54	3.95	1.31	3.19	4.44	
1	8/07/89	ST1-B-01		44	48	58	52	44 (INF)
2	8/08/89	ST1-B-02		29	53	58	58	
3	8/09/89	ST1-B-03		44	9.7 *	106 *	58	
4	8/10/89	ST1-B-04	14	34	50	53	63	
5	8/11/89	ST1-B-05		40	53	55	56	
6	8/12/89	ST1-B-06		46	53	55	56	
7	8/14/89	ST1-B-07		NA	60	54	55	
8	8/15/89	ST1-B-08		34	50	54	55	
9	8/16/89	ST1-B-09		34	46	57	55	
10	8/17/89	ST1-B-10	24	38	51	54	56	
11	8/18/89	ST1-B-11		34	50	55	56	54 (EFF)
12	8/19/89	ST1-B-12		34	51	56	55	
AVERAGE			19.00	37.36	51.36	55.36	56.25	
SD(n-1)			7.07	5.45	1.24	0.69	1.44	
1	8/21/89	ST1-C-01		41	53	55	54	
2	8/22/89	ST1-C-02	38	27	46	51	52	
3	8/23/89	ST1-C-03		29	51	53	54	
4	8/24/89	ST1-C-04		27	45	50	53	
5	8/25/89	ST1-C-05		26	43	54	55	
6	8/26/89	ST1-C-06		28	52	54	55	54 (EFF)
7	8/27/89	ST1-C-07		29	51	55	55	
8	8/28/89	ST1-C-08		29	51	52	55	
9	8/29/89	ST1-C-09		18	37	52	54	56 (EFF)
10	8/30/89	ST1-C-10		16 *	48	46	27	
11	8/31/89	ST1-C-11	12	28	46	46	42	24 (INF)
12	9/01/89	ST1-C-12		21	44	47	46	
AVERAGE			25.00	27.55	47.25	51.25	50.17	
SD(n-1)			18.38	5.70	1.67	1.40	4.50	

* - Not Included in Calculation of Average or Standard Deviation

TABLE 20. TOC ANALYTICAL RESULTS
TOC (mg/L)

DAY OF RUN	SAMPLE DATE	SAMPLE NUMBER	SAMPLING POINT					
			#01 WELL	#02 INFLUENT	#03 MID #1	#04 MID #2	#05 EFFLUENT	#14 DUPLICATE
1	7/24/89	ST1-A-01		63	32	52	56	
2	7/25/89	ST1-A-02		65	55	54	57	
3	7/26/89	ST1-A-03		62	55	56	66	
4	7/27/89	ST1-A-04		64	52	53	60	
5	7/28/89	ST1-A-05	79	63	51	50	61	69 (INF)
6	7/29/89	ST1-A-06		62	47	51	2450 *	
7	7/31/89	ST1-A-07		60	48	49	48	
8	8/01/89	ST1-A-08		57	47	48	46	
9	8/02/89	ST1-A-09		120 *	48 *	53 *	49 *	50 (EFF)
10	8/03/89	ST1-A-10	79	65	60	48	49	
11	8/04/89	ST1-A-11		58	51	49	46	
12	8/05/89	ST1-A-12		59	46	46	46	
AVERAGE SD(n-1)			79.0 0.0	61.6 2.8	49.5 2.5	50.5 1.2	53.5 3.8	
1	8/07/89	ST1-B-01		69	55	51	51	70 (INF)
2	8/08/89	ST1-B-02		72	58	51	52	
3	8/09/89	ST1-B-03		70	60	53	54	
4	8/10/89	ST1-B-04	82	69	57	54	51	
5	8/11/89	ST1-B-05		68	55	51	46	
6	8/12/89	ST1-B-06		68	54	49	50	
7	8/14/89	ST1-B-07		NA *	57	49	53	
8	8/15/89	ST1-B-08		75	59	53	50	
9	8/16/89	ST1-B-09		74	61	54	54	
10	8/17/89	ST1-B-10	82	70	58	51	50	
11	8/18/89	ST1-B-11		73	58	50	47	49 (EFF)
12	8/19/89	ST1-B-12		75	58	48	48	
AVERAGE SD(n-1)			82.0 0.0	71.2 2.7	57.5 0.7	51.2 0.8	50.5 1.4	
1	8/21/89	ST1-C-01		72	66	64	63	
2	8/22/89	ST1-C-02	80	85	66	63	61	
3	8/23/89	ST1-C-03		84	69	64	60	
4	8/24/89	ST1-C-04		82	66	65	56	
5	8/25/89	ST1-C-05		83	64	59	53	
6	8/26/89	ST1-C-06		82	72	70	68	64 (EFF)
7	8/27/89	ST1-C-07		79	65	58	55	
8	8/28/89	ST1-C-08		84	66	61	56	
9	8/29/89	ST1-C-09		84	68	68	61	60 (EFF)
10	8/30/89	ST1-C-10		81	68	80	68	
11	8/31/89	ST1-C-11	82	84	69	67	59	82 (INF)
12	9/01/89	ST1-C-12		79	67	71	60	
AVERAGE SD(n-1)			81.0 1.4	81.6 3.6	67.2 0.8	65.8 2.5	60.0 2.5	

* - Not Included in Calculation of Averages or Standard Deviations

TABLE 21. POTENTIAL CHLORIDE CONTRIBUTIONS FROM
PARTIALLY CHLORINATED PHENOLS

substance	detection limit PPM	chloride yield PPM (calc)
2-MONOCHLORO	2	0.6
2,4-DICHLORO	2	0.9
2,4,6-TRICHLORO	2	1.1
2,4,5-TRICHLORO	10	5.4
TETRACHLORO	NA, .2PCP*	5.1
POSSIBLE NON-PCP TOTAL.....		13.1
PENTACHLORO	42 found	27.9
GRAND TOTAL.....		41.0

*Estimated only, on the basis that PCP
may contain as much as 20% tetra isomers.

Removal of other pollutants such as residual oil or biomass may explain why the decreases in TOC levels are higher than calculated for PCP removal.

Polynuclear Aromatic Hydrocarbon Removal

Concentrations of the various polynuclear aromatic hydrocarbons (PAHs) in the incoming well water were lower than anticipated and below the detection limits in both the well water and the influent. The high detection limits for PAHs in the semivolatile organics GC/MS scans, often in the range of 2 ppm when analyzing groundwater or influent for pentachlorophenol in the 10-50 ppm range, precluded measurements for PAHs at ppb level, but do confirm that significant concentrations of the various PAHs were not present in the groundwater. Two values for total PAHs obtained during the predemonstration well drilling effort, 145 and 295 ppb, would be consistent with the absence at the indicated detection limits during the experimental portion of the project.

Specific PAHs were below the detection limits in the effluents as well, even with the detection limits now in the range of 10-100 ppb. One effluent sample exhibited a single PAH component, reported as 0.4 ppb of fluoranthene. The lack of numerical values for PAHs in the well water or the influent makes it impossible to assess the removal of these chemicals by the BATS at the MacGillis and Gibbs facility.

As noted earlier, It was only possible to carry out limited analyses, and only on a few sludge samples, for pentachlorophenol or the PAHs. These analyses indicated low but detectable quantities of PCP and selected PAH compounds of interest, as noted in Table 22. In every case the amount of sludge produced or collected was so small that daily sampling of the sludge was not practical. While not conclusive, the limited data does suggest that

accumulation of PCP or PAHs in the sludge is not a significant contributing mechanism for the removal of these species.

TABLE 22. SLUDGE ANALYSIS RESULTS

SAMPLE	POLLUTANT	CONC
		(mg/kg dry)
B-09-07S	PCP	34
	pyrene	15
	chrysene	5.3
	Benzo(b)fluoranthene	10
	benzo(a)pyrene	6.1
C-05-07S	PCP	170
	Anthracene	92
	Benzo(k)fluoranthene	74
C-10-07S	PCP	2.7
	Anthracene	3.0
	Pyrene	2.5
C-10-15S*	PCP	18
	phenanthrene	1.9

* This sample is "active" sludge found adhering to the walls of bioreactor.

Interestingly, monitoring of the exhaust air stream, in a 4 inch chimney in the lid over the bioreactor before and after the carbon adsorber, indicated that some stripping of polynuclear aromatic hydrocarbons does occur, probably due to the air bubbled through system (Table 23). It was necessary to introduce additional air to the stack during the monitoring to overcome the resistance of the carbon. Small amounts (≤ 1 ppb) of phenol, 2,4-dimethyl phenol, and higher molecular weight PAHs such as fluorene and dibenzofuran were found occasionally in the pre-carbon samples but not in the after-carbon samples. Only naphthalene was found to pass through the carbon at a detectable level (under 2 ppb), possibly by an air stripping "regeneration" phenomenon.

TABLE 23. PAHS IN AIR EMISSIONS FROM BIOREACTOR

Test #	Liquid flow at time of test	naphthalene		2-me naphthalene		acenaphthene	
		b.c.*	a.c.*	b.c.	a.c.	b.c.	a.c.
[----- (ppb) -----]							
1	1	6.5	0.6	4.7	nd #	0.5	nd
2	1	3.8	1.6	3.0	nd	0.3	nd
3	1	4.6	1.7	3.7	nd	nd	nd
4	3	4.6	0.6	6.7	nd	0.7	nd
5	5	34.6	1.1	47.9	nd	2.8	nd

* b.c. = before carbon adsorber

a.c. = after carbon adsorber

nd = not detected

Polychlorinated Dibenzo-p-Dioxins/Dibenzofurans

Historically, there has been concern about the possibility of chlorinated dibenzodioxins in manufactured chlorinated products such as pentachlorophenol. Consequently there was some concern about the possibility of these species being present in the groundwater. Selected samples were scanned for the various dioxins and furans using high resolution GC coupled with low resolution MS. A number of the chlorodioxin and furan species were found to be present in the influent and in the effluent, but only at nanogram/liter levels except for the octachloro- isomer (OCDD). The 2,3,7,8-TCDD isomer was reported at above detection limit in only one sample (62 ng/L in an effluent sample). Review of the data (Table 24) also discloses an increase in concentration for all the isomers as the wastewater moves through the reactor. The increases may be due to accumulation of the dioxins on the biomass, which then is sloughed off into the effluent.

TABLE 24. DIOXINS/FURANS FOUND IN SYSTEM

Week	Influent/Effluent Concentrations (ng/L)						
	HpCDD	HpCDF	HxCDD	HxCDF	OCDD	OCDF	TCDD 2378-
1	60/180	<10/20	-*	-	340/1100	<17/23	-
2	32/180	<2.8/30	<2.2/8.8	<1.5/4.1	170/910	<7.3/40	-
3	<4.4/4.3	-	-	-	28/42	-	-
4	-	-	-	-	<8.6/28	-	-
5	25/62	2.1/7.0	-	-	140/390	<4.8/12	-
6	-	-	-	-	-	-	<3.2/62

* An '-' indicates the isomer was absent or below detection limit in both influent and effluent.

Some dioxin/furan isomers were found in the sludge in the ng/Kg range, based on wet weights (Table 25). Recognizing the small

amount of sludge generated, it is not considered a problem except that the sludge may require disposal as a dioxin-contaminated material. This would add somewhat to the cost of the process.

TABLE 25. DIOXINS/FURANS FOUND IN SLUDGE

Week	Sludge Concentrations (ng/gm)							
	HpCDD	HpCDF	HxCDD	HxCDF	OCDD	OCDF	TCDD	2378-
1	260	46	13	13	1900	41	<.054	<.054
2	no sample							
3	no sample							
4	25	3.9	1.4	1.7	190	3.0	<.088	<.088
5	<.20	<.14	<.17	<.12	0.98	<.22	<.16	<.16
6	23	4	1.5	1.7	140	3.1	<.08	<.08

Heavy Metals

While low concentrations of arsenic and various heavy metals were found to be present in the groundwater, these appear to pass through the system with little change in concentrations (Table 26) - with the exception of the first effluent sample, which shows anomalous results. The remaining data in the table are groundwater and effluent data obtained on neighboring, but not necessarily the same, day. At the levels encountered, metals are not expected to interfere with the bioreaction. The analytical data show no evidence for accumulation of metals on the biomass and subsequent sloughing into the effluent.

