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Title: A Method for PCB Metabolite Determination in Anaerobic
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(ANBIOF).

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The biodegradation of five polychlorinated biphenyls (PCBs) by Hudson River and Silver Lake sediments was studied using gas chromatography with electron capture detection (GC/ECD) and gas chromatography with mass spectrometry (GC/MS) analyses. Methanogenic sediments from the Hudson River and Silver Lake were used to inoculate four anaerobic filter reactors. The upflow anaerobic filters were fed a synthetic wastewater containing the five PCB congeners, semi-continuously, at a 10 day hydraulic retention time. The PCBs were fed at increasing concentrations to stimulate bacterial degradation and metabolite formation. The production of an unknown metabolite was detected by observing the formation of a unique peak on the gas chromatogram. The peak clearly indicated a dependence on reactor sediment parent PCB concentrations by exhibiting a nine fold increase in peak area during a ten fold increase in parent compound feed concentrations. GC/MS analyses confirmed the unknown peak as a

tetrachlorobiphenyl (tetra-CB), and cochromatography identified the tetra-CB as 2,3,5,6-tetrachlorobiphenyl (2356-CB). Of the five congeners studied, 2,3,4,5,6-pentachlorobiphenyl (23456-CB) was clearly biodegraded. The parent compound, 23456-CB, was reductively dechlorinated at the para position to produce a 2356-CB. Reactors inoculated with Hudson River sediments exhibited dechlorination at an apparent ten fold lower sediment parent PCB concentration and at shorter lag times than observed for Silver Lake sediments. The results indicate anaerobic biodegradative competence exists for 23456-CB in Hudson River and Silver Lake sediments.

A Method for PCB Metabolite Determination in
Anaerobic Freshwater Sediments using a Upflow
Anaerobic Biofiltration Process (ANBIOF).

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TABLE OF CONTENTS

PREFACE

CHAPTER ONE: A method for PCB Metabolite Determination in Anaerobic Fresh Water Sediments using a Upflow Anaerobic Biofiltration Process (ANBIOF)	1
INTRODUCTION	1
MATERIAL AND METHODS	7
Reactor	7
Reactor Operation	9
Inocula	9
Feed Stock and PCBs	11
Sampling	12
Experimental Program	14
Analytical Techniques	15
pH, solids and chemical oxygen demand	15
Reactor Gases	16
PCB Extraction	17
PCB Quantification	18
RESULTS	20
Anaerobic Filter	20
PCBs and Unknown	24
Analysis of Metabolite	30
Identification of Parent Compound	32
DISCUSSION	34
Reactor Performance	34
Metabolite	35
Comparison to Environmental Transformation Data	37
CONCLUSIONS	40
ACKNOWLEDGEMENTS	40a
REFERENCES	41
BIBLIOGRAPHY	47
APPENDIX A: Physical/Chemical Properties of Chlorobiphenyls	57
APPENDIX B: Upflow Anaerobic Filter Degradation Results	59
APPENDIX C: Reactor Operation Results	69
APPENDIX D: Mass Spectra for Chlorobiphenyls	83
APPENDIX E: Cochromatography results	89

List of Figures

<u>Figure</u>	<u>Page</u>
1 Upflow Anaerobic Filter Detail	8
2 Structures of Parent Polychlorinated Biphenyls used in the PCB Feed Stock Solution	13
3 Reactor No.3 Chemical Oxygen Demand Conversion (%) during Phase I, II and III	23
4 Effluent Concentration of the Five Feed PCBs during Phase I, II and III	25
5 DB-5 Chromatographs of the Formation of the unknown metabolite vs. time at RT 24.15 minutes. (A) 8/24/87, 0.016 gms TVS, (B) 12/7/87, 0.015 gms TVS, (C) 2/3/88, 0.027 gms TVS, (D) 3/7/88, 0.082 gms TVS	27
6 Emergence of Metabolite at RT 24.15 Minutes. (A) Reactor No.1, C2, (B) Reactor No.2, F3, (C) Reactor No.3, H7, (D) Reactor No.4, TI	28
7 Mass Spectra of Metabolite and 2356-CB. (A) Peak at RT 24.15 Minutes (GC/ECD); Reactor No.3 Hexane Extract at 3/7/88. (B) 2,3,5,6-tetrachlorobiphenyl Reference Mass Spectra	31
8 Emergence of 23456-CB and 2356-CB in Reactor No.3	33
C-1 pH of Reactors No.1, No.2, No.3 and No.4	71
C-2 Chemical Oxygen Demand Removal Efficiency (%) for Reactors No.1, No.2, No.3 and No.4	72
C-3 Chemical Oxygen Demand of Reactor Influent and Reactors No.1, No.2, No.3 and No.4 Effluent	73
C-4 Experimental Gas Production of Reactors No.1, No.2, No.3 and No.4	74
C-5 Reactor No.1 Effluent PCB Concentration	75
C-6 Reactor No.2 Effluent PCB Concentration	76
C-7 Reactor No.3 Effluent PCB Concentration	77
C-8 Reactor No.4 Effluent PCB Concentration	78
C-9 Reactor No.1 Sediment PCB Concentration	79
C-10 Reactor No.2 Sediment PCB Concentration	80

Figure

Page

C-11 Reactor No.3 Sediment PCB Concentration 81

C-12 Reactor No.4 Sediment PCB Concentration 82

D-1 Total Ion Chromatograph of the Unknown Tetra-CB at RT
18.92 Minutes (Peak No.5) and the Internal Standard,
Tetrachloronaphthalene at RT 18.85 Minutes (Peak no.4) 87

D-2 Total Ion Chromatograph of the Sediment Extract showing
the Major Ions, and the Parent PCB Compounds at Peaks
No.16, No.17, No.18, No.19 and No.21 88

E-1 DB-5 Cochromatograph of the Unknown Peak at RT 24.15
Minutes and 2356-tetrachlorobiphenyl. (A) Unknown Peak
at RT 24.15 Minutes, (B) 2356-tetrachlorobiphenyl at RT
24.15 Minutes 91

List of Tables

<u>Page</u>	<u>Page</u>
1 Reactor Daily Feeding Schedule	10
2 Solids Characterization	21
A-1 Physical and Chemical Properties of Chlorobiphenyls	58
B-1 Reactor No.1 "Silver Lake C2" GC/ECD Results	61
B-2 Reactor No.2 "Silver Lake F3" GC/ECD Results	63
B-3 Reactor No.3 "Hudson River H7" GC/ECD Results	65
B-4 Reactor No.4 "Hudson River TI" GC/ECD Results	67
D-1 PCBs and Their Retention Times in GC/ECD Analysis	85

PREFACE

The processes affecting the fate of polychlorinated biphenyls (PCBs) in lake and river sediments are of great concern. It is important to understand the role of anaerobic bacteria in PCB degradation to assess the potential biological removal mechanisms inherent in the environment. Applications of environmentally selected PCB degrading organisms and the recent advances in fixed-film technology can provide effective wastewater treatment schemes which could affect the persistence of PCBs.

Traditional aerobic biological wastewater treatment processes alone do not remove all congeners present in complex PCB mixtures. Due to the inherent differences between aerobic and anaerobic degradation processes, anaerobic treatment may result in biodegradation of higher chlorinated PCBs refractory in aerobic conditions. However, virtually no data is available for the fate of PCBs in anaerobic wastewater treatment. With a better understanding of the factors affecting biodegradation of PCBs in anaerobic sediments, comprehensive wastewater treatment schemes could be developed.

The purpose of this research is to examine the removal mechanisms for PCBs in anaerobic sediments using an upflow anaerobic biofiltration process (ANBIOF).

Chlorinated biphenyls are a family of 209 congeners. They were originally formulated by Monsanto, by chlorinating biphenyls in an iron catalyzed process which resulted in complex mixtures of PCBs called Aroclors. Because of the large number of chlorinated congeners in Aroclor mixtures, potential biological removal processes would require

both aerobic and anaerobic biodegradation. Anaerobic degradation would be expected to remove predominantly the higher chlorinated congeners (Brown et al., 1987), leaving lower chlorinated congeners for aerobic degradation (Bedard et al., 1987).

Removal mechanisms for related chlorinated aromatic compounds such as chlorophenols and chlorobenzenes (Mikesell and Boyd, 1987; Fathepure et al., 1988) and the dechlorination patterns indicated in the environmental transformation of PCBs (Brown et al., 1987), suggest PCBs could be dechlorinated by a primary degradation process in which energy is derived from degradation. In reductive dechlorination, PCBs may act as electron acceptors and the carbon source as the electron donor. The increased concentration of both the electron donor and the electron acceptor species and the elimination of competing electron acceptors (NO_3 , NO_2 , SO_4 and FeIII) could enhance PCB dechlorination.

The objectives of this study were:

1. To develop an anaerobic filter reactor which results in PCB biodegradation.
2. To characterize PCB degradation by detection of metabolite(s).
3. To identify metabolite(s) using gas chromatography with electron capture detection (GC/ECD), gas chromatography with mass spectrometric detection (GC/MS) and cochromatography (GC/ECD).
4. To determine PCB degradation pathways.

The body of this research is contained in Chapter one. The experimental data for the reactors, the physical/chemical properties of PCBs and the mass spectra for PCBs are described in the appendices at the end of the thesis.

CHAPTER ONE

A Method For PCB Metabolite Determination in Anaerobic Fresh Water Sediments using a Upflow Anaerobic Biofiltration Process (ANBIOF).

INTRODUCTION

Chlorinated biphenyls are a family of 209 highly stable, water insoluble aromatic compounds. They were used extensively in industry between 1929 and 1978 as paint and dye additives, and in dielectric and hydraulic fluids (Hutzinger et al., 1974). Unfortunately, their attractive chemical properties have also contributed to their environmental persistence and bioaccumulation in food chains.

Treatment of polychlorinated biphenyls PCBs has traditionally focused on costly physical-chemical and incineration methods, and has not exploited their potential for biodegradation. Application of biological treatment schemes such as anaerobic and aerobic fixed film processes provide potential low cost and low maintenance alternatives. In-situ cleanup and of PCB contaminated "hot spots" could benefit the most because of the high volume of contaminated solids present. Biological treatment methods could be further enhanced by adding naturally selected and genetically engineered PCB degrading bacteria.

A broad range of aerobic bacteria are capable of biodegrading PCBs with three or fewer chlorines, but degradation becomes increasingly difficult for higher chlorinated congeners. Pure and mixed cultures isolated from activated sludge and PCB contaminated river sediments aerobically degraded 4-chlorobiphenyl and not 2-

chlorobiphenyl. The degradation products indicated a sequential reaction consisting of ring fission producing 4-chlorobenzoate followed by total mineralization to CO₂ (Kong and Sayler, 1983; Masse et al., 1984). Aerobic degradation of pure PCB isomers (with 5 or less chlorines) by Alcaligenes sp. strain Y42 and Acinetobacter sp. strain P6 suggested primary metabolism (dechlorination and ring cleavage) of mono-, di-, tri- and tetra-chlorobiphenyls (Furukawa et al., 1979, 1983; General Electric Company, 1984). The resulting metabolites consisted of mono and dichlorobenzoates, dihydroxybiphenyls, and many cleavage products with two or three chlorines. PCB congeners with single ring chlorinations were generally aerobically degraded faster, and preferential ring fission occurred on the lesser chlorinated ring. Pentachlorobiphenyls did not undergo primary degradation as observed by the production of dihydroxybiphenyls. The decreased degradative competence of pentachlorobiphenyl was a function of both increased chlorination and the complex chlorine substitution patterns on the biphenyl ring. Additionally, higher chlorinated congeners in commercial PCB mixtures exhibited decreased biodegradation while mono and dichlorobiphenyls were readily degraded by activated sludge (Tucker et al., 1975; Liu, 1980).

Although the increased chlorination of Aroclors 1248 and 1254 significantly decrease their biodegradability, several pure strain enriched bacterial cultures degraded tetra-, penta- and hexa-chlorobiphenyls. Alcaligenes eutrophus H850 isolated from PCB dredge spoils was enriched on biphenyl, and grew well on 2-chlorobiphenyl (2-CB) but not on 3-CB or 4-CB (Bedard et al., 1987; General Electric Company, 1984, 1985). The unique metabolism of 2-CB by H850 was not

observed for cultures mineralizing 4-CB. H850 degraded a wide range of tetra-, penta- and hexa-chlorobiphenyls in complex industrial PCB mixtures; Aroclor 1248 was reduced 81% and Aroclor 1254 was reduced 31% after 48 hours. In addition, most di-, tri- and tetra-chlorobiphenyls were completely eliminated (95-100% removed) by H850 in 48 hours. Similarly, pure strain bacteria Pseudomonas putida sp. LB400 degraded penta-CB and hexa-CB, and Corynebacterium sp. MBI degraded penta-CBs of Aroclors 1248 and 1254 (Bedard et al., 1986, 1987; Bopp, 1986).

In contrast to aerobic oxidative metabolism, anaerobic degradation of halogenated aromatic compounds proceeds by reductive dehalogenation. Biodegradation of chlorophenols, chlorobenzenes and chlorobenzoates by anaerobic bacteria occurs in methanogenic sediments and anaerobic sewage sludges (Horowitz et al., 1983; Suflita et al., 1984; Fathepure et al., 1988; Woods et al., 1988). Anaerobic degradation of chlorophenols proceeded with sequential replacement of chlorine atoms by hydrogen atoms in a reduction process (reductive dechlorination). The eventual dechlorination product of chlorophenol, phenol, was readily degraded to CH₄ and CO₂ by anaerobic bacteria, or CO₂ and H₂O by aerobic bacteria (Suflita and Miller, 1984). The dechlorination process exhibited by sewage sludge organisms (unacclimated), was shown to be selective for specific chlorine atom substitution patterns on the phenol molecule. The chlorine closest to the hydroxyl group (ortho) was removed first, followed by the next closest (meta) chlorine. Chlorine atoms opposite the hydroxyl group (para) were removed last (Boyd et al., 1983). Chlorine removal patterns for anaerobic sludge acclimated to monochlorophenols (ortho, meta and para substitutions) exhibited degradation patterns distinctly

different from unacclimated sludge. Cultures acclimated to 2-chlorophenol (2-CP), 3-CP and 4-CP removed chlorines with specificity ortho > para > meta. Similarly cultures acclimated to 3-CP degraded chlorophenols with meta or meta and para chlorine substituents (Boyd and Shelton, 1984). Biodegradation of chlorobenzenes was observed in sewage sludge acclimated to various industrial waste sources (Fathepure et al., 1988). Pentachlorobenzene was dechlorinated to produce a mixture of 1,3,5-trichlorobenzene (1,3,5-TCB) and dichlorobenzenes 1,2-DCB, 1,4-DCB and 1,3-DCB. The observed reductive dechlorination of chlorobenzenes extends the dechlorination reaction to water insoluble aromatic hydrocarbons (i.e. PCBs) which do not have polar functional groups like -OH and -COOH.

The similarity in structural and aromatic characteristics of chlorobenzenes and polychlorinated biphenyls suggest the dechlorinating ability inherent in chlorobenzene degrading bacteria may also exist for bacteria acclimated to PCBs. Reductive dechlorination of PCBs in anaerobic sediments was suggested from data showing alterations of original congener compositions; Aroclors 1248 and 1254 (Brown, 1987). Evidence from PCB profiles of Hudson River and Silver Lake sediments indicated preferential removal of higher chlorinated congeners (environmental transformations) (Brown et al., 1984). Environmental transformations exhibited complex ortho, meta and para chlorine removal patterns specific to sediment type and sampling location. Hudson River sediments exhibited distinct meta and para dechlorinations, and Silver Lake exhibited broader ortho, meta and para dechlorination specificity.

Environmental transformation of PCBs was determined using data collected from PCB contaminated sediment samples which were up to

30 years old. The observed removal patterns represented a history of selective congener removal, and was only suggestive of reductive dechlorination. Similar dechlorination patterns were observed in batch reactor experiments using a synthetic PCB wastewater and Hudson River sediment inocula (Tiedje et al., 1987). Experimental results showed penta- and hepta-chlorobiphenyl congeners were partially anaerobically degraded in 52 weeks. 43.8% of a synthetic 23456-CB was reductively dechlorinated to produce potential a mixture of para, 2356-CB and meta, 2346-CB dechlorination products. No ortho dechlorination was observed.

Data has shown the accumulation of specific chlorine substitution patterns in the degradation products of chlorophenols, chlorobenzenes and PCBs during anaerobic biotransformations (dechlorination). This evidence suggests the more easily removed chlorine atoms follow faster degradation kinetics, while the more persistent chlorine atoms are removed at slower kinetics. Anaerobic degradation of substituted chlorophenols showed the relative rates of dechlorination to follow a general order: ortho > meta > para (Boyd and Shelton, 1983). Additionally, dechlorination rates were the highest for pentachlorophenol, and the rates decreased as the number of chlorines decreased on the phenol molecule (Mikesell and Boyd, 1986; Woods et al., 1988). Archival sediment data (General Electric Company, 1984) for PCBs deposited during 1954 to 1974 indicated a 30% reduction of Aroclors 1242 and 1248 in 10 to 30 years. This rate of disappearance indicates in a biodegradative half life between 20 to 60 years. Similarly, 43.8% removal of 23456-CB in 43 months represented a 73 month (1.38 years) degradation half life (Tiedje et al., 1987).

Anaerobic degradation of PCBs is suggested from environmental

transformation data, but their long degradation half lives limit the practical application of biological wastewater treatment in degrading PCBs. Enhancing anaerobic biodegradation of PCBs would require the broad dechlorinating specificity of anaerobic sediments and the increased reaction kinetics associated with anaerobic fixed-film (biofilm) treatment processes. Fixed-film processes have traditionally shown increased reaction kinetics due to high concentrations of bacterial cells (biofilm) attached to the reactor media, and a high bacterial solids retention time. By virtue of the attached bacteria, the biofilm process exhibits a high tolerance to substrate toxicity and can degrade organic wastes at high COD loadings. (McCarty, 1964). Anaerobic treatment of chlorophenolic compounds was reported for anaerobic sludge blanket reactors (Hakulinen et al., 1985; Woods et al., 1988) and in an anaerobic fluidized bed reactor (Hakulinen and Salkinoja-Salonen, 1982). Results indicated biodegradation of chlorophenols, chloroveratroles and chloromethoxybenzenes in the sludge blanket reactor. Similarly, chlorophenols from pulp bleaching effluent were partially degraded in the anaerobic fluidized bed reactor.

The purpose of this study was to determine the biodegradative fate of a five synthetic PCB congeners fed to four anaerobic filter reactors inoculated with upper Hudson River and Silver Lake sediments. Particular emphasis was placed on acclimating and selecting for PCB degrading bacteria, and characterizing PCB degradation products.

MATERIAL AND METHODS

Four anaerobic filters were operated to treat a synthetic wastewater containing five chlorinated biphenyls. The major distinguishing feature between the reactors was the source of bacterial inocula used in each reactor.

Reactor

Reactors used in this experiment were modified upflow anaerobic filters. An anaerobic filter is an oxygen free, media filled reactor with wastewater delivered to either the top (stationary reactor type) or the bottom (upflow reactor type). Four upflow anaerobic filters (Figure 1) with recycle were constructed of Michel-Miller threaded chromatography glassware (Ace Glass Inc, Vineland, NJ). The reactor consisted of a 300 ml glass column and a 50 ml settling compartment coupled together and sealed at both ends with Teflon fittings. The reactor was packed with 6 x 6 mm Rasching rings (Ace Glass, Inc) which yielded a 3000 cm² surface area and a 250 ml void volume. The filter had three sampling points: reactor off gases were collected from a septum on the gas outflow line; effluent samples were collected off the recycle line at top of the reactor; and reactor sediments were collected from the port at the bottom of the reactor. Recycle was provided by a peristaltic pump (Cole Parmer, Chicago, IL) which delivered a flow rate between 450 and 500 mls/day. Teflon and brass shut-off valves were used to control influent, effluent and recycle streams. All fluid lines were 3.18 mm (1/8 in) OD FEP Teflon tubing.

