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**Cometabolic Bioreactor Demonstration at
the Oak Ridge K-25 Site:
Final Report**

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H. L. Jennings
M. I. Morris
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**MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
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OAK RIDGE K-25 SITE: FINAL REPORT**

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EXECUTIVE SUMMARY

The Oak Ridge National Laboratory (ORNL) conducted a demonstration of cometabolic technology for bioremediation of groundwater contaminated with trichloroethylene (TCE) and other chlorinated solvents. The technology demonstration was located at a seep from the K-1070-C/D Classified Burial Ground at the Oak Ridge K-25 Site. Funding for this demonstration was provided by the U.S. Department of Energy (DOE), Environmental Restoration/Waste Management Program, Office of Technology Development.

The technology demonstration was designed to evaluate the performance of two different types of cometabolic processes. In both cases, the TCE is cometabolized in the sense that utilization of a different primary substrate is necessary to obtain the simultaneous cometabolism of TCE. Trichloroethylene alone is unable to support growth and maintenance of the microorganisms. Methanotrophic (methane-utilizing) technology was demonstrated first; aromatic-utilizing microorganisms were demonstrated later. The demonstration was based on scaleup of laboratory and bench-scale prototype equipment that was used to establish the technical feasibility of the processes.

Cometabolic biotreatment of chlorinated organics in groundwater offers several potential advantages over air-stripping technologies now used for treatment of groundwater. The organics are destroyed biologically, and no large off-gas streams are created that require further treatment by activated carbon and/or incineration for disposal (no air permit was required for this demonstration). The cometabolic technologies are expected to generate very small quantities of biosludge. Equipment requirements are simple, and costs for cometabolic biotreatment of groundwater are projected to be comparable with costs for treatment of municipal and low-strength industrial wastewaters.

This report documents the operation of the methanotrophic bioreactor system to treat the seep water at the demonstration site. The initial objectives were to

1. demonstrate stable operation of the bioreactors and associated equipment, including the pretreatment and effluent polishing steps; and
2. evaluate the biodegradation of TCE and other organics in the seep water for the three operating modes — air oxidation pretreatment, steam-stripping pretreatment, and no pretreatment.

A bioreactor skid system was loaned to ORNL by the Air Force Civil Engineering Support Agency (AFCESA). It was modified and upgraded for the ORNL application and was contained within a van-type trailer installed at the demonstration site. Start-up was achieved in late September 1991 to meet an award-fee milestone. After a brief operating period in which difficulties were encountered with the steam supply for the steam stripper, winter operation was discontinued because of a lack of funding.

Operation in the air oxidation pretreatment mode was initiated in March 1992 following receipt of funds, and performance data were obtained during start-up and for one relatively stable extended operating period of ~2 weeks. Equipment malfunctions and delays in waste disposal interfered with operation on several occasions and limited the amount of data obtained. Evidence for degradation of TCE and other volatile organic compounds (VOCs) was seen early in the June 1992 operating period and in late August 1992. No sustained degradation was apparent in early August. (There was no operation in July 1992 because of waste disposal procedures.) Factors that may have contributed to the apparent lack of sustained degradation include frequent unsteady-state conditions that induced data variability, stress on the microorganisms caused by a pH excursion for several hours when the pH controller failed, and insufficient hydraulic residence time for treatment of low concentrations of VOCs. Operation in

the air oxidation pretreatment mode was discontinued on September 1, 1992, coincident with the need for waste disposal.

Following receipt of additional funds in January 1993, the monitoring and control system was upgraded to remedy operational difficulties encountered in the 1992 experiments. Operation in the steam-stripping mode was initiated in May 1993 upon completion of the upgrades. The analytical capabilities were expanded to include the ability to monitor samples for chloride ions generated by microbial destruction of the chlorinated organics.

The bioreactor system was operated successfully in the steam stripper mode for several periods when organics were fed as pulses for up to 2 h and two periods (1 and 2 weeks) when organics were fed continuously. During the pulse experiments, sustained methane utilization showed that the microorganisms were not adversely affected by the organics, and increases in the chloride ion concentrations indicated degradation of the chlorinated organics. Evidence for degradation of TCE and the other chlorinated organics was obtained for both continuous operation periods in 1993. Disappearance of the organics and generation of chloride ions indicated substantial degradation of TCE and the other organics during the June 1993 period. The degradation rates decreased considerably during July 1993, probably due to stress on the microorganisms from extremely high temperatures in the bioreactor system caused by high ambient temperatures.

Operation in the steam stripper mode was discontinued July 26, 1993, to concentrate efforts and conserve waste capacity for a Cooperative Research and Development Agreement (CRADA) with Envirogen, Inc., for the second cometabolic bioreactor system, which was based on aromatic-utilizing microorganisms. The technical report prepared by Envirogen, Inc., is included as Appendix A of this present report. No tests were conducted in the no-pretreatment mode.

1. INTRODUCTION

1.1 BACKGROUND

The Oak Ridge National Laboratory (ORNL) conducted a demonstration of two cometabolic technologies for biotreatment of groundwater contaminated with trichloroethylene (TCE) and other chlorinated compounds. The demonstration was based on scaleup of laboratory and bench-scale prototype equipment that was used to establish the technical feasibility of the processes. The technology demonstration was located at a seep from the K-1070-C/D Classified Burial Ground at the Oak Ridge K-25 Site. Funding for this demonstration was provided by the Office of Technology Development, within the U.S. Department of Energy's (DOE) Office of Environmental Management, under the In Situ Remediation Integrated Program.

The seep water contains TCE, perchloroethylene (PCE), benzene, toluene, chlorinated ethanes, and other VOCs at a total concentration of several parts per million (ppm) (Table 1). To maintain regulatory compliance, the treated water from the demonstration process was collected in a tanker trailer and transported to the Central Neutralization Facility (CNF), a licensed treatment facility at the K-25 Site.

Cometabolic biotreatment of chlorinated organics in groundwater offers several potential advantages over air-stripping technologies now used for treatment of groundwater. The organics are destroyed biologically, and no large off-gas streams are created that require further treatment by activated carbon and/or incineration for disposal. The cometabolic technologies are expected to generate very small quantities of biosludge and off-gas. (No air permit was required for this demonstration.) Equipment requirements are simple, and costs for cometabolic biotreatment of groundwater are expected to be comparable with costs for treatment of municipal and low-strength industrial wastewaters. Successful demonstration of this technology at the pilot scale will help to validate performance expectations and to encourage further application to DOE's environmental remediation and waste management problems.

Table 1. Contaminants detected in Storm Drain SD-180-04 (new sampling point designation: SU-31) at the K-25 Facility, April 1990.* All concentrations are reported in units of mg/L (ppm), except alpha and gamma activity (pCi/L).

Chemical	Number detected	Range of detection limits	Values above detection limits	Average value
1,1,1-Trichloroethane	4/4		4.9-6.8	5.9
1,1,2-Trichloroethane	2/4	0.25-0.25	0.025-0.033	0.029
1,1-Dichloroethane	4/4		0.98-1	0.995
1,1-Dichloroethene	4/4		0.51-0.64	0.57
1,2-Dichloroethene (total)	4/4		0.58-0.81	0.68
1-Ethyl-2-methyl-benzene	2/2		0.33-0.33	0.33
1-Methyl Naphthalene	2/2		0.068-0.069	0.0685
1-Pentanol	2/2		0.33-0.38	0.355
1 β -Indene, 1-ethylindene	1/1		0.042-0.042	0.042
1 β -Indene, 2,3-Dihydro-Methyl	2/2		0.033-0.06	0.0465
2-Butanone	1/4	0.2-0.5	0.022-0.022	0.022
2-Methylnaphthalene	5/5		0.076-0.092	0.087
3-Octanone	2/2		0.025-0.038	0.315
Acenaphthene	5/5		0.002-0.003	0.0026
Alpha Activity	1/5	1-2	1-1	1
Aluminum	3/5	0.04-0.104	0.091-0.144	0.12
Aroclor-1221	1/5	0.00057-0.0063	0.00071-0.00071	0.0071
Aroclor-1232	2/5	0.00057-0.0054	0.00091-0.0011	0.001
Aroclor-1242	2/5	0.00057-0.0025	0.00069-0.00078	0.000735
Aroclor-1248	1/5	0.00057-0.0006	0.0038-0.0038	0.0038
Barium	5/5		0.434-0.513	0.46
Benzene	4/4		1.2-1.3	1.2
Benzene 2-Ethyl-1,4-Dimethyl	1/1		0.033-0.033	0.033
Beryllium	1/5	0.001-0.001	0.001-0.001	0.001
Bromacil (ACN)	2/2		0.017-0.018	0.0175
Butane, 1,1'-oxybis(2,1-ethanediytoxy)bis	7/7		0.64-1.6	1.2
Butane, 2-Methyl-	4/4		0.27-0.45	0.345
Cadmium	1/5	0.005-0.005	0.005-0.005	0.005
Calcium	5/5		69.8-93.9	82.3
Chromium	3/5	0.01-0.01	0.014-0.03	0.02
Cobalt	2/5	0.02-0.02	0.021-0.032	0.0265
Copper	2/5	0.01-0.01	0.018-0.025	0.0215
Di-n-butylphthalate	2/5	0.011-0.012	0.003-0.004	0.0035
Diacetone alcohol	2/2		0.022-0.028	0.025
Dibenzofuran	3/5	0.011-0.012	0.002-0.003	0.0027
Diethyl Benzene	1/1		0.024-0.024	0.024
Dimethyl Naphthalene	2/2		0.015-0.032	0.0235
Ethenyl Methyl Benzene	2/2		0.05-0.08	0.065
Ethyl Dimethyl Benzene	4/4		0.024-0.031	0.027
Ethyl Methyl Benzene	7/7		0.06-0.19	0.14
Ethyl benzene	4/4		0.31-0.43	0.37
Fluorene	5/5		0.003-0.004	0.0038
Freon 113	3/3		1.9-2.8	2.2
Freon123	4/4		1.7-2.8	2.15
Gamma Activity	2/5	0-0	0-0	0
Heptachlor epoxide	1/5	0.000057-0.00006	0.00012-0.00012	0.00012
Hydroperoxide, 1-Methylpentyl	4/4		0.5-0.85	0.703
Iron	5/5		18.1-26.8	21.5

Table 1. (continued)

Chemical	Number detected	Range of detection limits	Values above detection limits	Average value
Methylcyclobutane	1/1		0.3-0.3	0.3
Methylcyclopentane	2/2		0.17-0.18	0.175
Methylene chloride	2/4	0.1-0.1	0.16-0.46	0.31
Methylpropylbenzene	6/6		0.014-0.038	0.026
Molybdenum	1/2	0.02-0.02	0.145-0.145	0.145
Naphthalene	5/5		0.093-0.13	0.11
Naphthalene, Dimethyl	3/3		0.017-0.024	0.02
Nickel	1/5	0.02-0.02	0.02-0.02	0.02
Pentane	3/3		0.31-0.55	0.44
Phenanthrene	5/5		0.004-0.005	0.0042
Potassium	4/5	1.9-1.9	2.23-2.73	2.5
Propane, 2-methoxy-2-methyl	2/2		0.11-0.15	0.13
Propenyl Benzene	1/1		0.077-0.077	0.077
Silicon	2/2		4.21-6.1	5.2
Silver	2/5	0.005-0.005	0.006-0.133	0.0695
Sodium	5/5		11.1-15.2	13.1
Strontium	2/2		0.053-0.105	0.079
Tetrachloroethene	2/4	0.25-0.25	0.063-0.067	0.065
Tetramethyl Benzene	4/4		0.02-0.031	0.023
Thorium	1/2	0.05-0.05	0.881-0.881	0.88
Toluene	4/4		2.7-3.1	2.9
Trichloroethene	4/4		0.33-0.43	0.385
Trimethylbenzene	21/21		0.058-0.46	0.16
Unknown	21/21		0.017-0.055	0.033
Unknown Hydrocarbon	28/28		0.018-0.23	0.060
Uranium 238	1/2	0.2-0.2	4.44-4.44	4.44
Vanadium	3/5	0.01-0.01	0.01-0.014	0.0127
Xylene (total)	4/4		1.4-1.9	1.625
Zinc	4/5	0.01-0.01	0.01-0.068	0.042
bis(2-Ethylhexyl)phthalate	1/5	0.11-0.12	0.004-0.004	0.004
α -propylbenzene	6/6		0.031-0.86	0.17
Lead	2/5	0.03-0.03	0.036-0.041	0.0385
Magnesium	5/5		9.78-12.9	11.3
Manganese	5/5		11.4-13.7	12.7
Methyl Methyl Ethyl Benzene	1/1		0.036-0.036	0.036
Methyl Naphthalene	1/1		0.044-0.044	0.044
Methyl Propyl Benzene	3/3		0.019-0.035	0.024

*Source: D. Miller, personal communication to S. E. Herbes, 10/8/90. Excerpted from Appendix C, Surface Water Sampling Data, Environmental Restoration Division/K-25 Environmental Restoration Division/K-25 Environmental Restoration Program, in "Site Characterization Summary: K-1070-C/D Classified Burial Ground." Report No. K/ER-4D1 (draft), March 1990.

1.2 BIODEGRADATION CHEMISTRY

Cometabolism is the term generally applied to the phenomenon in which utilization of a primary substrate enables the simultaneous cometabolism of another species that alone is unable to support growth and maintenance of the microorganisms. Chlorinated solvents are known to be degraded by these mechanisms. Methanotrophs are able to degrade TCE via a nonspecific enzyme called methane monooxygenase (MMO), whose principal function is to oxidize methane to provide energy for the microbial cells. MMO will also convert TCE to an epoxide; the epoxide is relatively unstable and spontaneously hydrolyzes to form several other chlorooxygenated compounds that are further biodegraded relatively easily by other microorganisms.¹ The process is represented below.

Certain aromatic-degrading microorganisms are also known to degrade TCE by a cometabolic pathway using another nonspecific enzyme, toluene dioxygenase.

Perchloroethylene and other chlorinated alkanes such as 1,1-dichloroethane (1,1-DCA) and 1,1,1-trichloroethane (1,1,1-TCA) are believed to be recalcitrant to oxidation in an aerobic environment, but they are degraded anaerobically by reductive dehalogenation mechanisms. Nevertheless, researchers at The University of Tennessee have seen apparent degradation of these compounds in an aerobic biofilm reactor.² They postulate that degradation occurs in

anaerobic niches within the biofilms. Thus, it is not known a priori if these and other compounds in the K-25 seep water will be degraded in the pilot-scale bioreactors. Other researchers have noted degradation of chlorinated alkanes such as 1,1,1-TCA and 1,1-DCA by methanotrophic microorganisms.³ These compounds were monitored in the seep water and bioreactor effluents to determine if degradation occurred.

1.3 SCOPE OF PILOT-SCALE FIELD TESTS

This report is a summary of the start-up phase and the operating campaigns for the methanotrophic technology using an upgraded bioreactor system on loan from the Air Force Civil Engineering Support Agency (AFCEA), Tyndall Air Force Base, Florida. ORNL has been a leader in the development of this technology through the applied research and bench-scale phases.^{4,5} The objectives of these field tests were to

1. demonstrate stable operation of the bioreactor and associated equipment, including the pretreatment and effluent polishing steps; and
2. evaluate the biodegradation of TCE and other organics in the seep water for the three operating modes — air oxidation pretreatment, steam-stripping pretreatment, and no pretreatment.

Operation of the pilot-scale process equipment has served to further characterize and improve the process performance. Development and testing of the second cometabolic technology, based on aromatic-degrading microorganisms, were conducted for the second phase of the project under a Cooperative Research and Development Agreement (CRADA) with Envirogen, Inc. The technical report prepared by Envirogen, Inc., is included as Appendix A. Additional detailed information concerning this technology demonstration can be found in the test plan,⁶ which includes the Safety Assessment, Health and Safety Plan, Waste Management Plan, and Quality Assurance/Quality Control (QA/QC) Plan.

1.4 PROJECT OVERVIEW AND CHRONOLOGY

Development of the technology for cometabolic biotreatment of chlorinated solvents began at ORNL in 1986 with the isolation and characterization of a type II methanotrophic microorganism from a groundwater well on the Oak Ridge Reservation.¹ Mixed cultures containing this microorganism were used in a laboratory-scale prototype bioreactor operated in a trickle-filter mode to provide oxygen and methane to the microbial culture, which was in the form of a biofilm on the surface of ceramic packing. This prototype bioreactor degraded approximately 50% of the TCE in a synthetic feed stream containing about 1 mg/L of TCE over several months of stable operation.⁴

Based on these results with the prototype bioreactor, ORNL provided guidance to Battelle on the design of a pilot-scale trickle-filter bioreactor system for Tyndall Air Force Base and provided an inoculum of the mixed microbial culture for use in the Battelle bioreactor for tests at Tinker Air Force Base. Several ORNL staff members also participated in the in situ bioremediation phase of the Integrated Demonstration at the DOE Savannah River Plant to treat TCE in the subsurface.

In FY 1990 funding was received from DOE for further development and pilot-scale testing at a DOE field site. Tests were first conducted using a series of laboratory-scale bioreactors to guide selection of a microbial culture for the pilot tests and to further define the range of satisfactory operating conditions. Five methanotrophic cultures were tested and compared for their ability to form stable active biofilms that degrade TCE. Although the bioactivity of the cultures were roughly comparable, it was found that a culture isolated from TCE-contaminated groundwater at the DOE Kansas City Plant exhibited better formation of stable biofilms and was more resistant to process upsets.⁵ Therefore, this culture was selected for the pilot-scale tests. It

was also shown that ammonia was inhibitory to degradation of TCE, and that use of formate in place of methane provided a short-term increase in TCE degradation rate that was not sustained.⁵ Evidence was also obtained that the pH must be maintained between 6.5 and 7.0, and that microbial growth and bioactivity were significantly better in the temperature range from 20 to 25°C than at 37°C.