TABLE 26. METALS FOUND IN SYSTEM

Week	Concentration of Metals (groundwater/effluent) (ug/L)					
	As	Cu	Ni	Cr	Pb	Zn
1	6.4/220	25/4400	60/390	ND/450	7.7/580	32/20,000
2	4.1/5.6	19/37	54/67	ND/8.0	11/ND	20/20
3	5.4/5.3	20/23	81/73	ND/ND	ND/11	ND/8.0
4	--/6.0	--/19	--/60	--/ND	--/8.1	--/13
5	6.5/7.7	--/23	67/71	ND/23	3.9/6.1	23/30
6	5.9/5.7	ND/30	91/87	7.0/ND	6.9/5.9	20/17
DL^	1.5	12	21	6.7	2.9	5.7

* An '--' indicates the analysis was not carried out; an ND indicates the concentration was below detection limit.

^ DL = Detection limit

Volatile Organics

Analyses for volatile organics indicated that few of these materials were present in the groundwater, even at low concentrations. Levels were further reduced by passage through the treatment system, probably by stripping. Interestingly, volatile organics were not detected in the exhaust air collected from the reactor during the Modified Method 5 testing.

Biomonitoring

Considering the nature of the contaminants, it was suspected that the groundwater could be toxic to aquatic species. With that in mind, biomonitoring with two different species, minnows and water fleas, was carried out on the groundwater, the influent, and the effluent. The results confirmed that the groundwater was toxic to these species and that treatment removed the cause of the toxicity. The results presented as LC_{50} values in Table 27 reflect the percentage of groundwater, influent, or effluent that could be tolerated in the water used for the test before 50% of the species succumbed. When 1% or even less of either groundwater or influent water is introduced to the test water, 50% or more of the test species die during the test period. After treatment in the BATS, the effluent has essentially no adverse effect on either species, even when 100% effluent is the test water.

TABLE 27. ACUTE BIOTOXICITY OF GROUNDWATER AND TREATED EFFLUENT

Week	Flow (gpm)	LC ₅₀ -Daphnia #			LC ₅₀ -Minnow *		
		grdwtr	infl.	effl.	grdwtr	infl.	effl.
		(% wastewater/test water)					
1	1	--	0.35	100	--	0.3	100
2	1	--	0.84	100	--	1.07	100
3	3	--	0.26	100	--	0.43	100
4	3	--	0.54	100	--	0.3	35
5	5	1.0	0.61	100	0.22	0.20	100
6	5	0.27	0.66	100	0.22	0.20	100

48 hour static test at 20°C, daphnia magna

* 96 hour static test at 20°C, pimephales promelas

SECTION 6

ECONOMICS

INTRODUCTION

The purpose of this economic analysis is to provide realistic costs and a knowledge of the basis for their determination, so that it is possible to estimate the cost for systems for other sites. The analysis is based on cost factors developed over the six weeks of operations at the demonstration site as well as other information provided by BioTrol, Inc. for operation at other sites. The key conclusions are based on the two weeks of operation of the mobile unit operating at 5 gpm with an influent containing approximately 30 ppm of pentachlorophenol and achieving 96% removal of that pollutant.

CONCLUSIONS

Operating costs total approximately \$3.45/1000 gallons when treating approximately 7200 gallons/day at 5 gpm in a 5 gpm BATS. The equivalent residence time is 1.8 hours.

Key components of the operating cost for the mobile unit were found to be heat and labor. Secondary items included: nutrients, electricity (pumps), and caustic. Related items such as permitting, sinking wells, residuals disposal, etc. are not included.

OPERATING COSTS

Cost data were provided by BioTrol, Inc. for operation of the mobile unit at a flow of 5 gpm, assuming an incoming groundwater with about 45 ppm of pentachlorophenol and a removal efficiency of about 95%. Operating costs were also provided by BioTrol for a 30 gpm unit on the basis of this demonstration and other data from the developer. Table 28 summarizes the essential operating cost data for systems of both sizes.

TABLE 28. OPERATING COST OF TREATMENT

Cost item	at 5 gpm	at 30 gpm
	(\$/1000 gal)	
nutrients	0.042	0.017
electricity	0.216	0.216
heat	1.46	1.46
labor*	1.49	0.50
caustic	0.24	0.24
TOTAL	3.45	2.43

* includes operation, maintenance, routine monitoring at \$15/hr

The estimates do NOT include operating costs for oil/water separation, suspended solids removal, exhaust air treatment, or effluent polishing since these items are site and waste specific. While carbon was used at the MacGillis and Gibbs site as part of the demonstration program, the exhaust from the reactor and the effluent from the reactor would have met the OSHA Permissible Exposure Limit (PEL) for naphthalene (10 ppm) and POTW discharge requirements (2 ppm PCP) without these controls.

In addition, the cost data do not reflect items such as well drilling, obtaining permits, disposing of solid residues or other wastes, site security, insurance, or decommissioning the site after treatment. While these items are part of EPA's list of 12 cost categories, these costs are expected to be comparable for any above ground system that was used to remediate a site. In addition, these costs would be very dependent on the site location and characteristics.

A more detailed discussion of each of the cost elements included in Table 28 is provided in the following paragraphs.

Nutrients: Urea and trisodium phosphate are added at the same dosage (0.16 lb urea and 0.31 lb TSP/lb PCP) regardless of system size. For the pilot scale system the cost reflects purchase of the ingredients at a local fertilizer supplier; for the larger system some economy of scale has been factored in on the assumption that the materials would be purchased in bulk. (Cost for storage facilities has not been included in the capital costs.)

Electricity: Groundwater (or other feedwater) is delivered to the system by a pump external to the system; the cost to operate that pump has not been included. Electricity, at \$0.06/kwh, is used to pump effluent from the bioreactor and to power the air sparger blower motor. The developer's calculations indicate that variations

between the requirements for a 5 gpm and a 30 gpm system appear to be nominal.

Heat: The amount of heat required at a particular site would be dependent to some extent on the incoming water temperature, the ambient temperature and resulting heat loss, as well as the exothermicity of the reactions for a particular wastewater. With the heat exchanger in use, the actual temperature difference between influent and effluent is only about 5°F and is essentially independent of the temperature of the water source except during startup. At the MacGillis and Gibbs site during July to September the average groundwater temperature was 55°F (13.25°C) because of ambient heating and the heater was not used. For the cost calculations, a 5°F difference in temperature is assumed.

Caustic: The cost for these estimates is based on the caustic used in the demonstration program at a price of \$2.60/gal of 50% solution. For the MacGillis and Gibbs demonstration project, total caustic use was about 15 gal over the six weeks. Depending on the pH and alkalinity of the incoming water to be treated, more or less caustic may be required at another site.

Labor: The vendor's experience is that operation of the 5 gpm system requires only about 5 hours/week for operation, on-site maintenance, replenishment of nutrient and caustic supply tanks, and sampling for off-site monitoring. With the larger system, it is estimated that labor requirements could increase to 10 hours/week.

Increasing the size of the system presents few economies of scale except in labor, which is very significant, and, to a much smaller extent, the quantity of nutrients that will be needed during the course of a cleanup.

Start-up of the system requires approximately two weeks and costs would be about the same as two weeks of operation. Clearly, acclimation time and costs contribute a more significant portion of total operating cost where a system is being used for a short duration cleanup.

Capital Costs

BioTrol, Inc. provided three bases to the capital cost of the equipment:

- a. A lease rate for a 5 gpm mobile unit of \$2400/month, which would be suitable for a short term cleanup;
- b. A purchase price of \$30,000 for a 5 gpm skid mounted installation, such as might be needed for long term treatment of a relatively low flow stream, leachate from a pond, etc.; and

- c. A purchase price of \$80,000 for a 30 gpm skid mounted installation, as might be needed for a larger aquifer.

These capital costs also do not include the equipment or installation costs for any pre- or post-treatment equipment nor the cost of a concrete pad, building enclosure for the equipment, or other site preparation. For the following comparisons, the capital costs for both the 5 gpm and the 30 gpm units have been amortized over 10 years and assigned a \$0.00 salvage value at that time.

HYPOTHETICAL CASE STUDIES

Using the above operating and capital cost figures provided by the vendor, various case studies can be formulated and conclusions drawn as to the time and actual cost that would be involved in remediations of specific sizes. For example, if a site is expected to yield 1,000,000 gallons of groundwater contaminated with 45 ppm of pentachlorophenol, and all other factors are comparable to those in the demonstration program, the most cost-effective scenario can be predicted, as shown in Table 29. At 5 gpm, the demonstration project approximates to the 0.1 MG example shown in the table.

While the 30 gpm unit would be the most cost-effective on these bases, short term use of this unit is probably unrealistic. Even for short term uses, lease of the 5 gpm mobile unit is more realistic than purchase of the 5 gpm unit unless other uses can be readily foreseen for the remainder of a purchased unit's life.

Mathematically, costs can be evaluated with the following general equation using the appropriate operating and capital costs for the system size selected:

$$\frac{\text{Total Cost}}{1000 \text{ gal}} = \frac{(\text{operating cost})}{1000} \times \frac{(\text{total throughput})}{1000} + \frac{(\text{capital cost})}{\text{amortize period}} \times \frac{(\text{total throughput})}{\text{throughput/day}}$$

Another way of examining the costs is to assume that a Superfund site is a large reservoir of contaminated water. Costs can then be estimated on the assumption that treatment (to a comparable removal level) will be carried out at the site for an extended time, for example, 5 years. For this analysis it would be assumed that the equipment is 50% amortized by the use and has 50% salvage value at the end of the five years. The results of such an analysis are presented in Table 30. Of course, this analysis results in the treatment of different volumes of wastewater over the course of the cleanup.

TABLE 29. ESTIMATED COST OF TREATING VARIOUS WASTEWATER VOLUMES*

System	0.1 MG	1 MG	10 MG

5 gpm skid mounted unit:			
days to treat #	28	153	1,403
operating cost \$3.45/1000 gal	\$ 690	3,795	34,845
capital cost of unit @ \$8.33/day	233	1,294	11,687
Total cost, \$	923	5,069	46,532
Cost, \$/1000 gallons	9.23	5.07	4.65

5 gpm mobile unit:	DEMONSTRATION		
days to treat #	28	153	1,403
operating cost \$3.45/1000 gal	\$ 690	3,795	34,845
lease cost (\$2,400/mo)	2,400	12,000	112,800
Total cost, \$	3,090	15,795	147,645
Cost, \$/1000 gallons	30.90	15.80	14.76

30 gpm skid mounted unit:			
days to treat #	17	37	243
operating cost \$2.43/1000 gal	1,713	3,900	25,770
capital cost of unit @ \$22.22/day	378	822	5,422
Total cost, \$	2,091	4,722	31,192
Cost, \$/1000 gallons	20.91	4.72	3.12

* At an assumed 45 ppm PCP concentration

Acclimation time of about 2 weeks is included in the "days to treat" and in capital and operating costs at the same operating cost

TABLE 30. TREATMENT COSTS OVER 5 YEARS (1800 days)

Cost item	5 gpm skid mounted	5 gpm mobile	30 gpm skid mounted

MG water treated	12.96	12.96	77.76
operating cost	\$ 44,712	\$44,712	\$188,957
equipment cost	\$ 15,000	\$144,000	\$ 40,000
total cost	\$ 59,712	\$188,712	\$228,957

Cost/1000 gal	\$ 4.61	\$14.56	\$ 2.94

An equation that can be used to estimate total cost on this basis would have the following form:

$$\text{Cost} = [\text{BATS rate} \times \text{total time} \times \text{operating cost}] + \text{depreciation}$$

SECTION 7

CONCLUSIONS

A mobile (trailer-mounted) BATS with 5 gpm capacity tested at the MacGillis and Gibbs Company site under the Superfund SITE program demonstrated the ability of the system to remove pentachlorophenol from groundwater. At the flow selected as optimum for the system, 5 gpm, removal of 96+% was achieved and an effluent with about 1 ppm of pentachlorophenol was attainable. At lower flow rates, 1 gpm and 3 gpm, pentachlorophenol removal increased to 99+% and final concentrations down to 0.1 ppm were achievable.