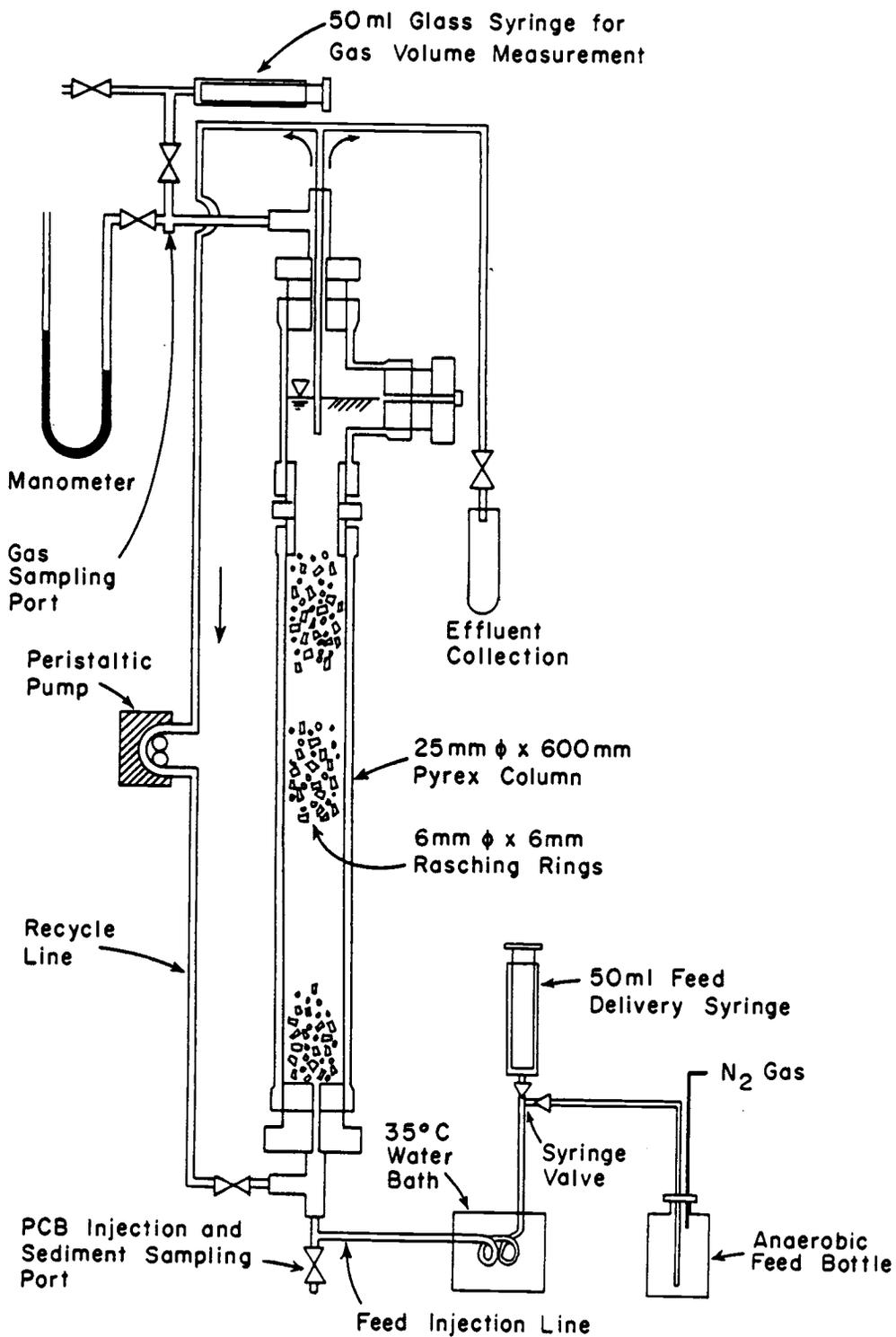


Figure 1. Upflow Anaerobic Filter Detail.

Reactor Operation

The anaerobic filter reactors were operated at 30 ± 0.5 °C throughout the experimental period. Each reactor was fed semicontinuously at a 10 day hydraulic retention time with daily batch injections of PCBs and a vitamin/mineral feed stock solution. Twenty five mls of the feed solution were fed simultaneously with PCBs (see feeding schedule for PCBs, Table 1) at the bottom port. The feed source was injected using a two step process in which the feed stock was first drawn into the 50 ml syringe from the anaerobic feed bottle through a two stage syringe valve, and then expelled into the feed injection line (Figure 1). The feed source was warmed to 35 °C by a recirculating water bath prior to injection into the reactor. Gas volumes were determined using manometers filled with a 5% (v/v) H_2SO_4 /saturated NaCl solution connected to the reactor effluent gas line. Volumes were measured by withdrawing an appropriate volume of reactor gas with a 50 ml syringe until the pressure exerted by the reactor head space on the manometer fluid was balanced with the atmosphere. Volumes were corrected to standard pressure (1 atm) and reactor operating temperature (30 ± 0.5 °C).

Inocula

Four PCB contaminated anaerobic sediments were used as reactor inocula. Samples C2 and F3 were collected from Silver Lake, a 10 ha urban pond located in Pittsfield, Massachusetts. Silver Lake received industrial discharges of Aroclor 1260 from 1950-1971, and Aroclor 1254

Table 1. Reactor Daily Feeding Schedule

Period	Beginning date	Feed component COD ^a				Total COD (mg/l)	PCB congener concentration ^{b,c}				
		Acetate	Methanol (mg/l)	Glucose	Acetone		Tetra	Penta	Hexa	Hepta	Octa
Stabilization	7/22/87	213	214	107	175	709	0	0	0	0	0
Phase I	8/24/87	281	297	150	175	903	0.18	0.15	0.15	0.14	0.12
Phase II	9/22/87	281	297	150	349	1078	0.36	0.31	0.29	0.27	0.24
Phase III	2/10/88	281	297	150	3490	4218	3.58	3.09	2.92	2.73	2.40

^a Theoretical chemical oxygen demand.

^b tetra: 23'44'-CB
 penta: 23456-CB
 hexa: 22'44'66'-CB
 hepta: 22'344'5'6-CB
 octa: 22'33'44'55'-CB

^c Based on PCB influent concentrations after PCBs are injected with 25 mls of feed stock addition.

during the period between 1971 and 1977. Samples C2 and F3 were bottom sediments which consisted of soft, black, oily, methanogenic muck. C2 was taken from sediments with PCB levels from 1 to 1300 ppm; F3 was taken from sediments containing 220 to 860 ppm PCBs. Sediment samples H7 and TI were collected from the Upper Hudson River between river miles 188.6 and 193.3 (between Thompson Island Dam and Ft. Edward Village). Upper Hudson River waters received industrial discharges of Aroclors 1248 and 1254 during the period between 1946 and 1977 (Brown, 1987). In contrast to C2 and F3, bottom sediments H7 and TI were sandy, silty and low in organic matter. H7 was collected one mile below Ft. Edward Village in sediments containing 50 to 380 ppm PCBs. TI was sampled above the Thompson Island Dam where PCB levels in the sediments ranged from 50 to 2500 ppm. All sediment samples were collected between February 3rd and 10th, 1987, and refrigerated at 0 °C at the General Electric Corporate Research and Development Laboratory, Schenectady NY (through June 11, 1987)(Brown, 1987). The inocula were stored at room temperature from June 12 to July 23, 1987, after which they were injected into the four anaerobic filter reactors.

Feed Stock and PCBs

A feed solution containing vitamins, minerals and carbon sources was used to support anaerobic growth. The feed solution was made up with deoxygenated distilled water. The water was deoxygenated by bubbling N₂ gas for 10 minutes with vigorous mixing. The inorganic nutrient stock solution was a modification of the media described by Owen et al., (1979) and contained: 0.175 g/l CaCl₂, 1.62 g/l

MgCl₂.6H₂O, 1.17 g/l KCl, 0.018 g/l MnCl₂.4H₂O, 0.0388 g/l CoCl₂.6H₂O, 5.2 mg/l H₃BO₃, 2.5 mg/l CuCl₂.2H₂O, 1.9 mg/l ZnCl₂, 2.3 mg/l Na₂MoO₄.2H₂O, 0.36 g/l NH₄Cl, 0.014 mg/l Biotin, 0.014 mg/l Folic Acid, 0.072 mg/l Pyridoxine HCl, 0.036 mg/l Riboflavin, 0.036 mg/l Thiamine, 0.036 mg/l Nicotinic Acid, 0.036 mg/l Pantothenic Acid, 0.072 ug/l Vitamin B12, 0.036 mg/l PABA, 0.036 mg/l Thiolic Acid and addition of the following minerals: 0.0257 g/l NiCl₂.6H₂O, 0.018 g/l FeCl₂.4H₂O and 0.22 g/l Na₂S. Buffering was accomplished using a carbonate and phosphate buffer containing: 0.25 g/l NaH₂PO₄.H₂O, 0.25 g/l Na₂HPO₄, and 2.77 g/l NaHCO₃. Glucose, acetic acid, methanol and acetone were added to yield a final chemical oxygen demand (COD) ranging from 709 mg/l during the reactor stabilization period to 4218 mg/l during Phase III. Concentrations of carbon sources during each phase are illustrated in Table 1.

The PCB stock solution contained five congeners (Figure 2); 2,3',4,4'-tetrachlorobiphenyl (23'44'-CB), 2,3,4,5,6-pentachlorobiphenyl (23456-CB), 2,2',4,4',6,6'-hexachlorobiphenyl (22'44'66'-CB), 2,2',3,4,4',5',6-heptachlorobiphenyl (22'344'5'6-CB) and 2,2',3,3',4,4',5,5'- octachlorobiphenyl (22'33'44'55'-CB) (Ultra Scientific Inc., Hope, RI). The PCB stock solution was made up in HPLC grade acetone. Final concentrations of the reactor feed solution are shown in Table 1.

Sampling

Effluent and sediment samples were taken from a sampling port on the recycle line and from a port at the bottom of the reactor, respectively (Figure 1). Daily effluent samples were collected with

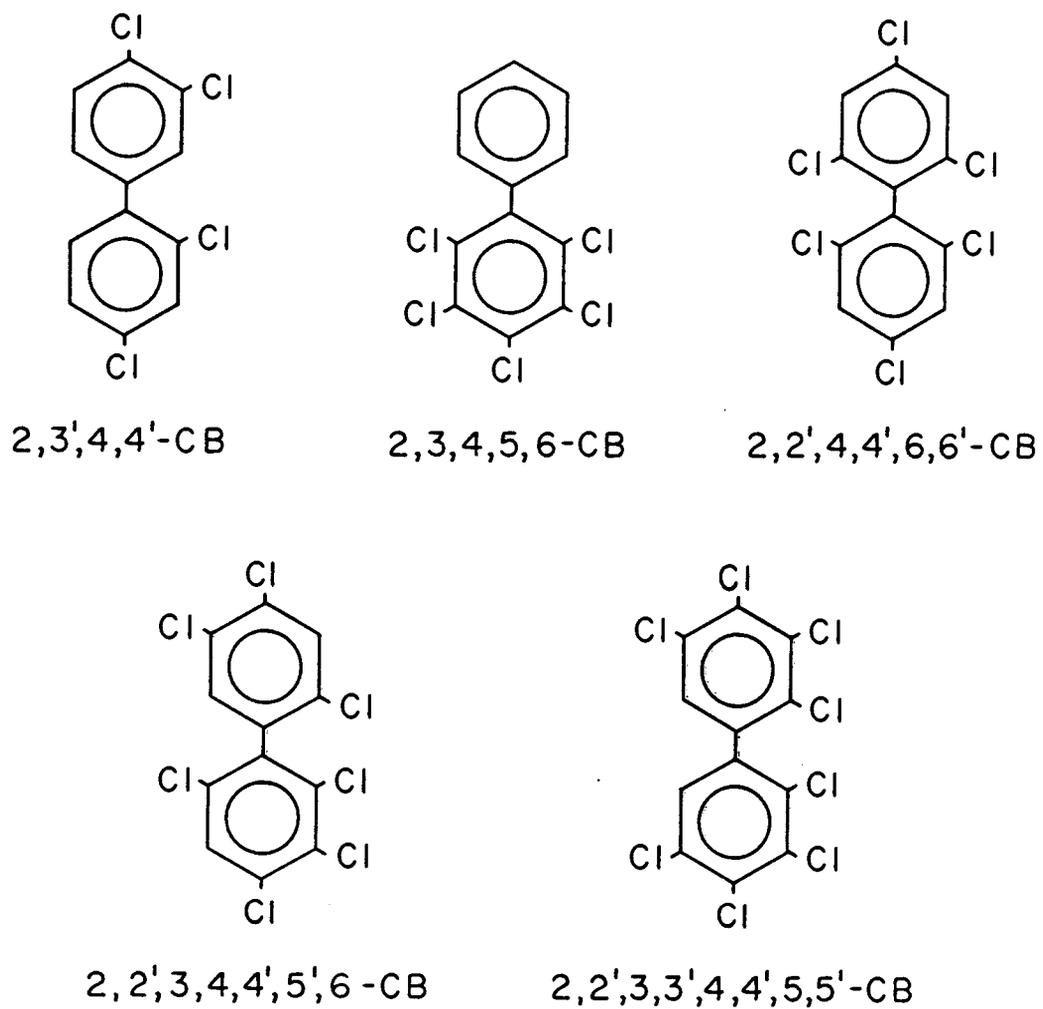


Figure 2. Structures of Parent Polychlorinated Biphenyls used in the PCB Feed Stock Solution.

simultaneous feed stock addition. pH was measured in each effluent sample immediately following sampling. A 25 ml effluent sample was placed in a 40 ml Teflon centrifuge tube and centrifuged at 20,000 rpm for 5 minutes. 20 mls of the supernatant was pipetted into a 22 ml glass vial with a Teflon lined cap, and extracted immediately.

Sediments were sampled prior to feed stock addition by collecting 5 mls of sediment sludge with a 10 ml syringe. The sediment sludge was placed in a preweighed 5 ml amber vial with a Teflon lined cap, and centrifuged at 7500 rpm for 10 minutes to separate the solids and supernatant. The supernatant was discarded and the sediment sludge was analyzed for solids composition, and extracted for PCB analysis.

Effluent COD samples were collected from the port on the recycle line. Samples were similarly centrifuged. A 10 ml aliquot of the supernatant was placed in a 20 ml glass vial with 10 mls distilled water. Influent COD samples were prepared identically using the stock feed solution and an appropriate volume of reagent grade acetone to simulate PCB addition.

Reactor off gases were sampled using a 250 μ l gas tight syringe. Gas samples were measured immediately by injecting a 100 μ l aliquot into the gas partitioner.

Experimental Program

The anaerobic filters were operated for 229 days in four experimental phases. The four phases included a stabilization phase in which no PCBs were added, and three experimental phases with a defined PCB feeding schedule (Table 1). During the four week stabilization

phase, the reactors were operated in batch mode to acclimate inocula to feed solution. After one week of batch operation, the reactors were switched to semicontinuous flow. The reactors were operated in semicontinuous plug flow for the remaining three weeks of the stabilization phase.

Phases I, II and III were characterized by increasing PCB concentrations. Throughout Phases I, II and III the reactors were fed semicontinuously by daily feed additions. Phase I was initiated with a 50 ug/l PCB feed concentration. Transition into Phase II was characterized by increasing the PCB feed concentration to 100 ug/l-day, and initiating semicontinuous flow with recycle. Phase III was the final phase of the experiment and was characterized by a 1000 ug/l-day PCB feed concentration. Reactors continued to operate in semicontinuous flow with recycle. Reactor effluent was sampled weekly during the beginning of Phase II and decreased to bimonthly for the remainder of Phase II and III. Sediments were extracted bimonthly in Phase I and II, and increased to once a week in Phase III. Daily pH and gas measurements and biweekly COD analyses were performed to monitor reactor operation during all three phases of PCB loading.

Analytical Techniques

pH, solids and chemical oxygen demand

The reactor pH was measured by taking pH readings of the reactor effluent immediately following effluent sampling. Special attention was made during pH measurement to gently mix the effluent with the pH probe to minimize CO₂ gas evolution. Reactor effluent and sediment

samples were analyzed for solids composition. COD measurements were performed on effluent samples only. Total solids (TS) and total volatile solids (TVS) were determined according to Standard Methods 209f (APHA, 1985). A 0.1 gm aliquot of sediment sludge was removed prior to solvent extraction, and the moisture content was determined by calculating the change in mass after the sample was dried in a 104 °C oven for one hour. Chemical oxygen demand (COD) was determined by the closed reflux colorimetric method (Standard Method 508C; APHA, 1985). COD samples were preserved by adding three drops of concentrated sulfuric acid to the sample and refrigerating them at 0 °C. (Metcalf and Eddy).

Reactor Gases

Major components in the reactor off gas were determined using a Fisher gas partitioner (Fisher Scientific, Pittsburgh, PA). Gas component mol fractions were determined by making standard curves for pure N₂, O₂, CO₂ and CH₄. Two packed columns were used to separate the individual gas components: column 1 (76.2 cm long x 6.35 mm Dia.) was packed with 30% HMPA on Columnpak 60 - 80 mesh, and column 2 (198 cm long x 4.76 mm Dia.) was packed with Molecular sieve 13X, 48 - 60 mesh. The carrier gas was helium, with a 10 psig column head pressure and a 35 ml/min flow rate.

PCB Extraction

PCBs were extracted from effluent supernatant and sediment sludge with hexane and acetone, and were measured by gas chromatography with electron capture detection (GC/ECD). Confirmation of unknown peak(s) were made using gas chromatography with mass spectrometric detection (GC/MS).

PCBs were extracted from liquid samples using glass distilled hexane. Ten μ ls of an internal standard, tetrachloronaphthalene (2.36 mg/l in HPLC grade acetone)(Ultra Scientific, Hope RI) was added to each sample before extraction. Two mls of hexane were added to 20 mls of supernatant (in 22 ml glass vial) and extracted for 10 minutes on a wrist shaker. The resulting hexane/aqueous emulsion was separated by centrifugation at 7500 rpm for 5 minutes. The hexane layer was removed and placed in two 1.8 ml amber autosampler vials, and refrigerated at 0 °C.

Sediments were extracted and purified using a modification of a technique developed by Georlitz and Law (1974). PCBs were extracted by a sequential addition of acetone and hexane. Purification was accomplished by adding copper pellets along with the solvent during mixing and extraction to precipitate sulfur components. The hexane/acetone solvent layer was mixed with concentrated sulfuric acid to remove oxidizable organic matter (Bellar and Lichtenberg, 1981). To a 5 ml glass vial containing the sediment sample, 5 gms of copper pellets, 10 μ ls of the tetrachloronaphthalene internal standard solution and 1 ml of HPLC grade acetone were added. The sediment was mixed for 20 minutes on a wrist shaker. Two mls of hexane were added and the

sample was extracted for 10 minutes. The hexane/acetone sample mixture was centrifuged at 7500 rpm for 10 minutes, and the solvent layer was pipetted in a 22 ml glass vial containing 10 mls of concentrated H₂SO₄ precooled to 0 °C. The solvent/acid mixture was mixed for one minute at 5 °C and centrifuged at 7500 rpm for 10 minutes. The bottom acidic layer was removed and 20 mls of distilled H₂O was added to the remaining solvent layer. The solvent/aqueous mixture was mixed for 2 minutes, centrifuged to separate the layers and the hexane layer was pipetted into two 1.8 ml amber autosampler vials. The hexane extract was stored at 0 °C until it was analyzed.

PCB Quantification

The five PCB congeners used as parent compounds were measured by preparing standard solutions which contained known masses of each congener and a fixed mass of internal standard (PCB standard curves). Standard solutions for each congener were analyzed by GC/ECD, and their corresponding retention times (RTs) and peak areas were used to identify and quantify the parent compounds in reactor samples. Standard solutions were made up for effluent and sediment samples separately. Effluent standards were made with 20 mls of distilled water, and sediment standards were made with 1 ml acetone and 2 mls hexane. The standard solutions were treated identically to effluent and sediment extraction procedures. The extract was analyzed by GC/ECD and the resulting peak areas for each congener were plotted against the ratio of congener to internal standard areas (The internal standard method; Shatkay, 1978). The resulting standard curves for each

congener were statistically analyzed, and the slopes and intercepts were used to calculate the concentration of each congener in the reactor sample.

PCB extracts were analyzed using splitless injection of a 1 μ l sample on a Hewlett Packard 5890 gas chromatograph fitted with an autosampler and an electron capture detector. A fused silica capillary column with DB-5 liquid phase and a 0.25 μ m film thickness (J and W Scientific Inc., 30 m x 0.329 mm id, ID# 142216) was used for separation. The conditions employed for the gas chromatographic analysis were: injector and detector temperature, 300 $^{\circ}$ C; initial temperature, 45 $^{\circ}$ C; initial time, 2 minutes; initial temperature ramp, 20 $^{\circ}$ C/min; final temperature 150 $^{\circ}$ C; temperature ramp A, 10 $^{\circ}$ C/min; ramp A final temperature, 200 $^{\circ}$ C; ramp A final time, 20 minutes; temperature ramp B, 4 $^{\circ}$ C/min; ramp B final temperature, 245 $^{\circ}$ C; ramp B final time, 18.5 minutes; column head pressure, 5 psig; flow rate, 23 ml/min; carrier gas, helium; makeup gas, 95% argon and 5% methane.

PCB parent compounds and potential metabolites were identified by splitless injection using a Hewlett Packard 5890 Gas chromatograph with a Hewlett Packard 5988 Mass spectrophotometer. The column used was identical to that used in our GC/ECD analysis. The conditions employed for the GC/MS analysis were: injector temperature, 300 $^{\circ}$ C, interface temperature, 280 $^{\circ}$ C; initial temperature, 45 $^{\circ}$ C; initial time, 2 minutes; initial ramp, 20 $^{\circ}$ C/min; final temperature 150 $^{\circ}$ C; temperature ramp A, 10 $^{\circ}$ C/min; ramp A final temperature, 170 $^{\circ}$ C; ramp A final time, 8 minutes; temperature ramp B, 10 $^{\circ}$ C/min; ramp B final temperature, 245 $^{\circ}$ C; ramp B final time, 7 minutes.