As noted earlier, a bioreactor skid unit was obtained on loan from Battelle for the pilot tests by ORNL. The aforementioned seep at the K-25 Site was selected for the field test. A list of the major events and dates associated with the pilot-scale phase of the project is given in Table 2. The bioreactor skid and associated support equipment were installed at the demonstration site during the summer of 1991 and operated briefly in a shakedown campaign.⁷ Treatment of seep water was carried out in 1992 in the air oxidation pretreatment mode⁷ and in 1993 in the steam-stripping pretreatment mode. The system was not operated in the no-pretreatment mode because available funds and waste capacity were concentrated on the other two modes.

Table 2. Major events during cometabolic bioreactor demonstration

Event	Date
Received bioreactor skid from AFCESA	8/90
Obtained van trailer	3/91
Completed installation of skid in trailer and equipment checkout	8/91
Completed safety review	8/91
Transported trailer from ORNL to K-25 Site	8/91
Completed installation at K-25 Site	9/91
Received approval for RCRA 90-d and Satellite Waste Accumulation Areas	9/91
Completed Readiness Review and received approval to operate	9/91
Inoculated bioreactors	9/20/91
First introduction of seep water	9/27/91
Total shutdown — insufficient funds	12/3/91
Receipt of FY 1992 funds (authorization to proceed)	2/15/92
Reinoculation	3/5/92
Introduction of seep water — air oxidation mode	5/28/92
Shutdown (total recycle) — Land Disposal Restrictions alert	6/6/92
Waste tanker emptied by Waste Transportation through K-25 CNF	7/31/92
Resume treatment of seep water	6/18/92
Replacement of main feed pump	7/1/92
Shutdown for waste disposal (total recycle)	7/6/92
Waste tanker emptied by Waste Transportation through K-25 CNF	7/31/92
Resume treatment of seep water	8/3/92
Shutdown for waste disposal (total recycle)	9/1/92
Waste tanker emptied by Waste Transportation through K-25 CNF	9/11/92
FY 1993 funds in place	1/18/93
Waste Transportation picked up tanker and emptied at CNF (rainwater)	3/16/93
Completed piping modifications	4/1/93
Inoculated system with microorganisms	4/1/93
Initiated experiment with dichloroethylene	4/27/93
Solenoid valve on steam generator repaired	5/7/93
Submitted request for waste disposal	5/17/93
Began pulse experiments	5/18/93
Cleaned orifice meter on steam stripper	5/26/93
Replaced the solenoid coils on steam generator	6/1/93
Replaced the solenoid valve on steam generator	6/10/93
Waste Transportation disposed of tanker waste at CNF	6/11/93
Methane feed ran out	6/14/93
Methane samples indicate drop in consumption	6/15/93
Initiated continuous flow	6/21/93
Shutdown due to drop in methane consumption at column A caused by recycle pump failure	6/29/93
Added more culture to recycle	7/8/93
Temperature reached 45.5°C in recycle	7/8/93
Added second cooler to system	7/9/93
Restarted steam stripper feed to bioreactors in continuous flow	7/17/93
Steam stripper mode discontinued to concentrate on CRADA	7/26/93
Submitted request for waste disposal	8/4/93
Pumped waste to temporary tanks in 90-d storage area while waiting for tanker to be emptied	9/9/93
Waste Transportation emptied tanker	9/13/93

Fig. 1. Process flow sheet for the cometabolic bioreactor system

(a)

(b)

Fig. 2. Koch packing (a) and liquid distributor (b) in the bioreactor columns.

2.2 PRETREATMENT SYSTEMS

Two pretreatment systems were added (see process flow sheet in Fig. 1) to prevent iron in the seep water (typically 20 mg/L; see Table 1) from entering the bioreactor columns where it would oxidize, precipitate, and likely interfere with the biofilms and perhaps plug the bioreactor. One pretreatment system is an air oxidation system, purchased locally from Continental Water Systems, for iron removal from the seep water. The second pretreatment system is a steam stripper. This unit removes the organics from the seep water for treatment in the bioreactors, while the iron remains with the seep water. The steam stripper was designed and constructed at ORNL and installed on the bioreactor skid frame. The stripper is an insulated column 6 in. in diameter and 8 ft tall packed with 5/8-in. stainless-steel pall rings.

2.3 FIELD INSTALLATION

The bioreactor skid and pretreatment equipment were installed in a van-type trailer (Fig. 3) and transported to the parking lot just east of Building K-1098-D at the K-25 Site and on the west side of Avenue D (Fig. 4). Electrical service (3 phase, 240 V, 100 A) was obtained at a pole beside the trailer. Premixed 3% methane in air was provided from compressed gas cylinders outside the trailer. Water from the K-1070-C/D seep on the east side of Avenue D was collected in an ~5-gal covered container (to minimize volatilization losses) and piped across the street via a 1/2-in.-diam stainless-steel line covered with a traffic ramp on the street. The feed pump was located in the trailer. Steam for the steam stripper was originally provided via a flexible hose from the utility steam service at Building K-1098-D. However, a stand-alone electrical steam generator was installed later in the trailer to provide a cleaner steam supply for

Fig. 3. Equipment layout in the process trailer for the cometabolic bioreactor demonstration.

Fig. 4. Site plot for the cometabolic bioreactor demonstration at the K-25 Site.

the steam stripper pretreatment mode. Off-gas from the bioreactors, containing <1% methane in air and parts-per-million levels of VOCs, was vented to the environment outside the trailer. The 6300-gal tanker trailer for effluent storage and a 1500-gal polypropylene surge tank were located in a 90-d Resource Conservation and Recovery Act (RCRA) storage area immediately adjacent to the process trailer.

2.4 WASTE DISPOSAL

Prior to disposal, all major aqueous effluent streams were treated using the steam stripper to remove VOCs. This step was part of the main process operation for the steam-stripping pretreatment mode. For the other modes, the steam stripper was used as an effluent polishing step. The stripped organics were collected in a 55-gal drum designated as a RCRA satellite waste accumulation area. After steam stripping, liquid effluents were routed to the 6300-gal tanker trailer located at the site and ultimately transported to the CNF at the K-25 Site for discharge through a National Pollution Discharge Elimination System (NPDES)-permitted point. The CNF required that this treated water in the tanker be sampled and analyzed to ensure compliance with the CNF waste acceptance criteria (Table 3) before it was released to the CNF.

Table 3. Waste acceptance criteria for the Central Neutralization Facility

Constituents	Criterion (mg/L)
Cadmium	2.6
Chromium	2.89
Copper	20.7
Lead	14.3
Nickel	17
Silver	1.2
Zinc	9.25
Cyanide	0.65
Total toxic organics	2.13
Oil and grease	26
Total suspended solids	270
PCBs	1.4E ⁻⁵ (detection)

3. OPERATING MODES

3.1 STEAM STRIPPING PRETREATMENT

This operating mode is depicted in Fig. 5. Raw seep water was introduced at the top of the steam stripper, and steam was added at the bottom via an automatic control valve to produce only a very small quantity of overhead vapor (~2% of the seep water feed). This vapor contained virtually all of the volatile organics and was sent to the bioreactors, which were operated in series in essentially total recycle. A small liquid purge stream, equal in mass to the vapor rate entering the bioreactors plus the nutrient feed (see Sect. 7.3), was sent back to the top of the steam stripper to maintain a constant liquid volume in the bioreactor recycle loop. Meanwhile, the seep water exited the bottom of the steam stripper, stripped of organics but still containing iron, other minerals, and nonvolatiles. This water was collected in the tanker trailer for ultimate disposal at the CNF.

3.2 AIR OXIDATION PRETREATMENT

A simplified block flow sheet for this mode is shown in Fig. 6. Air was bubbled through the seep water in one column to oxidize the iron, and then the ferric hydroxide was removed in a second sand filter column. Effluent water from the sand filter was then sent to the trickle-filter bioreactors. The sand column was backwashed periodically on an automatic timer circuit to remove the precipitates. The air feed to the oxidation unit was the same air/methane gas mixture for the bioreactors; the off-gas from the oxidation unit was fed to the first bioreactor (Column A) to maintain the methanotrophic microorganisms. This configuration allowed for biotreatment of

Fig. 5. Operational mode 1: steam stripper pretreatment.

Fig. 6. Operational mode 2: air oxidation pretreatment with steam-stripping post-treatment.

organics stripped from the seep water in the air oxidation unit. For this technology demonstration, the treated water from the bioreactors was polished with the steam stripper, as described previously, before it was sent to the tanker trailer for storage and analysis and eventual treatment at the CNF. Actual implementation of this technology for this or other applications may not require effluent polishing, depending on process performance and the applicable regulations for discharge of the treated water.

3.3 NO PRETREATMENT

This mode is the simplest and would require the least equipment. Tests were designed to determine if this mode would be practical for treatment of water containing significant iron. Raw seep water can be fed directly to the bioreactors, which may be operated with some liquid recycle to increase the hydraulic residence time if necessary. The effluent would be treated with the steam stripper as in the air oxidation pretreatment mode. This mode was scheduled to be tested last because of concern that precipitation of iron would foul the biofilms. However, decisions were made subsequently to focus resources on the other two modes, and this no-pretreatment mode was not tested.

4. PROCESS MONITORING AND SAMPLING

4.1 PROCESS CONTROL AND PERFORMANCE

The process equipment provided the capability to obtain liquid and gas samples at many different locations. For routine process monitoring, liquid and gas samples were obtained periodically at eight different locations, shown schematically in Fig. 7, for the steam-stripping mode. Liquid samples were obtained from the seep water feed line (L1), the treated effluent water to the tanker trailer (L2), the liquid flow between the two bioreactors (L3), and the liquid effluent from the second bioreactor (L4). Gas samples were obtained from the methane/air feed stream (G1) and the off-gas streams from each bioreactor column (G2 and G3). Location L2 (the effluent from the steam stripper) was not sampled routinely in the air oxidation mode because it was not required for the material balance calculation.

During start-up of the process equipment, two sets of samples were collected per day to obtain more information on process performance during this critical period. During stable operation, one set of samples per day was judged to be adequate to monitor the process performance. In addition to the liquid and gas samples described previously, operating conditions such as flow rates, temperatures, and pH were noted and recorded by the project staff during daily visits to the process trailer.

Several other parameters were measured periodically to aid in interpreting the volatile organic carbon (VOC) concentration data in terms of biodegradation. Samples of the liquids obtained from ports L1 through L4 were occasionally assayed for nutrients (nitrate and ammonia) to verify adequate levels for the microorganisms.

COMETABOLIC TECHNIQUES PROJECT MODE I SAMPLE DESIGNATIONS

Fig. 7. Location of sampling points for process performance monitoring.

4.2 WASTE DISPOSAL

Analysis of the treated effluent in the tanker trailer was required to ensure that the waste acceptance criteria for the CNF were met (Table 3). Upon request from the project engineer, the K-25 staff sampled the tanker and submitted the samples for analysis.

5. ANALYTICAL METHODS

5.1 ORNL SUPPORT LABORATORY

5.1.1 Liquid Samples

Liquid samples were collected from the bioreactor system using a separate 25-mL gastight syringe for each sample point. The syringe was first rinsed with the sample and then emptied. A 12-mL sample was then taken and injected into a 40-mL amber borosilicate vial containing 12 mL of hexane and 8 mL of acetone. The acetone partitioned wholly into the water and prevented formation of an emulsion. The vials were sealed using screw-cap closures with a Teflon-faced silicone rubber seal. These samples and a blank containing deionized water were extracted overnight on a rotator. Approximately 1.5 mL of the hexane phase was then pipetted into a 2-mL autosampler vial and sealed with a crimp-type septum seal. The vials were then placed on the autosampler tray for a Hewlett Packard (HP) Model 7673A automatic sampler/injector. Samples were analyzed using an HP 5890 gas chromatograph equipped with an electron-capture detector, located in Building 3017. Separation was achieved with an AT-624 60-m by 0.53-mm-ID capillary column with 1- μ m film thickness (Alltech, Inc.). The response of the detector was plotted and integrated with a HP model 3396A recording integrator. The integrator was programmed to calculate the concentrations of the target organics based on calibration with known standards.

The gas chromatograph was recalibrated weekly using standards prepared from a certified standard mix purchased from RESTEK, Inc., to EPA specifications. The calibration mix contained 2000 mg/L of each of the target compounds (TCE; 1,1,1-TCA;

1,2-*trans*-dichloroethylene (DCE); PCE; 1,1-DCA; and methylene chloride) prepared in purge-and-trap-grade methanol. These mixes were then diluted with hexane or water to make calibration standards in the concentration range of 1 µg/L to 1000 µg/L. The detection limits are estimated to be 1 µg/L for TCE; 1,1,1-TCA; and PCE in liquid and gas samples and 200 µg/L in liquid samples and 100 µg/L in gas samples for 1,1-DCA. The headspace gases in the extraction vials were assayed for VOCs; none were found. Furthermore, selected standards prepared in hexane gave results identical with standards prepared in water. On this basis, it was assumed that the extraction procedure recovered essentially all of the VOCs in the aqueous samples.

5.1.2 Gas Samples

Gas samples for both methane and organics analysis were obtained from the bioreactors using 2-L Tedlar bags. Five-µL samples from the Tedlar bags were injected into the gas chromatograph using a 10-µL gastight syringe. The Tedlar bags were then purged with ambient air and evacuated before reuse. Ambient air blanks were periodically run to verify that no cross contamination was occurring between uses. Gas samples were analyzed for the target organics using the gas chromatograph described previously without the autosampler. The integrator contained a separate program to calculate the concentrations based on runs with known standards. The calibration standards were prepared from the certified standard mix described previously.

5.2 K-25 ANALYTICAL LABORATORY

Samples for characterization of the effluent tanker contents were assayed by the K-25 Analytical Laboratory prior to disposal of each tanker load. The target VOCs were found

to be below detectable limits. However, the mixed contents of the tanker are not necessarily representative of the treated water discharged from the bioreactors for a variety of reasons, including steam stripping of the bioreactor effluent, possible volatilization of VOCs during transfers, and addition of uncontaminated rainwater from the diked area to the tanker. Thus, these data were not used to assess process performance.

6. DATA MANAGEMENT AND ANALYSIS

Concentration data for VOCs were entered into a Lotus® spreadsheet along with the liquid and gas flow rates for each column, pH, temperature, and additional comments concerning operation of the system. The spreadsheet automatically calculated a percent degradation for each compound detected. The degradation was calculated from a steady-state material balance around each bioreactor and a separate material balance around the bioreactor system. The amounts of each compound leaving the bioreactor in the off-gas and liquid streams were subtracted from the amount entering, and the difference was attributed to degradation. This calculation is summarized for TCE in Eq. (1) in terms of percent degradation of the mass flow (the product of the concentration of TCE and the volumetric flow rate) of TCE in the seep water fed to the system.

$$\% \text{ degradation} = \frac{\text{TCE}_{\text{liquid in}} - \text{TCE}_{\text{liquid out}} - \text{TCE}_{\text{off-gas}}}{\text{TCE}_{\text{liquid in}}} \times 100 \quad (1)$$

All terms on the right-hand side of the equation are measured in milligrams per minute. The degradations for the other compounds were obtained from similar calculations. The spreadsheet was saved on both floppy disk and the hard disk drive in the support lab every time it was updated, and it was backed up weekly on the hard disk drives in two nearby offices. Graphs of the data for each compound versus the date sampled were generated from the spreadsheet.

7. OVERVIEW OF OPERATING CAMPAIGNS

An overview of the major events associated with start-up and operation of the demonstration is given in Table 2. More details on daily events are shown in the comprehensive data tables in the Appendix B. Additional information on the 1991 and 1992 operating campaigns may be found in ref. 7.

7.1 FALL 1991 OPERATING CAMPAIGN

The system was inoculated with 2 L of dense microbial culture grown from a mixed culture enriched from TCE-contaminated groundwater obtained from the DOE Kansas City Plant.³ A liquid mineral salts medium was recirculated through both bioreactor columns (designated A and B) in series in total recycle. A 3% methane/air mixture was fed to both columns in parallel. This mode of operation was maintained for ~1 week to provide opportunity for development of biofilms on the packing in the columns. The pH was maintained at ~7.0. Mineral nutrients were replenished periodically by removing a portion of the liquid and replacing it with fresh medium.⁷

In fall 1991, seep water was first introduced to the system via the steam stripper for limited periods. The overhead VOC-rich vapors were sent to the bioreactors, which were operated in total liquid recycle. Following the addition of seep water, the methane consumption was monitored carefully for several hours to detect any adverse effects. This procedure was repeated on several occasions.

Addition of overhead vapors from the steam stripper to the bioreactors led to a significant decrease in methane consumption within an hour.⁷ The original methane utilization rate was recovered slowly over several days. After several replications of this response, the steam

stripper was operated alone (no seep water), and a comparable quantity of steam vapor was fed to the bioreactors. Again, the methane consumption dropped significantly, indicating that the behavior was caused by something other than the seep water.