Polynuclear aromatic hydrocarbons probably were also removed, either by biodegradation or by adsorption on/in the biomass but low concentrations in the groundwater source make it impossible to reach a firm conclusion.

Secondary pollutants such as oil, suspended solids, and even heavy metals do not appear to interfere with the reaction, at least at the concentrations present in this wastewater. Decreases in the Total Organic Carbon (TOC) beyond that attributable to pentachlorophenol suggest that the system removes other organic species as well.

Biomonitoring demonstrated that acute toxicity present in the raw groundwater was essentially totally removed. Coupled with the measured removal of specific chemical species, this suggests that any form of discharge or reuse would be safe for this wastewater.

Operating cost for the BATS ranges from \$3.45/1000 gal when using a 5 gpm system to \$2.43/1000 gal when using a larger (30 gpm) unit.

SECTION 8

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APPENDIX A

QUALITY ASSURANCE/QUALITY CONTROL EVALUATION

APPENDIX A

QUALITY ASSURANCE/QUALITY CONTROL EVALUATION

BioTrol Aqueous Biological Treatment of Wood Preserving Site Groundwater

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QUALITY ASSURANCE/QUALITY CONTROL EVALUATION

BioTrol Aqueous Biological Treatment of Wood Preserving Site Groundwater

1.0 INTRODUCTION

As a part of the USEPA Superfund Innovative Technology Evaluation (SITE) program, the BioTrol Aqueous Treatment System (BATS) technology was demonstrated at the MacGillis and Gibbs Superfund site in New Brighton, Minnesota. This appendix to the final report discusses the results of the comprehensive quality assurance program associated with this demonstration. Included in this discussion are: (1) data quality objectives (as defined in the Quality Assurance Project Plan), (2) analytical quality control, (3) additional studies undertaken during the project (including a method comparison study initiated in an effort to resolve an apparent discrepancy in pentachlorophenol influent concentrations as a function of sample location and system flow rate), (4) non-conformances encountered during the demonstration, (5) deviations from the QAPjP in field or laboratory protocols, (6) findings of audits conducted during the demonstration, and (7) conclusions and limitations of the data.

1.1 CRITICAL ANALYSES

The primary technical objective of this SITE demonstration was to determine the extent of removal of pentachlorophenol (PCP) by the BioTrol bioreactor treatment system. The project was also designed to obtain data on polynuclear aromatic hydrocarbons (PAHs) removal. Additionally, a secondary objective was to determine the fate and extent of removal of other semivolatile organic compounds, dioxins/furans, volatile organics, metals, oil and grease and total phenolics. Chloride ion production was determined along with total organic carbon as supporting measures of pentachlorophenol degradation/destruction. The toxicity reduction between well water/influent and effluent wastestreams was determined by conducting acute toxicity tests. Losses from the bioreactor via sloughed biomass and exhausted air were monitored by sludge analysis and emissions sampling and analysis, respectively. Residue and nutrient analyses were also performed in the laboratory as system condition measurements. Table A.1 summarizes the analyses performed, matrices sampled, location sampled and frequency of sampling. Each of these analyses will be summarized in sections 2.0

TABLE A.1

Sampling Summary: Biofrol Aqueous Treatment SITE Demonstration Project

Sample Type	Sampling Method	Parameter	Sampling Points ^a	Frequency ^b	Measurement Type ^c
Water	Composite	Pentachloro-phenol/PAHs	All bioreactor points	Daily	Critical
Water	Grab	PCP/PAHs	Carbon effluent	Weekly	Discharge
Water	Filtered Composite	Dissolved PCP/PAHs	All bioreactor points	3/week	Critical
Water	Grab (Filtered)	Dissolved PCP/PAHs	Well water	Weekly	Characterization
Water	Composite	Dioxins	Influent/effluent	Weekly	Critical
Water	Grab	Dioxins	Well water	Weekly	Characterization
Water	Composite	Priority Pollutant Metals	Influent/effluent	Weekly	Critical
Water	Grab	Priority Pollutant Metals	Well water	Weekly	Characterization
Water	Grab	Volatile Organics	Influent/effluent	Weekly	Critical
Water	Grab	Volatile Organics	Well water	Weekly	Characterization
Water	Composite	Semivolatile Organics (full scan)	Influent/effluent	Weekly	Critical
Water	Grab	Semivolatile Organics (full scan)	Well water	Weekly	Characterization
Water	Composite	Chloride	All bioreactor points	Daily	Critical
Water	Grab	Chloride	Well water	Weekly	Characterization
Water	Composite	Total Organic Carbon (TOC)	All bioreactor points	Daily	Critical
Water	Grab	Total Organic Carbon (TOC)	Well water	Weekly	Characterization

TABLE A.1 (Continued)
Sampling Summary: BioTrol Aquatic Treatment SITE Demonstration Project

Sample Type	Sampling Method	Parameter	Sampling Points ^a	Frequency ^b	Measurement Type ^c
Water	Filtered Composite	Dissolved TOC	All bioreactor points	3/week	Critical
Water	Grab (Filtered)	Dissolved TOC	Well water	Weekly	Characterization
Water	Composite	Residue: Total Suspended	All bioreactor points	3/week	System
Water	Grab	Residue: Total Suspended	Well water	Weekly	Characterization
Water	Composite	Residue: Volatile Suspended	All bioreactor	3/week	System
Water	Grab	Residue: Volatile Suspended	Well water	Weekly	Characterization
Water	Grab	pH (field measurements)	All bioreactor points	2/day	System
Water	Grab	pH (field measurements)	Well water	Weekly	Characterization
Water	Grab	Dissolved Oxygen (field measurement)	All bioreactor points	2/day	System
Water	Grab	Dissolved Oxygen (field measurement)	Well water	Weekly	Characterization
Water	Grab	Temperature (field measurement)	All bioreactor points	2/day	System
Water	Grab	Temperature (field measurement)	Well water	Weekly	Characterization

TABLE A.1 (Continued)
Sampling Summary: Biofrol Aqueous Treatment SITE Demonstration Project

Sample Type	Sampling Method	Parameter	Sampling Points ^a	Frequency ^b	Measurement Type ^a
Water	Composite	Alkalinity	All bioreactor points	Weekly	System
Water	Grab	Alkalinity	Well water	Weekly	Characterization
Water	Grab	Phenolics (total)	Influent/effluent	Weekly	Critical
Water	Grab	Phenolics (total)	Well water	Weekly	Characterization
Water	Composite	Nutrients: Ammonia Nitrate/Nitrite Phosphate	Influent/effluent	3/week	System
Water	Composite	Nutrients: Ammonia Nitrate/Nitrite Phosphate	Well water	Weekly	Characterization
Water	Composite	Biotoxicity Testing	Influent/effluent	Weekly	Critical
Water	Grab	Oil and Grease	All bioreactor points	3/week	Critical
Water	Grab	Oil and Grease	Well water	Weekly	Characterization
Emissions	Sorbent Trap	Pentachlorophenol/PAHs (semivolatile Organics)	Bioreactor stack exit, carbon column exit	At the beginning of each test period	Critical
Biosludge (sloughed)	Filtration/Centrifugation	PCP/PAHs	Bioreactor exit	Weekly	Critical
Biosludge (sloughed)	Filtration/Centrifugation	Phenolics (total)	Bioreactor exit	Weekly	Critical
Biosludge (sloughed)	Filtration/Centrifugation	Priority Pollutant Metals	Bioreactor exit	Weekly	Critical

TABLE A.1 (Continued)

Sampling Summary: Biofrol Aqueous Treatment SITE Demonstration Project

Sample Type	Sampling Method	Parameter	Sampling Points ^a	Frequency ^b	Measurement Type ^c
Biosludge (sloughed)	Filtration/Centrifugation	Residue	Bioreactor exit	Weekly	Critical
Biosludge (sloughed)	Filtration/Centrifugation	Dioxins	Bioreactor exit	Weekly	Critical
Biomass (active)	Grab (scraping)	PCP/PAH	Bioreactor sidewall	Once	Critical

^a All bioreactor points = influent, effluent and both midpoints; well water = groundwater sample taken at exit from well; carbon effluent = the effluent after carbon treatment being discharged to the POTW.

^b As proposed in the QAPJP, based on a 6 day/week sampling schedule.

^c Refers to critical measurement, raw water characterization, discharge permit requirement or system condition measurement.

and 3.0, including any potential bias, outlier data and precision and accuracy data.

1.2 DATA QUALITY OBJECTIVES

Quality assurance objectives were quantitatively defined in the QAPjP for precision, accuracy and completeness for the critical measurements for the project (excluding biotoxicity). A primary concern was the establishment of a comprehensive quality assurance program with defined objectives to ensure that the data produced during the demonstration were of known and acceptable quality, thus allowing an evaluation of the treatment technology and achievement of the project's technical objectives (the primary objective being the determination of the extent of removal of PCP). Overall, analytical measurements met data quality objectives with the following exceptions.

- o High levels of PCP in the samples required that many semivolatile extracts be diluted prior to analysis by GC/MS. As a result, a significant amount of surrogate recovery data was unobtainable, since the necessary dilution factors brought the surrogate compound concentrations below the detection limit. However, the available data suggest that overall approximately 90% of the recoveries were within control limits.
- o The high levels of PCP native to the samples also affected the calculation of pentachlorophenol spike recoveries. For half of the matrix spike duplicate pairs analyzed, the sample PCP concentration was 6-20 times higher than the spike concentration and therefore recovery could not be determined. The remaining available data met precision and accuracy objectives overall.
- o One set of emissions samples (from the 3 gpm flow rate) had significantly low surrogate recoveries for the semivolatile organic analysis of the MM5 sampling train, indicating that these results are biased low. However, the sampling episodes from the 1 gpm and 5 gpm flow rates, which had normal surrogate recoveries, indicate that losses to the exhaust air were minimal, and that no PCP was present in these emissions.
- o Completeness objectives for sludge (sloughed biomass) collection/analysis were not achieved for reasons detailed in section 6.1.

1.2.1 Data Quality Indicators:

Quality control analyses associated with the data quality indicators of precision and accuracy include matrix replicates, matrix spikes and matrix spike

duplicates. Precision, the ability of the measurement system to generate reproducible data, was calculated as the relative percent difference (RPD) between the results of duplicate samples or matrix spike/matrix spike duplicate (MS/MSD) pairs using the following equation:

$$\% \text{ RPD} = \frac{(R_1 - R_2)}{(R_1 + R_2)/2} \times 100$$

where R_1 and R_2 are the results of the sample and duplicate, or the MS and MSD, analyses. Accuracy, defined as the nearness of the analytical result to the "true" value, is assessed by the analysis of matrix spikes (or MS/MSD pairs) and reported as percent recovery according to the following equation:

$$\% \text{ Recovery} = \frac{C_i - C_o}{C_t} \times 100$$

where C_i = the measured concentration in the spiked sample, C_o = the measured concentration in the unspiked sample and C_t = the known concentration of analyte added to the sample. The data quality indicator of completeness is measured as the comparison of valid data obtained during the demonstration with the amount of data expected:

$$\% \text{ Completeness} = \text{Valid data points} / \text{Expected data points} \times 100$$

Completeness is discussed in section 2.1, and precision and accuracy are discussed for each of the analyses in sections 2.2-2.11.

2.0 ANALYTICAL QUALITY CONTROL

The following sections review the measure of completeness achieved for the project, followed by discussions of the analytical QC results for each of the parameters measured.

2.1 COMPLETENESS

QA objectives for completeness for all critical measurements were given in the QAPjP, generally as 90-95%, and results are summarized in Table A.2. The data presented in this table include the number of samples and duplicates proposed for collection in the QAPjP, the number actually collected during the 6-week demonstration and the number of samples analyzed. (Sample analyses which may have exceeded QC criteria for surrogate recoveries are included in the totals given for PCP/PAH, semivolatiles and emissions analysis).

