DOE/OR/21400--7492

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OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

CRADA Final Report
for
CRADA Number ORNL92-0093

FIELD DEMONSTRATION OF VAPOR PHASE TCE BIOREACTOR

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MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

C/ORNL--92-0093

MARTIN MARIETTA

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December 14, 1994

Mr. Peter D. Dayton
Director, Procurement and Contracts
Department of Energy, Oak Ridge Operations
Post Office Box 2001
Oak Ridge, Tennessee 37831-2001

Dear Mr. Dayton:

Final Report for CRADA No. ORNL92-0093 with Envirogen, Inc.

The subject CRADA has been completed and enclosed is the Final Report for this project.

This report does not contain proprietary information or Protected CRADA Information. Neither Energy Systems nor the participant object to public distribution of this report.

If you have any questions, please feel free to contact me.

Very truly yours,

C. A. Valentine

for Brian Bovee
Business Manager
Office of Technology Transfer

BBB:cav

Enclosure - As Stated.

cc: File - RC

DISCLAIMER

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

Submitted by:

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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 using groundwater at the Oak Ridge ~~National Laboratory~~ K-25 site 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 National Laboratory 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 and 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, 25µl of 2% 4-aminoantipyrene and 50 µl 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 µl of 8% $K_3Fe(CN)_6$ 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 µmole/(min • g protein). The rate of phenol disappearance from cell free controls was less than 0.01 µmole/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 µl 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 µl 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 µl 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 µl 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 µg/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 µl 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 µg/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 (❶ and ❷) (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.

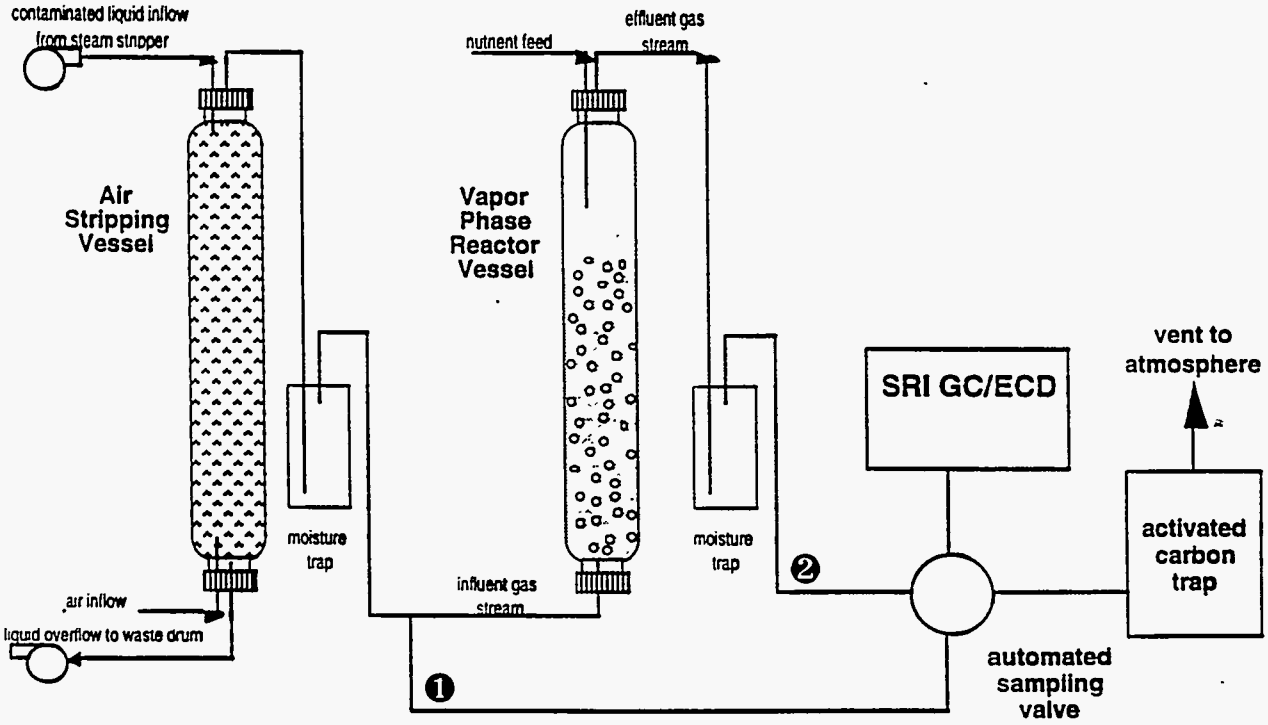

Figure 1: Process Flow Diagram for Vapor Phase TCE Bioreactor

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 μg/L air respectively. This difference represents the maximum abiotic losses of TCE since the concentration differential was the greatest. The loss of TCE from an operating reactor would be expected to be significantly less since the driving force would be much smaller.