Further investigation revealed that the steam fed to the stripper contained sufficient organics to create a film on a sample of the steam condensate and produce an odor. It was suspected that the source of these organics was the rubber lining of the new steam line installed to deliver steam to the process trailer from the plant steam supply at a nearby building. At this point, current funding for the project was exhausted and operation of the bioreactor system was suspended. The steam supply problem was solved by installation of a steam generator in the process trailer in the spring of 1992.

7.2 SPRING/SUMMER 1992 OPERATING CAMPAIGN

In March 1992, following authorization to resume work, the bioreactors were reinoculated in a manner similar to the initial inoculation. Methane consumption was monitored frequently as an indicator of bioactivity.⁷ Methane consumption was observed to be quite dependent on temperature, which is expected for microbial metabolism. When the ambient temperature dropped to $<5^{\circ}\text{C}$ overnight, the methane consumption observed in the morning was typically reduced by 20 to 40% compared with the methane consumption when the temperature was in the 25°C range late in the day.

Following shakedown of the air oxidation pretreatment equipment, operation with seep water feed commenced for several short-term periods of 1 to 2 h. Liquid flow was sequential through the air oxidation unit and the two bioreactors in series. Gas flow was in parallel, with separate feed streams to each bioreactor column at 0.5 L/min. The addition of seep water caused

no significant effect on methane consumption,⁷ so continuous feed of seep water was commenced at 0.5 L/min.

Samples of liquid were analyzed periodically to ensure that nitrate levels from nutrient addition remained in the milligram-per-liter range. After an initial sample in May 1992 indicated nitrate levels of 0.058 mg/L, nutrient addition rates were increased. Subsequent samples in August indicated nitrate levels of 6.2 and 12 mg/L.

After several weeks of operation in June, during which time samples were taken and analyzed daily, the system was returned to total recycle when the effluent tanker trailer became full. Approximately 1 month was required to sample and analyze the contents of the tanker and obtain permission to empty the tanker at the CNF. After disposal of the effluent, treatment of seep water in the air oxidation pretreatment mode resumed and continued for ~1 month until total recycle was again necessary while waiting for disposal of the contents of the waste tanker.

In July 1992, during operation in recycle while waiting for waste disposal, TCE and 1,1,1-TCA were added to the bioreactors via a saturated aqueous solution in lieu of seep water. The purpose was to provide TCE to the system for degradation tests in the event that waste disposal was substantially delayed. The saturated solution contained ~1000 mg/L each of TCE and 1,1,1-TCA.

A variety of operational problems prevented maintenance of stable operating conditions for extended periods, with the exception of one good stable operating period for about 2 weeks at the end of August. An air leak in the suction line from the sump at the seep to the pump in the trailer caused the centrifugal feed pump to discharge at erratic flow rates and eventually lose its prime. The pump was replaced with a positive-displacement gear pump, which worked satisfactorily. Other difficulties included erratic gas addition to the air oxidation unit in the presence of back pressure from the liquid stream. A pH controller failure during the second operational period

drove the pH up to 7.9 by unnecessary addition of base. This condition prevailed for several hours before the problem was discovered.

Operation was discontinued on September 1, 1992 because of the need for waste disposal and insufficient funds to continue.

7.3 SPRING/SUMMER 1993 OPERATING CAMPAIGN

Following receipt of new funding and authorization to begin work in January 1993, the bioreactor system was readied for operation in the steam stripper mode. Several approaches were considered to reduce the operational delays involved with disposing of the effluent from the system, including submission of the samples to an off-site laboratory (analysis of the effluent caused the longest portion of the delays) and disposal of the effluent at the Y-12 groundwater treatment facility (which would not require the analyses). All efforts to decrease the effluent disposal time were unsuccessful due to either prohibitive costs, long lead times to arrange, or regulatory compliance issues.

Preparation for operation of the bioreactors in the steam stripper mode included testing of the steam generator installed in 1992 and installing additional process control and monitoring equipment. A chloride ion-specific electrode was added to the analytical laboratory to provide an independent indicator of microbial degradation of the chlorinated organics from measurements of the appearance of chloride ions. To reduce the background levels of chloride ions, the several chloride salts in the mineral nutrient solution were replaced with non-chloride salts. The final nutrient recipe used for the 1993 operating campaign is shown in Table 4. As in 1992, samples were periodically analyzed for nitrate concentrations. Samples taken in April and May 1993 showed nitrate levels of 10 to 80 mg/L.

The bioreactors were reinoculated on April 1, 1993, upon completion of the piping modifications required for the monitoring equipment. After flow monitoring and control upgrades were complete in late April 1993, an experiment was conducted to measure the destruction of 1,2-*trans*-DCE added in a step input (data not shown). Disappearance of 1,2 *trans* DCE and appearance of DCE epoxide indicated a viable methanotrophic culture (Sect. 1.2).

Table 4. Nutrients concentrate recipe^a

Nutrient	Concentration
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.38 g/L
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2.0 g/L
KNO_3	1.0 g/L
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	3.36 mg/L
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.01 mg/L
$\text{Zn}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$	0.068 mg/L
CoSO_4	0.02 mg/L
MoO_3	0.03 mg/L

^aThis solution was added to the liquid recycle of the bioreactors at a rate of ~5 mL/min.

Between May 18 and June 15, several batch experiments were conducted in which seep water was treated in the steam stripper mode for 1 to 2 h to add VOCs to the bioreactor system. Concentrations of VOCs, chloride, and methane were measured during operation and periodically for 2 d afterwards. Continuous operation was initiated on June 21 and continued until the recycle pump failed on June 29. Operation resumed on July 13 and then was ceased on July 23 to conserve waste capacity and concentrate effort on the CRADA with Envirogen, Inc., to test the second bioreactor system.

The second bioreactor system, which was designed to destroy TCE using aromatic-utilizing microorganisms, was installed in the van trailer with the aid of Envirogen personnel during

August 1993 and tested during September and October 1993. The results are presented in Appendix A.

After completing the operation of the CRADA bioreactor system, the bioreactor site and associated utilities were decommissioned. The RCRA satellite accumulation area and the RCRA 90-d storage areas were dismantled after disposal of their contents. Health physics surveys were performed on the bioreactor trailer, its contents (including the bioreactor skid), and the tanker trailer.

The tanker trailer was salvaged because it was declared not roadworthy by K-25 garage personnel and no longer met Department of Transportation (DOT) specifications. The bioreactor skid and other internals of the bioreactor trailer were braced with wood for transportation and then transported to ORNL after the trailer passed a DOT annual inspection. The bioreactor skid was removed from the trailer by ORNL personnel and then returned to the Air Force.

8. RESULTS

A detailed discussion of the 1992 operating campaign is presented in ref. 7. The results for 1992 are summarized as follows.

8.1 SPRING/SUMMER 1992 OPERATING CAMPAIGN

8.1.1 Methane Consumption

Methane consumption during 1992 was consistent and substantial, typically around 90% of the amount fed.⁷ Decreased methane consumption was observed to correlate with lower ambient temperatures, which is to be expected. No adverse effect on methane consumption was observed when seep water was first fed to the system in the air oxidation pretreatment mode in May 1992 and again in August 1992, when treatment of seep water was resumed after waste disposal.

8.1.2 TCE Degradation

The TCE mass flow data during the June 1992 time period suggest >50% degradation of TCE⁷ based on a steady-state material balance in which the difference between the TCE in and TCE out is defined to be degradation [see Eq. (1)]. Non-steady-state conditions may cause accumulation or depletion of TCE in the system by means other than reaction, such as varying liquid and/or gas flow, varying inlet concentrations, adsorption/desorption, which will create uncertainties in the calculation of TCE degradation. Since the average liquid residence time in the system for this mode was ~1.5 h, about 6 h of stable operation was needed to achieve near

steady state from a hydraulic standpoint in this mode. The operating periods were as long as 2 weeks, so it seems plausible that most of the performance data were obtained during pseudo steady-state operation.

Performance of the bioreactors during a limited operating period in August was equivocal, in part due to perturbations believed to have been caused by a pulse test immediately prior to continuous operation. (See Sect. 7.2 and ref. 7 for more details.)

8.1.3 Degradation of Other Organics

Calculated degradation rates for 1,1-DCA; 1,1,1-TCA; and PCE are subject to the requirement for steady-state operation, just as for the TCE data. No methylene chloride or DCE was detected in the seep water during the 1992 operating campaign, although previous analyses of the seep water (Table 1) indicated 0.3 mg/L of methylene chloride and 0.7 mg/L of total DCE. In general, the data showed that the influent and effluent concentrations of the various organics often rise and fall together (but not always). This behavior suggests that common phenomena, such as varying influent concentrations and flow rates of seep water and gas streams, may have influenced all the constituents.

During the June 1992 operating period, apparent degradation of all VOCs was observed. The 1,1-DCA degradation was 20 to 30%, the 1,1,1-TCA degradation was 10 to 80%, and the PCE degradation was >50%. During the August operating period, the 1,1-DCA and PCE degradations varied widely and appeared to average ~0. The 1,1,1-TCA degradation was negative in early August 1992 (believed to be washout from the step feed experiment described earlier in Sect. 7.2) and then increased dramatically late in the month to >90%.

8.2 SUMMER 1993 OPERATING CAMPAIGN

8.2.1 Methane Consumption

Mass flow rates of methane to the bioreactors and in the effluents are shown in Fig. 8. Consumption of methane by the biofilm was sustained and substantial, usually above 97% in each column. The addition of organics during the pulse experiments and continuous-flow experiments produced no adverse effects on the methane consumption. The only decreases in methane usage observed in 1993 corresponded to specific operational incidents (Fig. 8). On June 15 the system operated several hours with organics fed after the methane feed tank was exhausted. On June 28 the recycle pump failed, and column A received hot concentrated organic vapor with no liquid recycle for several hours. In July 1993 extreme ambient temperatures regularly forced the recycle temperature over 38°C. Methane consumption appeared to recover quickly under total recycle in the absence of organics.

8.2.2 TCE Degradation

Mass flow rates of TCE in the influent seep water, the liquid effluent, and the off-gas are shown in Fig. 9. The TCE mass flow rate is the product of the TCE concentration and the volumetric flow rate for the various points in the system. Since the liquid effluent at the bottom of the steam stripper generally did not contain measurable TCE, the off-gas and biodegradation were the only means of removing TCE from the bioreactor system.

As described previously, the (apparent) degradation was derived from a steady-state material balance in which the difference between the TCE fed to the system and TCE leaving the system is defined to be degradation (Fig. 10). If the system were not operating at steady state

Fig. 8. Mass flow rates of methane into and out of process.

Fig. 9. Mass flow rates of TCE into and out of process.

Fig. 10. Degradation of TCE calculated from steady-state material balance.

and were experiencing accumulation or depletion of TCE by means other than reaction, then the actual degradation of TCE is uncertain. The average liquid residence time in the system for this mode is on the order of ~1 d since the only liquid flow through the system is the condensed overhead vapor plus the nutrient feed.

The data in Fig. 10 suggest >60% degradation of TCE for the entire system for much of the June operating period. Note that the feed rate is included for visual comparison with the degradation rate. During the July operating period, the degradation decreased to about 25%. The decrease was probably due to stress on the microorganisms caused by the high temperatures observed in July. A corresponding decrease in the methane consumption was observed during July (Fig. 8).

The data from the short-term pulse experiments in May and June show evidence of degradation of chlorinated VOCs. The chloride concentration increased substantially in one experiment (but not in all tests), and the VOCs decreased with time. These experiments were carried out as a contingency in the event that subsequent continuous operation could not be established, and the data were not analyzed in quantitative detail.

8.2.3 Degradation of Other VOCs

Mass flow rates and calculated degradation rates for 1,1,1-TCA; 1,1-DCA; and PCE are shown in Figs. 11 through 16. The determination of biodegradation from the mass flow data is subject to steady-state operation, as with the TCE data. Methylene chloride and DCE were not detected during the 1992 or 1993 operating campaigns, although previous analyses of the seep water had indicated their presence.

During the June operating period, all three compound appeared to be degraded. The 1,1,1-TCA degradation varied from about 20 to 50% (Figs. 11 and 12), the 1,1-DCA degradation

Fig. 11. Mass flow rates of 1,1,1-TCA into and out of process.

Fig. 12. Degradation of 1,1,1-TCA calculated from steady-state material balance.

Fig. 13. Mass flow rates of 1,1-DCA into and out of process.

Fig. 14. Degradation of 1,1-DCA in bioreactors calculated from steady-state material balance.

Fig. 15. Mass flow rates of PCE into and out of process.

was 80 to 90% (Figs. 13 and 14), and the PCE degradation was 40 to 80% (Figs. 15 and 16). During the July period, the degradation rates of all the compounds decreased. The 1,1,1-TCA degradation varied but averaged zero, and the PCE degradation averaged 0 to 10%. The degradation of 1,1-DCA decreased to about 60% during July. In general the graphs show the degradation often rising and falling with the feed rates of the organics.

8.2.4 Chloride Ion Generation

The rate of generation of chloride ions from degradation of chlorinated organics can be calculated from the chloride concentration measurements. This calculation is again subject to the steady-state assumption. Figure 17 shows a comparison of the chloride generation rate calculated from the chloride ion measurements, the total amount of chloride fed in the VOCs, and the expected generation rate calculated from loss of individual VOCs calculated by material balances. The generation rate of chloride ions is comparable with, but somewhat lower than, the expected rate from apparent degradation rates of the individual chlorinated VOCs. It would be expected to be lower if some of the organics that were degraded were not completely mineralized. The chloride generation data suggest 30 to 80% degradation of the chlorinated VOCs fed to the system in June and only 20% degradation in July, while the material balances suggest up to 90% degradation in June and 40% in July. These two independent analyses give comparable results, which supports the argument that chlorinated VOCs are indeed being biodegraded.

Fig. 17. Comparison of chloride ion generation rates, total chloride fed to the system as organics, and expected generation of chloride from loss of organics.

8.3 DEGRADATION KINETICS

The biodegradation rate of TCE and other organics is typically modeled as first-order in substrate concentration, such as

$$dC/dt = -kC, \quad (2)$$

where C is the concentration of organic substrate, t is time, and k is the first-order rate constant. (Degradation rates are also modeled by Monod or Michaelis-Menten equations that are first order in substrate at low concentrations and zero order at high concentrations.) Previous work at ORNL has indicated that the rate of TCE removal in trickle-filter bioreactors follows first-order kinetics.^{4,8} The removal rates in the pilot-scale bioreactors also appear to rise and fall with the concentrations (see Figs. 9 through 16 and the data in Appendix B), which is consistent with first-order kinetics.

For an ideal plug-flow reactor, Eq. (2) may be integrated to give

$$C_{\text{out}}/C_{\text{in}} = (-k\tau), \quad (3)$$

where τ is the residence time in the reactor. The residence time may be based on the superficial volume of the reactor or on the actual physical holdup of the liquid. The meaning of k will depend on the definition of τ . In either case, for a trickle-filter bioreactor, k is a lumped parameter that includes the effects of the biomass loading on the packing, the bioactivity, the surface area of the packing per unit volume of reactor, the distribution of liquid over the packing, and other complex factors.

Kinetics of removal of chlorinated VOCs may be compared for the several bench-scale^{4,8} and pilot-scale bioreactors on a superficial volume basis. In each case, τ is calculated from the geometric volume of the bioreactor and the liquid flow rate. Equation (3) is then used to determine k for the range of removals of organics that were obtained experimentally. The results are shown in Table 5. Also included are results from the demonstration at Tinker Air Force Base by Battelle using essentially the same type of bioreactor.⁹

Table 5 shows that the values of k for TCE removal are roughly comparable in the various bioreactors; that is, they are the same order of magnitude. This extent of agreement is perhaps all that should be expected since the packing, biofilms, and liquid flow distribution are undoubtedly different.

Experimental studies and mathematical modeling⁸ have shown that stripping can be significant. When the combination of stripping and biodegradation produce an effluent that has essentially no chlorinated VOCs, then the calculated rate constants are lower bounds since the VOC removals are restricted to total disappearance. The actual values of k may be larger. This was the situation for the experiments in the steam-stripping mode in the present study.

It has also been noted by various investigators that TCE concentration in the ppm range are more readily biodegraded than concentrations in the ppb range. The nominal TCE concentration at Tinker Air Force Base was 4 ppm, whereas the nominal TCE concentration at the Oak Ridge K-25 Site was 80 ppb, so this difference may also contribute to differences in removal kinetics at the two locations. Nevertheless, the data and calculations summarized in Table 5 provide an indication of the performance to be expected for these types of bioreactors at the present state of development.

Table 5. Kinetics of removal of chlorinated organics in trickle-filter bioreactors

Test system (τ , min) ^a	Compound	Observed removal (%)	k , (10^{-4} min ⁻¹)	Published reference
Bench-scale				4, 8
(430)	TCE	78	35	
(43)	TCE	40	119	
Pilot-scale				This project
Air oxidation mode (534)	TCE	>50	>13	
	1,1,1-TCA	10 to 80	2 to 30	
	1,1-DCA	20 to 30	4 to 7	
	PCE	>50	>13	
Steam-stripping mode (74 ^b)	TCE	10 to 30	14 to 48	
Pilot-scale				9
(133)	TCE	56 (average)	62 (average)	

^aBased on the geometric volume of the bioreactor.

^bBased on a single pass through one bioreactor. The system was operated at very high recycle, and the total liquid residence time in the packed region was about 1500 min. Rate constants for other compounds were generally similar to those for the single-pass air oxidation mode.