Almost all analyses met the QA objective for completeness, with the exception of PCP/PAHs (total and dissolved) and sludge analyses. The treatment technology was evaluated using average PCP concentrations for well water, influent and effluent waste streams. The loss of eight individual data points does not seriously impact data quality or the achievement of the project's technical objective, and as noted in Table A.2, the completeness objective only fell one-two percent short of the QAPjP objective. Sludge collection/analysis was hindered by the type of sample collected (see section 6.1). Sludge data was used qualitatively to estimate the potential PCP loss due to ad/absorption; thus data quality was not greatly impacted.

2.2 PCP/PAH (TOTAL, DISSOLVED) AND SEMIVOLATILE ORGANICS ANALYSIS

Aqueous samples were analyzed for PCP/PAHs (on samples as collected and after filtering), and occasionally for full-scan semivolatile organics, by SW846 method 3510/8270. Solid/sludge samples were analyzed for PCP/PAHs by SW846 method 3550/8270, and were phase-separated by centrifugation prior to extraction of the solids. Method blank data, surrogate recovery results, and precision and accuracy data (MS/MSD analysis) are summarized below. In addition to these quality control analyses, method specified protocols for calibration (tuning, multi-point standard curves, continuing calibration standards and internal standards) were followed and met QC criteria.

TABLE A.2

Completeness Data: Biofrol Aqueous Treatment SITE Demonstration

Matrix	Measurement	As Per QAP JP			Collection			Analysis		
		# of Samples (1)	# of Dupli.	Completeness Objective (%)	# of Samples (1)	# of Dupli.	Completeness Achieved (%)	# of Samples (1)	# of Dupli.	Overall Completeness Achieved (%)
Aqueous (2)	PCP/PAHs	138	6	95	134 (3)	6	94	130 (11)	6	94
	Dissolved PCP/PAHs	78	4	95	76 (4)	4	93	72 (11)	4	93
	Dioxins	18	1	90	18	1	100+	19 (12)	1	100+
	Metals	18	1	90	18	1	100	18 (13)	1	100
	Volatile Organics	18	1	90	18	1	100	18 (13)	1	100
	Semi-volatile Org.	18	1	95	18	1	100	18	1	100
	Chloride	150	7	90	149 (5)	7	99	149	7	99
	TOC	150	7	90	149 (5)	7	99	149	7	99
	Dissolved TOC	78	4	90	77 (5)	4	99	77	4	99
	Residue (TSS/TVSS)	78	4	85/NC	77 (5)	4	99	77	4	99
	Alkalinity	30	1	85/NC	30	1	100	30	1	100
	Total Phenolics	18	1	90	18	1	100	18	1	100
	Nutrients	42	2	85/NC	41 (5)	2	98	41	2	98
	Oil and Grease	78	3	90	78	4	99 (6)	77	4	99 (6)
	Biotoxicity	14 (7)	-	Not Specified	14	-	100	14	-	100
Sludge (8) (Sloughed biomass)	PCP/PAHs	6	1	95	4	0	50	3	0	50
	Metals	6	1	90	4	0	67	4	0	67
	Dioxin	6	1	90	4	0	67	4	0	67
	Total Phenolics	6	1	90	4	0	67	4	0	67
Biomass (active)	PCP/PAHs	6 (9)	0	N/A	1	0	N/A	1	0	N/A
	Emissions	6 (10)	2	90	6	4 (10)	100+	6	4	100+

TABLE A.2 (Continued)

Notes:

NC = Not a critical measurement; completeness QA objective given for guidance
N/A = Not applicable

1. Does not include field, trip or equipment wash blanks
2. Aqueous matrix includes: well water, influent, effluent, reactor midpoints and carbon effluent samples.
3. One influent sample lost in field; one influent, effluent and midpoint sample lost in lab (due to breakage).
4. One influent sample lost in field, one influent sample lost in lab (both due to breakage).
5. One influent sample lost in field (breakage).
6. An extra duplicate was collected for this measurement parameter. Completeness is calculated based only on the # of samples without the extra duplicate.
7. QAPP originally called for 2 samples/week. An additional well water sample was added the last 2 weeks.
8. Sludge collection severely hampered by type of filter used, generating wastewater-type sludge samples. The limited volume available prevented samples being collected during weeks 2 and 3 and made a field duplicate impractical (as qualified in the QAPP). Completeness calculated without including proposed duplicate.
9. Uncertainty about the opportunity to collect an active biomass sample was clearly documented in the QAPP. (Section 5.4, Table 5-5, Table 5-8, and 5.4.3.2-page 29) A single sample was obtained the last week of sampling. A completeness objective/calculation is not appropriate given the nature of the sampling activity.
10. The QAPP proposed an initial sampling episode at the start of the project, with subsequent bioreactor and carbon effluent being sampled once per test period, for a total of 8 samples. Three consecutive samples were to be taken with the first sampling episode, thus 1 sample and 2 "duplicates"; since both effluents were sampled there are actually 4 "duplicates". The initial sampling episode prior to the start of the demonstration was not performed due to schedule constraints; therefore only 6 samples were collected. The QAPP was not fully revised to reflect this altered schedule.
11. This total does include samples which had surrogate recoveries outside of control limits due to suspected matrix effect (see section 2.2).
12. An extra effluent sample was analyzed for dioxins/furans.
13. Eighteen samples were specified for collection in the QAPP; three grab samples were to be collected and analyzed in the laboratory as a composite (excluding the raw well water sample). Following the lab audit, the decision was made to analyze each individual grab separately. - thus the actual number of samples analyzed were 38 and the duplicate was actually 3 grab analyses.

2.2.1 Holding Time

The method-specified holding time for aqueous samples (7 days from sample collection to extraction and 40 days from extraction to analysis) was exceeded for the influent, midpoint 1, midpoint 2, effluent and equipment wash samples from day 3 of the 5 gpm flow test (STI-C-03-02/03/04/05/13), and were met for all other water samples. The results for samples exceeding hold time were not used in the evaluation of the bioreactor. The method-specified holding time for solid matrices (14 days from sample collection to extraction) was exceeded for two of the sludge samples by one and five days; all samples met the analysis hold time of 40 days. The elapsed time was considered to have minimal impact on data quality and these data were used in evaluating the extent of PCP removal via sloughed biomass. In addition, sludge data was used only as a quantitative estimate as previously stated.

2.2.2 Method Blank Results

Method blank results are summarized in Table A.3. The only consistent lab contaminant detected in aqueous method blanks was bis(2-ethylhexyl)phthalate (at an average concentration of 22 ug/l.) Phthalates were only a target compound for the 19 samples (and associated field blanks) analyzed for full-scan semivolatile organics. At the detected blank levels, there was no impact on sample data quality.

2.2.3 Surrogate Recovery

Seven surrogate compounds were spiked into each aqueous sample prior to the liquid-liquid extraction procedure. The percent recovery ranges and comparison to control limits are give in Table A.4. As discussed previously, a significant number of surrogate recovery data points were unobtainable when dilutions required, due to high sample PCP concentrations, resulted in surrogate concentrations below the detection limit.

Of the analyses for which surrogate recoveries were generated, an overall 90% of the recoveries were within specified control limits. However, approximately 18% of the samples had 2 or more surrogate recoveries (more than one each of the acid and base/neutral compounds) outside control limits. Significantly, two-thirds of these samples were collected from the second bioreactor midpoint or the effluent, mostly from the first two weeks of the demonstration (1 gpm flow

TABLE A.3

METHOD BLANK RESULTS: PCP/PAH AND SEMIVOLATILE ORGANIC ANALYSES

Compound	Number of Blanks	No. Above Detection Limit	Concentration Range (ug/L)	Detection Limit (ug/L)
<u>AQUEOUS MATRIX BLANKS</u>				
Diethylphthalate	22	1	34	10
Di-n-butylphthalate	22	1	16	10
Bis(2-ethylhexyl)phthalate	22	12*	13-140	10
Di-n-octylphthalate	22	1	17	10
Phenol	22	1	14	10
2-Chlorophenol	22	1	16	10
4-Chloro-3-methylphenol	22	1	11	10
All other compounds	22	0	--	10 - 50
<u>SOLID MATRIX BLANKS</u>				
All compounds	3	0	--	330 - 1600 mg/kg

* -- Also found in 2 additional blanks at levels just below the detection limit.

TABLE A.4

Surrogate Recovery: PCP/PAH (total, dissolved) and Semi-volatile Organic Analyses

Surrogate Compound	Number of Samples (1)	Number of Analyses (2)	Percent Recovery Ranges	AQUEOUS SAMPLES			
				Control Limits (%)	Number Within Control Limits	Number Outside Control Limits	Number of Analyses Diluted Out(3)
Nitrobenzene-d5	272	312	0-211	35-114	159	10	143
2-Fluorobiphenyl	272	312	0-186	43-116	158	17	137
Terphenyl-d4	272	312	0-278	33-141	165	12	135
Phenol-d5	272	312	0-57	10-94	139	27	146
2-Fluorophenol	272	312	0-92	21-100	140	27	145
2,4,6-Tribromophenol	272	312	0-256	10-123	167	13	132
Anthracene-d10	272	312	9-155	30-150	153	12	147(4)
Total		2184			1081	118	985

NOTES:

- (1) Includes field samples and duplicates, field blanks and equipment wash blanks.
- (2) Includes additional analyses requiring dilution of the extracts.
- (3) Includes sample analyses for which surrogates were diluted out in all analyses associated with a given sample (75% of this total) and analyses with the surrogates diluted out although there was another analysis which had reportable surrogate recovery (25%).
- (4) Determined by calculation; recovery data only available from control charts, which do not include analyses with surrogates which are diluted out.

SLUDGE/SOLID SAMPLES

Surrogate Compound	Number of Samples (a)	Number of Analyses	Percent Recovery Ranges	Control Limits (%)	Number Within Control Limits	Number Outside Control Limits	
Nitrobenzene-d5	5	5	9-86	23-120	4	1	
2-Fluorobiphenyl	5	5	8-75	30-115	4	1	
Terphenyl-d4	5	5	10-85	18-137	4	1	
Phenol-d5	5	5	10-93	24-113	4	1	
2-Fluorophenol	5	5	0-81	25-121	3	2	
2,4,6-Tribromophenol	5	5	9-98	19-122	4	1	
Anthracene-d10	5	5	12-116	30-150	4	1	
Total		35			27	8(b)	

NOTES:

- (a) Includes 3 sludge samples, one active biomass sample and an "excess media" sample.
- (b) All recoveries which were outside control limits (except one) were from the analysis of the "excess media" sample.

rate). Factors which appear to have contributed to this matrix effect include the suspended solids in the effluent which were highest during the first part of the demonstration (average TSS=54 mg/l at 1 gpm, 26 mg/l at 3 gpm and 18 mg/l at 5 gpm), and throughout the demonstration the samples collected at the second midpoint of the bioreactor and from the effluent would have been the most affected by biological activity (including any degradation by-products) thus causing a residual microbe population which may have interfered with the extraction or analysis.

In addition, the surrogate compounds d5-phenol and 2-fluorophenol were primarily affected and biased low; tribromophenol recoveries were reported both above and below the control limits and more frequently within limits. Similarly PCP concentrations did not appear to be biased low for samples with low surrogate recoveries - a review of influent samples from the 1 gpm flow rate indicated that the average PCP concentration was higher for samples (six out of twelve) with surrogate recoveries below the control limits than for samples with surrogate recoveries within limits.

It appears reasonable, therefore, to conclude that the low surrogate recoveries observed for d5-phenol and 2-fluorophenol are attributable, at least in part, to matrix effects, particularly for the bioreactor midpoint 2 and effluent samples from the first two weeks. It is also significant that extraction recovery/efficiency was generally within control limits for tribromophenol and for spiked pentachlorophenol - which for most samples was the only target acid extractable compound. Therefore, given the low percentage of samples with surrogates below specified limits there is considered to be minimal adverse impact on data quality basing conclusions on average PCP concentrations as a result of the low recovery for the two surrogate compounds. In addition, the comparison study of methods SW3510/8270 and the developer's HPLC method (which is not dependent on extraction efficiency) shows PCP recovery was not adversely affected in any given matrix (see section 4.1).