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 ± 9 % of 124 ± 47 μg 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. There was

essentially no loss of the 1,1,1-TCA, 12 ± 13 %, monitored during this time interval. 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 and the reactor continued to operate for about 3 days 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.

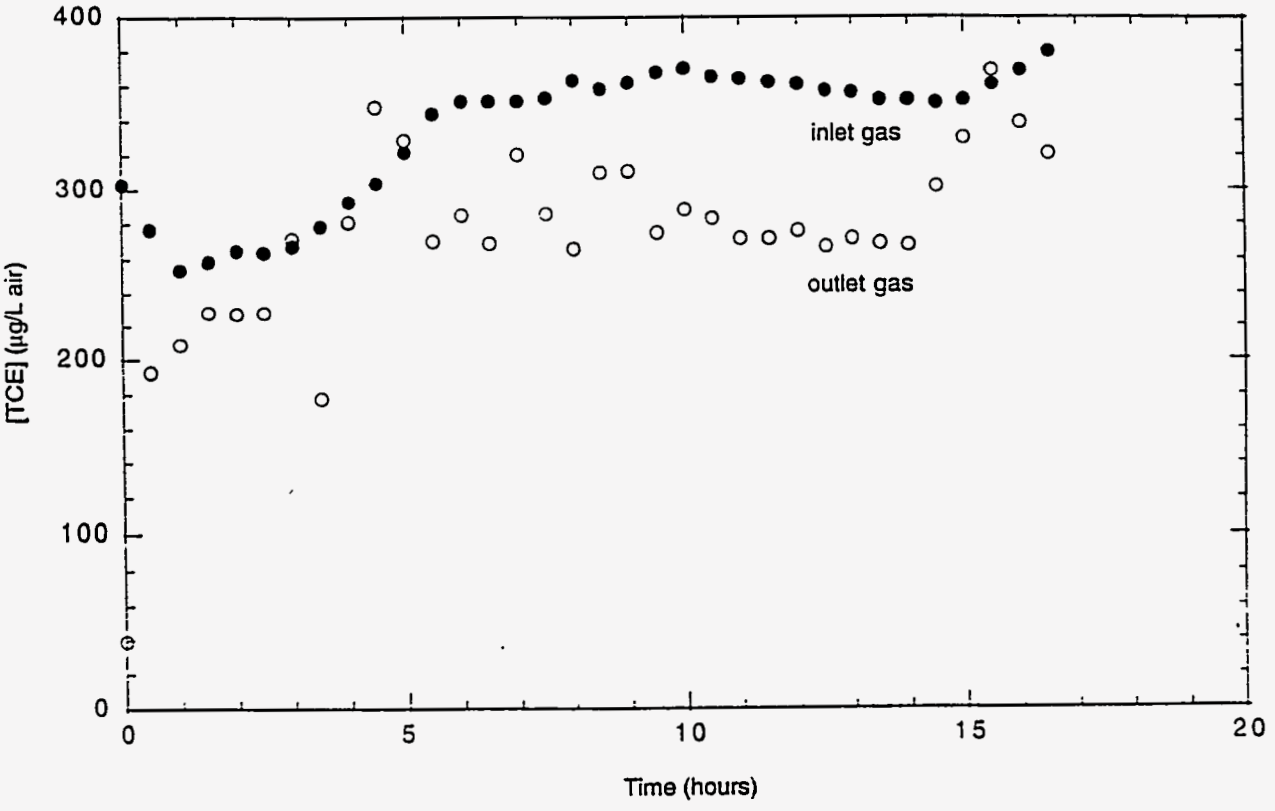

Figure 2: Control experiment for determining abiotic losses of TCE.