9. ECONOMICS

Although cometabolic biodegradation of chlorinated solvents is still in the demonstration stage, efforts have been made to project costs for full-scale treatment facilities. The Gas Research Institute (GRI) has funded process development and economic analyses for several years because methanotrophic technology represents a new market for natural gas. A recent report¹⁰ compares the costs for treatment of TCE in groundwater by methanotrophic cometabolism, air stripping with polishing of the off-gas by granular activated carbon (GAC), and liquid phase GAC. Methanotrophic cometabolism and air stripping/GAC were projected to be essentially identical in cost at about \$0.20 to \$0.25 per 1000 L of water. This cost is about 25% less than the projected cost for liquid-phase treatment by GAC.

The methanotrophic technology base for this economic analysis was a fluidized-bed bioreactor (perhaps because the GRI has primarily funded development of fluidized-bed technology). An early analysis by ORNL staff¹¹ for a large-scale trickle-filter process suggested that the cost could be about \$1.00 to \$1.70 per 1000 gal (\$0.25 to \$0.45 per 1000 L). These two estimates by GRI and ORNL are roughly comparable; the difference is probably not significant even though the estimates were derived for different types of bioreactors. Both estimates are for plants with treatment capacities of 1000 to 3000 L/min. The steam-stripping option¹² may add another \$2.00 to \$3.00 per 1000 gal of water for steam. For comparison, companies who discharge wastewater to a municipal aerobic treatment plant may typically be charged \$2.00 per 1000 gal.¹²

10. CONCLUSIONS

This demonstration project required significant collaborations among many people. These interactions were just as necessary for the success of the demonstration as was the technical operation of the pilot equipment. The following sections highlight aspects of the overall technology demonstration that went well and aspects that did not go as well as desired. The conclusions drawn from this project were derived from these various contributing factors.

10.1 PLANNING AND LOGISTICS

A variety of reviews and approvals were required prior to installation and operation of the pilot equipment at the demonstration site. These activities were generally completed smoothly. However, a significant perturbation occurred midway through the project when changes to the NPDES permit at the K-25 Site necessitated changes in the original requirements for waste disposal for the demonstration project. More extensive sampling and analyses were required prior to disposal of treated water. This change led to delays and unplanned costs for the project.

10.2 OPERATIONS

The experimental equipment experienced the typical failures and breakdowns of pumps, flowmeters, control systems, etc., that are often encountered in the operation of pilot-scale equipment. The impact was dependent on how quickly the problem could be solved and the equipment placed back in service. The most significant impact on the sustained operation of the equipment was the requirements for disposal of treated water, as highlighted above.

Much of the analytical chemistry work was done at a laboratory at the ORNL site where the requisite equipment was available. The approach necessitated transportation of samples by motor vehicle to the laboratory, which somewhat limited the timing and numbers of samples collected for analysis. Establishment of adequate on-site analytical capabilities (equipment and space to house it) would have cost significantly more on the front end but might have led to more experimental data. The significance of this trade-off was elevated when the ability to operate continuously at stable conditions was restricted by changes in the waste disposal requirements.

The project would have benefitted from better automated process-control equipment to maintain stable operating conditions. The desirability became apparent late in the project when it became clear that the length of operating campaigns would be limited because of waste disposal requirements and capabilities.

10.3 PROCESS PERFORMANCE

The field demonstration substantially met the initial objectives for the methanotrophic technology (Sect. 1.3), which were to

1. demonstrate stable operation of the bioreactor and associated equipment, including pretreatment and polishing steps; and
2. evaluate the biodegradation of TCE and the other chlorinated organics in the seep water for the three operating modes — air oxidation pretreatment, steam-stripping pretreatment, and no pretreatment.

A stable biofilm population containing methanotrophs was established on the structured packing material in the columns, as evidenced by sustained consumption of methane during hydraulic conditions that would wash unattached biomass from the columns. The system was operated successfully to treat seep water for periods up to 2 weeks; longer operation was limited

by effluent disposal requirements. Operation in the no-pretreatment mode was not tested in order to conserve resources for the tests with the pseudomonad system under the auspices of the CRADA with Envirogen, Inc., Lawrenceville, New Jersey.

Integrated biotreatment and physical/chemical treatment (air oxidation and steam stripping) to meet stringent discharge limits were demonstrated. The waste acceptance criteria for disposal of the effluent was effectively "no detectable VOCs," and the treated effluent from the integrated process never failed to meet these criteria.

Analytical methods were developed for successful simultaneous quantification of TCE; 1,1,1-TCA; 1,1-DCA; and PCE in gas and liquid samples to enable material balance calculations to assess degradation. In the air oxidation mode, capability was demonstrated to reduce 80 ppb of TCE by >50%; 1500 ppb of 1,1,1-TCA by 10 to 80%; 1500 ppb of 1,1-DCA by 20 to 30%; and 30 ppb of PCE by >50%. In the steam-stripping mode, reductions of chlorinated VOCs attributed to biodegradation were typically >50% for TCE; 20 to 50% for 1,1,1-TCA; 80 to 90% for 1,1-DCA; and 40 to 80% for PCE. Attribution of these reductions to biodegradation is supported by chloride generation comparable with the chloride in the lost VOCs. Simultaneous degradation of these compounds suggests the presence of both aerobic and anaerobic regions in the bioreactor, which is consistent with recent observations by other investigators.^{2,14} Values of first-order kinetic rate constants for degradation of TCE are consistent with values obtained from bench-scale experiments.

Microbiological sampling and characterization throughout the operation of the bioreactors were planned initially, but very little such data were actually obtained. Resources that were originally allocated to these issues were diverted to deal with increased waste disposal requirements. It was noted that methane utilization is a quick and easy way to monitor the general health of the methanotrophic culture; however, methane utilization does not appear to

correlate directly with degradation of chlorinated VOCs. It was observed that the bioactivity for degradation of chlorinated VOCs is threatened by a pH >7.5 and temperatures >30°C. No inhibition by VOCs was observed in this field demonstration. Good process control is desirable to stay within the acceptable operating window.

The bench-scale vapor-phase bioreactor system from Envirogen was capable of degrading TCE and other organics in the condensate from the steam stripper that contained a mixture of these organics. Pseudomonad (aromatic-utilizing) microbial cultures were used. Further technical information is available in the report from Envirogen, Inc. (Appendix A).

11. RECOMMENDATIONS

1. The maximum capabilities of the methanotrophic system have not yet been established.

Further extended tests are warranted to explore the total capabilities under conditions that do not restrict the long-term operation.

- 1.1 Two important parameters that have not been assessed are the maximum flow rate that can be treated and the maximum effluent quality that can be achieved. Further tests should focus on these variables.
- 1.2 Recent research has indicated that the oxygen content in air is greater than optimum and that methane concentrations $< 3\%$ also may increase the degradation rates. Further tests should examine dilution of the air with nitrogen, or recycle of the off-gas, and/or other means to reduce the oxygen concentration and the methane concentration. Improvements in performance are likely.

2. The apparent simultaneous aerobic/anaerobic degradation phenomena should be investigated further to improve the flexibility and adaptability of biofilm reactors such as the trickle-filter reactor used in this study. This apparent coexistence of aerobic and anaerobic regions offers opportunities for treatment of a variety of mixtures of contaminants by mixed microbial cultures in biofilm reactors.

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APPENDIX A

CRADA REPORT FROM ENVIROGEN, INC.

May 25, 1994

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Stephen E. Herbes, Ph.D.
Leader, Contaminant Transport Group
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6036

Subject: Final CRADA Report

Dear Steve:

On Friday, May 6th we met at ENVIROGEN to discuss closeout of the ENVIROGEN CRADA.

The report has been revised to include all the concerns from the ORNL project staff. ENVIROGEN has no objection to including our report as an appendix to your final Methanotroph report. This report contains no proprietary information or Protected CRADA Information, so the abstract can be openly distributed, when justified by the nature of the research efforts. We would also like to pursue publishing our report as a stand-alone document through the DOE office of Scientific and Technical Information (OSTI) or through other means if possible. Please let us know.

Over the course of the project, ENVIROGEN has incurred for in-kind labor and expenses more than \$95,000. Most of the money was spent on the eight weeks in the field and support labor from Operations and R & D.

We at ENVIROGEN feel this project was successful in achieving its goals and objectives and would like to thank you and your staff for their support and the opportunity to work at Oak Ridge National Laboratory.

Enclosed, please find (3) three copies of the final test report for you, Terry Donaldson and Bill Pader.

Please let me know if you require any additional information.

Sincerely,

James M. Caratura
Senior Project Manager

JMC/bt

Enclosure

Final Report
Field Demonstration of Vapor Phase TCE Bioreactor
Cooperative Research and Development Agreement
(ORNL92-0093)*

Submitted by:

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- * CRADA work performed in collaboration with the Environmental Sciences and Chemical Technology Divisions of Oak Ridge National Laboratory, which is managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under Contract DE-AC05-84OR21400.

Abstract

The objective of this Cooperative Research and Development Agreement (CRADA), was to demonstrate the effectiveness of a vapor-phase bioreactor system for the destruction of trichloroethylene (TCE) from contaminated groundwater. A field demonstration was performed with the cooperation of staff of Oak Ridge National Laboratory at the K-25 Site. Groundwater at this site is contaminated with a complex mixture of organic chemicals. This site is managed and operated by Martin Marietta Energy Systems, Inc. for the Department of Energy (DOE). Analysis of the data generated during the test can be summarized in three major observations. First, TCE was degraded in the presence of all the organics found in the steam strip condensate. This was observed during treatment of both the steam strip condensate and condensate amended with TCE to increase its concentration relative to the other components. The conclusion that TCE was being biodegraded was supported by performing mass balance control experiments with the reactor and by tracking recalcitrant chemicals also present in the steam stripper condensate. Second, there appeared to be an initial lag period of up to 24 hours before onset of TCE degradation in the reactor. The source of this lag was not determined but could be related to either an acclimation of the microorganisms to other chemicals found in the condensate or reversible inhibitory effects on TCE degradation. The duration of TCE degradative activity was relatively short, for only 2 to 5 days, compared to previous demonstrations where TCE was the sole contaminant. However, several of the runs were interrupted due to mechanical and not biological issues. Third, other chemical contaminants were also degraded by the bacteria used in the vapor phase reactor which is consistent with previous work performed both at ENVIROGEN and elsewhere.

Overview

The objective of the Cooperative Research and Development Agreement (CRADA), was to demonstrate the effectiveness of a laboratory-scale vapor phase bioreactor system for the destruction of trichloroethylene (TCE) from a groundwater seepage stream; i.e. the "garage seep" at the Oak Ridge K-25 Site. This site is managed and operated by Martin Marietta Energy Systems, Inc. for the department of Energy (DOE). This field demonstration at the K-25 Site was performed from August to October through a CRADA in cooperation of staff of Oak Ridge National Laboratory. The test represents one step towards full-scale demonstration of a bioreactor for the destruction of TCE in complex organic mixture of organic chemicals contaminating groundwater.

Methods and Materials

A. Bacterial strains.

Two strains of TCE degradative microorganisms were used in this study, *Pseudomonas cepacia* G4 and *Pseudomonas mendocina* KR1. Both strains were cultured in a defined basal salts medium (BSM)(6), pH 7.5 and shipped to the site at 4°C. Organisms were used as is or were diluted with BSM to preset cell densities.

B. Methods for quantifying phenol.

Phenol concentrations and phenol hydroxylase activities were determined using the modified colorimetric assay. In this assay, 25 μ l of 2% 4-aminoantipyrine and 50 μ l of 2 N NH_4OH were added to a microfuge tube. A 1 ml suspension was then added to the tube and mixed well. Finally, 25 μ l of 8% $\text{K}_3\text{Fe}(\text{CN})_6$ was added and the tube contents were again mixed. Following centrifugation to pellet out solids, the optical density of the supernatant was determined at 500 nm with phenol concentrations calculated from a standard curve. Rates of phenol disappearance were calculated and reported as $\mu\text{mole}/(\text{min} \cdot \text{g protein})$. The rate of phenol disappearance from cell free controls was less than 0.01 $\mu\text{mole}/\text{min}$.

C. TCE bottle assay protocol.

TCE degradation kinetics, toxicity and inhibitory interactions were determined using a bottle assay. In this standard assay, a 25 ml liquid microbial suspension was placed into a serum bottle (actual volume of 162 ml) with 125 ml of test liquid containing

either a known amount of TCE and/or other chemicals found at the K-25 Site. The bottle was immediately sealed with a Teflon lined septum and agitated at room temperature. At defined time intervals, 10 μ l of headspace gas was withdrawn through the septum using a gastight syringe and injected onto a GC. For volatile organic chemicals, which equilibrate rapidly between air and water, the gas phase analysis provides a clear representation of the total amount of chemical in the sealed bottle. Chemical concentrations in live experimental and killed controls are calculated by comparison to a standard curve. Degradation rates are calculated for the disappearance of total chemical from the bottle normalized to the microorganism content expressed as total protein.

D. Methods for quantifying TCE and other chlorinated hydrocarbons.

On site quantification of chlorinated hydrocarbon concentrations incorporated the use of an SRI gas chromatograph (GC) equipped with an electron capture detector and a stream selection valve. The concentrations of TCE and other chlorinated hydrocarbons were quantified by either direct injection of a 10 μ l headspace gas sample or use of an automated gas sampling valve. Direct injections used a gastight syringe. The automated gas sampling valve sampled influent and effluent air streams by drawing gas through a 50 μ l sample loop then injecting the contents of the loop onto the GC.

Concentrations were calculated from standard curves prepared by injecting a defined mixture of chlorinated organics at known concentrations. Standards were prepared in methanol and dilutions prepared in serum bottles. A 10 μ l gas sample was injected onto the GC and a calibration curve prepared and added to the integration software to calculate unknown concentrations. The detection limit was about 1 μ g/L for TCE using direct air phase injections. Standards were prepared fresh and run routinely to check calibration and reproducibility. The detection limit varied for the other chlorinated organics indirectly related to the extent of chlorination.

Analysis was also performed using ORBO tubes to trap the volatile organics which were not detectable using an electron capture detector. Samples were collected by passing gas through the ORBO tube at a known flow rate for a timed interval. Traps were assembled in series to determine the extent of chemical breakthrough during sample collection. The tube ends were then capped and shipped to ENVIROGEN for analysis. Each tube was extracted with 2.0 ml of carbon disulfide to remove the organic compounds. A 1 μ l liquid sample was injected onto the GC/PID and concentrations

determined against a known standard. Depending on the volume of air passed through the ORBO tube, detection limits varied between 0.1 and 1.0 $\mu\text{g/L}$ for the chemicals monitored. The benzene concentration was adjusted to account for benzene in the carbon disulfide extraction solvent.

E. Vapor phase reactor design and operation

The process diagram of the TCE vapor phase bioreactor for the degradation of TCE is depicted in Figure 1. The main reactor vessel was constructed from a 10 cm diameter by 60 cm glass chromatography column with threaded Teflon plugs in each end with an empty bed volume of 4.7 L. The reactor was filled with 3 L of a suspension of *P. cepacia* G4 or *P. mendocina* KR1 which had been grown at ENVIROGEN and shipped to the site. Contaminated groundwater seepage was pumped into a steam stripper to concentrate VOCs. The steam stripper condensate was pumped into an air stripping vessel and contaminated air then passed into the vapor phase reactor at a flow rate of 100 ml/min. The TCE concentration in the influent and effluent gas was monitored by GC (① and ②) (Fig. 1). The reactor was fed phenol in water at a rate of 0.4 g phenol per liter of liquid volume per day unless otherwise indicated.

Figure 1: Process Flow Diagram for Vapor Phase TCE Bioreactor

Results and Discussion

Initial assembly of the laboratory scale bioreactor system was initiated on August 23, 1993. By August 25, the reactor was operational with the GC functioning and calibrated at which time the first batch of bacteria was added to the reactor. Table 1 lists a chronology of events during the field study. Several major issues were encountered during the 7 week test period. First, separation and quantitation of TCE in the presence of 1,1,1-TCA was found to be difficult with the GC system used for automated sampling. Second, there was a chemical component present in the steam strip condensate which interfered with the standard colorimetric assay used to quantify phenol. This interference initially led to the incorrect conclusion that addition of steam strip condensate to the reactor immediately inhibited the biocatalyst's ability to metabolize phenol. Once this interference was deduced and characterized, continuous operation was achievable. In addition, there were numerous mechanical issues which also interfered with steady state operation of the test system for extended time periods. These mechanical problems included air leaks in the reactor, power shutdowns during weekend periods, high variability in organic concentrations and air flows to the reactor and difficulties with the automated gas chromatography equipment. In general, the test program did not go smoothly though all of the major hurdles were eventually overcome.

The first priority of the test program was to determine whether TCE could be effectively biodegraded from this complex mixture of organic chemicals found in the K-25 Site water. First, a control was performed to determine abiotic system losses. Once the water in the reactor was saturated with TCE, there was less than 15% difference between influent and effluent gas concentration (Figure 2). The average inlet and outlet gas concentrations following equilibration were 344 ± 31 and 291 ± 31 $\mu\text{g/L}$ air respectively. This difference in concentration represents the maximum abiotic losses of TCE from the system.

During several runs of the vapor phase reactor on steam stripper condensate, degradation of TCE was observed. Quantitation was difficult, so additional TCE was added to the condensate to enhance detection and quantitation. The amount of TCE added increased its concentration to nearly equal that of TCA in the steam stripper condensate. Addition of TCE also had the benefit of increasing our confidence that TCE was actually being biologically destroyed in the reactor by increasing the mass of TCE

Table 1: Major Events During Co-Metabolic Bioreactor Demonstration.