2.2.4 Precision and Accuracy

A summary of aqueous sample MS/MSD analysis results is presented in Table A.5. The full complement of spiking compounds was included for each MS/MSD analyzed although in many cases only PCP and PAHs were the target compounds. Due

TABLE A.5

QC Summary: Precision and Accuracy - Semivolatile Organic Compounds

Parameter	ACCURACY				PRECISION					
	Total Number Analyses(1)	Percent Recovery Ranges	Recovery Control Limits	Number Within Control Limits	Number Outside Control Limits	Total Number Analyses (1)	RPD Ranges (%)	RPD Control Limits	Number Within RPD Limits	Number Outside Control Limits
Semivolatile Organic Compounds										
Phenol	28	0-36	12-89	26	2	14	0-29	42	13	0(2)
2-chlorophenol	28	33-70	27-123	28	0	14	2-15	40	14	0
1, 4-dichlorobenzene	28	56-104	36-97	26	2	14	1-19	28	14	0
N-Nitroso-di-n-propylamine	28	41-93	41-116	28	0	14	1-27	38	14	0
1, 2, 4-Trichlorobenzene	28	47-85	39-98	28	0	14	0-14	28	14	0
4-Chloro-3-methylphenol	28	0-67	23-97	23	5	14	2-49	42	11	2(2)
Acenaphthene	28	46-103	46-118	28	0	14	3-26	31	14	0
4-Nitrophenol	28	8-71	10-80	26	2	14	0-35	50	14	0
2,4-Dinitrophenol	28	36-85	24-96	28	0	14	0-55	38	13	1
Pentachlorophenol	30	65-204	9-103	12	4(3)	15	2-31	50	8	0(3)
Pyrene	28	50-127	26-127	28	0	14	2-49	31	13	1
TOTAL:	310(4)			281	15	155(4)			142	4

NOTES:

- (1) There were a total of 15 MS/MSD pairs (30 spikes) analyzed. One pair required a dilution because of high levels of pentachlorophenol in the samples. All other spiked compound concentrations were diluted below the detection limit and recovery and RPD were not calculated. The spiked level was inappropriate, compared to the sample concentration, for pentachlorophenol.
- (2) One MS/MSD pair had 0% recovery for both spikes. An RPD was not calculated.
- (3) Seven MS/MSD pairs (14 spikes) were performed on samples containing high concentrations of pentachlorophenol. Sample concentrations were 6-20 times higher than the spike concentration. Recoveries and RPD values are not considered meaningful for these analyses and are not reported.
- (4) A total of 14 spike recoveries and 9 RPD values were not reported, therefore the totals do not tally correctly.

to the elevated background level of PCP in some of the samples spiked, pentachlorophenol recoveries were not considered meaningful and are not reported if the sample concentration was greater than 5 times the spike concentration.

Precision measurements for all PCP MS/MSD pairs reported were within control limits (RPD = 0-50%); RPD values were not reported for the MS/MSD pairs which had elevated PCP sample concentrations. However, if precision is calculated for these analyses using the observed spiked sample concentration (as opposed to using the calculated % recoveries to determine the RPD), then additional precision data is obtained which is particularly relevant for high PCP concentrations. This measure of precision generates an RPD range of 0.8-17.2% with all values within control limits.

Matrix spikes could not be performed on sludge/solid samples, due to limited volume.

2.3 CHLORIDE

During the initial stage of the analysis program, aqueous samples were analyzed for chloride by SW846 Method 9252. After the laboratory audit (see section 7.3), the method was changed to Standard Method 407C for the remainder of the program. All samples were analyzed within the method specified holding time of 28 days. Method blanks (see Table A.6) were analyzed with each sample batch, and chloride was less than the detection limit for all blanks. Precision and accuracy were determined by the analysis of matrix duplicates and matrix spikes/matrix spike duplicates (see Table A.7). Initial and continuing calibration standard analyses met applicable QC criteria.

2.4 TOTAL ORGANIC CARBON (TOC)

Samples were analyzed for TOC as collected and after filtering (soluble total organic carbon, STOC) by SW846 Method 9060. All samples were analyzed within the 28 day method specified hold time. One method blank had a TOC value of 1.4, all others were not detected at <1mg/L. Field and equipment wash blanks (19 out of 38 blanks) had detected TOC concentrations ranging from 1 mg/L to 83 mg/L, with an average concentration of 9.6 mg/L. However, sample concentrations ranged from 32 mg/L to 2450 mg/L (average concentration = 60 mg/L) and therefore this "background" bias would have little impact on the sample concentrations.

TABLE A.6

METHOD BLANK RESULTS: GENERAL CHEMISTRY, METALS, VOLATILE ORGANIC,
AND DIOXIN/FURAN ANALYSIS

<u>Parameter-Matrix (units)</u>	<u>Number of Blanks</u>	<u>Number Above Detec. Limit</u>	<u>Concentration Range</u>	<u>Detection Limit</u>
Chloride-Aqueous (mg/L)	28	0	--	<1.0
Total Organic Carbon-Aqueous (mg/L)	30	1	1.4	<1
Dioxins/furans-Aqueous (ng/L)				
OCDD	6	1	21	<4.5 ⁽¹⁾
Others	6	0	--	
Dioxins/furans-Solid (ng/g)	3	0	--	<0.24
Metals-Aqueous (ug/L)				
Chromium	6	1	9.0	<7.1
Nickel	6	1	31	<31
Lead	4	3	1.4-3.9	<1.2
Metals-Sludge (ug/L) ⁽²⁾	2	0	--	variable
Volatile Organics-aqueous (ug/L)				
Methylene chloride	11	2 ⁽³⁾	16-29	<5
Others	11	0	--	<5-<10
Oil and Grease - aqueous (mg)	14	9	0.2-3.2	0.0
Residue - aqueous (mg/L)	17	0	--	<1
Nutrients-Aqueous (mg/L)				
Nitrate-nitrite	11	0	--	<0.02
Ammonia	12	0	--	<0.02
Total phosphate	15	0	--	<0.02
Total phenolics-aqueous (mg/L)	7	0	--	<0.005

(1) MDLs varied from 4.5-11 ng/L

(2) Due to the aqueous nature of the sludge, an aqueous blank is applicable

(3) Four additional blanks contained methylene chloride at levels just below the detection limit

Table A.7

QC Summary: Precision and Accuracy - General Chemistry Analysis

Parameter	Accuracy			Precision		
	Total # Analyses	Percent Recovery Ranges	Control Limits	# Within Control Limits	# Outside Control Limits	Total # Analyses
Chloride	23	77.5-121.1	80-120	21	2	27
Total Organic Carbon	29	89.6-105.4	80-120	29	0	29
Oil and Grease	4(1)	94.0-109	75-125	4	0	3(1)
Residue	N/A	N/A	N/A	N/A	N/A	34
Nutrients:						
Ammonia	16	67.3-106.9	80-120	14	2	16
Nitrate-nitrite	16	74.0-103.5	80-120	14	2	16
Total phosphate	10	88-115.5	80-120	10	0	10
Total phenolics	9	90-102	80-120	9	0	9

NOTES:

(1) Limited sample volume prohibited additional matrix duplicates/matrix spike analyses. However, 12 QC check standards were analyzed with the sample batches; recoveries ranged from 80-101%.

(2) Control limits vary with sample concentration: if concentration is >50 mg/L, control limit = 15% RPD; 20-50 mg/L, 20% RPD; <20 mg/L, $R_1-R_2 \leq 4$ mg/L

N/A = Not Applicable

Precision and accuracy for TOC was evaluated by the analysis of matrix duplicates and matrix spikes and measurements met QC objectives. In addition, QC check standards were analyzed and had recoveries ranging from 96.8-103%. Calibration standard analyses met QC criteria.

2.5 POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS

Aqueous and sludge samples were analyzed for dioxins/furans by SW846 method 8280. Sludge samples were phase separated prior to extraction by decanting the water and only the solid fraction was analyzed. The procedure involves a matrix specific extraction and cleanup, followed by GC/MS analysis. Sample extracts, blanks and standards were spiked prior to analysis with $^{13}\text{C}_{12}$ -1,2,3,4-TCDD as a quantification standard, then analyzed by selective ion monitoring and identified/quantified based on isotope dilution techniques. All samples were analyzed within the method-specified holding time of 30 days from sample collection to extraction and 45 days for complete analysis.

All samples and blanks were spiked prior to extraction with labelled ($^{13}\text{C}_{12}$ -) PCDDs and PCDFs. Surrogate recoveries are summarized in Table A.8. Most compound recoveries were within control limits. In one instance, a sludge sample (STI-A-6-7) had high recovery of the labelled OCDD and OCDF surrogates (144% and 141%, respectively); the sample results reported for OCDD (1900 ng/g) and OCDF (41 ng/g) may consequently be biased somewhat high. For most of the other samples having surrogate recoveries outside of control limits, the related congener was not detected. Two sample results were reported as NC (not calculated) for PeCDF due to the associated surrogate being non-detected.

2.6 METALS

Aqueous samples and four sludge samples were analyzed for priority pollutant metals by SW846 methodologies. All samples were analyzed within the method-specified holding times of 28 days for mercury and 6 months for the other metals. Sludge samples were analyzed "as is" without phase separation, and reported as ug/g, wet weight.

Method blanks were digested/analyzed with each batch of aqueous and sludge samples. Three of the four lead analysis method blanks contained lead, at concentrations ranging from 1.4-3.9 ug/L. In addition, four equipment wash

TABLE A.8

Surrogate Recovery: Dioxin/furan Analysis

Surrogate	# of Analyses (1)	% Recovery Ranges	# Within Control Limits(%)	# Outside Control Limits	Control Limits
¹³ C ₁₂ -2,3,7,8-TCDD	31	35-108	40-120	30	1
¹³ C ₁₂ -2,3,7,8-TCDF	31	37-113	40-120	30	1
¹³ C ₁₂ -1,2,3,7,8-PeCDD	31	51-122	40-120	28	3
¹³ C ₁₂ -1,2,3,7,8-PeCDF	31	47-131	40-120	26 ⁽²⁾	3 ⁽²⁾
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	31	52-153	40-120	30	1
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	31	49-158	40-120	30	1
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	31	51-119	40-120	31	0
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	31	49-119	40-120	31	0
¹³ C ₁₂ -OCDD	31	38-144	40-120	26	5
¹³ C ₁₂ -OCDF	31	42-141	40-120	28	3
TOTAL	310			290 ⁽²⁾	18

NOTES:

(1) Includes field samples and duplicates and field QC blanks. Sludges are included since the control limits are the same for aqueous and solid matrices.

(2) Two surrogate recoveries were not calculated.

blanks and one field blank also had lead detected at concentrations ranging from 4.6-5.3 ug/l. Lead concentrations in the samples ranged from non-detected to 11 ug/L; one effluent sample had a concentration of 580 ug/L (all elements detected in this sample had much higher concentrations). Based on blank results, the low levels of lead detected in the samples may be biased due to the background lead level observed.

Precision and accuracy for metals analysis was determined by the analysis of matrix spike duplicates (MS/MSD) and these results are summarized on Table A.9. In addition, laboratory control samples were analyzed and generally met QC criteria.

2.7 VOLATILE ORGANICS

Aqueous samples were analyzed for volatile organics by SW846 Method 8240. All samples were analyzed within the method-specific holding time of 14 days for a preserved aqueous sample (pH < 2 with hydrochloric acid).

Method blanks were analyzed along with the samples each day. There were eleven method blanks associated with these samples; the only detected contaminant was methylene chloride in 6 blanks at concentrations ranging from 3J-29 ug/L. (The "J" refers to an estimated concentration reported below the MDL of 5 ug/L.) Most trip, field and equipment wash blanks (11 out of 15) were also contaminated with methylene chloride at concentrations ranging from 3J-28 ug/L. Sample concentrations ranged from non-detected to 48 ug/L. One sample which required a 50-fold dilution due to foaming during purging had a concentration of 1200 ug/L, which is equivalent to 24 ug/L prior to accounting for the dilution factor. Thus, all methylene chloride values should be considered biased high.

Surrogate recovery results, summarized in Table A.10 were all within control limits. Precision and accuracy were measured by the analysis of MS/MSD samples; the results are presented in Table A.11.