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

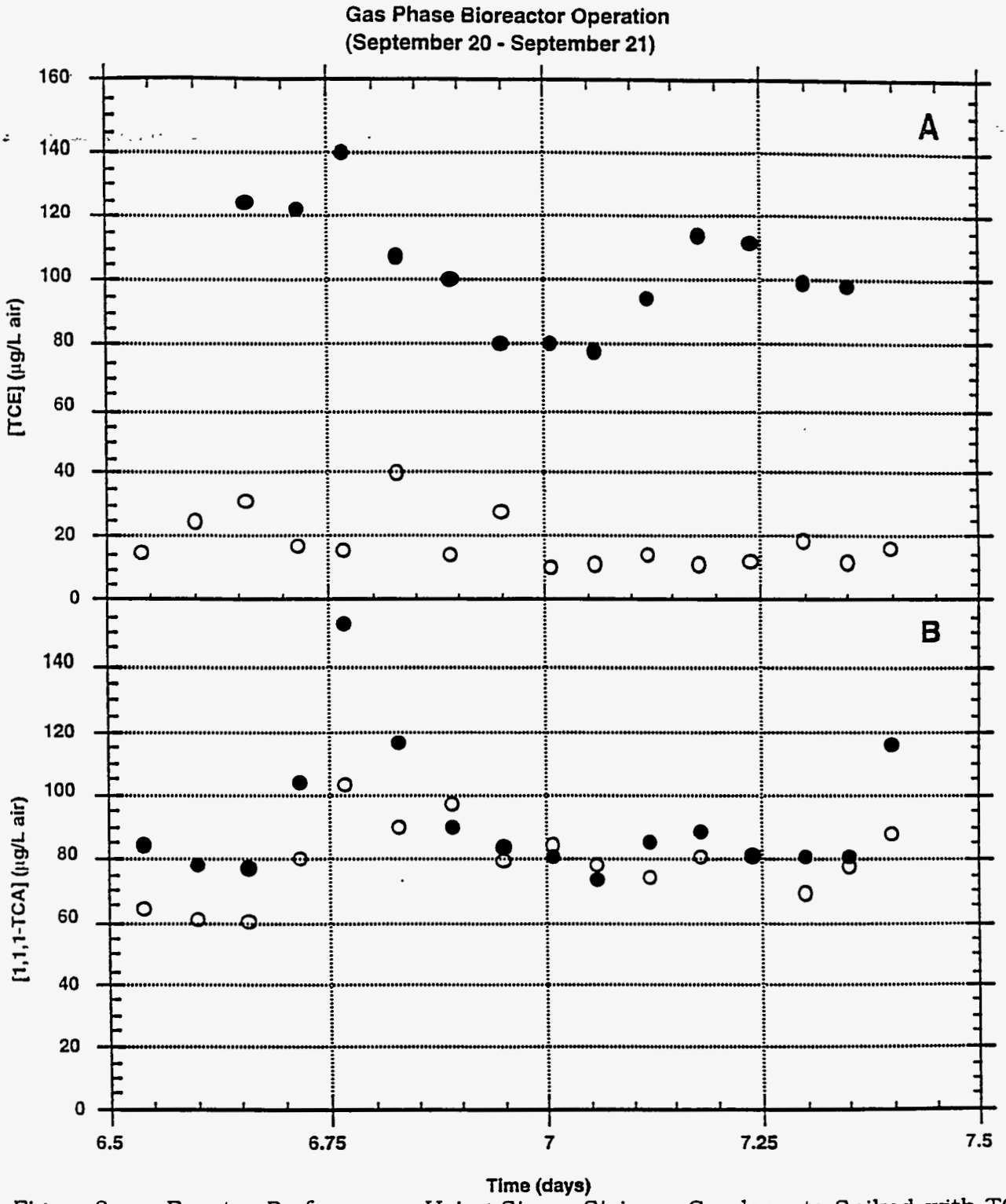

Figure 3: Reactor Performance Using Steam Stripper Condensate Spiked with TCE. A(500)= 3.8,. specific activity of phenol hydroxylase = 65 nmole/min/mg protein, 100 ml/min air flow. Plot A is for TCE and plot B is for 1.1.1-TCA.