RESULTS

Anaerobic Filters

Four upflow anaerobic filters were operated in a semicontinuous flow mode with a 10 day hydraulic retention time. Five synthetic chlorobiphenyls together with nutrients, vitamins and carbon sources (glucose, acetate, methanol and acetone) were fed daily into the reactors. The reactors differed in their mass and source of inocula, the percent of total volatile solids (%TVS) and the solids retention time (SRT). The results indicated the mass of TVS in the initial reactor inocula (time 0) varied between 17 to 74 gms (Table 2). The mass of effluent solids washed out per day (effluent solids flow rate) was determined in Phases II and III, and ranged between 0.39 to 0.67 gm TVS/l-day. From the effluent mass flow rate and the initial mass of TVS in each reactor, the SRT was calculated. The SRT varied from 30 days in Reactor No.4 to 193 days in No.2. At the end of Phase III, the mass of TVS in each reactor was estimated from the change in the %TVS (the difference in reactor %TVS from time 193 days and time 0). The results indicated the change in %TVS ranged from a 68% decrease in Reactor No.2 to a 378% increase in No. 4. A corresponding SRT was calculated from the estimated TVS mass in each reactor and the effluent solids flow rate in Phase III, and indicated the SRTs were converging to an approximate value of 100 days (Table 2).

Reactor performance was monitored daily by measuring reactor pH and gas production. COD analyses were completed biweekly during Phases I, II and III. Reactor pH fluctuated between 6.4 and 7.4 during Phase I and stabilized at 7.0 ± 0.1 throughout Phase II. At the end of

Table 2. Solids Characterization

Period	Reactor Solids				Effluent Solids ^d				TVS ^f				Solids Ret. Time			
	R1	R2	R3	R4	R1	R2	R3	R4	R1	R2	R3	R4	R1	R2	R3	R4
	(g TVS/l)				(g TVS/l-day)				(%)				(DAYS)			
Stabilization	23 ^a	74 ^a	31 ^a	17 ^a	ND	ND	ND	ND	16	28	5	4	59 ^b	193 ^b	69 ^b	30 ^b
Phase I	-	-	-	-	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-
Phase II	-	-	-	-	0.40	0.39	0.6	0.67	40 ^d	60 ^d	40 ^d	25 ^d	-	-	-	-
Phase III	35 ^c	50 ^c	43 ^c	60 ^c	0.38	0.37	0.43	0.47	24 ^d	19 ^d	7 ^d	15 ^d	88 ^e	132 ^e	97 ^e	104 ^e

- a Estimated from initial reactor sediment inocula solids analyses taken before reactor startup
- b Calculated from effluent solids determined in Phase III
- c Estimated from reactor %TVS increase
- d Averaged value
- e Calculated from estimated solids concentration
- f $(TVS/TS) \times 100\%$
- ND Not determined

Phase II, when the COD of the feed was increased four fold, the pH began to fall and stabilized at 6.7 ± 0.1 in Phase III (Figure C-1).

COD removal efficiency varied little between inocula sources in Reactors No.1 through No.4 during Phases I, II and III. COD removal efficiency for Reactor No.3 which was inoculated with H7 sediment (Hudson River) is shown in Figure 3. The COD removal efficiency varied between 45 and 70% during Phase I, and increased to 90% by the end of Phase I. Phase II was dominated by 90% COD removal, increasing to 95% by the end of the phase. The mean soluble COD concentration in the effluent was 110 mg/l (S.D. = 25mg/l) which corresponded to $97 \pm 0.4\%$ removal. During Phase III, the removal efficiency was consistently above 97%. The other three reactors exhibited similar COD removal efficiencies during Phases I and II, and removal was above 97% in Phase III (Figure C-2).

There was little variation in gas production between the four reactors. Gas production during Phase I for all reactors varied between a high of 6 mls/day to a low of 2 mls/day. At the end of Phase I, gas production stabilized at 8 mls/day. Phase II was characterized by wide fluctuations in gas production with the mean gas production rate at 8 ± 2 mls/day. The gas production rate increased rapidly to 32 to 36 mls/day at the beginning of Phase III, in response to a four fold increase in the influent COD loading. By the middle of Phase III, gas production decreased to 28 ± 2 mls/day (Figure C-4).

Analysis of reactor off gases in all reactors indicated the methane fraction was $33 \pm 2\%$ of the gases, N_2 , O_2 , CO_2 and CH_4 . The remaining gas fraction was $53 \pm 2\%$ N_2 , $8 \pm 1\%$ CO_2 and $2 \pm 1\%$ O_2 .

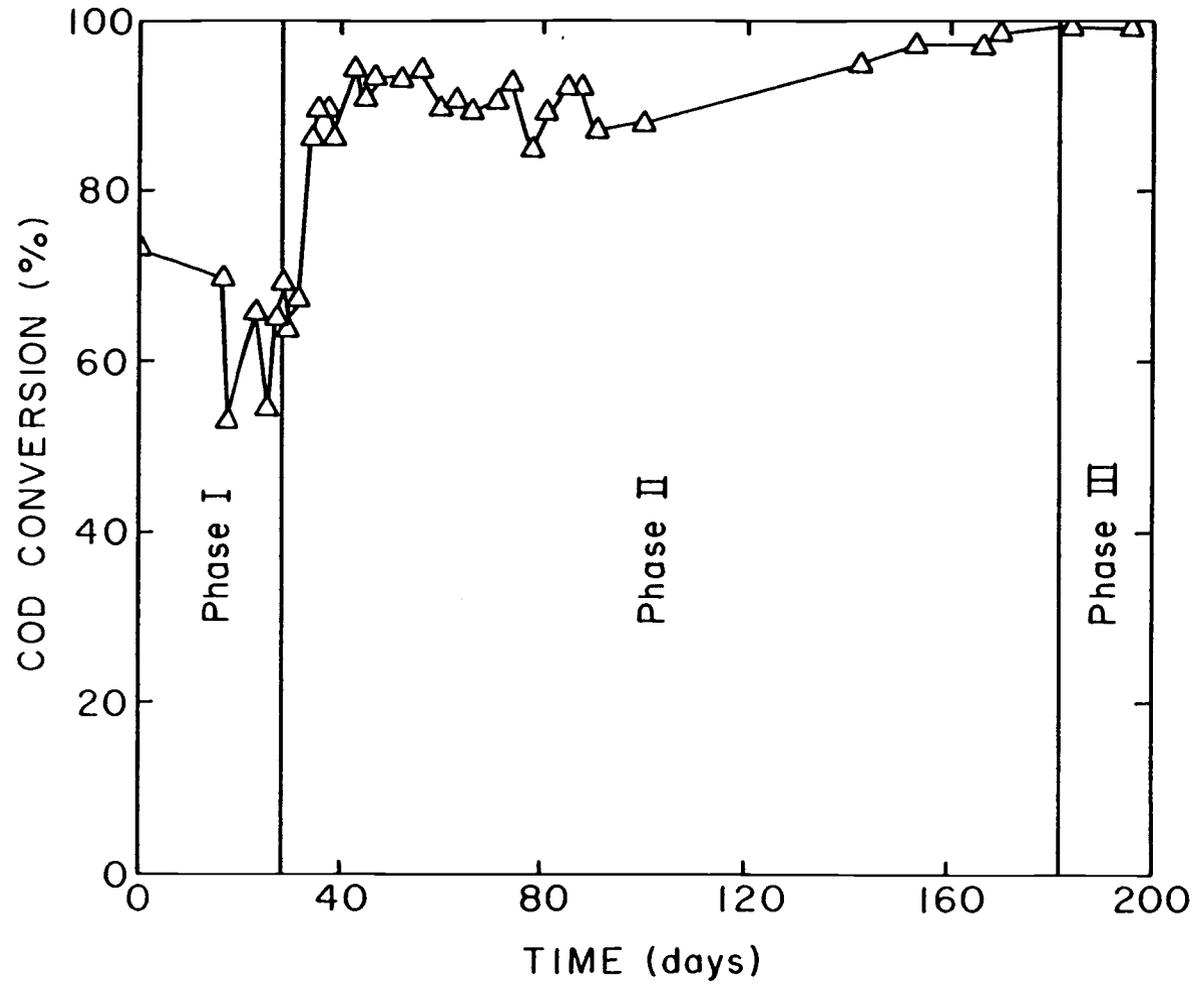


Figure 3. Reactor No. 3 Chemical Oxygen Demand Conversion (%) during Phase I, II and III.

PCBs and Unknown

The experimental program was designed to accumulate PCBs in the sediment solids of each reactor with the intent of stimulating bacterial uptake of the parent compounds and increasing metabolite formation. The five PCB congeners (Figure 2) were chosen because their potential dechlorination products clearly separated during GC/ECD analysis (General Electric Company, 1985). Characterization of each of the five parent compounds in reactor effluents were measured with time (Figure C9, C10, C11 and C12). All reactors had an initial period of complete PCB removal (influent PCB concentrations were below levels of detection) followed by breakthrough of the PCBs through the filter. The effluent concentrations of the parent compounds for Reactor No.3 are shown in Figure 4. However, each reactor behaved similarly. Breakthrough occurred at 60 ± 10 days in all reactors for all congeners except octa-CB. Octa-CB first appeared in all reactors between 90 and 110 days. The PCBs reached effluent concentrations between 3.0 to 4.0 nmol/l for tetra-CB, 1.0 to 1.5 nmol/l for penta-CB, 2.0 to 2.5 nmol/l for hexa-CB, 2.0 to 3.0 nmol/l for hepta-CB and 1.0 to 2.0 nmol/l for octa-CB by the end of Phase III. These concentrations were approximately 0.02 to 0.03% of the influent PCB concentrations during Phase III (Table 1), and corresponded to greater than 99.9% removal efficiencies.

Characterization of PCBs in sediment inocula indicated the congeners used in the PCB feed were not detected in C2, H7 and TI reactor inocula. However, in Reactor No.2 (inocula F3), the higher chlorinated, hexa- hepta- and octa-CBs were initially present.

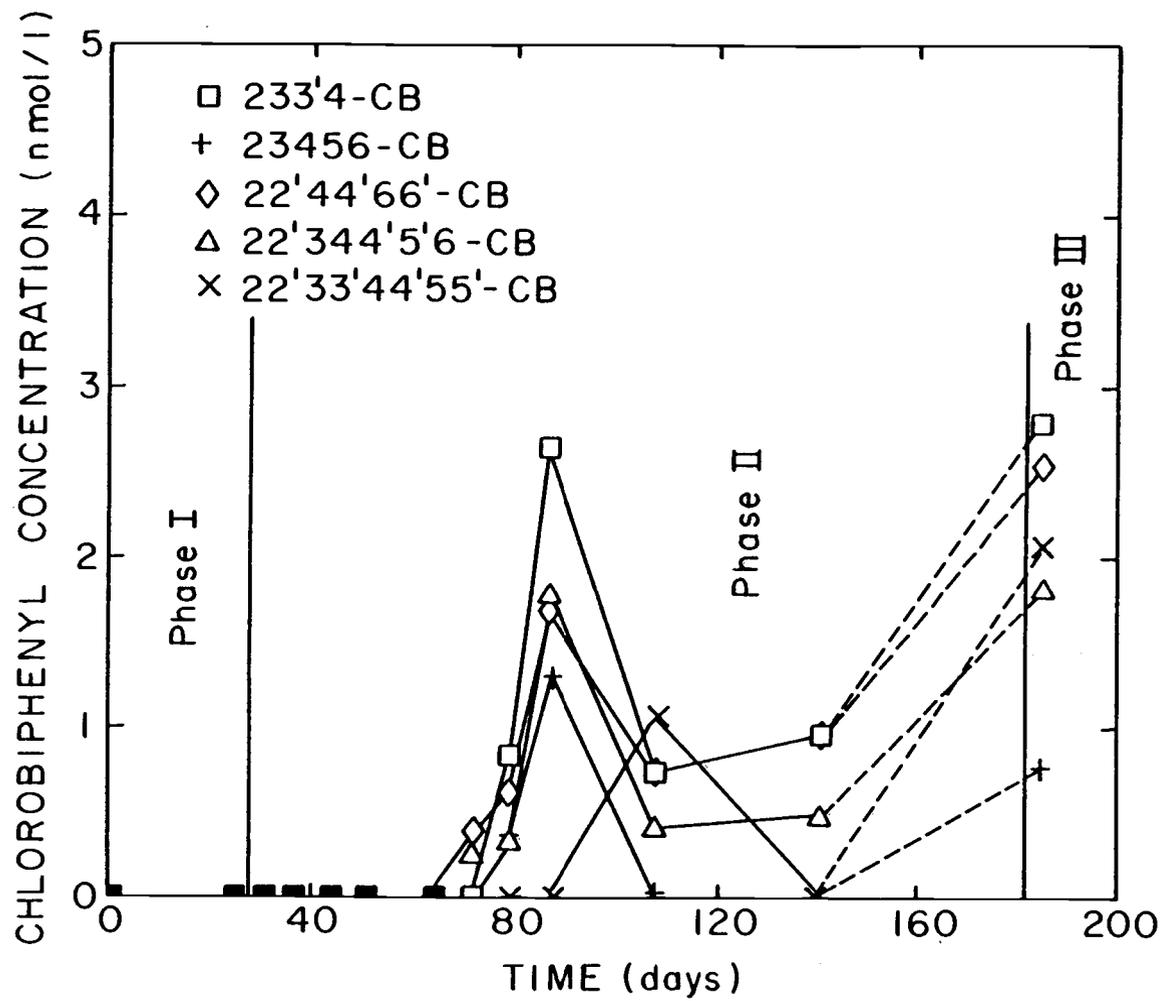


Figure 4. Effluent Concentration of the Five Feed PCBs during Phase I, II and III.

Measurement of PCB parent compound concentrations in reactor sediments indicate a moderate increase in concentrations during Phase I and II, and a rapid increase during Phase III (Figure C-10, C-11, C-12, and C-13). PCB concentrations ranged between 0.4 and 1.2 $\mu\text{mol/g TVS}$ for the individual parent compounds accumulated in all reactors by the end of Phase III. Sediment PCB concentrations during Phase I and II, varied between 0.1 to 0.3 $\mu\text{mol/g TVS}$. Sediment parent compound concentrations increased between 300 and 400% during Phase III. Reactor No.1 indicated the highest PCB concentrations at 1.2 $\mu\text{mol/g TVS}$, and Reactor No.4 the lowest concentration at 0.6 $\mu\text{mol/g TVS}$.

Characterization of reactor solid extracts revealed the formation of a potential PCB degradation product in Reactors No.1, No.3 and No.4. The unknown compound was detected by observing the formation of a new peak at a retention time (RT) of 24.15 minutes in sediment hexane extracts analyzed by GC/ECD. The unknown peak was first detected in Reactor No.3 at 93 days, at the base of the tetrachloronaphthalene internal standard peak (Figure 5-B). The peak continued to increase (Figure 5-C) until it dominated the internal standard peak (Figure 5-D). Figure 5-A represents the absence of the peak at 24.15 minutes in the initial sediment inocula (time zero).

Analyses of Data from Reactors No.1, No.3 and No.4 was performed by normalizing the unknown raw peak areas to the area of internal standard and the mass of TVS extracted. Once the peak was identified, concentrations in the sediments were determined. The increase in concentration of the unknown with respect to time for the four reactors is shown in Figure 6. The unknown in Reactors No.3 and No.4 followed similar accumulation patterns during Phase II, except the unknown

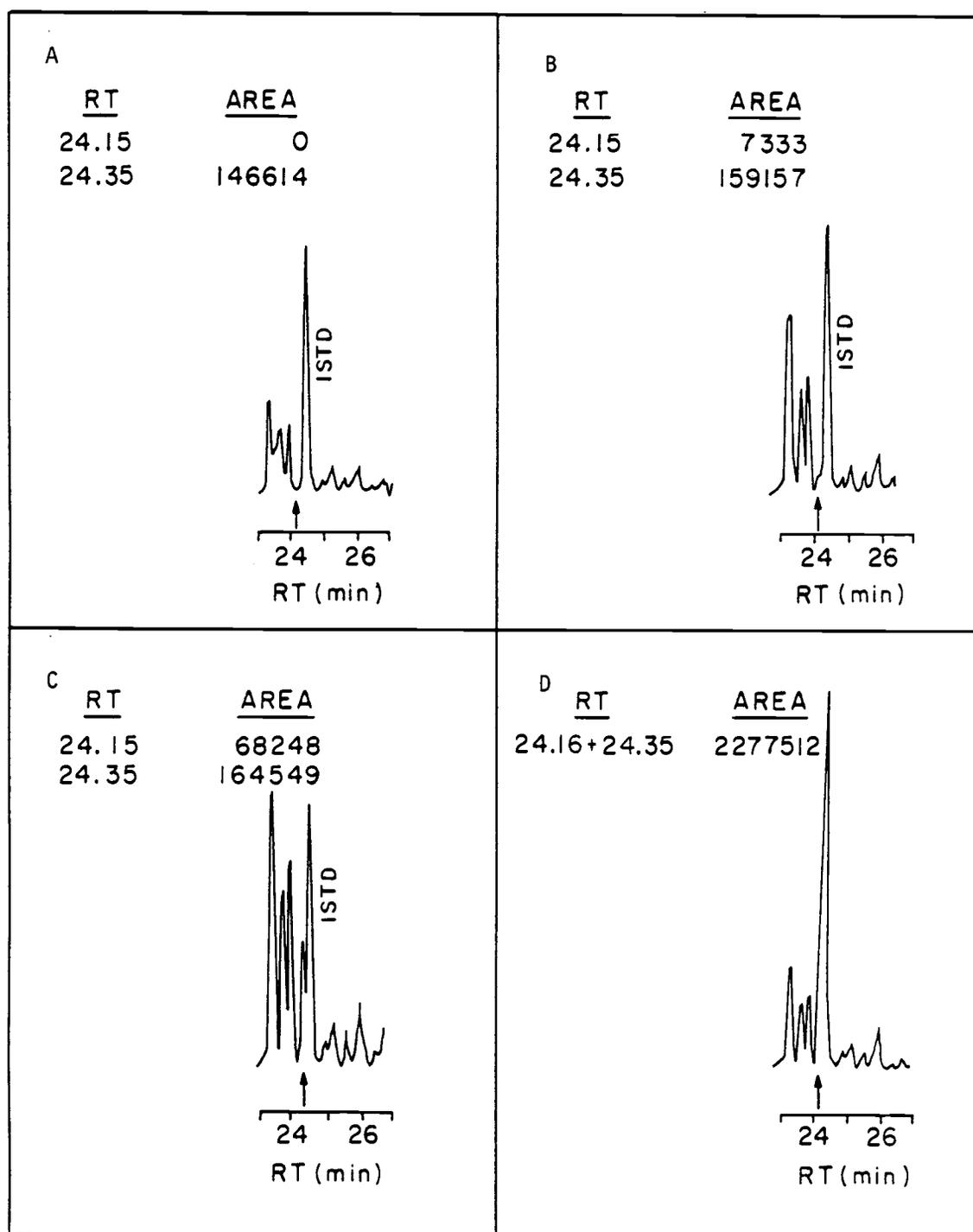


Figure 5. DB-5 Chromatographs of the Formation of the Unknown Metabolite vs. Time at RT 24.15 minutes. (A) 8/24/87, 0.016 gms TVS, (B) 12/7/87, 0.015 gms TVS, (C) 2/3/88, 0.027 gms TVS, (D) 3/7/88, 0.082 gms TVS.