2.8 OIL AND GREASE

Samples were analyzed for oil and grease by SW846 Method 9070. All samples were analyzed within the method-specified holding time of 28 days.

QC Summary: Precision and Accuracy - Metals

2-15
(83)

Table A.10

Surrogate Recoveries: Volatile Organic Analysis

Compound	# of Analyses	Percent Recovery Ranges	Control Limits (2)	Number Within Control Limits	Number Outside Control Limits
Toluene-d8	58	89-109	88-110	58	0
p-Bromofluorobenzene	58	88-114	86-115	58	0
1,2-Dichloroethane-d4	58	78-112	76-114	58	0
TOTAL	174			174	0

Table A.11

QC Summary: Precision and Accuracy - Volatile Organics

Parameter	Total # Analyses	Accuracy			Precision		
		Percent Recovery Ranges	Control Limits	# Within Control Limits	RPD Ranges	Control Limits	# Outside Control Limits
1,1-Dichloroethene	10	66-111	61-145	10	2-19	0-14	4
Trichloroethene	10	92-123	71-120	9	1-18	0-14	4
Benzene	10	76-127	76-127	10	4-18	0-11	4
Toluene	10	78-121	76-125	10	1-7	0-13	5
Chlorobenzene	10	77-123	75-130	10	3-9	0-13	5
TOTAL	50			49			22
				1			3

Precision and accuracy were to be determined by the analysis of matrix replicates and matrix spikes; due to limited sample volume this was not always possible. In addition, QC check standards were analyzed with each sample batch and all recoveries were acceptable, ranging from 80-101%.

2.9 TOTAL PHENOLICS

Aqueous samples and sludge samples were analyzed for total phenolics by SW846 Method 9066. Sludge samples were analyzed as received, basically as aqueous samples and reported as mg/L. All samples were analyzed within the method recommended hold time of 28 days. Method blanks were free from any contamination. All precision and accuracy measurements were within control limits.

2.10 RESIDUE

Aqueous samples were analyzed for total suspended solids (TSS) and total volatile suspended solids (TVSS). Sludge samples were analyzed for total solids. All samples were analyzed within the 7 day method-specified hold time. All associated method blanks had non-detected (<1 mg/L) results. Matrix replicate analyses were used to assess method precision and results were within control limits.

2.11 NUTRIENTS

Samples were analyzed for ammonia, nitrate-nitrite, and total phosphate as system condition measurements. Samples were analyzed within the 28 day holding times for each of these analyses excluding the following samples which exceeded the holding time for phosphate: days 1 and 3 of the 1 gpm flow test, influent/effluent/equipment washes (ST1-A-1-2/5/13, ST1-A-3-2/5/13). All method blanks for these analyses were free from any laboratory contamination. Method precision was evaluated by the analysis of matrix duplicates and accuracy was determined by the analysis of matrix spike analyses; results are summarized in Table A.7.

2.12 FIELD DUPLICATES

Field duplicates were collected and analyzed at a frequency of 5%. As discussed in the QAPjP, field duplicates inherently measure the precision of both the collection procedure and the analytical methodology. When the results of the

field duplicate analyses meet the analytical precision objectives, then both the sampling and analysis can be considered to be within control. If, however, the measurements exceed the precision objectives, then it is difficult to ascertain whether the collection procedures resulted in non-representative samples or if the analysis was in error. A total of eight field duplicates, analyzed for a variety of parameters, were collected during the demonstration. Table A.13 summarizes the results of the field duplicate analyses.

2.12.1 Pentachlorophenol

Since the measurement of PCP was the most critical of the measurements, the individual sample results for the field duplicate pairs are given in Table A.13 for total and dissolved PCP.

Of the eleven duplicate pair analyses, seven RPD values were less than the analytical control limit (RPD 0-50%). This indicates both sampling and analytical precision were in control. In the cases where the analysis for total and/or dissolved PCP exceeded the control limit, other parameters analyzed for the sample pairs generally met the control limits. For sample pair ST1-C-6-05/14 the RPD for total PCP was 85.7%, but dissolved PCP and other analyzed parameters had RPD values within the applicable analytical control limits. Similarly, sample ST1-C-09-05 and the duplicate had dissimilar PCP concentrations, but results for TOC and chloride agreed. For sample pair ST1-B-01-02/14 both total and dissolved PCP had RPD values outside of control limits, although the duplicate sample dissolved PCP concentration is suspect due to analysis at an inappropriate dilution. In addition, other parameters analyzed for this field duplicate pair were generally within the applicable control limits. This suggests that sample collection techniques resulted in representative samples; if differences in PCP concentrations were a result of non-representative sample composition this would be reflected in other analyses. The PCP analyses which exceeded the control limit are more likely a result of differences in extraction efficiency or analytical measurements which were affected by large dilution factors. PCP extraction is known to be highly variable by SW846 Method 3510 and because of this variability several field duplicates showed precision to be above specified objectives. However, a majority of the field duplicate pairs, as well as MS/MSD analyses, indicate that overall variability was in control for the measurement system.

Table A.12

Field Duplicate Analysis Summary

<u>Analysis Parameter</u>	<u>Total # of Analyses</u>	<u>RPD Ranges</u>	<u>Analytical RPD Control Limit</u>
Pentachlorophenol	7	0-200	0-50
Dissolved Pentachlorophenol	4	0-195	0-50
Chloride	7	0-61	0-25
Total Organic Carbon (TOC)	7	1.4-9.1	0-25
TOC-dissolved	4	0-9.2	0-25
Total Phenolics	1	33	0-25
Oil and Grease	3	0-33	0-30
Volatile Organic Compounds: Methylene Chloride	3	0-200	NA ⁽¹⁾
Metals: Arsenic	1	5.3	0-20
Copper	1	12	0-20
Lead	1	15	0-20
Nickel	1	20	0-20
Zinc	1	0	0-20
Dioxin/furans:			
HpCDD	1	45	0-30
HpCDF	1	35	0-30
OCDD	1	44	0-30
OCDF	1	20	0-30
Alkalinity	1	1.2	0-20
Residue - TSS	4	3.8-40	0-20
TVSS	4	0-40	0-20
Nutrients - Ammonia	2	0-6.1	0-20
Nitrate-nitrite	2	4.1-12	0-20
Phosphate	2	0-23	0-20

⁽¹⁾ There are no established control limits for this compound.

TABLE A.13

Pentachlorophenol Field Duplicate

Analytical Results

<u>Sample/Duplicate ID⁽¹⁾</u>	<u>PCP Concentration (ug/L)</u>			<u>Dissolved PCP (ug/L)</u>		
	<u>Sample</u> <u>Conc.</u>	<u>Dupl.</u> <u>Conc.</u>	<u>%</u> <u>RPD</u>	<u>Sample</u> <u>Conc.</u>	<u>Dupl.</u> <u>Conc.</u>	<u>%</u> <u>RPD</u>
STI-A-5-02/14	7200	11000	41.7	NA	NA	--
STI-A-9-05/14	<50	<50	0	<50	<50	0
STI-B-1-02/14	8800	17000	63.6	15000	200*	195
STI-B-9-02/14	24000	24000	0	22000	22000	0
STI-B-11-05/14	230	160	35.9	NA	NA	--
STI-C-6-05/14	1100	440	85.7	810	810	0
STI-C-9-05/14	300	<50	200	NA	NA	--

(1) The last number in the sample ID relates to influent (-02), effluent (-05) and the field duplicate (-14).

* = Extract was not re-analyzed at an appropriate dilution

2.12.2 Other Analyses

One chloride field duplicate RPD value (61%) exceeded the analytical RPD control limit; all other chloride RPD values were well within limits, again indicating that any problem was limited to individual sample analysis. The one sample pair collected as the field duplicate for total phenolics had an RPD of 33%. One oil and grease duplicate analysis also had an RPD of 33%. These estimates of precision are considered to be indicative of an overall system (sampling and analysis) which is in control, even though the analytical RPD values were slightly exceeded. Methylene chloride was the only detected compound in the volatile organic analysis of the field duplicate collected (as 3 grabs over 24 hours) for this parameter. Due to the background levels encountered in the laboratory for this compound, the high RPD can be attributable to lab contamination of the duplicate. One effluent sample collected in duplicate for dioxins/furans had RPD values which exceeded the analytical control limit for three out of four detected congeners. The duplicate pair analyses for TOC, STOC and metals all had results which met the precision objectives for the analysis.

3.0 BIOMONITORING AND EMISSIONS MONITORING

3.1 BIOMONITORING

Acute toxicity was determined on influent, effluent and well water samples. The fathead minnow tests were performed at five concentrations, each in replicate, using a total of 20 organisms. Controls were performed, in replicate, with each test. Survival for the controls was well within the 80% survival requirements; in most cases no mortality was observed (except a few tests exhibiting 90% survival). The water flea bioassay tests also were performed at five concentrations, using a total of 20 organisms divided between two or four vessels. All control samples exhibited 100% survival.

Reference toxicant tests were performed using cadmium chloride and sodium pentachlorophenate. (This latter compound could only be obtained as a technical grade reagent since it is no longer available from EPA.) The replicate 48 hour LC50 values for cadmium chloride for the water flea were 0.08 mg/L and 0.09 mg/L. The reported EPA ranges were 0.01-0.09 mg/L. The replicate 96 hour LC50 values for cadmium chloride for the minnow was 0.48 mg/L and 0.60 mg/L; the reported EPA ranges were 0.10-0.41 mg/L. The replicate 96 hour LC50 values for sodium pentachlorophenate were determined for the minnow to be 0.09 mg/L and 0.12 mg/L (it was not run with the water flea). The values referenced in the literature indicate LC50 values ranging from 0.198-0.60 mg/L.

3.2 EMISSIONS MONITORING

3.2.1 Sample Collection

Gaseous samples were collected from the exhaust in the lid of the bioreactor at locations before (upstream) and after (downstream) the carbon adsorption system using EPA Modified Method 5 sampling procedures (SW846 Method 0010). Pre- and post-sampling leak tests were conducted per the Method to assure that the sampling systems were within tolerance of the leak specifications in the method.

EPA guidelines for acceptable results based on percent isokinetic sampling are $100\% \pm 10\%$. Isokinetic sampling percentages for the upstream and downstream samples collected during Run 1 were 80.6% and 99.1% respectively. The low

measured percent of isokinetic for the upstream sample was probably a result of turning the bioreactor fan on and off during the sampling run. During the first sampling run, flow measurements were made with the fan on and off to determine impacts the fan had on flowrates. It was decided that the fan was necessary for isokinetic sampling; therefore, the booster fan was left on for the remaining runs. The percent of isokinetic sampling maintained for all of the remaining runs (Periods 2 and 3) was within the acceptance criteria of 90 - 110%.

3.2.2 Sample Analysis

Each emissions sample was comprised of the particulate filter, XAD sorbent trap, impinger condensate and the probe/nozzle solvent washings. The filter and trap were combined, spiked with phenol-d5, 2-fluorobiphenyl and anthracene-d10 as surrogate standards, and extracted by SW846 Method 3540 (soxhlet extraction). The condensate was spiked with nitrobenzene-d5 and 2,4,6-tribromophenol, the washings fraction was spiked with 2-fluorophenol and terphenyl-d14 (see section 6.3); both were extracted (individually) by SW846 Method 3510 (liquid-liquid separatory funnel). The three extracts were combined prior to analysis for PCP, PAHs and phenols by SW846 Method 8270. Reagent blanks were prepared using XAD and an aqueous blank and were extracted with each batch of samples.

Four reagent blanks were analyzed; one contained 11 ug of naphthalene. Four field blanks were collected and three had naphthalene detected at 15-100 ug. Sample concentrations of naphthalene ranged from 92-780 ug for inlet samples and 11-40 ug at the outlet; therefore the outlet levels of naphthalene may be suspect.

Table A.14 summarizes surrogate recoveries achieved for the analysis of MM5 samples. All surrogate recoveries which were outside control limits were for the samples collected during the 3 gpm flow rate period. All of these field samples (inlet, outlet, and field blanks), along with the associated reagent blank, had low surrogate recoveries for almost all compounds (average recoveries were 16% for the trap/filter fraction, 14% for the condensate fraction and 8% for the washings fraction). All results for these samples should therefore be considered significantly biased low.