EVENT	DATE
• Received CRADA approval	6/22/93
• ENVIROGEN arrived at site and completed GET	7/93
• Setup bioreactor system in trailer at K-25	8/93
• Completed installation of bioreactor in trailer and equipment checkout	8/93
• Completed safety review	8/93
• Completed readiness review and received approval to operate	8/93
• Inoculated bioreactor, no apparent growth, bacteria possible killed during shipment	8/24/93
• First introduction of seep water to bioreactor, difficulties in separating and quantifying key chemical components with automated GC system, repaired leaks in system, phenol breakthrough with no apparent degradation of TCE	9/3 - 9/6
• Reinoculated bioreactor, continued difficulties with GC analysis, positive growth and enzymatic activity of bacteria	9/7 - 9/13
• Reinoculated bioreactor, apparent phenol breakthrough when seep water initiated, characterized interference of seep liquor with phenol assay which had given false positive results, positive growth and enzymatic activity	9/14 - 9/20
• TCE being degraded for approximately 20 hours, data collected for Table 2 and Figures 3 A & B	9/20 - 9/22
• Reinoculated bioreactor, positive growth and enzymatic activity	9/25
• Resume treatment of seep water using hand injection for GC data points, data collected for Table 3 and Figures 4 A & B	9/27
• Spiked TCE into seep water to elevate concentrations, ORBO tube samples collected for Table 4	9/28 - 9/29
• TCE spike discontinued, ORBO tube samples collected for Table 4, power shut off to trailer for 24 hours	9/30 - 10/3
• Reinoculated bioreactor, positive growth and enzymatic activity, phenol breakthrough, could not sustain activity	10/5 - 10/21
• Operation terminated due to construction	10/21

entering the reactor. The data presented in Figure 3a & b is a compilation of automated GC analyses collected over a 20 hour period of stable operation. On average, $84 \pm 9 \%$ of $124 \pm 47 \mu\text{g TCE/L-air}$ was removed from the air during this time interval. This was clearly in excess of losses determined for TCE in control experiments. As expected,

there was essentially no loss of the 1,1,1-TCA, $12 \pm 13 \%$, monitored during this time interval. Since TCA is not biodegradable by this bacterial system, it acts as a conservative organic tracer. Though the relative concentrations of TCE to the other contaminants was greater by spiking TCE into the steam stripper condensate, this experiment demonstrated that TCE could be successfully degraded within this mixture of chemicals. These data were collected during the second day of operation under these conditions. The reactor continued to operate for about 3 days maintaining specific rates of phenol degradation above greater than 100 nmole/(min mg protein) before activity was lost. In general, although TCE was degradable in this mixture of chemicals, longevity of reactor operation was shorter than previous experiences with TCE as the sole contaminant. The nature of this instability was not determined.

Figure 2: Control experiment for determining abiotic losses of TCE.

In a subsequent run, the reactor was again set up and inoculated with fresh organisms to determine whether TCE could be degraded at concentrations found in the steam stripper condensate. To achieve concentrations of TCE which could be detected reliably with our analytical equipment, the stripper was operated at its optimum output. There was a high degree of variability in chemical concentrations over this time interval as seen in Figures 4a & b. Analysis was performed by manual injections with a gas tight

syringe which accounts for the timing and frequency of analysis. Although removal of TCA and TCE from the contaminated air stream varied as the influent concentration

Gas Phase Bioreactor Operation
(September 20 - September 21)

Figure 3: Reactor Performance Using Steam Stripper Condensate Spiked with TCE. $A(500) = 3.8$, specific activity of phenol hydroxylase = 65 nmole/min/mg protein, 100 ml/min air flow. Plot A is for TCE and plot B is for 1,1,1-TCA. Filled symbols are for inlet concentrations and open symbols are for outlet concentrations

Gas Phase Bioreactor Operation
(September 27 - September 29)

Figure 4: Reactor Performance Using Steam Stripper Condensate. $A(500) = 3.7$, specific activity of phenol hydroxylase = 100 nmole/min/mg protein, 100 ml/min air flow. Plot A is for TCE and plot B is for 1,1,1-TCA. Filled symbols are for inlet concentrations and open symbols are for outlet concentrations

fluctuated, TCE removal was much greater than that observed for 1,1,1-TCA. These data support the conclusion that TCE can be biodegraded from steam stripper condensate containing a complex mixture of organics found at the K-25 Site.

This run of the reactor continued past 4 days with active degradation of TCE. On days 4 and 5, GC analysis was not performed at the site, however, ORBO tube samples were collected and analyzed at ENVIROGEN for a wider range of chemicals. Analysis was performed using a PID which will detect aromatic (BTEX) and unsaturated chlorinated aliphatic compounds (TCE) but will not detect unsaturated aliphatics (TCA and DCA). Two ORBO tubes were connected in series to determine whether there was any breakthrough due to overloading. Benzene concentrations were not tabulated from the data collected because there was interference from benzene in the CS_2 extraction solvent. DCE was detected in only half of the inlet samples analyzed, possibly due to its greater volatility and potential losses during collection and handling. In general, there was evidence of breakthrough for only *m*-xylene (raw data and calculations found in Appendix A). Following 4 and 5 days of continuous operation, not only was the TCE biodegraded, but most of the aromatic hydrocarbons were also being effectively removed (Table 2). This activity against the aromatic hydrocarbons is not unexpected since it has previously been demonstrated the bacteria used in the reactor are capable of degrading all of the chemicals listed in Table 2 in addition to benzene. These data indicate that the composition and concentration of chemicals in the steam stripper condensate was as variable as the TCE and TCA components monitored previously. The detection limits were different for the two sets of samples. The higher air flow rate and greater collection time used on day 5 allowed for a lower minimum detection limit than samples collected on day 4. Unfortunately, power was shut off to the trailer following day 5 so reactor operation was suspended.

Table 2: Reactor Performance, ORBO Tube Analysis.

compound	Day 4 ($\mu\text{g/L air}$) (5A&B, 6A&B)		Day 5 ($\mu\text{g/L air}$) (11A&B, 12A&B)		Day 7 ($\mu\text{g/L air}$) (13A&B, 14A&B)		Day 7 ($\mu\text{g/L air}$) (17A&B, 18A&B)	
	in	out	in	out	in	out	in	out
TCE	86	5	46	7	16	< 1	22	3
toluene	26	< 1	476	5	264	< 1	356	< 1
ethylbenzene	16	< 1	242	8	180	< 1	248	4
<i>o,p</i> -xylene(s)	53	< 1	276	11	211	< 1	232	5
<i>m</i> -xylene	127	65	398	23	239	74	318	26

A(500)= 3.8 (day 4) and 4.1 (day 5), specific activity of phenol hydroxylase = 54 (day 4) and 75 (day 5) nmole/min/mg protein, 100 ml/min air flow.

Conclusions

Analysis of the data generated during the test can be summarized in three major observations. First, TCE was degraded in the presence of all the organics found in the steam strip condensate. This was observed during treatment of both the steam strip condensate and condensate amended with TCE to increase its concentration relative to the other components. The conclusion that TCE was being biodegraded was supported by performing mass balance control experiments with the reactor and by tracking recalcitrant chemicals also present in the steam stripper condensate. Second, there appeared to be an initial lag period of up to 24 hours before onset of TCE degradation in the reactor. The source of this lag was not determined but could be related to either an acclimation of the microorganisms to other chemicals found in the condensate or reversible inhibitory effects on TCE degradation. The duration of TCE degradative activity was relatively short, for only 2 to 5 days, compared to previous demonstrations where TCE was the sole contaminant. However, several of the runs were interrupted due to mechanical and not biological issues. Third, other chemical contaminants were also degraded by the bacteria used in the vapor phase reactor which is consistent with previous work performed both at ENVIROGEN and elsewhere.

During the course of this test at the K-25 Site, many operational obstacles were overcome in the development of the data presented in this report. Though operation was not always as smooth as planned, an initial body of data was generated to support the conclusion that TCE can be biodegraded within a complex mixture of organic chemicals. Ultimately, sustained degradation of TCE and many of the other chemical contaminants may be achievable in a stable bioreactor system. Additional work would be required to optimize operating conditions. Recently, we have made major advances in increasing the stability of operation for our vapor phase TCE bioreactor system and have begun to successfully treat TCE directly from contaminated groundwater in the presence of a similar mixture of aromatic hydrocarbons as found at the K-25 Site.

Acknowledgments

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Appendix A

ORBO Tube Raw Data and Calculations

ORBO Tube analysis information

#	date	description
3A	9/30	inlet, tube 1, 10 min, 90 ml/min
3B	9/30	inlet, tube 2, 10 min, 90 ml/min
4A	9/30	outlet, tube 1, 10 min, 45 ml/min
4B	9/30	outlet, tube 2, 10 min, 45 ml/min
5A	9/30	inlet, tube 1, 10 min, 73 ml/min
5B	9/30	inlet, tube 2, 10 min, 73 ml/min
6A	9/30	outlet, tube 1, 10 min, 60 ml/min
6B	9/30	outlet, tube 2, 10 min, 60 ml/min
9A	10/1	inlet, tube 1, 10 min, 95 ml/min
9B	10/1	inlet, tube 2, 10 min, 95 ml/min
10A	10/1	outlet, tube 1, 10 min, 50 ml/min
10B	10/1	outlet, tube 2, 10 min, 50 ml/min
11A	10/1	inlet, tube 1, 60 min, 80 ml/min
11B	10/1	inlet, tube 2, 60 min, 80 ml/min
12A	10/1	outlet, tube 1, 60 min, 50 ml/min
12B	10/1	outlet, tube 2, 60 min, 50 ml/min
13A	10/3	inlet, tube 1, 10 min, 120 ml/min
13B	10/3	inlet, tube 2, 10 min, 120 ml/min
14A	10/3	outlet, tube 1, 10 min, 55 ml/min
14B	10/3	outlet, tube 2, 10 min, 55 ml/min
17A	10/3	inlet, tube 1, 60 min, 95 ml/min
17B	10/3	inlet, tube 2, 60 min, 95 ml/min
18A	10/3	outlet, tube 1, 60 min, 55 ml/min
18B	10/3	outlet, tube 2, 60 min, 55 ml/min

GC/FID
(CRADA ORBO data 9/30/93a)

		standard run on: 9/30/93			ppm	ARF					
Compound	RT				100.00	(area/ppm)					
1 DCE	6.89				2464378	24,644					
2 benzene	7.62				2289955	22,900					
3 TCE	8.77				1107111	11,071					
4 toluene	11.29				558406	5,584					
5 PCE	12.54				337343	3,373					
6 ethylbenzene	14.46				363612	3,636					
7 op-xylene	14.61				1187104	11,871					
8 m-xylene	15.56				448790	4,488					
9 DCB 1 (1,3)	19.39				645072	6,451					
10 DCB 2 (1,4)	19.63				550766	5,508					
11 DCB 3 (1,2)	20.45				506131	5,061					
12 naphthalene	24.84				740610	7,406					
GC run date: 9/30/93											
extraction volume (ml):		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
sample volume (ml):		900.00	900.00	900.00	450.00	450.00	450.00	730.00	730	730	730
concentration factor:		450.00	450.00	450.00	225.00	225.00	225.00	365.00	365.00	365.00	365.00
Integrated Peak Area		CS2 blank	orbo 3A 9/30 Inlet	orbo 3B 9/30 Inlet	Detection Limit #3	orbo 4A 9/30	orbo 4B 9/30	Detection Limit #4	orbo 5A 9/30 Inlet	orbo 5B 9/30 Inlet	Detection Limit #5
1 DCE	6.89		291,890		1,000			1,000			1,000
2 benzene	7.62	3,568,082	3,828,250	3,894,478	3,569,082	3,670,921	4,112,464	3,569,082	3,997,346	3,354,498	3,569,082
3 TCE	8.77		453,808		1,000	20,994		1,000	348,184		1,000
4 toluene	11.29		65,183		1,000			1,000	53,250		1,000
5 PCE	12.54				1,000			1,000			1,000
6 ethylbenzene	14.46		24,543		1,000			1,000	21,545		1,000
7 op-xylene	14.61		271,615		1,000			1,000	229,155		1,000
8 m-xylene	15.56		189,525	43,552	1,000	32,313	47,509	1,000	167,601	40,529	1,000
9 DCB 1 (1,3)	19.39		127,385		1,000			1,000	113,704		1,000
10 DCB 2 (1,4)	19.63		187,043		1,000			1,000	162,059		1,000
11 DCB 3 (1,2)	20.45		221,705		1,000			1,000	200,644		1,000
12 naphthalene	24.84				1,000			1,000			1,000
ppm (extracted sample)											
1 DCE	6.89		11.84		0.04			0.04			0.04
2 benzene	7.62		(11.36)	(14.25)	(0.04)	(4.49)	(23.77)	(0.04)	(18.75)		(0.04)
3 TCE	8.77		40.99		0.09	1.90		0.09	31.45		0.09
4 toluene	11.29		11.67		0.18			0.18	9.54		0.18
5 PCE	12.54				0.30			0.30			0.30
6 ethylbenzene	14.46		6.75		0.28			0.28	5.93		0.28
7 op-xylene	14.61		22.88		0.08			0.08	19.30		0.08
8 m-xylene	15.56		42.23	9.70	0.22	7.20	10.59	0.22	37.35	9.03	0.22
9 DCB 1 (1,3)	19.39		19.75		0.16			0.16	17.63		0.16
10 DCB 2 (1,4)	19.63		33.96		0.18			0.18	29.42		0.18
11 DCB 3 (1,2)	20.45		43.80		0.20			0.20	39.64		0.20
12 naphthalene	24.84				0.14			0.14			0.14
µg/l air	RT	CS2 blank	orbo 3A 9/30 Inlet	orbo 3B 9/30 Inlet	Detection Limit #3	orbo 4A 9/30	orbo 4B 9/30	Detection Limit #4	orbo 5A 9/30 Inlet	orbo 5B 9/30 Inlet	Detection Limit #5
1 DCE	6.89		26.32		0.09			0.18			0.11
2 benzene	7.62		(25.25)	(31.67)	(0.10)	(19.96)	(105.66)	(0.19)	(51.36)		(0.12)
3 TCE	8.77		91.09		0.20	8.43		0.40	86.16		0.25
4 toluene	11.29		25.94		0.40			0.80	26.13		0.49
5 PCE	12.54				0.66			1.32			0.81
6 ethylbenzene	14.46		15.00		0.61			1.22	16.23		0.75
7 op-xylene	14.61		50.85		0.19			0.37	52.89		0.23
8 m-xylene	15.56		93.84	21.57	0.50	32.00	47.05	0.99	102.32	24.74	0.61
9 DCB 1 (1,3)	19.39		43.88		0.34			0.69	48.29		0.42
10 DCB 2 (1,4)	19.63		75.47		0.40			0.81	80.61		0.50
11 DCB 3 (1,2)	20.45		97.34		0.44			0.88	108.61		0.54
12 naphthalene	24.84				0.30			0.60			0.37

GC/FID
(CRADA ORBO data 9/30/93a)