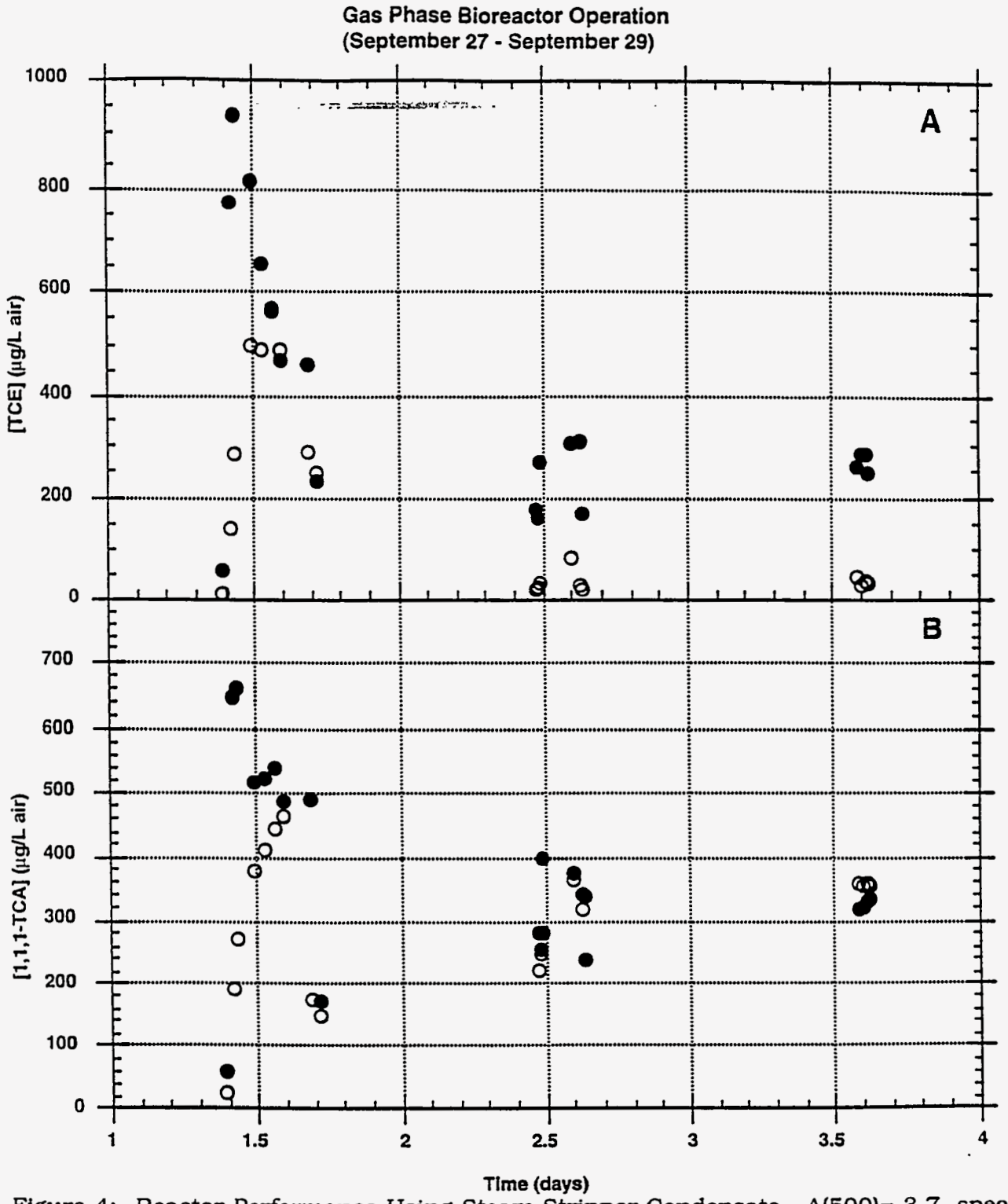

Figure 4: Reactor Performance Using Steam Stripper Condensate. A(500)= 3.7, specific activity of phenol hydroxylase = 100 nmole/min/mg protein, 100 ml/min air flow. Plot A is for TCE and plot B is for 1,1,1-TCA.

fluctuated, similar results were observed as described earlier. In general, 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. A drop in degradative activity was observed during the first 24 hours of operation indicating an adaptation or acclimation period. One possible explanation for this decrease in degradative activity could have resulted from a transient increase in phenol within the reactor. Phenol buildup would stimulate growth while competitively inhibiting TCE degradation though direct evidence of phenol accumulation was not documented.

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 and DCE) 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 listed are suspect due to interference from benzene found in the 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	Inlet day 4 (µg/L air) ORBO 5A & B	Outlet day 4 (µg/L air) ORBO 6A & B	Inlet day 5 (µg/L air) ORBO 11A & B	Outlet day 5 (µg/L air) ORBO 12A & B
DCE	< 1	< 1	44	< 1
TCE	86	5	46	7
toluene	26	< 1	476	5
ethylbenzene	16	< 1	242	8
o,p-xylene(s)	53	8	276	11
m-xylene	127	64	398	23

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.

Appendix A

ORBO Tube Raw Data and Calculations

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
	sample volume (ml):			900.00	900.00	900.00	450.00	450.00	450.00	730.00	730	730
	concentration factor:			450.00	450.00	450.00	225.00	225.00	225.00	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		43.60		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/µg)					100.00				
	Compound	RT										
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	
	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	
	µg/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
	sample volume (ml):		4800.00	4800.00	4800.00	3000.00	3000.00	3000.00	1200.00	1200	1200
	concentration factor:		2400.00	2400.00	2400.00	1500.00	1500.00	1500.00	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	
	concentration factor:		275.00	275.00	275.00	2850.00	2850.00	2850.00	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	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	

MARTIN MARIETTA

Internal Correspondence

MARTIN MARIETTA ENERGY SYSTEMS, INC.

Date: December 6, 1994

To: W. P. Painter, 6026E, MS-6396

From: Stephen Herbes, 1505, , MS-6036 SE Herbes

Subject: CRADA Number ORNL92-0093 (Envirogen, Inc.); Final Report

The following certification is made for the subject final report:

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2) that Energy Systems and the participant has no objection to public distribution of the final report, and

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