Table A.14

Surrogate Recovery: MW5 Sample Analysis

<u>Fraction</u>	<u>Surrogate Compound</u>	<u># of Analyses</u>	<u>% Recovery Ranges</u>	<u>Control Limits (%)</u>	<u># w/in Control Limits</u>	<u># Outside Control Limits</u>
Trap, filter	2-Fluorobiphenyl	14	4-97	33-153	10	4
	Phenol-d5	14	3-100	27-154	10	4
	Anthracene-d10	14	5-108	50-150	10	4
Condensate	Nitrobenzene-d5	14	2-86	20-158(1)	10	4
	Trifluorophenol	14	4-109	0-223(1)		
Washings	2-Fluorophenol	14	3-78	21-159(1)	12	2
	Terphenyl-d14	14	0-100	0-179(1)		
	TOTAL	98				

(1) These limits are based on recovery of the surrogates from the XAD trap fraction for which historical data existed to generate control limits. It is not common lab practice to split the surrogates between the various MW5 fractions, and therefore no historical data existed to generate fraction specific control limits.

Three samples were collected during the 1 gpm flow rate period as a means of evaluating sampling precision. Triplicate analyses were not possible, therefore these three consecutive samples were the best alternative. Naphthalene, phenol and 2-methylphenol were measured in all three inlet samples; the relative standard deviations (RSD) were 27.9%, 23.4%, and 21.7%, respectively. Naphthalene was detected in all three outlet samples, with an RSD-46%; the elevated RSD is probably a function of the concentration bias discussed previously (based on contaminated reagent and field blank analyses). Acenaphthene was detected in two of the three inlet samples, but at levels barely above the MDL for the compound. Overall, the results for these analyses indicate that the sampling and analyses protocols were in-control and generated representative concentrations.

4.0 ADDITIONAL STUDIES

4.1 PENTACHLOROPHENOL SAMPLING LOCATION BIAS

As initial pentachlorophenol results were reported for samples collected during the first two weeks of the demonstration, it became apparent that there was a significant difference between the PCP concentration in the raw well water, and the concentration in the sample collected as the influent. The well sample was collected as a grab sample from a tap in the line prior to the groundwater entering the conditioning tank. The influent samples were collected as 22 hour composites taken from the bioreactor pre-chamber above the underflow weir where the water entered the first cell of the bioreactor. As additional data became available, the difference in PCP concentration between the well water and the influent decreased as the flow rate increased, as shown below:

<u>Flow Rate</u>	<u>Average Concentration (ug/L)</u>	
	<u>Well Water</u>	<u>Influent</u>
1 gpm	42000	6900
3 gpm	34500	18300
5 gpm	27500	24200

Data available from grab samples collected and analyzed by the developer (using an HPLC method), and data from samples split with Lockheed as part of the field immunoassay project provided additional data. The following observations were made.

- o The developer collected samples from a tap in the line after the conditioning tank, but prior to the water entering the bioreactor. Results indicated a fairly constant sample concentration averaging 42000 ug/L.
- o Samples analyzed by GC/MS (SW846 Method 8270) by EMSL-LV as part of the field immunoassay project were split samples of the composites collected from the bioreactor. Results were comparable to the influent concentrations obtained by the SITE contract laboratory.
- o Other analyses - chloride and residue - showed a reverse trend in concentration: the well water concentrations were lower than the influent sample, suggesting that some change was occurring in the bioreactor prechamber.

It was postulated that backmixing within the bioreactor, from one chamber to the preceding chamber, could be occurring. Thus, the PCP concentration of the "influent" would decrease as wastewater from midchamber in the bioreactor, having a lower PCP concentration after undergoing biodegradation, mixed with and diluted the incoming groundwater. Likewise, chloride and residue concentrations would be higher within the cells of the bioreactor due to degradation by-product and sloughed biomass, respectively, and would therefore increase the "influent" concentrations after mixing with the incoming groundwater.

To determine whether the variation between the influent sample collected/analyzed by the developer and the composite influent sample collected from the bioreactor pre-chamber could be due to differences in methodology versus sample location and to document how the methods compared, as well as to determine if the developer's data could be used in support of the other demonstration data, the following steps were taken:

1. Compared the developer's sample results (HPLC) with the SITE contract lab sample results (SW8270) for high flow rate influent and effluent samples where possible. Also determine what, if any, QC/validation data the developer had available for the HPLC method.
2. Have the SITE contract lab re-analyze several of their composite influent samples (low and high flow rate) by SW8270 to evaluate hold time effect.
3. Have the SITE contract lab re-analyze several developer influent samples (low and high flow rate) by SW8270 to compare methodology.
4. Have the developer re-analyze several of their influent grab samples by HPLC to evaluate hold time effect.
5. Have the developer re-analyze several of the composite influent samples by HPLC to compare methodology.
6. Have each lab analyze the standard used for calibration by the other.

Eight samples (four each from the low and high flow tests) were chosen for re-analysis by both labs; two were to be performed in duplicate. By re-analyzing the samples which were also being sent to the other lab, data would be comparable from within the same analysis time frame, and in addition, information on the effects of holding time would be generated. Results of this study are discussed below.

Holding Time: The re-analysis of samples by both laboratories provided inconclusive results. Twenty reanalyses, total, were performed with a majority of the re-analyzed values lower than the original sample concentrations; however, the percent decrease ranged from 4.7-100%. (A few re-analysis sample concentrations actually increased.) The results indicated that the effect of compound degradation over time was unpredictable.

Method Comparison: Regardless of the effect of hold time on the samples, since both laboratories were re-analyzing samples at the same time, the results could be used to compare the GC/MS and HPLC methods used. Table A.15 presents the re-analysis values of composite samples (collected from the bioreactor pre-chamber) re-analyzed by both laboratories. Six of the eight analysis pairs had RPD values less than 50 percent (the SW8270 precision criteria for MS/MSD pairs for pentachlorophenol).

Each laboratory also analyzed the other's analytical standard. The SITE contract laboratory analyzed the 38.4 ppm standard used by the developer at 25.0 and 26.0 ppm (average 66.4% recovery). The developer analyzed the 2.0 ppm standard used by the SITE contract lab at 1.8 and 2.1 ppm (average 98% recovery).

The average of the 8270 values compared to the HPLC data were approximately 35% lower. The GC/MS method used the 3510 extraction procedure, which is known to exhibit fair to moderate extraction efficiency for PCP. The SITE contract lab MS/MSD recoveries, while highly variable (65-204%), also suggest PCP recovery efficiency was biased low. Therefore it appears the two different methods are comparable, that extraction efficiency causes the GC/MS analysis to be biased low, and that HPLC methodology may be more accurate for PCP concentrations above 1 PPM.

Precision: Several samples were analyzed in duplicate by both laboratories. The precision estimates are presented in Table A.16. In general, the HPLC duplicate analyses performed by the developer's lab showed excellent agreement (maximum RPD = 12). The GC/MS analyses performed by the SITE contract lab were also within QC limits, meeting the method criteria for precision for pentachlorophenol, RPD ≤ 50%, in 7 out of 8 analyses. The larger RPD for the SITE contract lab result was primarily a function of variable extraction efficiency.

The results of these analyses indicated that the lower-than-expected influent concentrations for the composite samples collected from the bioreactor prechamber during the demonstration, specifically during the 1 gpm and 3 gpm flow rates, were probably due to the suspected backmixing as opposed to method bias. (See reported concentrations in the Technical Evaluation Report) In general, the extraction/analysis method used for the analysis of the well water demonstration

TABLE A.15

PCP Method Comparison

<u>Sample Date</u>	<u>Concentration, ug/L</u>		
	<u>SW846-3570/8270 Re-Analysis</u>	<u>HPLC Re-Analysis</u>	<u>RPD</u>
7/26/89	ND(4J)	ND (<500)	--
7/27/89, dupl.	3400, 5600	5700, 5700	24*
8/01/89, dupl.	2900, --	3700, 3300	19*
8/03/89, dupl.	6100, 5500	8400, --	37*
8/24/89	18000	37900	71
8/26/89, dupl.	33000, 35000	37300, 37500	9.5*
8/28/89, dupl.	28000, 15000	33400, 33600	44*
8/29/89	9700	35800	115

* - RPD value calculated using the average concentration(s) of the duplicate pair

TABLE A.16

METHOD PRECISION DATA FOR GC/MS AND HPLC PCP ANALYSIS

Sample Date	Sample ID#	GC/MS Analysis			HPLC Analysis		
		Sample ug/L	Replicate ug/L	RPD	Sample ug/L	Replicate ug/L	RPD
7/25/89	(Developer)	NA	NA	NA	9600	8500	12
7/27/89	STI-A-4-2	3400	5600	49	5700	5700	0
7/27/89	4404	23000	17000	30	NA	NA	NA
8/01/89	STI-A-8-2	NA	NA	NA	3700	3300	11
8/03/89	STI-A-10-2	5500	6100, 7700	18(1)	NA	NA	NA
8/03/89	4451	20000	25000, 28000	17(1)	NA	NA	NA
8/04/89	(Developer)	NA	NA	NA	18100	18500	2.2
8/26/89	STI-C-6-2	33000	35000	5.9	37300	37500	0.5
8/26/89	4611	21000	24000	13	NA	NA	NA
8/28/89	STI-C-8-2	28000	15000	60	33400	33600	0.6
8/28/89	4615	21000	26000	21	NA	NA	NA

* = "STI" sample id's reference composite influent samples; "XXX" numbers or the (Developer) designation indicate g' grab sample collected by the developer.

NA = Not Analyzed

(1) Three sample aliquots were actually extracted and analyzed; one on 12/12/89, and two on 12/19/89. The three concentrations were used to calculate the RSD which is the precision estimate value reported.

samples, SW846 Method 3510/8270, did appear to achieve somewhat lower absolute recovery (60-70%) when compared to the HPLC method.

Well water PCP concentrations analyzed by GC/MS were similar to BioTrol's influent PCP concentrations analyzed by HPLC when a correction for a 65% extraction efficiency was performed.

The QA data from the study indicated that the developer's results could be used to support the demonstration data, and that the well water PCP concentrations were more representative of the actual "influent" concentration.

4.2 EXTENDED PENTACHLOROPHENOL CALIBRATION STUDY

Many sample extracts for PCP, particularly the well water and the influent, required analyses at multiple dilutions to bring the PCP concentration within the calibration range of the analysis. Time constraints resulted in a number of samples with reported PCP concentrations which exceeded the calibration range; the highest concentration standard analyzed was 160 ng/uL which, for a one liter sample extracted and concentrated to one milliliter, is equivalent to a sample concentration of 160 ug/L. After reviewing the sample and calibration data, it was felt that the actual linear range of PCP analysis extended beyond 160 ng/uL. Therefore, three studies were performed to determine the actual linear range of PCP. Standards were analyzed at eight concentrations for the tests: 20, 50, 80, 120, 160, 200, 250 and 300 ng/uL. The first two tests used all eight points, the third excluded the 20 ng/uL standard. (The routine laboratory calibration range for PCP is 50-160 ng/uL.) The average response factors and relative standard deviations were calculated for all eight standards (20-300 ng/uL) and a second time excluding the lowest concentration standard (since PCP has a method detection limit of 50 ug/L). The results are summarized below:

<u>Test</u>	<u>20-300 ng/uL</u>		<u>50-300 ng/uL</u>	
	<u>RF</u>	<u>%RSD</u>	<u>RF</u>	<u>%RSD</u>
1	0.1183	41.8	0.1316	26.4
2	0.1168	29.9	0.1257	20.8
3	NA	NA	0.1310	13.4

where the response factor (RF) = area PCP/area internal standard x concentration internal standard/concentration PCP. The method requirement for linearity for

a compound designated as a calibration check compound (CCC), which PCP is not, is an RSD $\leq 30.0\%$. If this criteria is applied to the PCP results for the seven-point calculations, then the % RSD all meet the linearity requirement. Therefore, it was determined that pentachlorophenol was linear within 50-300 ng/uL, and almost all sample data did indeed fall within this range, and therefore was determined to be useable for calculating process efficiency.