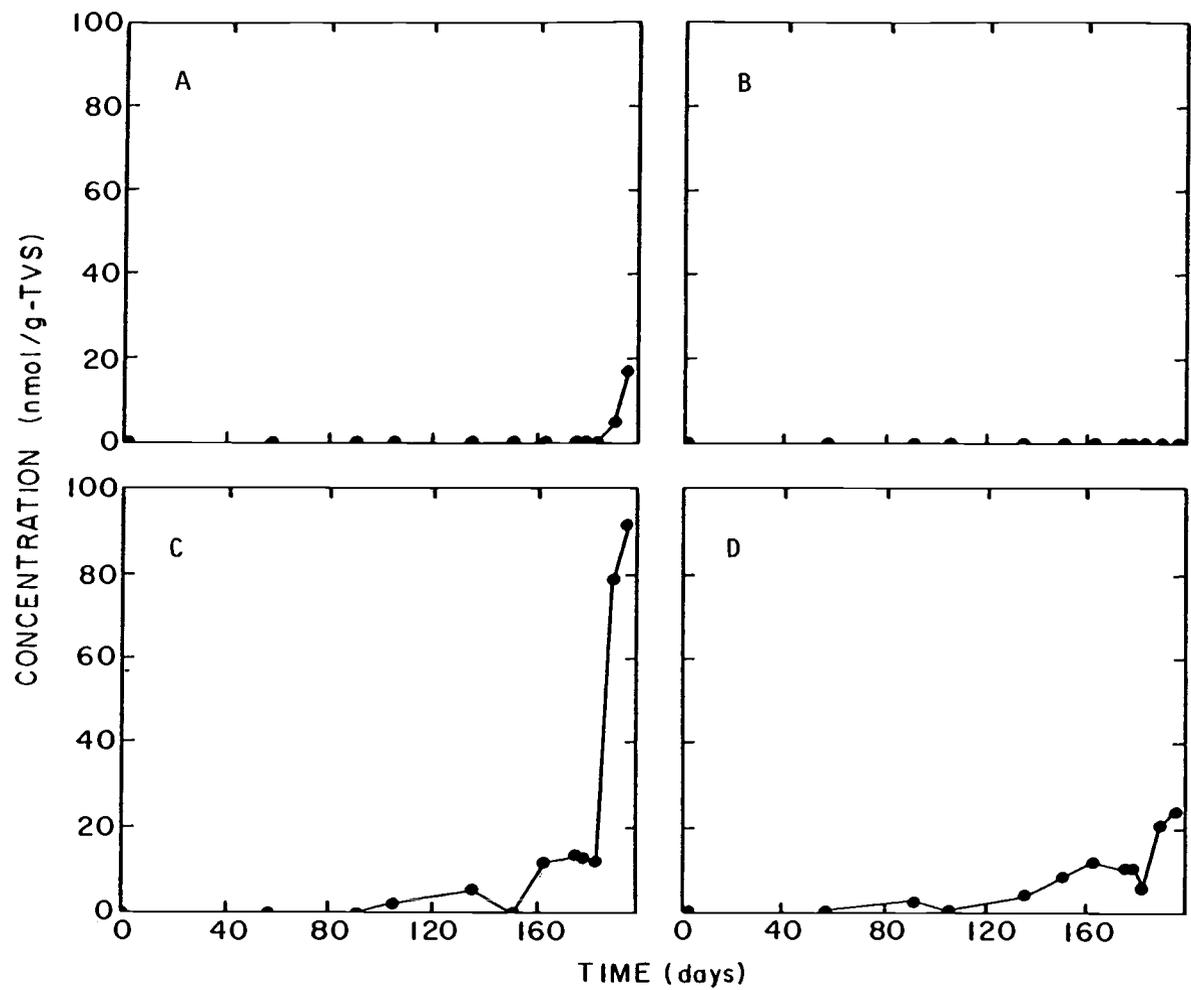


Figure 6. Emergence of Metabolite at RT 24.15 Minutes. (A) Reactor No.1, C2, (B) Reactor No.2, F3, (C) Reactor No.3, H7, (D) Reactor No.4, TI.

emerged at 58 days in Reactor No.4 compared to 93 days in Reactor No.3 (Figure 6-C and 6-D). The unknown in Reactors No.1 and No.2 was undetected throughout Phase II (Figure 6-A and 6-B). Phase III accumulations indicated similar sharp increases in the unknown concentrations for Reactors No.1, No.3 and No.4 (Figure 6). The largest increase in the unknown's concentration was observed for Reactor No.3. The concentration of the metabolic product increased from 10 nmol/g TVS at the beginning of Phase III, day 172, to 90 nmol/g TVS at day 196, corresponding to a 900% increase (Figure 6-C). Similarly there was a 360% increase in Reactor No.4. Silver Lake sediment (Reactor No.1) also showed formation of the unknown. Reactor No.1 accumulated a concentration that was 20% of the concentration accumulated in Reactor No.3 at the end of Phase III. The compound clearly emerged after the parent compounds had been fed to the reactors and responded to an order of magnitude increase in parent compound concentrations.

The increased concentration of the unknown indicated a correlation between a factor in the sediments and the increased concentration of parent compound in the reactor influent. Formation of the unknown occurred uniquely in the sediments and not during the PCB extraction and cleanup procedure. This assumption was verified from GC/ECD analysis of the PCB standard curve, made up to quantify PCBs in the sediment extracts. The results clearly showed no alteration of the five PCB parent compounds during the acetone/hexane extraction with copper metal and concentrated sulfuric acid treatment. Additionally, Reactor No.2, with no metabolite formation, served as a control. The pH and redox conditions of No.2 were similar to the other reactors.

Analysis of Metabolite

The unknown compound occurring at 24.15 minutes was identified by gas chromatography with mass spectrometric detection (GC/MS) and by GC/ECD. Hexane extracts from Reactor No.1, No.3 and No.4 were analyzed but only No.3 had sufficient mass to give positive identification in GC/MS analysis. However the unknown's RT (GC/ECD) indicated that the unknown in the three reactors were identical. The unknown was identified as a tetrachlorobiphenyl (tetra-CB) by comparing its mass spectra with the mass spectra of tetra-CBs from a limited library of known chlorobiphenyl congeners. The library used for GC/MS analysis was derived from a library of PCB mass spectra used by the National Institute of Health and The Environmental Protection Agency (Roberts, 1987). The unknown showed a dominant molecular ion at M/Z 292 and auxiliary ions at M/Z 290 and 294 characteristic of chlorine atoms (Figure 7). The ion was characteristic of ten tetrachlorobiphenyls: 22'44'-CB, 33'44'-CB, 23'4'5-CB, 23'55'-CB, 2356-CB, 2345'-CB, 22'66'-CB, 33'55'-CB, 22'45'-CB, and 22'55'-CB. The compounds are listed in order of decreasing goodness of match; best match was given for 22'44'-CB.

The unknown was positively identified by Cochromatography. Tetra-CB solutions of the best eight tetra-CB matches (all ten tetra-CB except 22'45'-CB and 22'55'-CB)(UltraScientific Inc., Hope, RI), were made up individually in hexane and analyzed by GC/ECD using identical procedures as the unknown. Cochromatography of Reactor No.3 hexane extract, and a 2356-CB stock solution identified the unknown as 2,3,5,6-tetrachlorobiphenyl. Its RT matched perfectly (Figure E-1).

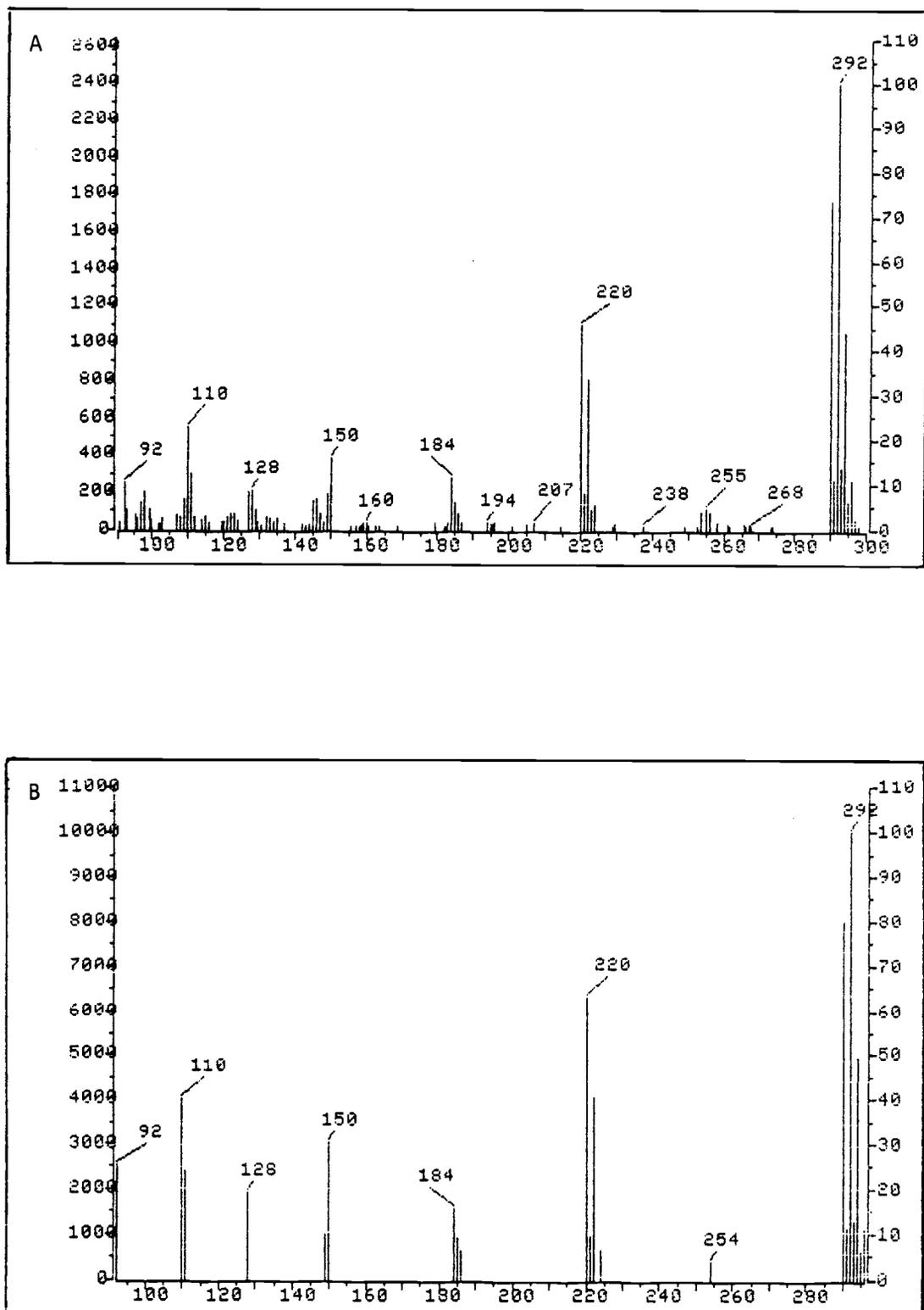


Figure 7. Mass Spectra of Metabolite and 2356-CB. (A) Peak at 24.15 Minutes (GC/ECD); Reactor No.3 Hexane Extract at 3/7/88, (B) 2,3,5,6-tetrachlorobiphenyl Reference Mass Spectra.

The seven remaining tetra-CBs each had unique RTs with a minimum of 0.95 minutes difference from the retention time of the unknown.

Identification of Parent Compound

Since 2356-CB clearly responded to increases in the parent compound, and was not present in the parent PCB standard solutions or Reactor No.2, it is a metabolic product. Based on the molecular structure of the parent compounds (Figure 2) 2356-CB could only be formed from 23456-CB. Thus, the parent compound, 23456-CB, was dechlorinated at the para position to form 2356-CB (Figure 8).

The concentration of 2356-CB was determined from a standard curve and compared to the concentration of the parent compound, 23456-CB (Figure 8). Based on these results the metabolite clearly showed a concentration increase in the later part of Phase II, and a sharp increase in Phase III. Additionally, the increased metabolite concentration during Phase III in Reactors No.3 and No.4 indicated a significant decrease in lag time compared to the initial lag time observed in Phase II (see figure 6).

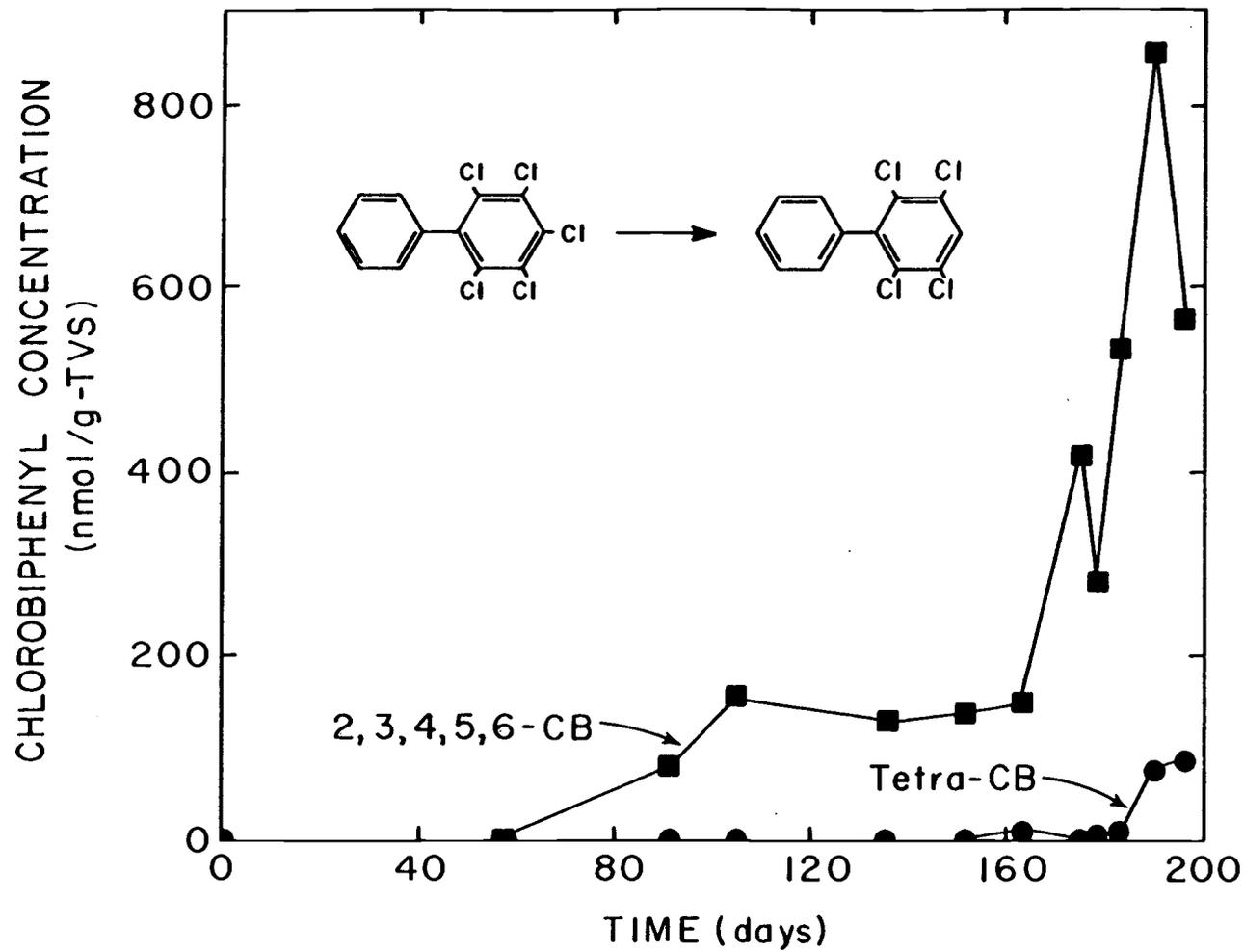
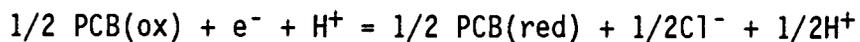


Figure 8. Emergence of 23456-CB and 2356-CB in Reactor No.3.

DISCUSSION

The results reported here indicate active methanogenic cultures were developed in four anaerobic filter reactors degrading PCBs. PCB Toxicity was not indicated because of the observed high COD removal efficiency and rapid metabolite formation in Phase III. Results also indicated PCB contaminated anaerobic sediments from the upper Hudson River and Silver Lake have the ability to degrade 23435-CB.

Degradation products were not detected for the remaining four parent compounds, 23'44'-CB, 22'44'66'-CB, 22'344'5'6-CB and 22'33'44'55'-CB within the experimental time period. Formation of the metabolite, 2356-CB, indicated that the parent compound 23456-CB, was dechlorinated at the para position in a reductive dechlorination process:



It is apparent from these data that similar PCB degradation pathways exist in anaerobic microorganisms of both Hudson River and Silver Lake sediments.

Reactor Performance

Reactor performance during Phase I and II PCB addition indicated an active methanogenic culture. This observation was supported by: (1) rapid gas production during phase II; (2) an immediate four fold increase in methane production resulting from a four fold increase in feed COD; (3) COD removal efficiency was greater than 90% in Phase II and greater than 97% in Phase III; (4) and rapid metabolite formation

during high PCB loading in Phase III. Toxicity by PCBs or by the high acetone concentration in Phase III was not indicated, but localized toxicity to high sediment PCB concentrations at the bottom of the reactor was not discounted. Toxicity would have been detected with a sudden drop in COD removal efficiency.

Metabolite

2356-tetrachlorobiphenyl's spectra and RT perfectly matched to the unknown metabolite. However, the similarity between mass spectra of the 42 possible tetra-CB congeners suggests one or more tetra-CBs could coelute with 2356-CB in the unknown peak at 24.15 minutes. Positive identification of the unknown peak would require the comparison of its RT with the RTs of the 42 possible tetra-CBs. However, many of the compounds are unavailable. Mullin et al. (1984) identified the RTs of 209 possible chlorobiphenyl congeners with GC/ECD using a capillary column, phase SE-54, which was identical to the phase used in the DB-5 column of our analysis. Their results indicated two pairs of tetra-CBs with indistinguishable RTs. Additionally, RTs for 2356-CB and the remaining 38 tetrachlorobiphenyl congeners were unique. The tetra-CBs which would elute closest to the unknown were identified by their RTs as 22'45-CB and 2346-CB. The difference between the retention times of 2356-CB and 22'45-CB, and 2356-CB and 2346-CB was calculated. The calculations showed the differences in RTs for 22'45-CB and 2346-CB were within 0.25 and 0.175 minutes of 2356-CB, respectively.

Therefore, the possibility of the unknown being 2346-CB or 22'45-

CB was further evaluated. Production of 2346-CB would suggest meta dechlorination of 23456-CB or 3 dechlorinations of 22'344'5'6-CB at the 2', 4' and 5' positions. Formation of 22'45-CB would suggest 3 dechlorinations of 22'344'5'6-CB at the 3, 4 and 6 positions or 4 dechlorinations of 22'33'44'55'-CB at the 3, 3' 4' and 5' positions on the biphenyl ring.

However, because 22'45-CB and 2346-CB were not available for cochromatography, the hexane extract containing the tetra-CB metabolite was analyzed by M. D. Mullin at the US EPA Laboratory (Large Lakes Research Station, Grosse Ile, MI). Results from Mullin's analysis confirmed our results that 2356-CB was the only tetra-CB metabolite in the unknown peak at RT 24.15 minutes (Figure 5) in Reactors No.1, No.3 and No.4.

The formation of 2356-CB in Reactors No.1 (Silver Lake sediment, C2), and No.3 and No.4 (Hudson River sediments, H7 and TI respectively) indicated that the reactors responded differently to the parent compound, 23456-CB. These differences were observed in the initial lag times in metabolite formation and the final concentration of the metabolite during Phase III (see figure 6 for comparison). The observed lag times for Reactors No.1, No.3 and No.4 (186 days, 93 days and 58 days, respectively) indicated more similarity between Reactors No.3 and No.4 (Hudson River sediments). However, the final metabolite concentration in Phase III for Reactor No.1, No.3 and No.4 (18, 90 and 24 nmol/g TVS) showed more similarity between Reactor No.1 (Silver Lake) and No.4 (Hudson River). The increase in metabolite formation for Reactor No.3 during Phase III clearly showed a correlation to the increased influent parent PCB compound concentration. The observed

nine fold increase in metabolite concentration showed a stoichiometric response (approximately 1:1) to a ten fold increase in the influent parent compound concentration. Reactors No.1 and No.4 indicated noticeable increases in metabolite formation during Phase III, but did not show the stoichiometry observed for No.3.

In addition to the different responses in metabolite formation observed for each reactor, characterization of the reactor inocula showed differences in % total volatile solids (%TVS), and background PCB contamination. Characterization of the %TVS for each reactor (Table 2) indicated a 3 to 5 fold higher %TVS fraction for Silver Lake compared to Hudson River sediments. Analysis of metabolite formation and the %TVS of each reactor indicated a correlation between the higher %TVS and the longer lag times observed in Silver Lake (Reactor No.1). However the similarity in %TVS in Reactors No.3 and No.4 (5 and 4.5 %TVS) showed no correlation to their difference in lag times (93 days vs. 58 days, No.3 and No.4 respectively). Characterization of the background PCB contaminants during GC/ECD analysis showed variations in the apparent mass (peak area), but not in the congeners detected. All reactors indicated similar congener compositions by observing nearly identical RTs of the background peaks.

Comparison To Environmental Transformation Data

Although one or a combination of factors appear to affect the concentration of metabolite and the initial lag times in each reactor, we were unable to distinguish between them. However, these observed variations in metabolite formation suggest different species, or mass

of anaerobic bacteria degrade 23456-CB in Hudson River and Silver Lake sediments. This observation is consistent with data from environmental transformation of PCBs, which showed distinctly different degradation patterns for Hudson River and Silver Lake sediments (Brown et al., 1987). Hudson River sediments showed characteristic degradation patterns which resulted from the loss of chlorine atoms located in positions meta and para to the adjacent phenyl ring in the biphenyl molecule. Degradation was observed for moderately chlorinated congeners up to hexa-CB. In comparison, Silver Lake sediments exhibited chlorine removal patterns indicating ortho, meta and para dechlorination processes. Dechlorination in Silver Lake was selective for the highly chlorinated penta-, hepta-, octa-, and nano-CBs.

The different dechlorination patterns observed in PCB transformations by Hudson River and Silver Lake sediments indicate which of the five PCB feed congeners could be potentially degraded in each sediment system. Analysis of the specific congener dechlorination patterns indicate 23456-CB would be more degradable in Silver Lake (Brown et al., 1987). Additionally, congener selectivity in Hudson River sediments indicated potential dechlorination of 23'44'-CB, 22'344'5'6-CB and 22'33'44'55'-CB. In comparison to Hudson River sediments, Silver Lake indicated decreased dechlorination potential for 23'44'-CB and increased potential for 22'344'5'6-CB and 22'33'44'55'-CB. Both sediment types indicated no dechlorination competence for 22'44'66'-CB.

It is apparent from our experimental results that the enhanced degradation of 23456-CB observed in Reactor No.3 and No.4 (Hudson River sediments) compared to Reactor No.1 (Silver Lake sediment) was

opposite to the expected results derived from environmental PCB transformation data (Brown et al., 1987). Additionally, degradation products of 23'44'-CB, 22'44'66'-CB, 22'344'5'6-CB and 22'33'44'55'-CB were not detected throughout the 196 day experimental period. Because of the experimental design and the observed background interference during GC analysis, only the degradation products which produced unique GC peaks were detectable. The likelihood of detecting other degradation products from the remaining four PCB congeners was low, but it did not preclude the absence of degradation.