		ARF (area/ug)									
Compound	RT										
1 DCE	6.89	-	-	-	-	-	-	-	-	100.00	
2 benzene	7.62	-	-	-	-	-	-	-	-	24,644	
3 TCE	8.77	-	-	-	-	-	-	-	-	22,900	
4 toluene	11.29	-	-	-	-	-	-	-	-	11,071	
5 PCE	12.54	-	-	-	-	-	-	-	-	5,584	
6 ethylbenzene	14.46	-	-	-	-	-	-	-	-	3,373	
7 op-xylene	14.61	-	-	-	-	-	-	-	-	3,636	
8 m-xylene	15.56	-	-	-	-	-	-	-	-	11,871	
9 DCB 1 (1,3)	19.39	-	-	-	-	-	-	-	-	4,488	
10 DCB 2 (1,4)	19.63	-	-	-	-	-	-	-	-	6,451	
11 DCB 3 (1,2)	20.45	-	-	-	-	-	-	-	-	5,508	
12 naphthalene	24.84	-	-	-	-	-	-	-	-	5,061	
		-	-	-	-	-	-	-	-	7,406	
GC run date:											
extraction volume (ml):	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	
sample volume (ml):	600	600	600	950	950	950	500	500	500		
concentration factor:	300.00	300.00	300.00	475.00	475.00	475.00	250.00	250.00	250.00		
Integrated Peak Area		orbo 6A 9/30 outlet	orbo 6B 9/30 outlet	Detection Limit #6	orbo 9A 10/1 Inlet	orbo 9B 10/1 Inlet	Detection Limit #9	orbo 10A 10/1 outlet	orbo 10B 10/1 outlet	Detection Limit #10	
1 DCE	6.89			1,000			1,000			1,000	
2 benzene	7.62	4,062,785	4,085,421	3,569,082	4,605,386	3,706,789	3,569,082	3,942,502	3,650,107	3,569,082	
3 TCE	8.77	17,377		1,000	177,610		1,000			1,000	
4 toluene	11.29			1,000	863,434		1,000			1,000	
5 PCE	12.54			1,000			1,000			1,000	
6 ethylbenzene	14.46			1,000	230,294		1,000			1,000	
7 op-xylene	14.61			1,000	1,166,334		1,000			1,000	
8 m-xylene	15.56	42,978	45,390	1,000	486,750	39,120	1,000	48,909	41,600	1,000	
9 DCB 1 (1,3)	19.39			1,000	226,792		1,000			1,000	
10 DCB 2 (1,4)	19.63			1,000	214,095		1,000			1,000	
11 DCB 3 (1,2)	20.45			1,000	368,706		1,000			1,000	
12 naphthalene	24.84			1,000			1,000			1,000	
ppm (extracted sample)											
1 DCE	6.89			0.04			0.04			0.04	
2 benzene	7.62	(21.60)	(22.59)	(0.04)	(45.30)	(6.06)	(0.04)	(16.35)	(3.58)	(0.04)	
3 TCE	8.77	1.57		0.09	16.04		0.09			0.09	
4 toluene	11.29			0.18	(154.62)		0.18			0.18	
5 PCE	12.54			0.30			0.30			0.30	
6 ethylbenzene	14.46			0.28	63.34		0.28			0.28	
7 op-xylene	14.61			0.08	98.25		0.08			0.08	
8 m-xylene	15.56	9.58	10.11	0.22	(108.46)	8.72	0.22	10.90	9.27	0.22	
9 DCB 1 (1,3)	19.39			0.16	35.16		0.16			0.16	
10 DCB 2 (1,4)	19.63			0.18	38.87		0.18			0.18	
11 DCB 3 (1,2)	20.45			0.20	72.85		0.20			0.20	
12 naphthalene	24.84			0.14			0.14			0.14	
	ug/l air	RT	orbo 6A 9/30 outlet	orbo 6B 9/30 outlet	Detection Limit #6	orbo 9A 10/1 Inlet	orbo 9B 10/1 Inlet	Detection Limit #9	orbo 10A 10/1 outlet	orbo 10B 10/1 outlet	Detection Limit #10
1 DCE	6.89				0.14			0.09			0.16
2 benzene	7.62		(72.01)	(75.31)	(0.15)	(95.36)	(12.75)	(0.09)	(65.40)	(14.33)	(0.17)
3 TCE	8.77		5.23		0.30	33.77		0.19			0.36
4 toluene	11.29				0.60	(325.53)		0.38			0.72
5 PCE	12.54				0.99			0.62			1.19
6 ethylbenzene	14.46				0.92	133.34		0.58			1.10
7 op-xylene	14.61				0.28	206.84		0.18			0.34
8 m-xylene	15.56		31.92	33.71	0.74	(228.33)	18.35	0.47	43.59	37.08	0.89
9 DCB 1 (1,3)	19.39				0.52	74.02		0.33			0.62
10 DCB 2 (1,4)	19.63				0.61	81.84		0.38			0.73
11 DCB 3 (1,2)	20.45				0.66	153.36		0.42			0.79
12 naphthalene	24.84				0.45			0.28			0.54

GC/FID
(CRADA ORBO data 9/30/93b)

		standard run on: 9/30/93		ppm		ARF					
Compound	RT			100.00	(area/ppm)						
1 DCE	6.89			2464378	24,644						
2 benzene	7.62			2289955	22,900						
3 TCE	8.77			1107111	11,071						
4 toluene	11.29			558406	5,584						
5 PCE	12.54			337343	3,373						
6 ethylbenzene	14.46			363612	3,636						
7 op-xylene	14.61			1187104	11,871						
8 m-xylene	15.56			448790	4,488						
9 DCB 1 (1,3)	19.39			645072	6,451						
10 DCB 2 (1,4)	19.63			550766	5,508						
11 DCB 3 (1,2)	20.45			506131	5,061						
12 naphthalene	24.84			740610	7,406						
GC run date:		9/30/93									
extraction volume (ml):		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
sample volume (ml):		4800.00	4800.00	4800.00	3000.00	3000.00	3000.00	1200.00	1200	1200	1200
concentration factor:		2400.00	2400.00	2400.00	1500.00	1500.00	1500.00	600.00	600.00	600.00	600.00
Integrated Peak Area		CS2 blank	orbo 11A 10/1 Inlet	orbo 11B 10/1 Inlet	Detection Limit #11	orbo 12A 10/1 outlet	orbo 12B 10/1 outlet	Detection Limit #12	orbo 13A 10/3 Inlet	orbo 13B 10/3 Inlet	Detection Limit #13
1 DCE	6.89		2,605,130		1,000			1,000			1,000
2 benzene	7.62	3,568,082	8,948,304	3,683,298	3,569,082	4,520,068	3,735,740	3,569,082	4,689,747	3,813,328	3,569,082
3 TCE	8.77		1,212,678		1,000	110,565		1,000	103,216		1,000
4 toluene	11.29		6,383,319		1,000	54,702		1,000	885,517		1,000
5 PCE	12.54		119,943		1,000	27,470		1,000			1,000
6 ethylbenzene	14.46		2,113,951		1,000	45,078		1,000	391,668		1,000
7 op-xylene	14.61		7,880,113		1,000	200,971		1,000	1,499,763		1,000
8 m-xylene	15.56		4,249,281	40,563	1,000	151,659	42,418	1,000	594,642	49,462	1,000
9 DCB 1 (1,3)	19.39		2,547,985		1,000	23,774		1,000	319,958		1,000
10 DCB 2 (1,4)	19.63		1,891,755		1,000	99,555		1,000	286,767		1,000
11 DCB 3 (1,2)	20.45		4,003,216		1,000	60,350		1,000	595,458		1,000
12 naphthalene	24.84				1,000			1,000			1,000
ppm (extracted sample)											
1 DCE	6.89		(105.71)		0.04			0.04			0.04
2 benzene	7.62		(234.95)	(5.03)	(0.04)	(41.57)	(7.32)	(0.04)	(48.98)	(10.71)	(0.04)
3 TCE	8.77		(109.54)		0.09	9.99		0.09	9.32		0.09
4 toluene	11.29		(1,143.13)		0.18	9.80		0.18	(158.58)		0.18
5 PCE	12.54		35.56		0.30	8.14		0.30			0.30
6 ethylbenzene	14.46		(581.38)		0.28	12.40		0.28	(107.72)		0.28
7 op-xylene	14.61		(663.81)		0.08	16.93		0.08	(126.34)		0.08
8 m-xylene	15.56		(946.83)	9.04	0.22	33.79	9.45	0.22	(132.50)	11.02	0.22
9 DCB 1 (1,3)	19.39		(394.99)		0.16	3.69		0.16	49.60		0.16
10 DCB 2 (1,4)	19.63		(343.48)		0.18	18.08		0.18	52.07		0.18
11 DCB 3 (1,2)	20.45		(790.94)		0.20	11.92		0.20	(117.65)		0.20
12 naphthalene	24.84				0.14			0.14			0.14
μg/l air	RT	CS2 blank	orbo 11A 10/1 Inlet	orbo 11B 10/1 Inlet	Detection Limit #11	orbo 12A 10/1 outlet	orbo 12B 10/1 outlet	Detection Limit #12	orbo 13A 10/3 Inlet	orbo 13B 10/3 Inlet	Detection Limit #13
1 DCE	6.89		(44.05)		0.02			0.03			0.07
2 benzene	7.62		(97.90)	(2.10)	(0.02)	(27.71)	(4.88)	(0.03)	(81.64)	(17.85)	(0.07)
3 TCE	8.77		(45.64)		0.04	6.66		0.06	15.54		0.15
4 toluene	11.29		(476.31)		0.07	6.53		0.12	(264.30)		0.30
5 PCE	12.54		14.81		0.12	5.43		0.20			0.49
6 ethylbenzene	14.46		(242.24)		0.11	8.26		0.18	(179.53)		0.46
7 op-xylene	14.61		(276.59)		0.04	11.29		0.06	(210.56)		0.14
8 m-xylene	15.56		(394.51)	3.77	0.09	22.53	6.30	0.15	(220.83)	18.37	0.37
9 DCB 1 (1,3)	19.39		(164.58)		0.06	2.46		0.10	82.67		0.26
10 DCB 2 (1,4)	19.63		(143.12)		0.08	12.05		0.12	86.78		0.30
11 DCB 3 (1,2)	20.45		(329.56)		0.08	7.95		0.13	(196.08)		0.33
12 naphthalene	24.84				0.06			0.09			0.23

GC/FID
(CRADA ORBO data 9/30/93b)

Compound	RT	ARF (area/μg)				100.00				
1 DCE	6.89	-	-	-	-	24,644				
2 benzene	7.62	-	-	-	-	22,900				
3 TCE	8.77	-	-	-	-	11,071				
4 toluene	11.29	-	-	-	-	5,584				
5 PCE	12.54	-	-	-	-	3,373				
6 ethylbenzene	14.46	-	-	-	-	3,636				
7 op-xylene	14.61	-	-	-	-	11,871				
8 m-xylene	15.56	-	-	-	-	4,488				
9 DCB 1 (1,3)	19.39	-	-	-	-	6,451				
10 DCB 2 (1,4)	19.63	-	-	-	-	5,508				
11 DCB 3 (1,2)	20.45	-	-	-	-	5,061				
12 naphthalene	24.84	-	-	-	-	7,406				
GC run date:										
extraction volume (ml):	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
sample volume (ml):	550	550	550	5700	5700	5700	3300	3300	3300	3300
concentration factor:	275.00	275.00	275.00	2850.00	2850.00	2850.00	1650.00	1650.00	1650.00	1650.00
Integrated Peak Area		orbo 14A 10/3 outlet	orbo 14B 10/3 outlet	Detection Limit #14	orbo 17A 10/3 inlet	orbo 17B 10/3 inlet	Detection Limit #17	orbo 18A 10/3 outlet	orbo 18B 10/3 outlet	Detection Limit #18
1 DCE	6.89			1,000	2,217,627		1,000			1,000
2 benzene	7.62	3,688,834	3,763,982	3,569,082	8,714,101	4,214,097	3,569,082	4,505,369	3,604,475	3,569,082
3 TCE	8.77			1,000	698,323		1,000	47,186		1,000
4 toluene	11.29			1,000	5,672,656		1,000			1,000
5 PCE	12.54			1,000	94,192		1,000	28,354		1,000
6 ethylbenzene	14.46			1,000	2,571,843		1,000	25,913		1,000
7 op-xylene	14.61			1,000	7,845,438		1,000	98,626		1,000
8 m-xylene	15.56	45,664	45,177	1,000	3,986,434	87,172	1,000	139,787	53,797	1,000
9 DCB 1 (1,3)	19.39			1,000	2,947,372		1,000			1,000
10 DCB 2 (1,4)	19.63			1,000	1,731,400		1,000	266,135		1,000
11 DCB 3 (1,2)	20.45			1,000	4,770,913		1,000	197,244		1,000
12 naphthalene	24.84			1,000			1,000			1,000
ppm (extracted sample)										
1 DCE	6.89			0.04	89.99		0.04			0.04
2 benzene	7.62	(5.27)	(8.55)	(0.04)	(224.72)	(28.21)	(0.04)	(40.93)	(1.59)	(0.04)
3 TCE	8.77			0.09	63.08		0.09	4.26		0.09
4 toluene	11.29			0.18	(1,015.87)		0.18			0.18
5 PCE	12.54			0.30	27.92		0.30	8.41		0.30
6 ethylbenzene	14.46			0.28	(707.30)		0.28	7.13		0.28
7 op-xylene	14.61			0.08	(660.89)		0.08	8.31		0.08
8 m-xylene	15.56	10.17	10.07	0.22	(888.26)	19.42	0.22	31.15	11.99	0.22
9 DCB 1 (1,3)	19.39			0.16	(456.91)		0.16			0.16
10 DCB 2 (1,4)	19.63			0.18	(314.36)		0.18	48.32		0.18
11 DCB 3 (1,2)	20.45			0.20	(942.62)		0.20	38.97		0.20
12 naphthalene	24.84			0.14			0.14			0.14
μg/l air										
μg/l air	RT	orbo 14A 10/3 outlet	orbo 14B 10/3 outlet	Detection Limit #14	orbo 17A 10/3 inlet	orbo 17B 10/3 inlet	Detection Limit #17	orbo 18A 10/3 outlet	orbo 18B 10/3 outlet	Detection Limit #18
1 DCE	6.89			0.15	31.57		0.01			0.02
2 benzene	7.62	(19.17)	(31.11)	(0.16)	(78.85)	(9.90)	(0.02)	(24.81)	(0.96)	(0.03)
3 TCE	8.77			0.33	22.13		0.03	2.58		0.05
4 toluene	11.29			0.65	(356.44)		0.06			0.11
5 PCE	12.54			1.08	9.80		0.10	5.09		0.18
6 ethylbenzene	14.46			1.00	(248.18)		0.10	4.32		0.17
7 op-xylene	14.61			0.31	(231.89)		0.03	5.04		0.05
8 m-xylene	15.56	37.00	36.61	0.81	(311.67)	6.82	0.08	18.88	7.26	0.14
9 DCB 1 (1,3)	19.39			0.56	(160.32)		0.05			0.09
10 DCB 2 (1,4)	19.63			0.66	(110.30)		0.06	29.29		0.11
11 DCB 3 (1,2)	20.45			0.72	(330.75)		0.07	23.62		0.12
12 naphthalene	24.84			0.49			0.05			0.08

APPENDIX B

DATA FROM 1993 OPERATING CAMPAIGN

DATE PRINTED		11/22/93		FLOW RATES				CHLORIDE CONC.			NITROGEN-OXYGEN				METHANE CONC.					
LEGEND		Sample not taken																		
ND		Not detected																		
RC		Recycle																		
SS		Steam-Stripper																		
DATE	TIME	COMMENTS	Initials	Seep Flow	Col. A Liquid Flow	Col. B Liquid Flow	Recycle Liquid Flow	Col. A Gas Flow	Col. B Gas Flow	Col. A Inlet	Col. A Outlet	Col. B Outlet	Col. A N2	Col. B N2	Col. A O2	Col. B O2	Col. A Inlet Eff.	Col. B Inlet Eff.		
				L/min.	L/min.	L/min.	L/min.	L/min.	L/min.	ppm	ppm	ppm	%	%	%	%	%	%		
05/18/93	10:20 AM	Baseline	LJK	0.00	2.08	2.08	2.08	0.55	1.11	6	6	6	--	--	--	--	--	0.01	0.02	
	11:20 AM	1 Hr after start-up	LJK	0.44	2.08	2.08	2.08	0.49	0.98	--	--	--	--	--	--	--	--	0.11	0.02	
	03:10 PM	HexAce contaminated with	LJK	0.00	2.08	2.08	2.08	0.49	0.98	6	7	7	--	--	--	--	--	0.10	0.04	
05/19/93	10:15 AM	approx. 500 ppb of TCE	LJK	0.00	2.08	2.08	2.08	0.49	0.98	9	10	9	--	--	--	--	--	--	--	
	03:30 PM	corrections will be made	LJK	0.00	2.08	2.08	2.08	0.49	0.98	--	9	9	--	--	--	--	--	--	--	
05/20/93	09:00 AM	Ran CH4N2O2 before organics	LJK	0.00	2.06	2.06	2.06	0.49	0.98	--	9	9	78.18	79.99	15.70	14.66	--	0.03	0.03	
06/03/93		Experiment No. 2																		
	12:15 PM	Initial readings	LJK	0.00	2.02	2.02	0.00	0.49	0.98	4	5	5	--	--	--	--	--	2.72	0.01	0.02
	12:30 PM	Organics added	LJK	0.91	2.02	2.02	0.00	0.49	0.98	--	--	--	--	--	--	--	--	--	--	
	02:30 PM	SS turned off	LJK	0.91	2.02	2.02	0.00	0.49	0.98	20	30	30	--	--	--	--	--	2.60	0.06	0.02
06/04/93	09:50 AM		LJK	0.00	1.87	1.87	0.00	0.49	0.98	20	20	20	--	--	--	--	--	2.30	0.05	0.08
	01:33 PM		LJK	0.00	1.96	1.96	1.96	0.49	0.98	20	20	20	--	--	--	--	--	0.04	0.02	
06/07/93		Experiment No. 3																		
	09:20 AM	Initial Readings	LJK	0.00	1.96	1.96	0.00	0.49	0.97	7.16	7.03	7.58	--	--	--	--	--	2.75	0.01	0.01
	11:40	SS turned off	LJK	1.92	1.96	1.96	0.00	0.49	0.98	--	--	--	--	--	--	--	--	--	--	
	12:00		LJK	0.00	1.96	1.96	1.96	0.49	0.98	9.04	8.33	8.77	--	--	--	--	--	0.11	0.03	
06/08/93	11:10		LJK	0.00	1.96	1.96	1.96	0.49	0.98	--	10.80	9.92	--	--	--	--	--	2.38	0.01	0.04
06/09/93	09:30		LJK	2.66	1.91	1.91	1.91	0.49	0.98	8.92	8.51	8.62	--	--	--	--	--	2.84	0.03	0.05
06/11/93		Experiment No. 4																		
	09:00	Started SS & SEEP	LJK	2.36	2.13	2.13	0.00	0.49	0.98											
	10:30	SS shut off	LJK																	