5.0 NON-CONFORMANCES

Most analytical QC results, including blank analyses, precision and accuracy data, surrogate recovery results and QC check sample results, were discussed in detail in previous sections (2.2 through 2.11) of this review. Therefore, nonconformances regarding QC analysis results which did not meet QC criteria have already been discussed. However, a few additional non-conformances are presented below.

- o Dioxin/furan extraction was to be performed on a phase-separated solid sample of the sludge. Percent solids were to have been determined in this phase-separated sample to allow the calculation of dry-weight concentrations. Percent solids were not performed and dioxin/furan results for the sludge were reported as wet-weight concentrations.
Corrective Action: None possible.
- o Trip blanks were often received (at the field and/or at the lab) with air bubbles.
Corrective Action: Document on Chain-of-Custody. (This problem was not encountered with the samples.)

6.0 DEVIATIONS FROM THE QAPjP

In some instances the procedures and methods referenced in the QAPjP for use during the BioTrol demonstration project were modified or changed in response to physical constraints of the system, field requirements/limitations, laboratory needs and/or EPA concerns. These deviations are listed below; each includes in parentheses the QAPjP section reference and page number which applies.

6.1 FIELD PROCEDURES

Samples for biotoxicity testing were to be collected as composites. Due to the limited hold time, and large volume requirements, these samples were actually collected as grab samples (5.4, pg. 32).

Total organic carbon (TOC) samples were to be preserved with hydrochloric acid to a pH of less than 2. At the laboratory's request, the preservative used was changed to sulfuric acid (5.4, pg. 16) in order to accommodate their TOC analyzer.

Samples to be analyzed for dissolved parameters (TOC and PCP/PAHs) were to be filtered in the field prior to preservation; time constraints in the field required that samples for dissolved PCP/PAHs be filtered in the laboratory. (Dissolved TOC samples were filtered in the field, preserved and then shipped to the lab.) (5.4, pg. 28).

Oil and grease samples of the bioreactor midpoints could not be obtained by direct immersion of the sample bottle; the Teflon suction line of the auto-sampler was used to collect a sample (no equipment wash blank was collected) (5.4, pg. 27).

Samples for total phenolics and volatile organic compounds analysis were to be taken as three grabs over 24 hours and composited in the laboratory prior to analysis. Instead, each individual grab sample was analyzed separately for volatile organics, and samples for total phenolics were collected as a field composite. (A measured volume was collected, preserved, poured into a sample bottle and refrigerated. During the day, two more volumes were collected,

preserved and added to the bottle which was then shipped as a composite of the three grab aliquots.) (5.4, pg. 27).

The sample numbering system was modified to include two additional sample identifiers. The last digit(s) of the sample number specifies the discreet sample location (e.g., influent, sludge). Field replicates were assigned a sample point number "-14" (e.g., STI-A-9-1-14). An additional sludge sample was collected from the walls of the bioreactor (not proposed in the QAPjP) and was assigned a sample number "-15". [5.4, page 35]

Sludge samples were to be collected at the bioreactor filter location on a weekly basis. The type of filter utilized (described as a felt sock bag filter) hindered the collection of a true sludge sample. Volume was limited, and the sludge was collected as a composite by combining samples obtained each time the filter was changed. [5.4, pg. 29]

Emissions monitoring was originally planned to take place during system start-up, and once during each of the three test periods. At the time the QAPjP was approved, it was no longer feasible to sample during the start-up period and most references in the QAPjP to this proposed sampling were omitted. However, Table 5-5, an overall sampling summary for the project, [5.4, pg. 8] still (incorrectly) specified a total of four samples (plus samples for precision) at each sample point. Only three were collected (plus samples for precision), one for each flow rate test.

6.2 SAMPLING SCHEDULE

Seven more trip blanks (TB) than originally proposed were collected. The raw well water was grab sampled once/week for all parameters including volatile organics on a different day than planned, necessitating one additional TB per week. An additional TB was also required when the field blank was collected and sent for analysis.

As a result of the field audit, an equipment wash blank for dissolved TOC was added to the sampling plan on a weekly basis, beginning with week 4.

As a result of concerns expressed during the EPA audit of the procedure used by laboratory for biotoxicity testing, the raw well water was added for biotoxicity testing on a weekly basis (in addition to the influent/effluent samples proposed).

An additional sludge sample was obtained the last week of sampling by collecting scrapings from the side walls of the bioreactor. This sample, STI-C-10-15, was analyzed for PCP/PAHs.

6.3 ANALYTICAL METHODS

Total phenolics were cited in the QAPJP as analysis method SW846 9065; the laboratory actually used SW9066 which is an automated application of the same procedure. (5.5, pg. 11).

During the EPA audit of the laboratory performing chloride it was agreed to change the procedure referenced for chloride analysis, SW9252, to the Standard Methods procedure 407C. (5.5, pg. 10).

Metals determinations require the analysis of a laboratory control sample (LCS), often a known solution provided by EPA with statistically determined 95% confidence limits. The lab performing metals used an NBS standard for the LCS, and has established an acceptance criteria for the analysis of $\pm 15\%$ of the true value. (5.7, pg. 4).

Sludge samples were expected to be a very wet solid sample. A wastewater type sample was actually obtained. The sample was treated "as-is" for total phenolics and metals as proposed in the QAPJP, and results were calculated on a wet-weight basis. Samples for dioxin and PCP/PAH analysis were separated into phases and the solid phase was extracted. Total solids were used to calculate dry-weight results for PCP/PAH; dioxins were reported as wet weight. (5.4, pg. 29).

Samples for semivolatile analysis (full scan or PCP/PAHs only) which exhibited low surrogate recoveries of d5-phenol and 2-fluorophenol were re-analyzed to confirm results. However, due to time constraints, this re-analysis

was discontinued after it was determined that the re-analysis was confirming the original results. (5.7, pg. 2).

7.0 AUDIT FINDINGS/RESULTS

A series of audits were conducted in the field and of the laboratories involved with this BioTrol SITE demonstration project. The findings and results of the audits and corrective actions taken in response to any concerns noted during the audits are summarized below.

7.1 FIELD AUDIT, WATER SAMPLING

An audit of the water sampling operations was conducted by an EPA contractor on July 26-27, 1989. The audit rating was satisfactory. A few issues were identified and prompt corrective action was taken to resolve these issues.

Prior to the audit, it had been noted during the first few days of sampling that the dissolved oxygen meter was not functioning properly and steps were taken to obtain an additional D.O. meter. Dissolved oxygen was a system condition measurement, not a critical measurement. One day's worth of measurements were lost (and the two prior day's measurements were suspect). While waiting for the new meter to arrive on site, dissolved oxygen measurements were taken using the Winkler titration method. After receiving a new D.O. meter, problems were still encountered with calibration, and the decision was made to continue using the Winkler method for dissolved oxygen determinations.

A second item of concern noted by the auditor was the manner in which samples were labelled for shipment. A question arose as to whether or not samples which were preserved with acid to pH <2 required shipment as corrosive material. After shipments made according to DOT regulations were unsuccessful and, after evaluating the regulations, the following procedure was implemented. The samples were not considered corrosive and were shipped via regular overnight carrier. All samples were preserved to a pH <2 without over-acidifying (generally only a few drops of acid per several hundred milliliters of sample). Bottles were sorbent wrapped, bubble wrapped, packed with ice, placed in a plastic bag and shipped in a cooler.

A third issue noted on the audit corrective action form involved field filtration of samples for dissolved TOC. The field filtration kit erroneously

included an organic-based filter paper and consequently inorganic-based filter paper was promptly obtained and substituted.

7.2 FIELD AUDIT, EMISSIONS SAMPLING

An audit of the emissions monitoring MM5 sampling protocols was conducted by an EPA contractor on August 2-3, 1989. The audit rating was satisfactory. One issue was raised concerning the representativeness of the MM5 samples. Previously, a memorandum from Guy Simes dated July 20, 1989 raised the issue of isokinetic sampling. As a result, the sampling team obtained a 4" PVC pipe to attach to the BioTrol reactor exhaust for MM5 sampling. This was done to increase duct size as required by the method. In order to measure the velocity of both the reactor exhaust and carbon filter exhaust, an exhaust fan attached to the reactor lid needed to be turned on. Once this decision was made, an issue of representativeness was raised. Without the fan running it was evident that no vacuum was pulled on the reactor bed, nor were there leaks in the system. It was also obvious that since the fan increased the flow in the reactor outlet, the extra air flowing through the system resulted from system leaks. Leaks into the exhaust flow would produce a non-representative sample. Without the exhaust fan operating, sample flow in the exhaust outlet would be almost impossible to measure and the exhaust for the carbon bed filter had no measurable flow. This presented a problem for obtaining isokinetic samples in the reactor exhaust and for obtaining a sample at all in the carbon filter exhaust. All parties involved were in agreement that isokineticity was non-critical because there were no particles in the reactor exhaust. Not being able to obtain a measurement of the carbon bed filter emission, however, would have presented a problem if it was decided to turn off the exhaust fan. It was determined that representativeness of the sample was not a problem providing no significant PCP or PAH concentration existed in the dilution air. In order to do a mass balance of the system all that was needed was a total PCP/PAH concentration regardless of whether or not it was diluted. After close examination of the calculations used to determine PCP/PAH concentration in air emissions, all involved parties were satisfied with the decision to keep the exhaust fan operating. It was therefore decided that sampling should take place only while the exhaust fan was operating. Additional concerns about pulling a vacuum on the reactor or if operating the fan upset reactor operations proved to be negligible.

7.3 LABORATORY AUDITS

Audits of the three laboratories involved with the analysis of the BioTrol demonstration samples were conducted by EPA contractors. Two audit ratings were satisfactory and one was rated conditional.

On August 4, 1989 an audit was conducted of the laboratory performing PCP/PAH analysis, full scan semivolatile organics, volatile organics and metals analysis. The audit rating was satisfactory. During the audit, the volatile compositing procedure described in the QAPjP was changed. Rather than compositing the three grabs collected over 24 hours into a single sample prior to analyses, each of the grabs was to be analyzed separately as a discrete sample.

The August 7, 1989 audit covered the analyses of total organic carbon, dissolved organic carbon, oil and grease, residue and alkalinity. A conditional rating was assigned. The major concern noted involved the procedure being used for distillation in the oil and grease method, a modification of the reference method SW9070. The laboratory responded to the concern by providing documentation of the distillation temperature and by performing duplicate analyses comparing the modified procedure and the referenced method. Based on these determinations, which indicated that data quality was not compromised by the variation, a change in audit rating was requested. To date, a final audit report and rating have not been received.

A final audit was conducted August 14-15, 1989 covering the analysis of dioxins/furans, chloride, phenolics, ammonia, phosphate, nitrate-nitrite, biotoxicity, and the MM5 sampling trains for PCP/PAHs. The audit rating was satisfactory. Minor concerns were noted regarding the biotoxicity method, and the shipment of MM5 samples.

8.0 CONCLUSIONS AND LIMITATIONS OF DATA

As noted throughout this Appendix, most of the data generated during the BioTrol SITE demonstration can be used in its current form with the exceptions noted below. Process efficiency was most representative when determined using well water contaminant concentrations, as opposed to bioreactor influent sample concentrations. The additional study performed on PCP influent concentrations supports the use of these well water sample concentrations which were similar to data obtained by the developer in an independent collection/analysis program.

Data which have limitations include the following; however, these qualifications to the data did not preclude the ability to adequately evaluate the treatment technology.

- o Emissions samples collected during the 3 gpm flow rate period were significantly biased low. However, sampling during the 1 gpm and 5 gpm flow rates indicated that losses to the exhaust air were minimal and that PCP was not present in these emissions, therefore mass balance calculations were not affected.
- o Sludge samples were not the wet solids expected, but rather an almost aqueous wastewater type sample. Analyses performed on the samples were either reported on an as-is, wet weight basis (which could easily be converted to dry weight) or on a phase-separated sample. Samples were phase-separated for PCP/PAH by centrifugation and reported on a dry-weight basis, and by decanting for dioxins/furans. Without percent moisture on the solids obtained after decanting, overall mass balances can only be estimated for dioxins.