Undoubtably, many physical and biological factors affect PCB dechlorination patterns. Brown et al.,(1987) observed high variability in environmental PCB dechlorination patterns within sediment sampling sites, and the location of PCB degrading sediments appeared to be random. With this variability in sediment samples (inocula) along with the potential organic solids effect and the variability in reactor sediment sampling techniques, the differences observed in the formation of the metabolite was expected. However, the observation of identical metabolite formation in Reactors No.1, No.3 and No.4 clearly indicated biodegradative competence for 23456-CB in both Hudson River and Silver Lake sediments.

CONCLUSIONS

1. The metabolite formed in Reactors No.1, No.3 and No.4 was confirmed by GC/MS and cochromatography as 2356-CB.
2. The parent compound, 23456-CB, was dechlorinated at the para position to form 2356-CB.
3. Both Hudson River sediments, H7 and TI, and Silver Lake sediment, C2, dechlorinated 23456-CB by producing the formation of 2356-CB.
4. Metabolite formation in Hudson River sediments, Reactors No.3 (H7) and No.4 (TI), had the shortest lag times, and No.4 (TI) indicated the most rapid production of 2356-CB.
5. Reactor No.2 (Silver Lake sediment, F3) indicated no formation of 2356-CB, and served as a control; physical-chemical dechlorination processes (abiotic dechlorination) were ruled out.

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APPENDICES

APPENDIX A

Physical and Chemical Properties of
Polychlorinated Biphenyls

Table A-1
Physical and Chemical Properties of Chlorobiphenyls

Compound	MW	Vapour Pressure (mm Hg, 25 ^o C) ^a	Log K _{ow} ^c	Solubility ^b in H ₂ O (ppm)	Melting point ^o C
23'44'-CB ^e	291.99	4.6x10 ⁻⁵	6.67 ^d	0.058	124
23456-CB	326.44	-	6.85	0.0068 ^d	123
22'44'66'-CB	360.88	1.3x10 ⁻⁵	7.12	0.00091 ^d	112.5
22'344'5'6-CB	395.33	-	-	-	-
22'33'44'55'-CB	429.77	-	8.42	0.0014 ^d	156.5

^a Neely, 1983

^b Hutzinger et al., 1974

^c Bruggenman et al., 1982

^d Yalkowsky et al., 1983

^e 2,3',4,4'-tetrachlorobiphenyl (typical)

APPENDIX B

Upflow Anaerobic Filter Degradation Results

The following tables contain the results from the semicontinuous upflow anaerobic filter degradation of PCBs during the period from 8/24/87 to 3/7/88. The raw and normalized peak areas are contained in symphony worksheets; file names: RXR-S1A.WR1, RXR-S2A.WR1, RXR-S3A.WR1 and RXR-S4A.WR1. (corresponding to Reactors No.1, No.2, No.3 and No.4).

Table B-1. Reactor No.1 "Silver Lake C2" GC/ECD Results

Reactor no.1 "SILVER LAKE C2"													
NORMALIZED DATA(NORMALIZED TO ISTD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
10.100		0.00	0.00	0.00	0.19	0.33	0.00	0.00	0.60	0.32	0.35	0.30	0.30
10.610		0.00	0.00	1.50	0.00	0.49	2.56	0.00	0.00	0.00	0.38	0.37	0.35
11.000		1.13	1.19	4.27	0.79	1.87	0.00	0.00	2.22	1.33	1.44	1.41	1.15
11.560		23.03	7.69	27.47	5.72	9.35	68.72	6.40	6.39	4.07	3.24	9.70	4.11
11.760		0.00	0.00	2.57	0.42	1.06	0.00	0.00	0.00	0.75	0.65	1.03	0.56
12.170		0.00	0.00	0.49	0.11	0.42	0.00	0.00	0.00	0.15	0.00	0.20	0.09
12.420		0.00	0.00	0.00	0.41	0.00	7.44	1.46	0.00	0.00	0.00	0.00	0.00
13.180		0.70	3.35	5.28	0.96	1.60	8.02	1.61	0.44	0.37	0.21	0.19	0.27
13.760		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.52
14.080		1.24	0.00	7.15	32.83	10.62	46.29	57.08	3.19	1.78	0.38	0.84	2.55
14.830		0.00	1.48	0.00	5.69	0.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15.250		0.00	0.00	1.91	2.35	1.39	0.00	0.00	0.45	0.78	0.00	0.37	0.29
15.700		0.00	0.00	1.69	1.65	0.94	0.00	0.00	0.00	0.00	0.22	0.00	0.00
15.850		0.00	0.00	0.00	3.24	3.47	5.34	1.62	0.77	1.36	0.43	0.80	0.65
16.470		0.00	0.00	2.07	3.63	1.92	2.13	0.42	0.00	0.81	0.33	0.22	0.34
16.630		0.00	1.42	0.92	1.75	1.04	0.00	0.00	0.00	0.41	0.00	0.00	0.00
17.270		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.25	0.20
17.970		0.00	0.00	0.00	0.00	0.45	4.45	0.84	1.11	0.52	0.51	1.83	4.21
18.580		0.00	0.00	0.00	0.00	1.91	0.00	0.00	0.91	1.08	0.63	0.89	0.89
19.080		1.07	0.00	2.95	108.17	19.75	79.04	117.34	7.79	6.84	3.81	4.37	6.55
19.500		0.00	0.00	0.00	115.44	0.00	0.00	15.37	0.00	0.59	0.30	0.47	0.39
19.930		0.00	0.00	0.00	10.81	0.00	0.00	12.20	0.00	0.00	0.00	0.00	0.00
20.410		1.62	1.77	3.33	10.60	6.43	10.74	7.37	13.24	13.59	9.33	9.72	11.35
20.580		0.00	0.00	0.00	7.45	3.42	11.80	4.68	8.70	7.58	5.59	9.96	22.98
20.900		0.00	0.00	0.00	7.99	1.23	0.00	1.59	2.33	2.24	1.54	2.14	2.85
21.620		1.61	0.00	5.50	17.20	5.96	8.36	4.65	5.98	6.67	4.66	4.97	5.61
21.950		0.00	0.00	9.31	16.50	8.25	11.53	3.62	2.94	3.82	2.36	2.33	2.48
22.990		0.00	0.00	19.05	32.45	15.16	18.95	3.31	3.66	5.94	3.19	3.08	2.69
23.210		7.24	3.01	52.85	55.27	67.05	85.93	29.24	36.65	43.48	28.08	28.19	30.99
23.560		7.51	0.00	16.99	40.89	28.68	38.15	20.04	28.78	31.61	21.35	22.18	25.39
23.800		2.20	0.00	0.00	0.00	0.00	0.00	5.41	8.04	9.35	5.97	6.17	7.35
24.150		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.71	19.91
24.350	ISTD	89.29	131.58	166.67	64.90	80.00	235.57	93.42	88.03	64.94	52.52	46.15	40.37
24.830		2.19	0.00	0.00	1.62	7.15	12.39	6.62	7.83	11.38	6.01	6.32	7.95
25.070		0.00	0.00	0.00	24.64	6.16	0.00	4.29	5.40	7.68	4.28	45.97	5.61
25.500		0.00	0.00	0.00	21.24	0.00	0.00	1.13	1.02	1.38	0.71	0.79	0.95
25.910		0.00	0.00	0.00	0.00	1.87	2.23	0.00	3.55	3.64	4.39	5.07	5.99
26.750		0.00	0.00	0.00	0.00	4.86	0.00	0.00	3.58	3.32	2.19	2.42	3.06
27.200		0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.83	2.62	3.39	3.87	5.49
27.530		1.73	0.00	19.05	4052.29	176.14	3086.16	7712.30	18.46	6.85	2.57	1.21	10.83
28.060		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59	0.72
28.510		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
28.910	GE PCB#1	0.00	18.88	171.02	256.64	443.45	755.93	374.49	784.34	666.79	1234.23	1307.78	1443.26
29.700		1.30	0.00	0.00	1.32	1.85	2.62	2.00	2.51	3.92	1.85	2.73	3.49
30.600	GE PCB#3	0.00	20.58	213.63	250.74	423.63	818.20	394.24	838.25	575.99	1010.03	1081.18	1231.51
30.900		2.31	0.00	0.00	3.57	0.00	0.00	7.00	0.00	9.88	0.00	0.00	0.00
31.450		1.17	0.00	0.00	2.04	2.62	3.16	3.83	6.11	6.20	3.34	3.45	4.27
31.710		2.35	0.00	0.00	3.20	4.00	5.71	5.98	9.78	9.80	5.89	6.58	7.95
32.420		1.18	0.00	0.00	1.42	0.96	0.00	0.00	4.34	4.28	2.31	2.63	3.13
33.200		0.00	0.00	0.00	0.66	0.96	0.00	0.00	1.71	1.76	1.26	1.46	1.74

Table B-1. Reactor No.1 "Silver Lake C2" GC/ECD Results

Reactor no.1 "SILVER LAKE C2"													

NORMALIZED DATA(NORMALIZED TO 1STD AND SOLIDS CONCENTRATION)													

RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
33.750		0.00	0.00	0.00	0.98	1.61	0.00	0.00	21.66	2.23	1.50	1.68	1.97
34.360		0.00	0.00	0.00	0.48	0.00	0.00	0.00	1.13	1.02	0.57	0.87	0.72
35.050	GE PCB#2	0.00	20.28	350.92	594.05	974.59	1614.11	857.43	1987.89	1555.35	2856.73	3009.16	3350.50
35.720		0.82	0.00	0.00	0.74	4.30	0.00	1.03	1.73	0.00	1.22	1.58	1.84
36.030		3.24	0.00	10.78	3.93	9.86	*****	6.24	10.47	10.96	7.75	9.25	133.36
37.030		0.00	0.00	23.38	7.41	15.02	19.39	2.26	2.92	3.26	1.59	1.59	1.07
37.310		0.54	0.00	9.87	3.15	7.28	7.60	2.57	3.76	4.39	2.76	2.94	3.12
37.750		1.10	0.00	6.21	21.67	5.03	5.13	2.29	3.24	3.48	2.30	2.88	2.82
38.165		0.00	0.00	0.00	6.89	14.55	18.16	4.02	4.43	6.07	3.39	3.72	3.17
38.510		3.39	1.98	0.00	45.29	57.96	72.76	25.52	29.50	38.42	24.12	28.60	25.82
38.650		0.00	0.00	98.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39.430		2.30	0.00	0.00	0.00	0.00	0.00	0.00	1.96	2.12	1.33	1.34	1.34
39.630		0.00	0.00	0.00	45.29	0.00	0.00	0.00	0.00	0.00	0.00	0.56	1.02
39.960		0.00	0.00	5.83	0.98	3.01	2.58	0.00	0.72	0.92	0.77	1.02	0.83
40.200		0.84	0.00	12.18	8.24	15.63	21.50	7.12	11.71	10.95	12.68	15.25	16.93
40.730		3.33	1.61	18.15	17.82	25.16	46.80	0.00	50.91	37.63	60.31	69.35	82.51
41.920		2.31	0.00	9.93	6.55	2.07	16.94	23.69	3.46	0.95	0.73	1.38	0.86
42.530		0.00	0.00	10.04	4.62	2.16	0.00	8.97	3.93	0.55	0.42	2.18	0.93
42.940		2.69	0.00	24.25	6.37	5.23	15.55	8.38	8.21	6.50	4.62	5.25	6.27
43.170		0.00	0.00	0.00	3.53	0.00	0.00	0.00	0.00	0.00	0.00	0.85	1.15
43.680		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65	0.61	0.08	0.51
44.100		0.00	0.00	0.00	0.61	0.00	0.00	1.00	0.66	0.33	0.64	1.38	0.83
44.340		0.00	0.00	3.67	3.14	6.64	5.96	4.71	10.12	7.49	12.03	14.57	17.79
44.730	GE PCB#4	0.00	28.22	596.21	573.46	924.53	1750.45	862.63	2063.60	1279.97	2332.35	2331.70	2935.04
45.780		7.79	0.00	3.20	0.42	0.00	8.63	2.91	0.00	0.00	0.00	0.00	0.00
46.250		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.58	1.22	0.49	3.43
46.710		0.00	0.00	0.00	1.04	1.48	0.00	0.89	1.65	1.61	0.95	1.15	1.61
47.130		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.50	0.68	0.63
48.170		0.00	0.00	0.00	1.01	1.91	2.35	1.47	3.18	3.43	3.79	4.82	5.92
48.800		0.00	0.00	0.00	2.70	3.36	7.26	2.70	2.93	5.11	1.89	3.11	2.44
49.965		0.00	0.00	0.00	0.00	1.37	0.00	0.00	1.03	2.74	2.02	1.00	2.52
50.520		11.65	22.16	167.93	112.38	282.02	185.60	31.41	100.26	39.03	28.04	720.45	18.64
51.750		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.83	3.63	2.04	2.31	2.94
52.230		0.71	0.00	1.70	1.81	3.46	11.21	0.00	0.00	2.78	0.00	0.00	0.00
52.750		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.44
53.370		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.57	1.06	0.54	0.66
55.100		0.00	0.00	2.64	2.32	39.86	6.23	3.29	9.10	5.84	11.35	14.90	18.92
59.860	GE PCB#5	0.00	33.97	1073.49	1104.89	1797.35	3177.81	1657.78	4113.64	2384.04	4315.92	4709.55	5462.14

Table B-2. Reactor No.2 "Silver Lake F3" GC/ECD Results

Reactor no.2 "SILVER LAKE F3"													
NORMALIZED DATA(NORMALIZED TO ISTD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
10.100		0.37	0.30	0.00	0.35	0.00	0.00	0.98	0.68	1.25	1.09	0.75	0.85
10.610		0.00	0.00	1.29	0.33	0.00	0.00	0.00	0.00	1.13	0.40	0.00	0.41
11.000		0.31	0.19	4.00	1.22	0.61	0.00	0.00	2.17	3.17	1.30	0.35	1.05
11.560		3.02	1.16	6.29	5.92	8.30	4.19	3.49	5.49	21.71	12.81	12.75	5.88
11.760		0.33	0.34	0.00	0.00	0.00	1.64	0.48	2.26	0.00	0.00	0.98	0.79
12.170		0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.69	0.00	1.37	0.46	0.16
12.420		0.11	0.00	0.00	0.30	0.54	1.15	0.83	0.00	0.00	0.00	0.00	0.00
13.180		0.15	0.15	1.17	0.54	0.57	1.27	2.11	0.45	0.36	0.00	0.00	0.12
13.760		0.14	0.20	1.39	0.47	0.29	0.45	2.90	0.64	2.67	2.19	2.70	2.80
14.080		2.73	1.68	0.00	9.48	6.79	3.69	21.38	0.00	0.97	0.60	7.57	1.57
14.930		0.00	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15.250		0.00	0.06	0.00	0.00	0.51	0.00	0.51	0.73	0.00	0.48	0.64	0.23
15.470		15.80	7.05	0.00	5.54	2.36	4.55	18.47	9.57	33.97	28.28	27.07	25.27
15.700		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15.850		0.00	0.00	0.00	0.36	1.80	0.91	1.20	1.63	0.00	1.47	1.27	0.19
16.270		0.22	1.25	3.20	1.34	0.58	1.17	4.67	2.29	9.13	7.89	9.87	8.89
16.470		0.00	0.00	0.00	0.00	0.81	0.42	0.85	0.90	0.00	0.00	0.51	0.00
16.630		0.44	1.29	0.00	1.05	0.88	1.26	3.87	2.23	6.86	5.77	7.05	6.21
17.270		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.19
17.650		47.29	14.25	0.00	9.03	4.22	7.59	32.55	16.72	61.38	48.20	52.94	49.46
17.970		0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18.700		100.72	34.37	1.25	21.16	11.18	18.93	80.47	39.86	142.06	112.32	126.58	115.64
19.080		103.49	35.27	1.07	44.90	22.93	20.62	121.63	29.21	111.21	92.80	116.13	97.96
19.500		12.34	3.89	0.00	1.76	0.82	1.56	9.08	3.59	13.46	11.66	15.11	12.84
19.930		0.43	0.27	0.00	0.00	0.00	0.00	1.05	0.99	1.01	0.87	0.50	0.97
20.270		3.65	1.06	0.00	0.00	0.00	0.00	2.26	1.30	4.83	3.77	4.21	3.96
20.410		22.35	8.05	0.00	4.87	3.14	4.80	18.00	8.86	30.10	25.92	30.99	29.28
20.580		40.20	15.30	0.00	7.40	4.03	7.27	31.59	15.53	56.47	50.02	61.94	56.64
20.900		7.23	4.53	0.00	2.28	0.85	2.43	9.61	4.55	17.34	15.00	18.70	17.33
21.620		39.29	11.98	1.56	7.85	5.84	8.03	29.51	17.26	52.81	41.58	45.97	42.66
21.950		23.42	7.15	1.53	5.42	6.20	5.80	19.67	13.35	31.81	25.75	29.40	25.91
22.450		5.51	1.32	0.00	0.70	0.46	0.63	2.93	1.65	5.17	4.54	5.42	4.80
23.210		71.91	23.64	10.42	22.18	31.49	25.09	81.05	65.51	110.20	89.61	104.06	87.81
23.560		84.89	26.03	0.00	17.45	15.06	18.62	119.54	39.52	110.52	87.73	96.55	91.13
23.800		85.99	23.49	0.00	12.86	8.82	9.99	54.95	28.74	92.15	77.04	88.29	82.34
24.150		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24.350	ISTD	14.08	10.47	125.00	39.68	54.79	48.78	82.16	84.03	117.10	48.35	32.94	42.83
24.830		11.92	4.09	0.00	1.37	2.48	1.26	11.30	5.63	11.05	10.27	16.07	82.34
25.070		26.21	6.41	0.00	2.88	3.94	2.76	17.83	9.40	21.84	19.27	26.22	23.04
25.500		5.53	1.55	0.00	0.78	0.80	0.58	5.83	1.59	4.57	3.97	5.14	4.80
25.910		25.69	7.48	0.00	4.93	2.91	3.69	21.98	8.64	25.98	23.83	30.73	27.55
26.680		17.10	6.43	0.00	9.39	5.29	4.15	31.16	4.78	15.36	13.22	18.04	14.55
27.200		10.52	0.00	0.00	0.00	0.00	0.00	0.00	3.69	9.19	8.63	14.20	9.58
27.530		15.11	133.01	3.47	924.52	269.20	102.04	2244.28	2.29	11.85	5.48	40.37	9.49
28.060		5.54	2.11	0.00	0.80	0.95	1.23	3.69	2.49	8.30	7.02	8.56	7.98
28.510		2.08	0.90	0.00	0.00	0.00	0.00	1.19	0.25	1.52	1.55	2.94	3.44
28.910	GE PCB#1	0.00	26.63	49.34	143.41	125.28	211.71	405.70	647.15	585.36	876.02	1112.87	973.53
29.700		37.50	9.66	1.68	5.18	3.29	5.35	21.24	10.22	38.38	32.23	36.83	34.52
30.600	GE PCB#3	0.00	8.80	62.04	148.87	138.57	207.06	379.96	658.64	568.70	677.80	805.75	701.25
30.900		46.62	11.09	0.00	7.03	4.93	7.67	26.97	15.29	47.05	39.42	42.64	41.22