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION PROJECT

DATE PRINTED		11/22/93		FLOW RATES						CHLORIDE CONC.			NITROGEN-OXYGEN				METHANE CONC.		
LEGEND	--	Sample not taken		Col. A	Col. B		Col. A	Col. B		Col. A	Col. A	Col. B	Col. A	Col. B	Col. A	Col. B	Col. A	Col. B	
	ND	Not detected		Inlet	Inlet	Recycle	Inlet	Inlet		Inlet	Outlet	Outlet					Inlet	Col. A	
	RC	Recycle		Seep	Liquid	Liquid	Liquid	Gas	Gas								Eff.	Col. B	
	SS	Steam-Stripper		Flow	Flow	Flow	Flow	Flow	Flow								Eff.		
DATE	TIME	COMMENTS	Initials	L/min.	L/min.	L/min.	L/min.	L/min	L/min.	ppm	ppm	ppm	N2	N2	O2	O2	G1	G2	
													%	%	%	%	%	%	
Changed calibrations to linear; previous data will be corrected																			
Experiment No. 7																			
07/12/93	09:50	CH4 CHECK	LJK	0.00	1.40	1.40	1.40	0.50	0.50	--	--	--	--	--	--	--	3.80	0.11	0.12
07/13/93	09:45	CH4 CHECK	LJK	0.00	2.04	2.04	2.04	0.51	0.51	--	--	--	--	--	--	--	2.74	0.00	0.06
	13:45		LJK	0.30	1.83	1.83	1.83	0.51	0.51	14.56	13.80	13.40	--	--	--	--	2.96	0.14	0.03
07/14/93	12:35		LJK	0.41	1.91	1.91	1.91	0.51	0.51	11.40	10.40	11.00	--	--	--	--	2.80	0.05	0.04
07/15/93	08:55		LJK	0.41	1.79	1.79	1.79	0.51	0.51	13.50	13.30	13.50	--	--	--	--	2.64	0.30	0.02
	14:15		LJK	0.41	1.91	1.91	1.91	0.34	0.46	11.50	12.10	11.30	--	--	--	--	2.77	0.14	0.02
07/16/93	09:00		LJK	0.44	1.79	1.79	1.79	0.51	0.52	13.00	12.20	12.10	--	--	--	--	2.94	0.61	0.03
	13:50		LJK	0.44	1.87	1.87	1.87	0.52	0.52	11.20	11.20	12.80	--	--	--	--	2.94	0.60	0.03
07/19/93	09:20		LJK	0.47	1.83	1.83	1.83	0.52	0.52	13.20	12.50	14.30	--	--	--	--	2.78	2.22	0.12
	13:30		LJK	0.44	1.91	1.91	1.91	0.50	0.50	13.20	12.50	14.30	--	--	--	--	2.72	2.01	0.06
07/20/93	10:30		LJK	0.44	1.83	1.83	1.83	0.56	0.56	12.80	12.50	11.20	--	--	--	--	2.84	2.26	0.21
	14:40	CH4 CHECK	LJK	0.41	1.83	1.83	1.83	0.56	0.56	--	--	--	--	--	--	--	--	1.99	0.14
07/21/93	10:00		LJK	0.44	1.74	1.74	1.74	0.56	0.56	11.00	11.00	11.20	--	--	--	--	3.02	2.37	0.35
	14:00	Flow rate in ?????	LJK	0.44	2.83	2.83	2.83	0.56	0.56	9.74	9.10	10.90	--	--	--	--	2.84	2.07	0.14
07/22/93	08:45		LJK	0.44	1.79	1.79	1.79	0.56	0.56	10.90	10.70	11.90	--	--	--	--	2.69	1.82	0.29
	15:00		LJK	0.00	--	--	--	--	--	--	--	--	--	--	--	--	2.59	1.93	0.17
07/23/93	09:00		LJK	0.34	0.40	0.40	0.40	0.56	0.57	8.84	8.02	8.06	--	--	--	--	2.09	1.11	0.16
	12:45		LJK	0.44	0.40	0.40	0.40	0.57	0.57	7.30	8.25	7.82	--	--	--	--	3.11	1.82	0.10
Mass Balance																			
08/11/93	12:15		LJK	2.95	1.79	1.79	1.79	0.51	0.51	--	--	--	--	--	--	--	2.92	1.20	0.34
08/13/93	14:30	Col. B sump 25.1 C, no gas flow	LJK	2.36	1.87	1.87	1.87	0.00	0.00	--	--	--	--	--	--	--	2.64	--	2.64
08/16/93	09:30	Col.B sump 24.5 C	LJK	2.95	1.87	1.87	1.87	0.00	0.00	--	--	--	--	--	--	--	--	--	--
08/18/93	09:30	Col.B sump 28.1 C	LJK	2.95	1.87	1.87	1.87	0.00	0.00	--	--	--	--	--	--	--	--	--	--
Mass Balance																			
11/05/93	13:40		LJK	0.59	0.00	1.62	1.62	0.51	0.45	200	200	200					2.65	2.33	2.40
11/09/93	08:45		LJK	0.58	1.36	1.36	1.36	0.00	0.56	4000	4000	4000							
11/11/93	09:10	Seep reading for flow was fluctuat	LJK	0.56	1.53	1.53	1.53	0.57	0.57	700	600	700					1.08	1.00	0.95
11/12/93	09:10		LJK	1.18	1.62	1.62	1.62	0.57	0.57	500	500	500					1.08	1.03	0.88
	14:00		LJK	1.24	1.66	1.66	1.66	0.57	0.57	800	600	500							

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION

DATE PRINTED

11/22/93

1,1 DCA

LEGEND		Sample not taken	Initials	Steam		Col. A		Col. B		Liquid Feed	Liquid Effluent	Combined off-gas	Degraded	Percent Degraded
				Stripper	Seep	Eff.	AIR	Eff.	AIR					
DATE	TIME	COMMENTS		L1	L2	G2	G3	system	system	µg/min.	µg/min.	µg/min.	µg/min.	
05/18/93	10:20 AM	Baseline	LJK					0.00	0.00	0.00	0.00	0.00	0.00	ERR
	11:20 AM	1 Hr after start-up	LJK					0.00	0.00	0.00	0.00	0.00	0.00	ERR
	03:10 PM	Hex: Ace contaminated with	LJK			56.1	84.4	0.00	0.00	109.83	-109.83	ERR		
05/19/93	10:15 AM	approx. 500 ppb of TCE	LJK			ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	03:30 PM	corrections will be made	LJK			ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
05/20/93	09:00 AM	Ran CH4/N2/O2 before organics	LJK			ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
								0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/03/93		Experiment No. 2												
	12:15 PM	Initial readings	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	12:30 PM	Organics added	LJK	1171.5	ND	--	--	1071.35	0.00	0.00	1071.35	100%		
	02:30 PM	SS turned off	LJK	--	--	105.6	70.8	0.00	0.00	120.78	-120.78	ERR		
06/04/93	09:50 AM		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	01:33 PM		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
								0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/07/93		Experiment No. 3												
	09:20 AM	Initial Readings	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	11:40	SS turned off	LJK	1670.2	ND	--	--	3202.69	0.00	0.00	3202.69	100%		
	12:00		LJK	--	--	316.8	251.0	0.00	0.00	399.63	-399.63	ERR		
06/08/93	11:10		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/09/93	09:30		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
								0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/11/93		Experiment No. 4												
	09:00	Started SS & SEEP	LJK	1272.4	ND			3002.91	0.00	0.00	3002.91	100%		
	10:30	SS shut off	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	13:15		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	15:10		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
								0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/14/93		Experiment No. 5												
	09:46	Initial Readings	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	10:06	Started SS	LJK					0.00	0.00	0.00	0.00	0.00	0.00	ERR
	14:25		LJK	1317.9	ND	ND	ND	544.28	0.00	0.00	544.28	100%		
06/15/93	10:00	Ran out of CH4	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
		at 9 last night						0.00	0.00	0.00	0.00	0.00	0.00	ERR
	13:35	Low CH4 consumption	LJK	1197.8	ND	ND	ND	282.68	0.00	0.00	282.68	100%		
	15:45	Shut SS & SEEP off						0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/16/93	09:30	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	01:35	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/18/93	09:55	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
								0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/21/93		Experiment No. 6												
		SS on continuous run						0.00	0.00	0.00	0.00	0.00	0.00	ERR
	10:18	CH4 & Cl- check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	14:05	Rev SSin/SSout	LJK	1363.3	ND	ND	49.1	482.62	0.00	24.81	457.81	95%		
06/22/93	10:00		LJK	2214.8	ND	192.3	ND	784.05	0.00	98.44	685.61	87%		
	14:00	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/23/93	09:05		LJK	2114.0	ND	ND	100.3	498.91	0.00	50.13	448.78	90%		
	15:30	Blew SS trap	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/24/93	09:30	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	14:15		LJK	2219.4	ND	ND	105.7	0.00	0.00	53.71	-53.71	ERR		
06/25/93	09:30		LJK	2094.3	ND	210.6	ND	864.96	0.00	105.30	759.66	88%		
	13:20		LJK	2241.1	ND	207.1	ND	793.35	0.00	103.57	689.79	87%		
06/28/93		CH4 check; liq. level high, col. B	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	13:30		LJK	2110.2	ND	ND	ND	1120.51	0.00	0.00	1120.51	100%		
06/29/93	10:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	13:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	13:45	Shut SEEP feed off	LJK					0.00	0.00	0.00	0.00	0.00	0.00	ERR
06/30/93	10:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	14:40	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
		End of exp. due to low CH4 usage						0.00	0.00	0.00	0.00	0.00	0.00	ERR
								0.00	0.00	0.00	0.00	0.00	0.00	ERR
07/01/93	09:30	Monitoring CH4	LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
07/02/93	09:40		LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
07/07/93	09:00		LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	14:30		LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
07/08/93	09:30		LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR
	14:30		LJK	--	--	--	--	0.00	0.00	0.00	0.00	0.00	0.00	ERR

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION

DATE PRINTED

11/22/93

1,1 DCA

LEGEND	--	Sample not taken		Steam	Col. A	Col. B							
	ND	Not detected		Stripper	Eff.	Eff.	Liquid	Liquid	Combined	Degraded	Percent		
	RC	Recycle		Seep	Eff.	AIR	AIR	Feed	Effluent	off-gas		Degraded	
	SS	Steam-Stripper		L1	L2	G2	G3	system	system				
DATE	TIME	COMMENTS	Initials	µg/L	µg/L	µg/L	µg/L	µg/min.	µg/min.	µg/min.	µg/min.		
		Changed calibrations to linear;						0.00	0.00	0.00	0.00	ERR	
		previous data will be corrected						0.00	0.00	0.00	0.00	ERR	
07/12/93		Experiment No. 7						0.00	0.00	0.00	0.00	ERR	
	09:50	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
07/13/93	09:45	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	13:45		LJK	658.4	ND	278.4	252.5	194.22	0.00	270.72	-76.50	-39%	
07/14/93	12:35		LJK	2134.3	ND	347.1	289.4	881.48	0.00	325.23	556.26	63%	
07/15/93	08:55		LJK	2592.2	ND	357.4	361.9	1070.57	0.00	367.54	703.04	66%	
	14:15		LJK	2048.3	ND	394.1	334.4	845.96	0.00	287.81	558.15	66%	
07/16/93	09:00		LJK	2073.8	ND	339.7	269.8	917.65	0.00	313.83	603.82	66%	
	13:50		LJK	2072.5	ND	382.5	313.3	917.09	0.00	361.84	555.26	61%	
07/19/93	09:20		LJK	2123.8	ND	286.0	248.4	1002.45	0.00	277.87	724.58	72%	
	13:30		LJK	2134.3	ND	292.8	228.9	944.41	0.00	260.84	683.57	72%	
07/20/93	10:30		LJK	2163.0	ND	230.2	185.5	957.14	0.00	232.83	724.31	76%	
	14:40	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
07/21/93	10:00		LJK	2141.8	ND	271.7	222.9	947.73	0.00	274.96	672.77	71%	
	14:00	Flow rate in ????	LJK	2208.9	ND	260.8	233.0	977.44	0.00	276.58	700.87	72%	
07/22/93	08:45		LJK	2193.5	ND	155.7	103.1	970.61	0.00	144.93	825.69	85%	
	15:00		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
07/23/93	09:00		LJK	1424.4	ND	202.4	168.5	483.23	0.00	209.40	273.83	57%	
	12:45		LJK	2193.5	ND	264.1	205.7	970.61	0.00	266.31	704.31	73%	
								0.00	0.00	0.00	0.00	ERR	
		Mass Balance						0.00	0.00	0.00	0.00	ERR	
08/11/93	12:15		LJK	2142.2	ND	--	--	6319.43	0.00	0.00	6319.43	100%	
08/13/93	14:30	Col. B sump 25.1 C, no gas flow	LJK	2263.5	ND	--	--	5341.97	0.00	0.00	5341.97	100%	
08/16/93	09:30	Col.B sump 24.5 C	LJK	2201.4	ND	--	--	6494.14	0.00	0.00	6494.14	100%	
08/18/93	09:30	Col.B sump 28.1 C	LJK	2134.7	ND	--	--	6297.29	0.00	0.00	6297.29	100%	
		Mass Balance											
11/05/93	13:40		LJK	ND	ND	55.46	51.53	0.00	0.00	51.82	-51.82	ERR	
11/09/93	08:45		LJK	ND	ND	27.02	ND	0.00	0.00	0.00	0.00	ERR	
11/11/93	09:10	Seep reading for flow was fluctuat	LJK	ND	ND	ND	48.71	0.00	0.00	27.99	-27.99	ERR	
11/12/93	09:10		LJK	ND	ND	ND	ND	0.00	0.00	0.00	0.00	ERR	
	14:00		LJK	ND	ND	ND	ND	0.00	0.00	0.00	0.00	ERR	

11/22/93

1.1.1 TCA

1

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION

DATE PRINTED

11/22/93

1.1.1 TCA

LEGEND

--

Sample not taken

ND

Not detected

RC

Recycle

SS

Steam-Stripper

DATE

TIME

COMMENTS

Initials

Seep

L1

L2

G2

G3

Liquid

Feed

Liquid

Effluent

Combined

off-gas

Degraded

Percent

Degraded

µg/L

µg/L

µg/L

µg/L

µg/min.

µg/min.

µg/min.

µg/min.

ERR

Changed calibrations to linear;

previous data will be corrected

07/12/93

Experiment No. 7

09:50

CH4 CHECK

LJK

--

--

--

--

0.00

0.00

0.00

0.00

ERR

07/13/93

09:45

CH4 CHECK

LJK

--

--

--

--

0.00

0.00

0.00

0.00

ERR

13:45

LJK

1102.1

-2.0

289.5

151.7

325.13

-0.59

224.70

101.02

31%

07/14/93

12:35

LJK

1013.0

-3.3

497.0

239.8

418.37

-1.34

376.23

43.49

10%

07/15/93

08:55

LJK

1026.5

-2.7

387.7

449.1

423.94

-1.12

427.67

-2.61

-1%

14:15

LJK

1110.8

0.9

915.6

574.3

458.77

0.36

575.48

-117.07

-26%

07/16/93

09:00

LJK

1109.8

-3.1

485.9

700.9

491.09

-1.36

611.40

-118.95

-24%

13:50

LJK

1077.1

-1.8

773.0

554.0

476.60

-0.79

690.03

-212.65

-45%

07/19/93

09:20

LJK

1088.8

-2.8

630.0

466.4

513.90

-1.32

570.12

-54.90

-11%

13:30

LJK

1099.0

-3.2

649.3

394.8

486.29

-1.42

522.07

-34.36

-7%

07/20/93

10:30

LJK

1101.6

-3.2

525.4

311.8

487.45

-1.40

468.85

20.00

4%

14:40

CH4 CHECK

LJK

--

--

--

--

0.00

0.00

0.00

0.00

ERR

07/21/93

10:00

LJK

1098.2

-2.7

518.8

362.8

485.96

-1.19

490.15

-2.99

-1%

14:00

Flow rate in ????

LJK

1015.1

1.2

518.3

364.0

449.20

0.54

494.09

-45.42

-10%

07/22/93

08:45

LJK

1037.2

-1.4

270.9

108.2

458.96

-0.61

212.31

247.25

54%

15:00

LJK

--

--

--

--

0.00

0.00

0.00

0.00

ERR

07/23/93

09:00

LJK

1029.5

-0.8

443.3

290.2

349.24

-0.28

413.98

-64.45

-18%

12:45

LJK

995.4

3.9

501.1

268.5

440.45

1.73

436.17

2.55

1%

0.00

0.00

0.00

0.00

ERR

Mass Balance

0.00

0.00

0.00

0.00

ERR

08/11/93

12:15

LJK

1027.5

1.9

--

--

3031.23

5.59

0.00

3025.63

100%

08/13/93

14:30

Col. B sump 25.1 C, no gas flow

LJK

1102.7

1.2

--

--

2602.33

2.91

0.00

2599.43

100%

08/16/93

09:30

Col. B sump 24.5 C

LJK

1106.8

1.8

--

--

3265.09

5.23

0.00

3259.87

100%

08/18/93

09:30

Col. B sump 28.1 C

LJK

1079.4

2.4

--

--

3184.28

6.94

0.00

3177.34

100%

Mass Balance

11/05/93

13:40

LJK

33330.54

<1

1134.66

4338.39

19676.82

0.00

2548.47

17128.35

87%

11/09/93

08:45

LJK

23259.34

19.63

1837.64

<1

13379.94

11.29

0.00

13368.64

100%

11/11/93

09:10

Seep reading for flow was fluctuat

LJK

5563.94

126.76

2374.19

1894.01

3118.59

71.05

2449.66

597.88

19%

11/12/93

09:10

LJK

4834.12

<1

3215.01

2665.23

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION

DATE PRINTED

11/22/93

LEGEND

--

Sample not taken

ND

Not detected

RC

Recycle

SS

Steam - Stripper

DATE

TIME

COMMENTS

Initials

TCE

Steam

Col. A

Col. B

Stripper

Eff.

Eff.

Seep

AIR

AIR

L1

L2

G2

G3

L1

L2

G2

G3

L1

L2

G2

G3

L1

L2

G2

G3

L1

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G2

G3

Steam	Col. A	Col. B	Liquid	Liquid	Combined	Degraded	Percent
Stripper	Eff.	Eff.	Feed	Effluent	off-gas		Degraded
Seep	Eff.	AIR	AIR	system	system		
L1	L2	G2	G3	μg/min.	μg/min.	μg/min.	μg/min.
05/18/93	10:20 AM	Baseline	LJK	--	--	0.00	0.00
	11:20 AM	1 Hr after start-up	LJK	--	--	0.00	0.00
	03:10 PM	Hex: Ace contaminated with	LJK	7.6	15.9	0.00	19.22
05/19/93	10:15 AM	approx. 500 ppb of TCE	LJK	ND	3.5	0.00	3.44
	03:30 PM	corrections will be made	LJK	ND	ND	0.00	0.00
05/20/93	09:00 AM	Ran CH4N2O2 before organics	LJK	ND	ND	0.00	0.00
				0.00	0.00	0.00	0.00
06/03/93		Experiment No. 2		0.00	0.00	0.00	0.00
	12:15 PM	Initial readings	LJK	--	--	0.00	0.00
	12:30 PM	Organics added	LJK	84.3	ND	77.11	77.11
	02:30 PM	SS turned off	LJK	--	--	0.00	12.66
06/04/93	09:50 AM		LJK	--	--	0.00	0.00
	01:33 PM		LJK	--	--	0.00	0.00
				0.00	0.00	0.00	0.00
06/07/93		Experiment No. 3		0.00	0.00	0.00	0.00
	09:20 AM	Initial Readings	LJK	--	--	0.00	0.00
	11:40	SS turned off	LJK	69.8	ND	133.82	133.82
	12:00		LJK	--	--	0.00	36.66
06/08/93	11:10		LJK	--	--	0.00	0.01
06/09/93	09:30		LJK	--	--	0.00	0.00
				0.00	0.00	0.00	0.00
06/11/93		Experiment No. 4		0.00	0.00	0.00	0.00
	09:00	Started SS & SEEP	LJK	60.7	ND	143.16	143.16
	10:30	SS shut off	LJK	--	--	0.00	33.89
	13:15		LJK	--	--	0.00	23.47
	15:10		LJK	--	--	0.00	21.20
				0.00	0.00	0.00	0.00
06/14/93		Experiment No. 5		0.00	0.00	0.00	0.00
	09:46	Initial Readings	LJK	--	--	0.00	0.00
	10:06	Started SS	LJK	--	--	0.00	0.00
	14:25		LJK	51.2	ND	21.14	7.55
06/15/93	10:00	Ran out of CH4	LJK	--	--	0.00	0.00
		at 9 last night		--	--	0.00	0.00
	13:35	Low CH4 consumption	LJK	50.2	ND	11.84	20.98
	15:45	Shut SS & SEEP off		--	--	0.00	0.00
06/16/93	09:30	CH4 check	LJK	--	--	0.00	0.00
	01:35	CH4 check	LJK	--	--	0.00	0.00
06/18/93	09:55	CH4 check	LJK	--	--	0.00	0.00
				0.00	0.00	0.00	0.00
06/21/93		Experiment No. 6		0.00	0.00	0.00	0.00
		SS on continuous run		0.00	0.00	0.00	0.00
	10:18	CH4 & Cl- check	LJK	--	--	0.00	0.00
	14:05	Rev SSin/SSout	LJK	47.4	ND	16.79	5.67
06/22/93	10:00		LJK	46.6	ND	16.50	5.71
	14:00	CH4 check	LJK	--	--	0.00	0.00
06/23/93	09:05		LJK	42.7	ND	10.07	2.31
	15:30	Blew SS trap	LJK	--	--	0.00	0.00
06/24/93	09:30	CH4 check	LJK	--	--	0.00	0.00
	14:15		LJK	44.0	ND	0.5	2.93
06/25/93	09:30		LJK	43.5	ND	17.96	5.59
	13:20		LJK	43.9	ND	15.55	5.41
06/28/93		CH4 check; liq. level high, col. B	LJK	--	--	0.00	0.00
	13:30		LJK	38.3	ND	20.32	25.70
06/29/93	10:30	CH4 CHECK	LJK	--	--	0.00	0.00
	13:30	CH4 CHECK	LJK	--	--	0.00	0.00
	13:45	Shut SEEP feed off	LJK	--	--	0.00	0.00
06/30/93	10:30	CH4 CHECK	LJK	--	--	0.00	0.00
	14:40	CH4 CHECK	LJK	--	--	0.00	0.00
		End of exp. due to		--	--	0.00	0.00
		low CH4 usage		--	--	0.00	0.00
				0.00	0.00	0.00	0.00
07/01/93	09:30	Monitoring CH4	LJK	--	--	0.00	0.00
07/02/93	09:40		LJK	--	--	0.00	0.00
07/07/93	09:00		LJK	--	--	0.00	0.00
	14:30		LJK	--	--	0.00	0.00
07/08/93	09:30		LJK	--	--	0.00	0.00
	14:30		LJK	--	--	0.00	0.00

TCE								
Seep Li	Steam Stripper Eff.	Col. A AIR	Col. B Eff. AIR	Liquid Feed system μg/min.	Liquid Effluent system μg/min.	Combined off-gas μg/min.	Degraded μg/min.	Percent Degraded
	L2	G2	G3					
μg/L	μg/L	μg/L	μg/L					
				0.00	0.00	0.00	0.00	ERR
				0.00	0.00	0.00	0.00	ERR
				0.00	0.00	0.00	0.00	ERR
--	--	--	--	0.00	0.00	0.00	0.00	ERR
--	--	--	--	0.00	0.00	0.00	0.00	ERR
22.9	ND	1.8	10.8	6.74	0.00	6.40	0.34	5%
21.8	ND	5.9	2.5	9.00	0.00	4.29	4.71	52%
21.6	ND	4.6	5.6	8.90	0.00	5.22	3.68	41%
39.4	6.6	18.6	7.7	16.27	2.74	9.87	3.66	23%
27.8	ND	10.9	11.2	12.30	0.00	11.40	0.90	7%
26.6	ND	15.2	9.0	11.76	0.00	12.59	-0.84	-7%
26.4	ND	10.8	11.7	12.44	0.00	11.69	0.74	6%
26.2	ND	11.9	7.7	11.58	0.00	9.79	1.79	15%
25.7	ND	9.7	5.0	11.37	0.00	8.18	3.19	28%
--	--	--	--	0.00	0.00	0.00	0.00	ERR
25.4	ND	8.4	6.2	11.26	0.00	8.15	3.11	28%
25.0	ND	10.3	6.5	11.08	0.00	9.38	1.70	15%
24.4	ND	4.5	2.5	10.78	0.00	3.88	6.90	64%
--	--	--	--	0.00	0.00	0.00	0.00	ERR
24.0	ND	6.4	5.3	8.14	0.00	6.58	1.57	19%
23.4	0.3	8.6	4.8	10.35	0.12	7.59	2.65	26%
				0.00	0.00	0.00	0.00	ERR
				0.00	0.00	0.00	0.00	ERR
26.8	ND	--	--	79.05	0.00	0.00	79.05	100%
27.6	ND	--	--	65.11	0.00	0.00	65.11	100%
27.7	ND	--	--	81.82	0.00	0.00	81.82	100%
24.3	ND	--	--	71.66	0.00	0.00	71.66	100%
5563.7	<1	4753.4	4338.4	3282.58	0.00	4405.61	-1123.02	-34%
3448.1	<1	7039.9	<1	1983.52	0.00	0.00	1983.52	100%
837.5	27.9	465.9	382.9	469.42	15.62	487.16	-33.36	-7%
866.3	104.8	518.5	469.7	1022.25	123.70	566.08	332.47	33%
757.0	43.6	910.8	797.6	937.93	53.99	972.76	-88.82	-9%

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION

DATE PRINTED

11/22/93

PCE

LEGEND	--	Sample not taken	Initials										
ND		Not detected											
RC		Recycle											
SS		Steam - Stripper											
DATE	TIME	COMMENTS	Initials	µg/L	µg/L	µg/L	µg/L	µg/min.	µg/min.	µg/min.	µg/min.	Percent Degraded	
05/18/93	10:20 AM	Baseline	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	11:20 AM	1 Hr after start-up	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	03:10 PM	Hex: Ace contaminated with	LJK					0.00	0.00	6.91	-6.91	ERR	
05/19/93	10:15 AM	approx. 500 ppb of TCE	LJK					0.00	0.00	3.30	-3.30	ERR	
	03:30 PM	corrections will be made	LJK					0.00	0.00	0.60	-0.60	ERR	
05/20/93	09:00 AM	Ran CH4,N2,O2 before organics	LJK					0.00	0.00	3.50	-3.50	ERR	
								0.00	0.00	0.00	0.00	ERR	
06/03/93		Experiment No. 2						0.00	0.00	0.00	0.00	ERR	
	12:15 PM	Initial readings	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	ERR	
	12:30 PM	Organics added	LJK	28.0	ND	--	--	25.62	0.00	0.00	25.62	100%	
	02:30 PM	SS turned off	LJK	--	--	4.7	1.3	0.00	0.00	3.55	-3.55	ERR	
06/04/93	09:50 AM		LJK	--	--	0.2	0.2	0.00	0.00	0.29	-0.29	ERR	
	01:33 PM		LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	ERR	
								0.00	0.00	0.00	0.00	ERR	
06/07/93		Experiment No. 3						0.00	0.00	0.00	0.00	ERR	
	09:20 AM	Initial Readings	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	ERR	
	11:40	SS turned off	LJK	25.4	ND	--	--	48.65	0.00	0.00	48.65	100%	
	12:00		LJK	--	--	21.5	6.1	0.00	0.00	16.44	-16.44	ERR	
06/08/93	11:10		LJK	--	--	0.2	0.0	0.00	0.00	0.12	-0.12	ERR	
06/09/93	09:30		LJK	--	--	0.0	0.0	0.00	0.00	0.03	-0.03	ERR	
								0.00	0.00	0.00	0.00	ERR	
06/11/93		Experiment No. 4						0.00	0.00	0.00	0.00	ERR	
	09:00	Started SS & SEEP	LJK	25.3	ND			59.61	0.00	0.00	59.61	100%	
	10:30	SS shut off	LJK	--	--	2.1	6.4	0.00	0.00	7.35	-7.35	ERR	
	13:15		LJK	--	--	0.8	8.5	0.00	0.00	8.71	-8.71	ERR	
	15:10		LJK	--	--	8.5	10.1	0.00	0.00	13.99	-13.99	ERR	
								0.00	0.00	0.00	0.00	ERR	
06/14/93		Experiment No. 5						0.00	0.00	0.00	0.00	ERR	
	09:46	Initial Readings	LJK	--	--	ND	ND	0.00	0.00	0.00	0.00	ERR	
	10:06	Started SS	LJK					0.00	0.00	0.00	0.00	ERR	
	14:25		LJK	22.4	ND	7.2	3.0	9.24	0.00	5.00	4.24	46%	
06/15/93	10:00	Ran out of CH4	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
		at 9 last night						0.00	0.00	0.00	0.00	ERR	
	13:35	Low CH4 consumption	LJK	20.2	ND	12.3	10.1	4.76	0.00	10.89	-6.14	-129%	
	15:45	Shut SS & SEEP off						0.00	0.00	0.00	0.00	ERR	
06/16/93	09:30	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	01:35	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
06/18/93	09:35	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
								0.00	0.00	0.00	0.00	ERR	
06/21/93		Experiment No. 6						0.00	0.00	0.00	0.00	ERR	
		SS on continuous run						0.00	0.00	0.00	0.00	ERR	
	10:18	CH4 & Cl- check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	14:05	Rev SSin/SSout	LJK	22.1	ND	0.1	0.6	7.83	0.00	0.33	7.49	96%	
06/22/93	10:00		LJK	21.3	ND	6.7	0.2	7.53	0.00	3.53	4.01	53%	
	14:00	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
06/23/93	09:05		LJK	20.8	ND	0.2	2.1	4.90	0.00	1.15	3.76	77%	
	15:30	Blew SS trap	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
06/24/93	09:30	CH4 check	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	14:15		LJK	21.0	ND	0.3	2.6	0.00	0.00	1.45	-1.45	ERR	
06/25/93	09:30		LJK	21.2	ND	5.8	0.1	8.75	0.00	2.98	5.77	66%	
	13:20		LJK	21.5	ND	5.4	0.5	7.60	0.00	2.95	4.66	61%	
06/28/93		CH4 check; liq. level high, col. B	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	13:30		LJK	20.2	ND	8.4	6.0	10.71	0.00	7.18	3.53	33%	
06/29/93	10:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	13:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	13:45	Shut SEEP feed off	LJK					0.00	0.00	0.00	0.00	ERR	
06/30/93	10:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	14:40	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
		End of exp. due to low CH4 usage						0.00	0.00	0.00	0.00	ERR	
								0.00	0.00	0.00	0.00	ERR	
07/01/93	09:30	Monitoring CH4	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
07/02/93	09:40		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
07/07/93	09:00		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	14:30		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
07/08/93	09:30		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	
	14:30		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR	

SPREADSHEET FOR DATA FROM COMET DEMONSTRATION

DATE PRINTED

11/22/93

PCE

LEGEND

--

Sample not taken

ND

Not detected

RC

Recycle

SS

Steam - Stripper

DATE

TIME

COMMENTS

Initials

PCE

Steam

Col. A

Col. B

Stripper

Eff.

Eff.

Liquid

Liquid

Combined

Degraded

Percent

Degraded

Seep

Eff.

AIR

Feed

Effluent

off-gas

Degraded

Degraded

L1

L2

G2

G3

system

system

μg/min.

μg/min.

μg/min.

DATE	TIME	COMMENTS	Initials	μg/L	μg/L	μg/L	μg/L	μg/min.	μg/min.	μg/min.	μg/min.	ERR
		Changed calibrations to linear;						0.00	0.00	0.00	0.00	ERR
		previous data will be corrected						0.00	0.00	0.00	0.00	ERR
07/12/93		Experiment No. 7						0.00	0.00	0.00	0.00	ERR
	09:30	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR
07/13/93	09:45	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR
	13:45		LJK	16.7	ND	9.0	1.0	4.94	0.00	5.08	-0.14	-3%
07/14/93	12:35		LJK	16.4	ND	5.2	1.7	6.78	0.00	3.51	3.27	48%
07/15/93	08:55		LJK	16.7	ND	3.7	5.0	6.88	0.00	4.42	2.46	36%
	14:15		LJK	22.8	5.4	16.0	6.6	9.40	2.22	8.49	-1.31	-14%
07/16/93	09:00		LJK	18.1	1.0	7.4	8.1	8.02	0.42	7.98	-0.39	-5%
	13:50		LJK	17.5	ND	12.9	7.2	7.73	0.00	ERR	ERR	ERR
07/19/93	09:20		LJK	17.5	ND	7.6	7.4	8.26	0.00	7.78	0.48	6%
	13:30		LJK	17.8	1.1	9.1	5.3	7.89	0.46	7.20	0.23	3%
07/20/93	10:30		LJK	17.0	ND	5.7	2.5	7.51	0.00	4.58	2.93	39%
	14:40	CH4 CHECK	LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR
07/21/93	10:00		LJK	17.9	0.7	5.6	3.7	7.91	0.31	5.17	2.42	31%
	14:00	Flow rate in ????	LJK	17.0	ND	7.4	4.4	7.51	0.00	6.58	0.93	12%
07/22/93	08:45		LJK	17.2	ND	2.6	1.3	7.59	0.00	2.18	5.41	71%
	15:00		LJK	--	--	--	--	0.00	0.00	0.00	0.00	ERR
07/23/93	09:00		LJK	16.7	ND	4.4	3.3	5.66	0.00	4.36	1.30	23%
	12:45		LJK	16.6	ND	6.6	3.1	7.33	0.00	5.47	1.86	25%
								0.00	0.00	0.00	0.00	ERR
		Mass Balance						0.00	0.00	0.00	0.00	ERR
08/11/93	12:15		LJK	17.2	8.7	--	--	50.71	25.52	0.00	25.19	50%
08/13/93	14:30	Col. B sump 25.1 C, no gas flow	LJK	19.2	0.8	--	--	45.41	1.84	0.00	43.57	96%
08/16/93	09:30	Col. B sump 24.5 C	LJK	18.9	ND	--	--	55.85	0.00	0.00	55.85	100%
08/18/93	09:30	Col. B sump 28.1 C	LJK	18.9	1.3	--	--	55.72	3.95	0.00	51.77	93%
		Mass Balance										
11/05/93	13:40		LJK	3188.1	<1	2277.4	2211.0	1880.98	0.00	2170.79	-289.81	-15%
11/09/93	08:45		LJK	2003.0	<1	3239.4	<1	1152.23	0.00	0.00	1152.23	100%
11/11/93	09:10	Seep reading for flow was fluctuat	LJK	529.5	2.8	284.1	212.1	296.79	1.55	284.78	10.47	4%
11/12/93	09:10		LJK	481.6	<1	267.9	227.3	568.31	0.00	283.65	284.66	50%
	14:00		LJK	499.3	<1	518.4	432.7	618.63	0.00	541.52	77.11	12%

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