Table B-2. Reactor No.2 "Silver Lake F3" GC/ECD Results

Reactor no.2 "SILVER LAKE F3"													
NORMALIZED DATA(NORMALIZED TO ISTD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
31.450		23.85	6.60	0.00	3.87	2.29	3.84	15.15	8.47	26.73	22.99	26.37	25.50
31.710		68.14	17.23	5.83	9.42	6.18	10.06	38.25	20.90	67.56	57.51	65.09	63.65
32.420		47.94	11.50	3.28	6.24	4.11	6.62	25.07	13.72	44.83	38.75	44.95	42.55
33.200		15.76	3.23	0.00	1.65	1.05	1.74	7.06	3.70	12.34	11.29	13.67	12.25
33.750		10.18	2.20	0.00	1.16	0.78	1.10	4.92	2.68	8.30	7.52	9.14	8.52
34.360		7.89	2.15	0.00	1.12	1.07	0.80	4.49	2.69	7.94	6.66	8.46	8.55
35.050	GE PCB#2	0.00	17.08	81.91	299.33	254.69	409.53	816.67	1598.02	1265.23	1932.50	2410.13	2081.24
35.720		18.26	4.43	0.00	2.09	3.76	2.23	11.66	4.61	20.13	13.39	14.66	16.76
36.030		82.86	21.75	5.08	9.86	8.79	10.22	48.42	21.43	76.62	69.02	83.44	83.23
37.030		0.00	0.00	6.19	1.83	9.25	2.54	0.00	6.22	0.00	0.00	0.00	0.00
37.310		38.47	8.44	3.51	6.74	5.34	5.61	27.90	12.17	38.20	31.18	36.02	30.20
37.750		34.29	7.38	2.45	4.27	2.45	4.68	18.37	10.10	29.52	26.33	29.23	25.97
38.165		13.21	2.92	4.66	3.47	1.00	4.29	12.49	10.96	14.49	13.37	16.34	11.38
38.510		134.87	36.66	39.94	30.98	39.47	37.03	116.95	90.20	170.51	150.74	171.18	135.78
38.650		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39.430		13.77	2.56	0.00	1.83	1.14	2.13	7.34	4.74	8.82	10.14	11.91	8.88
39.630		9.76	1.59	0.00	0.00	0.00	0.00	3.29	1.77	4.87	5.80	7.06	5.36
39.960		0.00	0.00	0.00	0.00	1.08	0.45	0.00	1.45	0.00	0.00	0.00	0.00
40.200		45.74	9.41	5.85	7.83	9.49	8.58	27.52	21.64	44.15	42.25	49.84	39.50
40.730		100.54	22.66	10.87	18.41	14.85	22.63	67.44	73.02	115.12	110.73	126.06	111.20
41.500		1.11	0.20	0.00	0.00	0.00	0.00	0.91	0.00	1.30	0.66	0.85	0.77
41.920		17.32	3.67	2.90	7.83	2.83	3.02	8.90	6.85	15.37	12.78	14.20	12.88
42.530		15.37	2.92	5.06	2.00	2.74	1.86	7.12	4.06	12.23	10.29	11.77	10.78
42.940		138.47	29.16	11.71	13.60	9.25	15.29	60.79	29.99	107.64	101.12	115.10	103.92
43.170		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43.680		16.43	2.89	0.00	2.75	2.34	1.46	5.19	3.87	9.95	9.78	11.25	10.52
44.100		2.18	0.28	0.00	0.00	0.00	0.35	1.81	0.75	1.61	1.56	1.89	2.02
44.340		61.43	12.05	4.57	26.16	6.51	8.10	28.59	18.76	46.60	47.53	54.70	47.70
44.730	GE PCB#4	21.79	19.82	264.57	319.25	289.62	466.43	844.60	1492.31	1303.81	1508.52	1793.02	1527.37
45.150		16.58	3.36	0.00	0.00	0.00	0.00	10.76	0.00	18.58	16.17	16.79	16.08
45.610		3.72	0.56	0.00	0.00	0.00	0.00	2.83	0.00	4.02	3.20	3.73	4.28
46.250		25.12	4.60	1.30	3.33	1.38	3.12	8.42	4.98	16.09	14.74	18.83	14.90
46.710		33.60	6.53	2.47	3.89	2.62	4.15	13.01	8.25	23.99	22.66	26.30	22.40
47.130		26.82	4.81	3.59	2.63	1.72	2.81	9.03	5.56	16.98	16.41	19.89	16.58
48.170		7.90	1.30	0.00	0.88	0.86	1.21	4.45	5.00	6.01	6.50	8.47	6.91
48.800		104.53	17.19	7.88	7.43	7.95	9.17	35.72	23.85	57.31	57.51	68.26	55.87
49.965		2.20	0.59	0.00	0.00	0.00	0.00	0.00	0.00	3.49	3.65	2.80	1.94
50.520		75.81	4.96	46.64	29.29	306.45	31.92	62.21	95.74	53.33	27.22	626.54	93.39
51.750		55.59	8.64	3.23	3.72	2.23	4.25	19.80	14.20	29.74	30.92	35.70	30.55
52.230		1.59	4.23	0.00	0.00	1.41	0.00	0.00	0.00	4.03	1.99	0.00	0.00
52.750		23.95	3.73	0.00	1.65	1.25	1.70	8.37	5.23	14.49	12.98	13.62	12.50
53.370		28.79	4.23	0.00	1.74	1.04	2.12	7.96	4.16	15.15	13.81	15.60	13.89
55.100		2.40	0.48	0.00	1.33	1.31	1.99	4.23	6.77	6.76	8.12	11.96	9.21
57.010		11.53	1.89	0.00	0.82	0.00	1.07	3.45	2.09	6.60	6.11	6.87	5.98
59.860	GE PCB#5	28.26	28.70	506.50	580.52	539.59	918.54	1688.81	3092.73	2497.92	2776.09	3194.23	2788.27

Table B-3. Reactor No.3 "Hudson River H7" GC/ECD Results

Reactor no.3 "UPPER HUDSON H7"													
NORMALIZED DATA(NORMALIZED TO ISTD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
10.100		0.00	0.00	0.00	0.45	0.16	0.00	0.26	0.36	0.43	0.17	0.22	0.13
10.400		0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.00	0.00	0.00	0.00	0.00
11.530		1.30	0.34	27.42	13.49	7.03	28.44	9.02	0.93	3.69	1.54	7.15	1.79
12.170		0.00	0.00	0.34	0.00	0.49	0.00	0.00	1.36	0.25	0.49	0.17	0.09
12.420		0.00	0.00	0.00	0.50	0.36	7.88	0.30	0.00	0.00	0.00	0.00	0.00
13.180		0.16	0.17	1.51	1.27	0.50	3.82	1.05	0.40	0.37	0.14	0.06	0.09
13.750		0.99	0.26	2.24	6.87	2.50	5.73	5.11	2.81	4.17	4.50	6.89	5.03
14.080		0.56	0.00	3.91	18.09	5.05	1.92	8.68	0.94	0.00	0.23	0.25	0.55
14.830		0.38	0.14	0.00	0.71	1.46	0.00	0.61	0.73	0.80	0.94	1.48	0.92
15.475		6.67	2.21	13.68	76.62	27.03	60.00	57.07	36.90	44.90	37.66	55.73	42.56
16.250		0.27	0.13	0.58	2.50	1.02	1.73	2.33	1.25	2.03	2.13	3.42	2.44
16.630		0.97	0.35	2.46	6.68	3.51	5.26	6.02	5.69	5.66	5.74	9.05	6.28
16.950		4.36	1.66	8.64	33.31	13.97	24.22	29.98	18.63	27.44	26.57	42.23	28.75
17.660		8.02	1.70	18.99	75.93	30.16	60.54	65.89	43.12	45.01	35.77	47.54	40.86
18.175		0.00	0.00	0.00	0.00	0.06	0.00	0.38	0.00	0.00	0.28	0.53	0.00
18.450		0.18	0.10	0.00	0.00	0.00	0.00	0.69	1.16	1.15	1.91	1.13	
18.700		5.98	2.32	11.20	39.04	15.73	25.63	34.44	18.84	31.88	28.06	42.96	28.32
19.090		8.31	1.71	23.30	140.31	39.47	51.56	99.96	44.15	50.76	45.88	65.14	51.82
19.505		3.27	0.69	7.24	27.62	10.78	16.89	26.36	14.95	18.18	18.60	28.72	21.57
19.940		0.45	0.10	1.43	4.56	1.65	3.18	4.25	2.97	2.92	2.67	3.99	3.18
20.270		0.16	0.00	1.08	3.27	0.00	0.00	3.23	2.72	1.69	1.33	0.00	1.78
20.420		3.24	0.91	7.40	20.49	11.02	18.41	20.64	14.18	16.47	1.57	23.52	15.48
20.580		0.94	0.39	2.53	7.25	3.72	7.18	7.84	6.82	9.99	9.59	50.07	58.96
20.910		6.58	2.09	13.53	39.94	18.03	30.26	39.56	27.81	37.04	36.73	58.76	40.45
21.640		3.96	0.81	17.61	34.59	17.80	28.69	32.81	39.44	23.50	19.70	25.06	21.06
21.965		1.20	0.00	17.92	12.34	11.89	10.66	11.23	43.68	10.00	9.26	6.61	9.29
22.060		0.00	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22.440		0.45	0.10	1.95	4.53	2.20	2.82	4.55	5.79	3.18	2.97	3.98	3.55
23.230		4.07	0.86	120.66	55.06	72.78	44.47	45.09	320.89	52.43	40.78	42.10	32.28
23.570		4.11	2.12	28.20	26.52	20.61	22.52	24.99	88.72	20.61	18.26	21.54	17.00
23.800		2.87	0.67	14.18	28.16	14.61	20.01	28.94	0.00	20.65	18.83	24.01	19.71
24.150		0.00	0.00	0.00	3.03	7.24	0.00	15.56	15.51	14.65	13.95	93.95	109.18
24.350	ISTD	10.00	9.89	84.03	65.83	58.07	213.68	37.52	116.86	61.67	17.73	19.49	12.17
24.845		0.38	0.11	0.00	2.55	3.76	1.81	2.85	49.74	4.19	3.93	3.92	2.96
25.120		1.27	0.46	11.37	8.54	7.09	6.48	8.69	22.85	10.71	9.93	12.60	9.32
25.520		0.51	0.13	2.47	5.04	2.41	3.67	4.98	4.18	3.92	3.48	4.20	35.46
25.935		1.31	0.34	4.70	15.30	5.42	9.43	13.71	8.32	10.29	11.48	18.06	14.30
26.385		0.17	0.00	0.80	5.08	1.21	0.00	3.07	1.71	1.11	0.88	0.89	0.97
26.680		0.52	0.00	2.31	15.48	3.53	2.98	9.08	4.76	2.99	2.58	3.45	2.96
27.530		5.73	0.39	19.26	1774.29	79.78	27.75	514.14	1.52	0.86	0.00	0.00	2.12
28.120		2.62	0.26	1.79	4.48	2.26	6.12	4.64	2.84	3.81	3.38	5.19	4.24
28.510		1.47	0.18	1.09	2.76	1.12	2.46	2.98	1.36	2.29	1.89	3.57	2.56
28.920	GE PCB#1	0.00	6.33	130.13	270.45	213.27	276.41	258.64	544.10	385.60	713.01	1171.48	799.52
29.720		0.47	0.00	2.19	5.12	2.18	3.79	5.45	2.64	2.91	2.39	3.34	3.32
30.605	GE PCB#3	0.00	5.12	171.98	269.83	202.26	356.75	254.00	557.29	389.87	572.69	895.12	600.82
30.995		1.36	0.00	6.24	12.54	5.27	0.00	10.28	0.00	8.36	0.00	0.00	0.00
31.465		0.42	0.00	2.20	5.12	2.12	4.45	5.00	3.29	3.46	2.20	3.05	2.94
31.735		0.71	0.00	3.12	6.75	2.97	5.41	6.80	4.49	5.12	3.78	5.77	4.64
32.155		0.00	0.00	0.00	1.53	0.59	0.00	1.44	1.14	1.18	0.58	0.90	0.77
32.405		0.35	0.00	1.14	2.43	1.28	0.00	2.96	1.62	2.20	1.61	2.49	2.04

Table B-3. Reactor No.3 "Hudson River H7" GC/ECD Results

Reactor no.3 "UPPER HUDSON H7"													
NORMALIZED DATA(NORMALIZED TO 1STD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
33.225		0.15	0.00	0.00	1.19	0.60	0.00	1.39	0.75	0.81	0.79	1.20	0.97
33.470		0.29	0.00	2.39	2.43	1.43	3.40	2.71	2.83	1.71	1.61	2.20	1.90
33.750		0.00	0.00	2.11	0.00	1.25	0.00	1.29	3.68	0.00	0.88	1.09	0.94
34.360		0.00	0.00	0.00	1.15	1.31	0.00	1.33	1.93	1.28	1.00	1.21	0.99
35.035	GE PCB#2	0.00	7.63	278.01	538.14	454.58	469.62	529.36	1302.81	864.00	1627.20	2554.43	1686.69
35.720		0.74	0.13	5.71	3.54	4.45	4.27	4.48	3.93	1.95	1.58	1.83	1.96
36.030		2.34	0.66	16.45	17.72	15.61	18.64	20.63	14.93	18.37	15.49	32.10	30.59
37.330		1.19	0.25	22.32	17.48	14.26	20.89	15.79	43.34	9.89	8.54	10.65	9.18
37.750		0.59	0.15	11.55	6.77	7.37	15.20	6.77	18.61	4.45	3.80	4.18	3.81
38.165		0.17	0.00	0.00	5.18	0.00	9.18	3.59	0.00	7.29	5.91	3.90	2.73
38.505		0.57	0.12	187.50	31.33	95.82	33.39	23.60	442.02	20.04	19.57	13.55	11.08
38.650		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	17.37	10.79
39.450		0.17	0.00	23.81	2.92	4.68	0.00	2.56	0.00	2.61	2.23	1.87	1.57
39.645		0.34	0.00	4.25	3.70	3.29	0.00	4.76	9.92	3.84	2.51	0.59	6.20
40.205		0.50	0.16	14.24	11.36	17.98	2.95	11.15	34.22	13.21	13.70	17.64	13.73
40.730		0.49	0.31	18.94	20.42	16.78	25.68	21.00	53.21	25.37	40.31	63.66	44.05
41.925		0.38	0.29	3.80	8.41	5.34	64.93	4.15	6.53	2.11	1.94	2.08	2.06
42.535		0.14	0.25	0.83	7.81	3.40	84.36	1.59	1.14	1.35	0.77	1.02	0.89
42.955		1.79	0.30	7.05	17.39	9.73	56.02	15.52	9.42	8.78	8.41	11.63	10.00
43.680		0.87	0.08	4.45	9.40	8.80	21.89	8.28	5.12	3.58	3.15	3.70	3.65
44.110		0.00	0.00	0.00	0.00	0.00	8.76	0.26	0.49	0.37	0.58	0.82	0.59
44.340		0.98	0.41	5.70	8.89	6.43	9.90	9.66	10.38	7.26	1.03	16.32	12.36
44.745	GE PCB#4	0.00	7.91	391.54	569.79	450.36	708.03	567.86	1375.33	887.15	1297.00	1996.29	1324.51
45.900		0.23	0.00	0.00	2.25	0.60	14.06	0.00	0.00	0.00	0.00	0.00	0.00
46.250		0.12	0.00	1.33	2.76	1.06	0.00	2.15	0.00	0.61	0.60	0.64	0.70
46.725		0.29	0.00	5.57	4.36	3.35	3.28	4.38	19.16	2.71	2.28	2.29	2.24
47.080		0.43	0.00	2.76	3.72	2.11	2.77	3.88	8.73	2.03	1.85	2.10	1.98
47.780		0.00	0.00	0.00	0.79	0.57	4.53	1.18	0.00	0.67	0.38	0.49	0.39
48.185		0.00	0.00	2.63	1.41	1.90	0.00	3.05	31.51	2.75	3.35	6.48	5.38
48.800		0.26	0.09	8.33	2.67	5.56	2.13	6.43	0.00	6.40	4.53	3.72	2.90
49.965		0.00	0.00	4.77	0.00	2.57	0.00	2.29	43.27	0.00	1.64	1.38	1.11
50.520		10.32	2.20	1375.96	49.14	490.10	71.48	22.78	879.27	71.60	97.91	220.73	30.30
51.760		0.17	0.00	0.00	2.18	0.00	0.00	4.52	16.52	4.39	1.85	2.96	2.41
52.255		0.33	0.00	2.25	1.06	2.68	0.00	2.49	21.16	0.00	0.52	0.44	0.37
52.770		0.33	0.00	2.68	4.59	2.42	2.87	6.03	16.59	3.40	1.83	2.01	2.03
53.370		0.22	0.00	0.00	2.99	1.19	2.35	4.12	3.74	1.56	1.17	1.37	1.45
55.095		0.00	0.00	1.39	2.29	2.13	4.56	3.27	6.69	3.57	6.69	12.92	8.66
56.935		0.16	0.00	1.42	3.30	1.88	10.99	4.47	1.77	1.29	0.92	0.90	1.04
57.985		0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.09
59.885	GE PCB#5	0.28	8.98	703.23	1032.18	896.55	1232.27	1075.19	2861.69	1670.79	2225.25	3382.92	2117.80

Table B-4. Reactor No.4 "Hudson River TI" GC/ECD Results

Reactor no.4 "UPPER HUDSON TI"													
NORMALIZED DATA(NORMALIZED TO 1STD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
10.100		0.00	0.00	0.18	0.72	0.00	0.35	0.30	0.20	0.36	0.42	0.18	0.25
10.400		0.00	0.15	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.29
11.530		1.29	0.34	2.69	7.90	8.33	3.51	2.70	2.90	0.59	0.65	4.24	3.94
12.170		0.00	0.07	0.31	1.23	0.00	0.46	1.04	1.20	0.31	5.69	0.91	0.51
12.420		0.00	0.00	0.36	1.21	1.64	0.00	0.52	0.00	0.00	0.00	0.00	0.00
13.180		0.30	0.42	0.56	1.21	1.55	1.23	1.04	0.31	0.12	0.23	0.05	0.31
13.750		0.95	0.71	6.65	36.33	16.77	20.27	20.77	12.03	13.16	13.43	13.73	12.61
14.080		0.14	0.21	9.33	24.12	10.55	5.93	16.27	0.00	0.89	0.00	0.42	0.00
14.830		0.61	0.26	0.61	2.40	2.33	1.76	2.91	1.11	1.46	2.08	2.10	1.76
15.100		0.00	0.00	0.00	0.53	0.00	0.00	0.00	0.00	0.37	0.00	0.56	0.00
15.250		0.00	0.00	0.39	1.80	0.00	0.80	0.00	0.13	0.95	0.00	0.00	0.00
15.475		2.32	4.80	56.09	192.68	105.55	124.13	129.46	80.89	87.06	82.52	78.49	76.41
15.850		0.00	0.00	1.18	13.26	2.07	4.96	42.66	0.71	5.68	0.00	0.21	0.00
16.250		0.33	0.72	9.41	27.29	14.57	19.37	22.45	14.24	14.17	14.80	15.96	14.32
16.470		0.00	0.00	0.27	4.09	0.00	1.39	0.00	0.00	1.87	0.00	0.00	0.00
16.630		3.17	2.31	17.29	49.32	27.07	33.92	104.54	23.45	27.30	28.73	29.21	25.75
16.850		10.60	13.97	141.70	394.68	225.20	278.58	314.48	197.54	211.40	220.96	219.54	201.18
17.660		0.00	3.67	56.40	152.82	89.11	109.09	121.12	77.25	79.10	70.78	67.90	69.56
18.160		0.15	0.23	1.00	2.48	2.29	1.71	1.89	1.11	1.30	1.78	1.74	1.62
18.450		0.41	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18.580		1.54	2.32	21.19	51.96	32.54	37.44	42.66	26.95	30.72	33.57	30.13	28.24
18.680		3.21	5.10	52.63	124.37	71.77	89.31	104.54	65.22	67.94	68.57	65.50	62.89
19.080		4.67	7.06	133.86	336.45	163.68	192.23	250.77	134.11	133.32	123.90	127.67	120.94
19.500		6.24	7.03	108.49	250.24	142.00	184.31	214.80	140.13	137.38	128.17	133.08	125.60
19.930		0.22	0.29	4.56	9.92	5.50	7.33	8.90	5.91	5.49	5.17	6.03	5.44
20.270		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20.410		5.95	7.75	82.96	182.50	110.97	138.72	161.79	107.26	112.59	113.21	97.08	93.49
20.580		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	21.56	25.37
20.900		11.62	14.06	135.38	293.25	178.93	221.19	255.73	168.18	177.79	196.77	175.69	170.04
21.620		4.45	4.63	61.40	140.70	82.52	102.44	111.91	74.88	79.43	66.53	64.56	65.34
21.950		0.00	0.00	26.66	68.39	36.29	44.64	43.25	31.44	39.01	16.10	17.00	28.26
22.060		1.96	2.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.05	0.00
22.430		0.62	0.61	11.35	33.16	12.58	18.53	20.56	15.63	13.39	11.34	13.39	12.31
22.990		0.00	0.00	6.12	17.87	6.46	14.47	4.85	4.29	21.04	4.12	5.56	3.74
23.210		6.10	8.70	108.71	309.40	139.33	189.37	166.26	116.60	181.41	107.01	104.53	99.86
23.560		7.66	7.82	83.10	188.36	109.78	133.46	142.79	96.66	107.79	85.48	82.63	82.87
23.800		4.41	4.34	80.27	160.87	90.59	120.14	139.26	93.96	89.49	75.21	78.93	73.58
24.150		0.00	0.00	2.61	0.00	3.74	10.30	14.42	10.81	10.88	5.34	24.01	28.10
24.350	1STD	19.61	16.95	32.45	99.30	75.98	55.06	47.26	42.77	58.80	55.56	19.20	36.08
24.830		0.22	0.41	5.05	12.53	2.73	6.88	7.47	4.54	7.62	5.08	8.39	14.67
25.120		1.29	2.03	22.92	49.58	20.44	31.18	37.24	23.23	28.02	24.03	28.38	24.77
25.500		0.52	0.60	11.73	23.55	10.21	14.30	20.00	12.05	10.95	8.96	11.59	11.18
25.910		2.34	2.89	49.71	95.52	47.82	66.01	86.70	55.03	53.15	49.49	57.74	51.97
26.360		0.00	0.00	5.64	13.29	3.33	4.42	9.50	3.46	2.86	1.87	2.74	2.88
26.660		0.33	0.32	15.35	34.06	11.41	12.54	25.14	8.49	7.78	6.91	8.73	7.53
27.200		0.27	0.39	0.00	0.00	33.78	18.45	0.00	4.64	3.95	4.28	5.24	4.80
27.530		2.80	2.32	831.77	2894.37	233.33	144.23	1553.40	5.12	1.32	4.66	1.47	3.84
28.060		0.48	0.63	5.18	12.48	7.51	7.34	6.16	5.84	5.73	6.20	6.30	5.53
28.510		0.23	0.34	1.82	3.12	1.48	2.17	2.59	1.38	2.08	2.80	2.93	2.44
28.910	GE PCB#1	0.00	99.89	175.96	392.42	349.43	322.44	347.12	389.93	433.86	788.96	822.58	778.49

Table B-4. Reactor No.4 "Hudson River TI" GC/ECD Results

Reactor no.4 "UPPER HUDSON TI"													
NORMALIZED DATA(NORMALIZED TO ISTD AND SOLIDS CONCENTRATION)													
RT	descript	8/24/87	10/20/87	11/23/87	12/7/87	1/6/88	1/22/88	2/3/88	2/15/88	2/18/88	2/23/88	3/1/88	3/7/88
min		AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N	AREA.N
29.700		0.73	0.55	13.75	24.04	14.72	19.34	22.53	15.68	13.73	10.96	13.06	12.98
30.600	GE PCB#3	0.00	83.95	154.68	306.89	311.14	249.04	272.46	362.66	376.18	642.41	625.27	600.76
30.990		1.09	0.00	18.59	32.60	20.89	29.35	30.02	21.22	19.99	17.81	0.00	17.58
31.450		0.65	0.57	12.36	22.52	13.96	17.98	20.90	14.96	13.60	11.96	13.67	12.91
31.710		0.00	0.61	9.31	16.52	10.36	13.01	15.28	10.72	10.19	9.97	10.73	9.71
32.125		0.00	0.00	2.34	4.19	2.50	3.29	3.89	2.75	2.61	2.39	3.42	2.51
32.380		0.00	0.00	3.40	5.86	3.74	4.67	5.63	3.95	4.31	3.68	3.98	0.00
33.200		0.00	0.17	3.21	5.53	3.44	4.25	5.15	3.71	3.10	2.91	3.45	3.29
33.450		0.00	0.00	3.95	7.26	4.48	5.26	6.18	4.84	4.31	3.72	4.54	4.07
33.750		0.00	0.00	2.73	5.68	3.21	3.38	3.75	3.29	3.44	2.62	3.12	2.68
34.360		0.82	0.00	1.27	2.66	0.00	1.19	1.19	1.42	1.35	1.49	1.59	1.35
35.020	GE PCB#2	0.00	203.81	342.44	702.62	662.97	566.94	639.19	891.41	941.49	1766.69	1800.11	1696.38
35.720		0.89	0.65	8.65	17.14	10.74	9.96	13.10	8.58	7.21	5.27	5.96	6.33
36.010		2.04	2.58	31.91	60.82	36.16	40.02	49.41	34.54	35.95	32.79	37.04	36.08
37.030		0.00	0.00	3.68	25.98	9.22	4.65	0.00	0.00	15.29	0.00	0.00	0.00
37.310		1.16	2.73	27.64	56.63	32.10	34.90	39.29	32.36	31.26	20.79	24.06	21.60
37.750		0.51	0.50	12.06	25.32	15.43	14.64	16.83	14.78	12.97	8.77	9.27	9.00
38.165		0.00	0.47	8.06	32.63	11.89	13.90	4.80	5.47	19.95	4.50	5.76	3.38
38.510		0.70	3.89	41.18	91.19	54.94	82.34	26.39	26.88	93.84	14.37	20.00	22.37
39.430		0.21	0.33	6.45	15.75	8.56	9.04	8.29	7.65	8.91	4.61	5.37	4.44
39.630		0.00	0.00	5.35	9.88	6.38	6.58	7.68	6.08	5.27	3.50	4.84	4.94
40.200		0.61	1.36	16.11	44.33	22.41	24.56	17.99	18.91	29.85	15.26	19.63	15.75
40.730		0.50	4.37	16.84	39.88	34.98	29.33	32.23	45.07	33.80	46.98	50.80	44.36
41.420		0.00	0.00	0.00	1.38	6.77	0.36	0.94	10.34	0.36	3.13	0.00	0.00
41.920		0.38	0.29	6.46	14.72	20.99	9.06	11.20	30.84	7.20	11.54	5.15	5.23
42.530		0.22	0.39	2.58	8.12	19.07	3.89	4.87	19.25	2.56	7.02	2.22	2.37
42.940		1.62	1.54	26.46	52.32	45.40	34.92	43.26	48.28	24.78	28.45	27.75	26.30
43.680		0.73	1.09	11.07	17.48	19.46	135.65	16.86	18.70	9.35	8.24	8.56	8.76
44.080		0.00	0.00	0.41	0.41	1.06	0.39	0.58	2.13	0.41	0.80	0.58	0.55
44.340		4.05	1.43	13.20	19.33	13.79	15.78	19.98	17.31	12.65	12.89	16.55	15.73
44.730	GE PCB#4	0.00	18.87	368.28	652.91	657.36	529.00	601.20	895.24	837.55	1467.99	1405.83	1355.76
45.600		0.00	0.38	1.83	0.76	0.00	1.04	1.68	0.33	0.00	0.00	0.27	2.27
46.250		1.59	0.00	2.93	4.41	20.97	7.54	8.20	2.65	2.47	1.54	2.24	2.11
46.710		0.33	0.20	5.94	10.98	6.33	7.63	8.53	6.05	7.14	3.85	4.98	4.52
47.060		0.37	0.25	5.91	10.65	6.14	7.46	8.66	6.31	6.31	3.64	4.77	4.56
47.780		0.00	0.00	1.59	3.87	1.27	2.49	2.31	1.64	2.57	0.85	1.13	1.26
48.170		0.00	0.30	2.69	8.25	1.93	5.63	4.11	3.34	22.09	3.20	4.97	4.35
48.600		0.51	0.31	12.32	36.00	9.68	21.77	14.76	9.69	22.09	7.26	9.40	8.42
49.965		0.00	0.00	4.29	17.30	9.68	11.94	2.59	2.10	13.14	1.18	1.43	1.47
50.520		23.70	19.21	55.76	249.87	284.46	98.47	14.95	15.61	173.74	73.95	189.77	30.81
51.750		0.22	0.26	4.61	19.44	4.51	12.25	8.35	5.87	12.80	3.78	4.79	5.12
52.230		0.21	0.23	0.42	6.79	1.44	3.75	2.26	1.54	5.53	0.00	0.43	0.90
52.750		0.36	0.36	9.39	20.36	8.15	14.52	14.63	10.22	12.02	5.00	6.02	6.92
53.350		0.38	0.25	7.81	13.68	6.77	11.16	12.35	8.67	7.07	4.13	5.11	6.06
55.070		0.00	0.73	2.00	3.80	3.49	2.87	3.34	4.73	3.84	6.77	8.24	7.28
56.920		0.00	0.00	5.48	11.42	6.37	9.33	8.03	6.96	4.04	2.09	3.28	4.05
57.960		0.00	0.00	1.93	3.42	0.75	2.80	2.98	1.94	1.40	0.00	0.91	0.34
59.860	GE PCB#5	0.91	351.97	714.36	1233.25	1269.43	1028.60	1132.85	1751.54	1514.20	2689.78	2380.74	2374.25

APPENDIX C

Reactor Performance During Phase I, II and III

The following figures represent the results from pH, COD, reactor off gas, effluent PCB concentration and sediment PCB concentration collected from Reactors No.1 through No.4 during the period 8/24/87 to 3/7/88. The raw data is contained in symphony worksheets with the following file names: pH data, CH4-PH.WR1, PH-DATA.PIC; gas production, CH4-PH.WR1, EXP-CH4.PIC; COD of effluent and feed, COD-1A.WR1, COD-EFF.PIC; COD conversion %, COD-1A.WR1, COD-%COD.PIC; PCB effluent concentration, RXR-1A.WR1, RXR-2A.WR1, RXR-3A.WR1, RXR-4A.WR1, RXR-E1A.PIC - RXR-E4A.PIC; PCB sediment concentration, RXR-S1A.WR1, RXR-S2A.WR1, RXR-S3A.WR1, RXR-S4A.WR1, RXR-S1A.PIC - RXR-S4A.PIC.

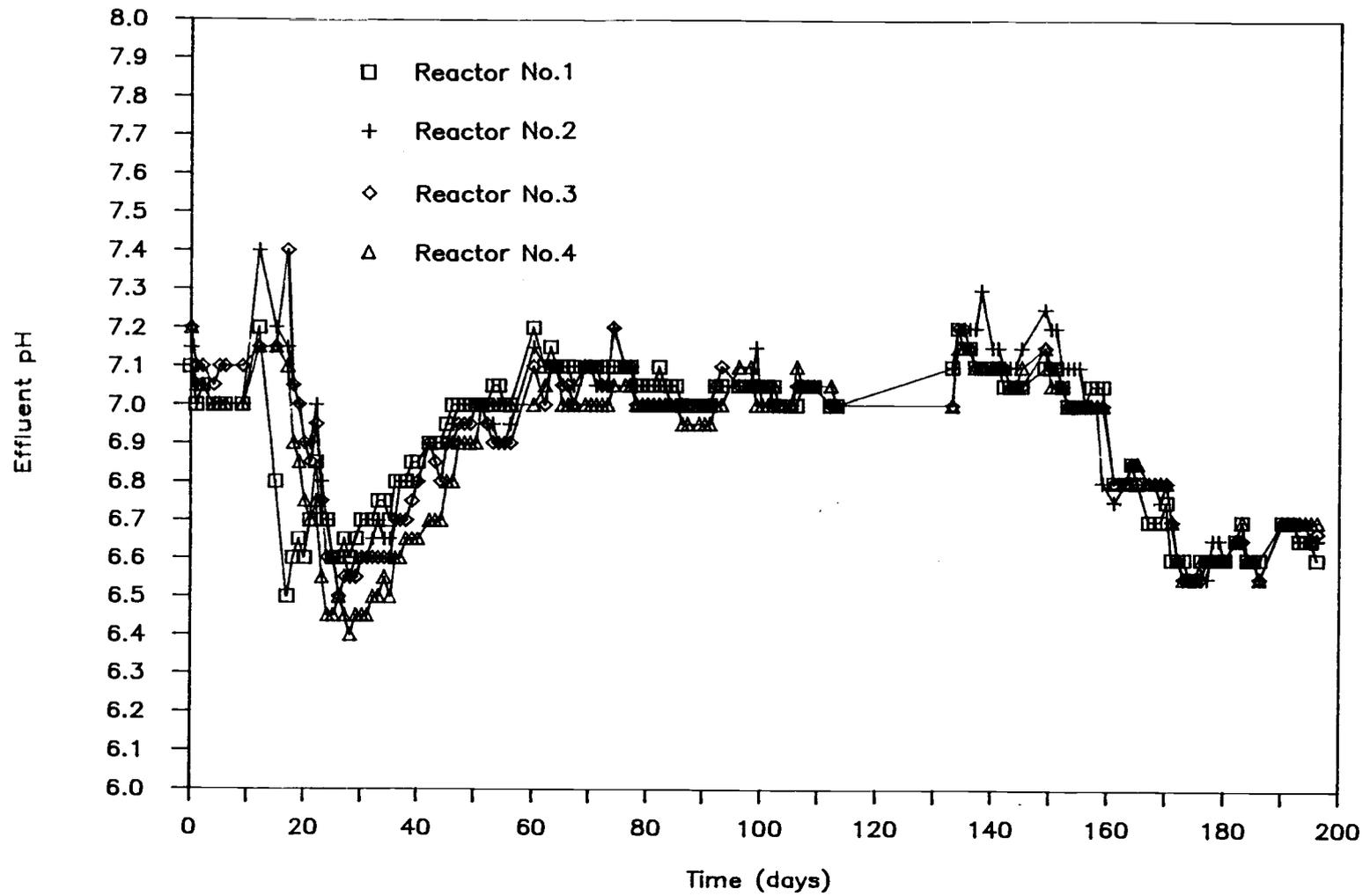


Figure C-1. pH of Reactors No.1, No.2, No.3 and No.4.

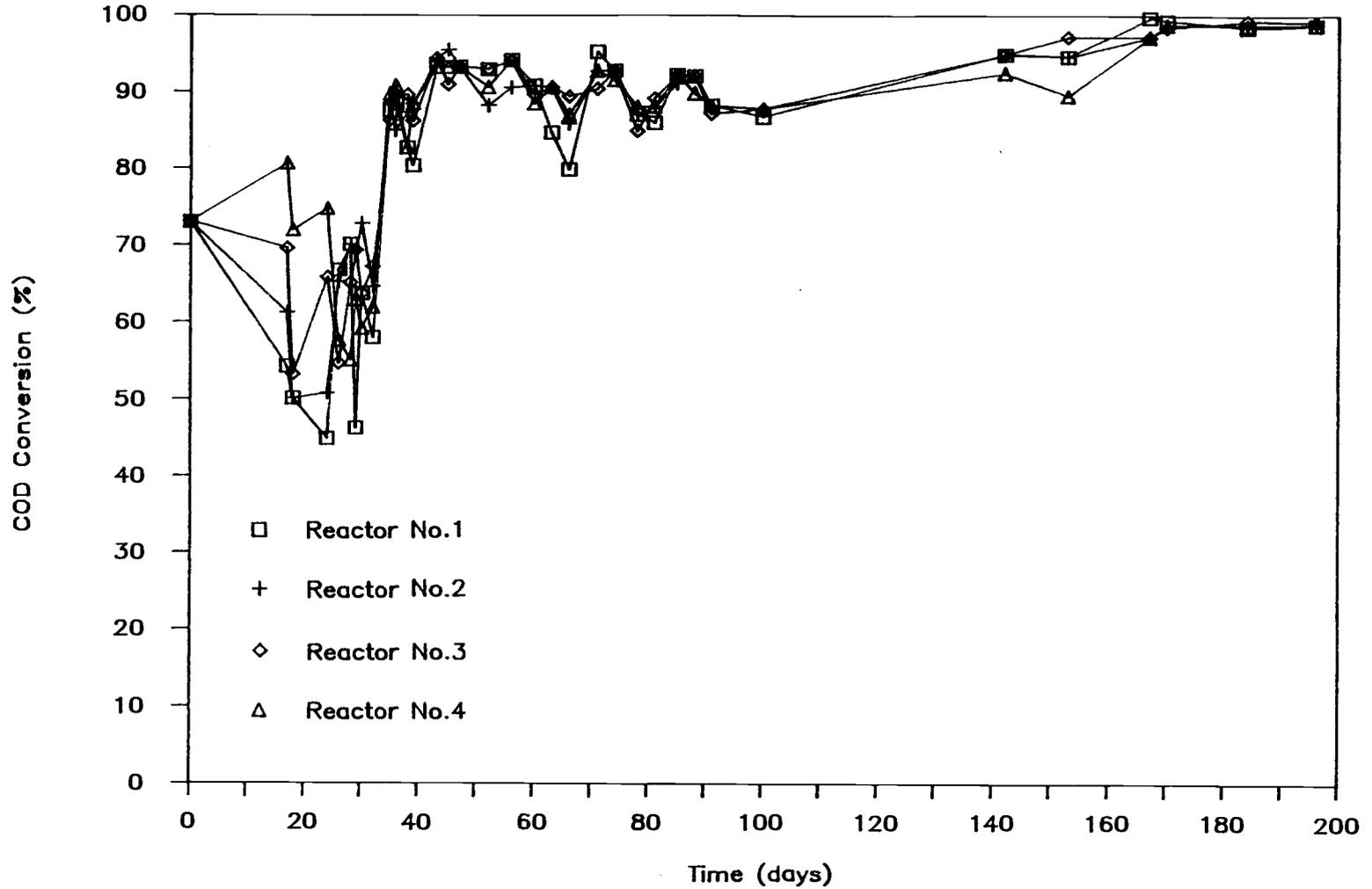


Figure C-2. Chemical Oxygen Demand Removal Efficiency (%) for Reactors No.1, No.2, No.3 and No.4.

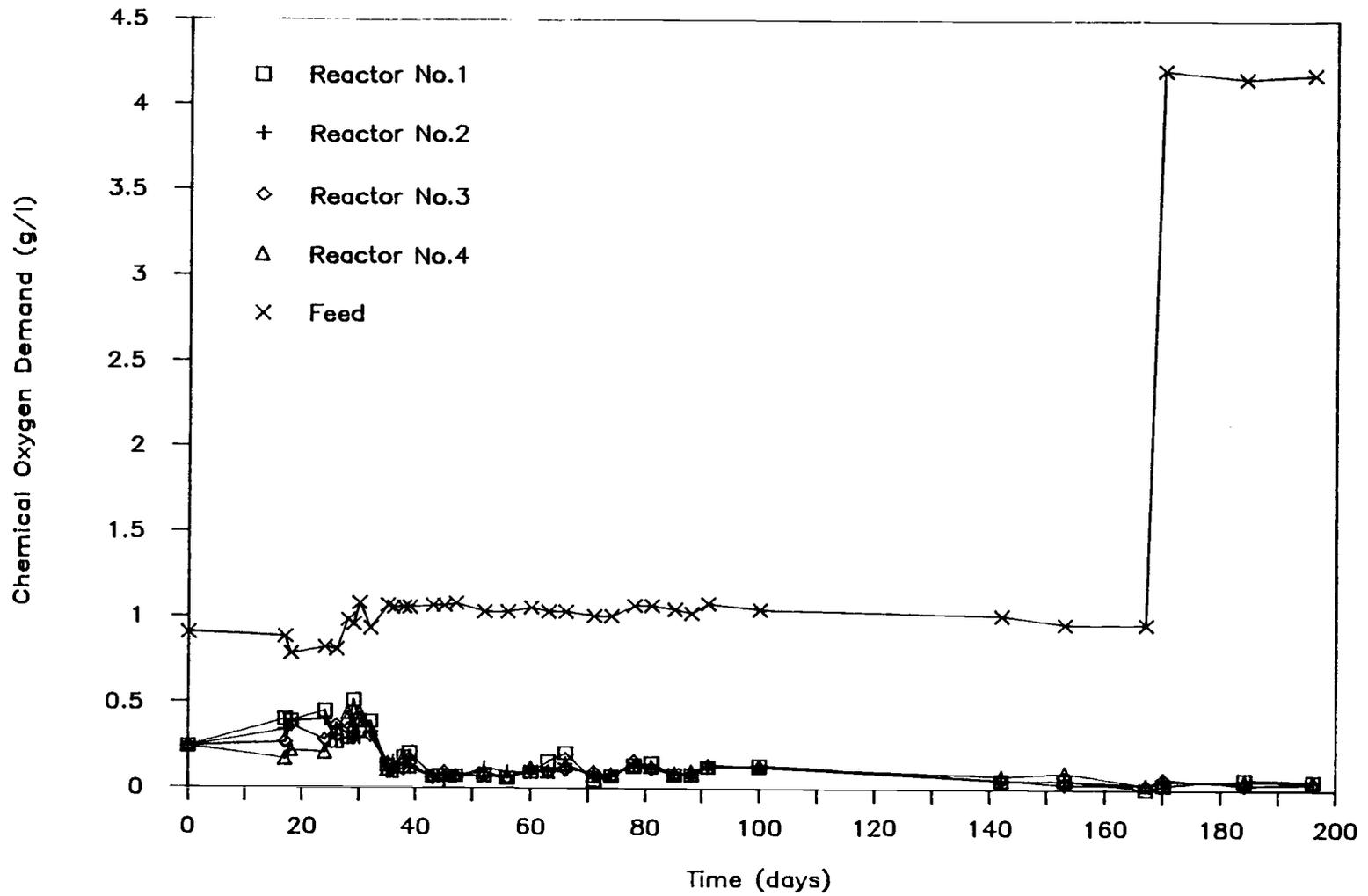


Figure C-3. Chemical Oxygen Demand of Reactor Influent and Reactors No.1, No.2, No.3 and No.4 Effluent.

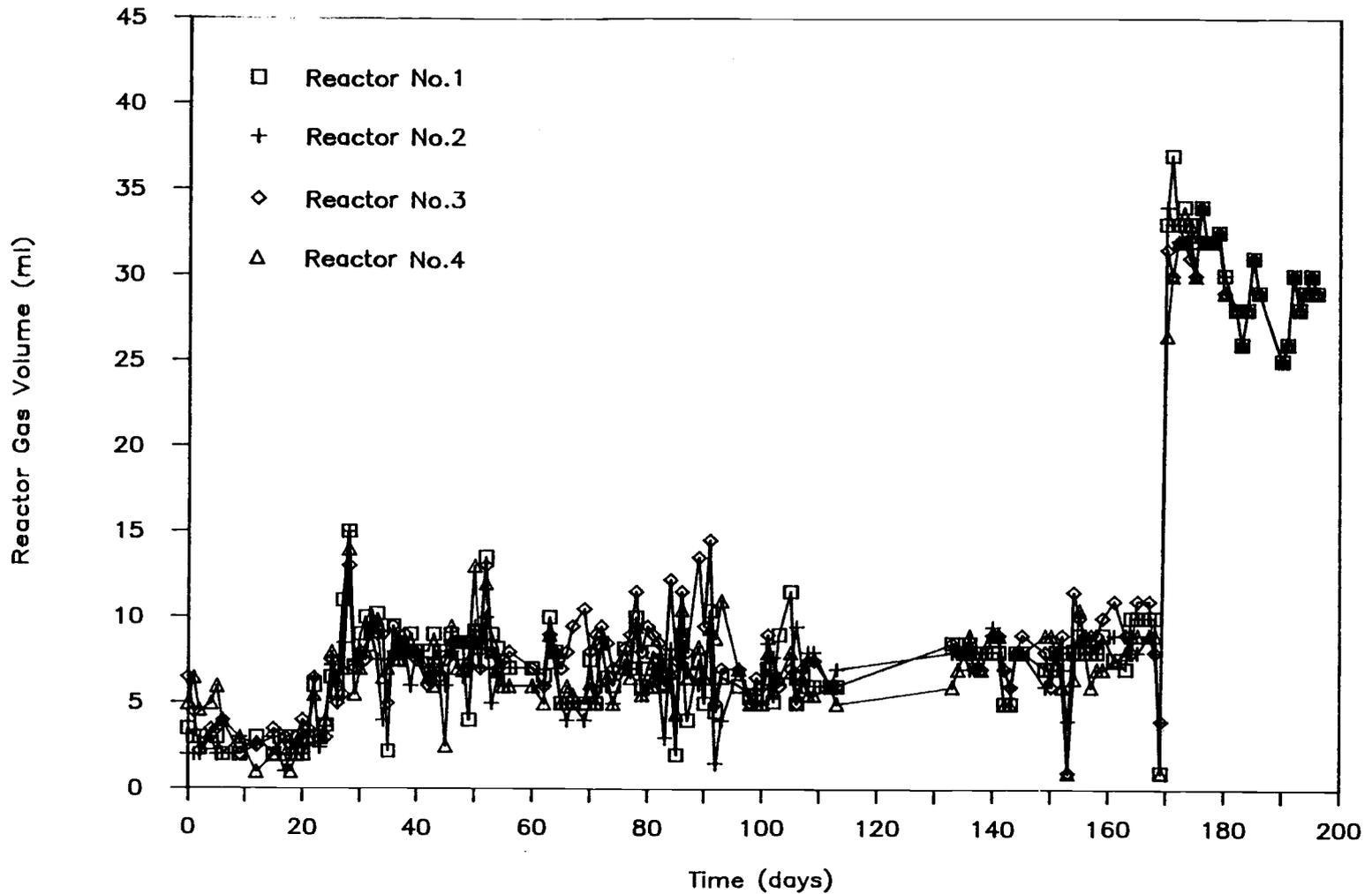


Figure C-4. Experimental Gas Production of Reactors No.1, No.2, No.3 and No.4.

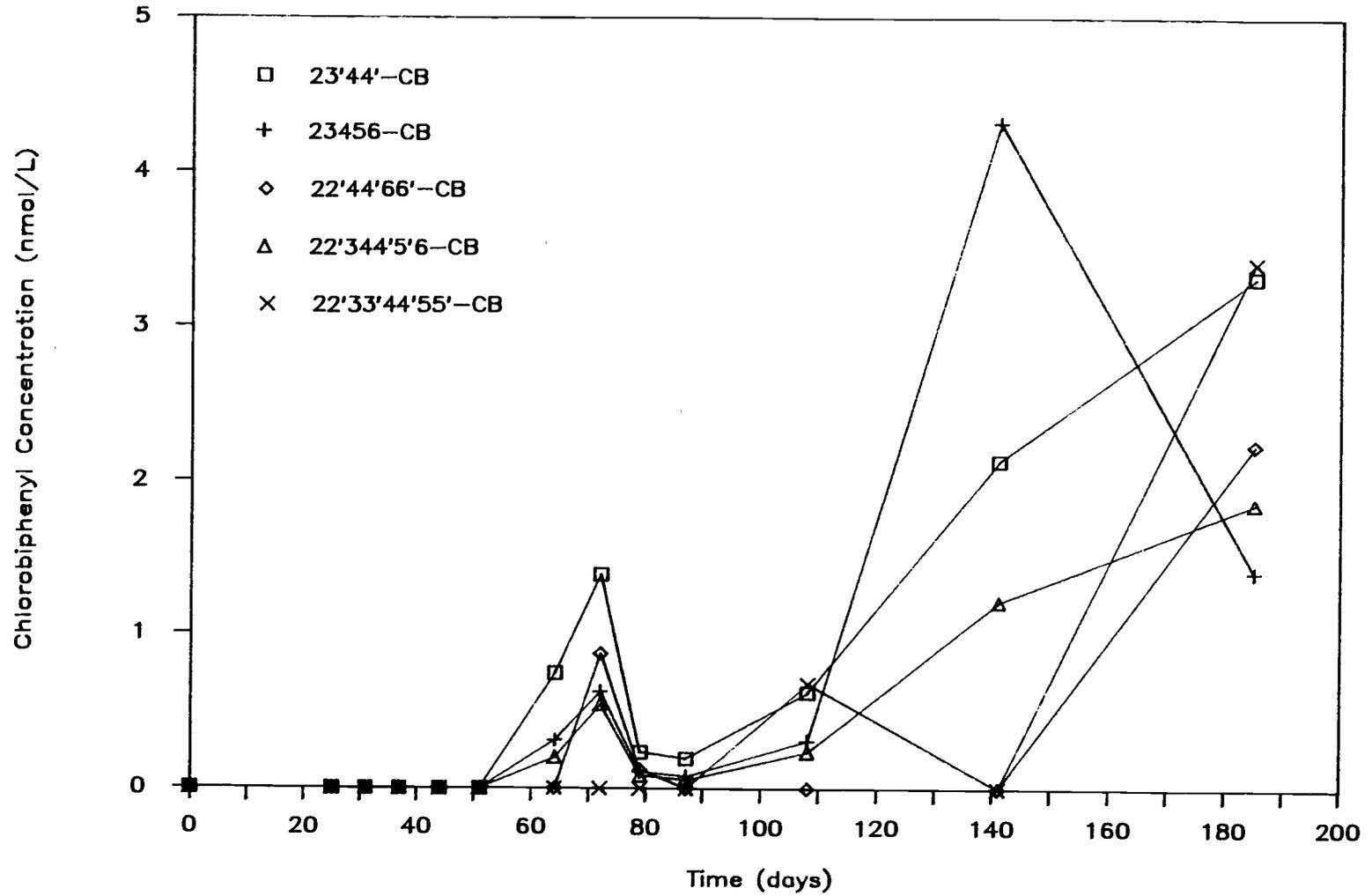


Figure C-5. Reactor No.1 Effluent PCB Concentration.

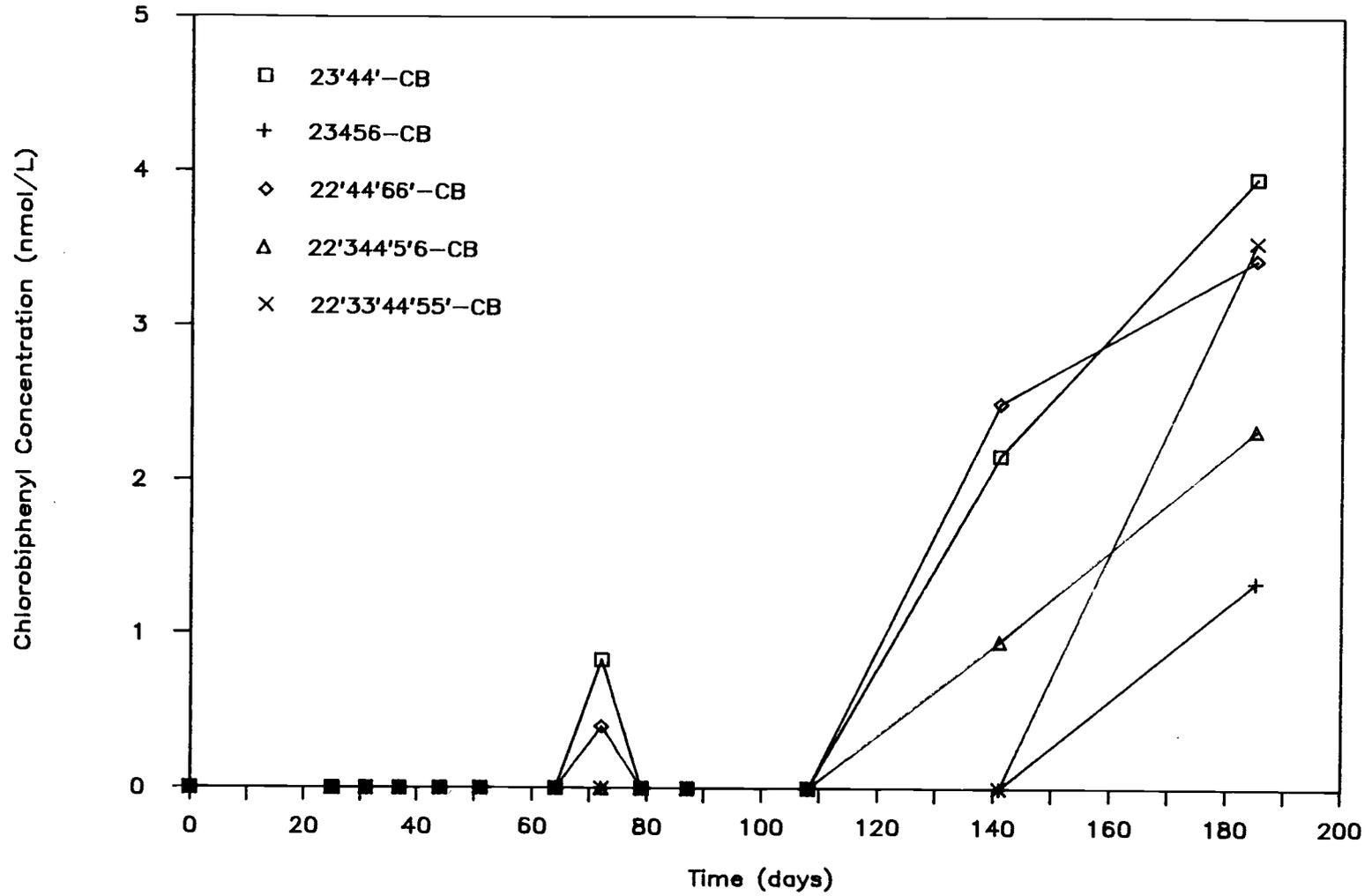


Figure C-6. Reactor No.2 Effluent PCB Concentration.

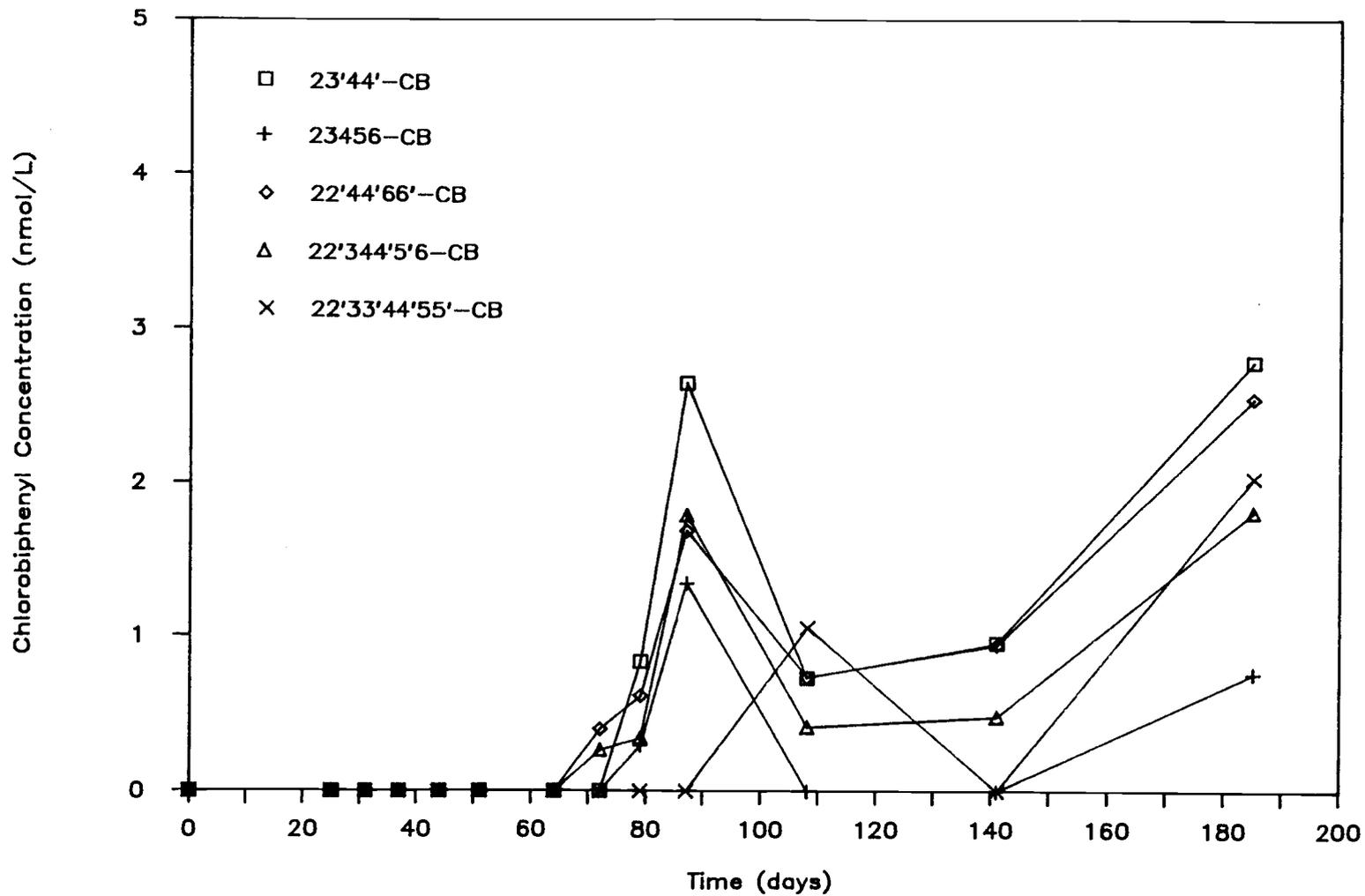


Figure C-7. Reactor No.3 Effluent PCB Concentration.

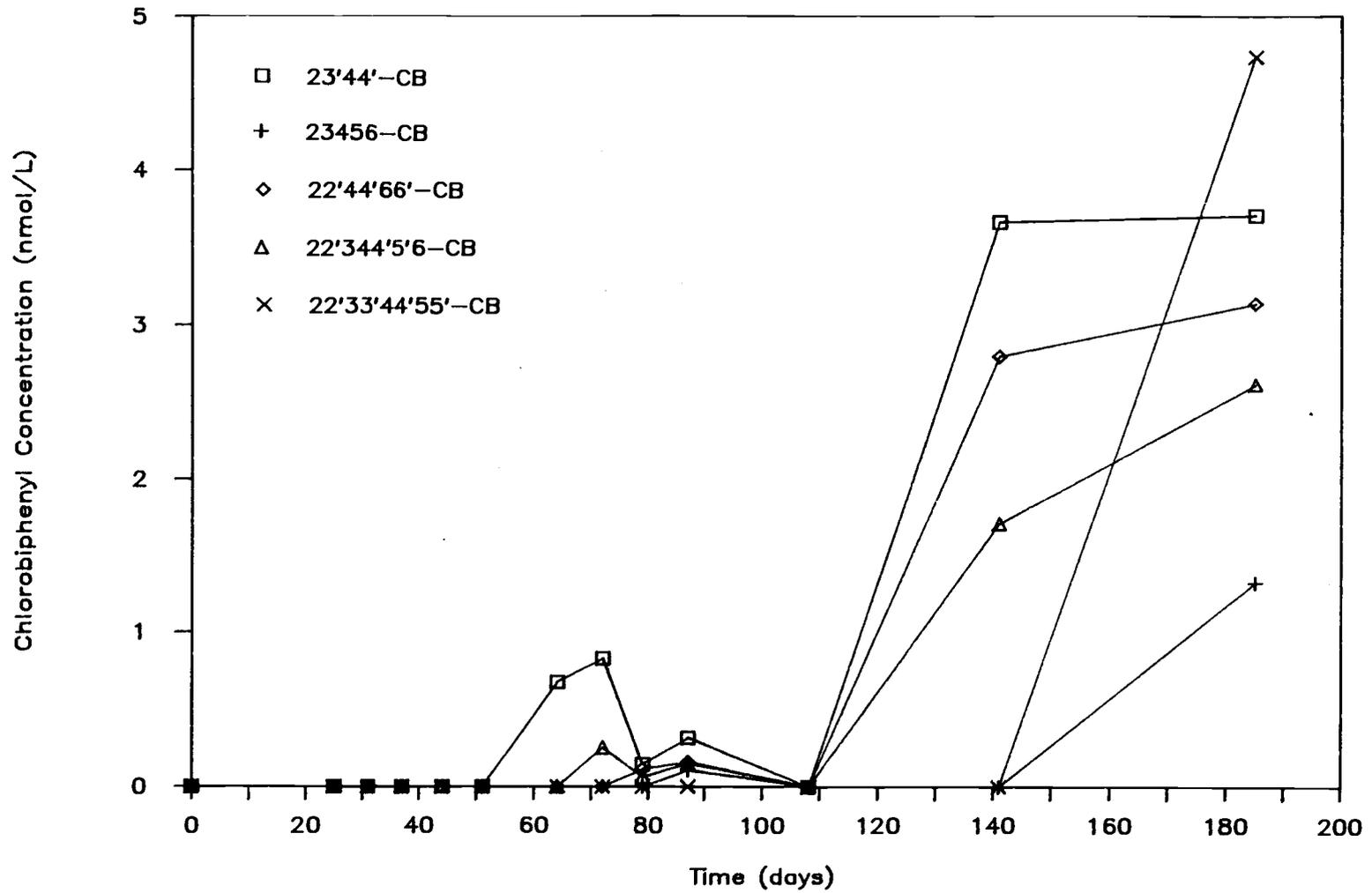


Figure C-8. Reactor No.4 Effluent PCB Concentration.

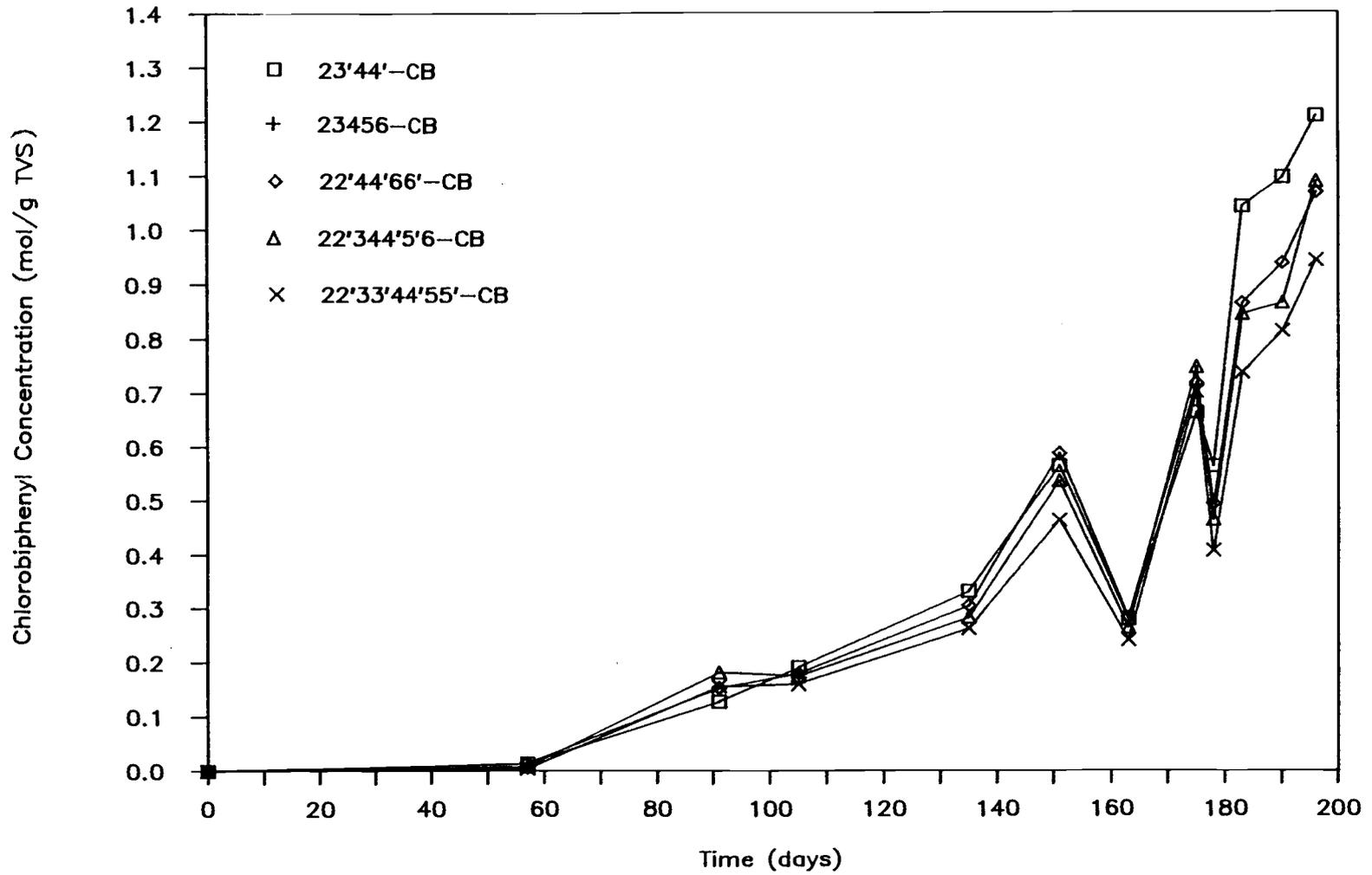


Figure C-9. Reactor No.1 Sediment PCB Concentration.

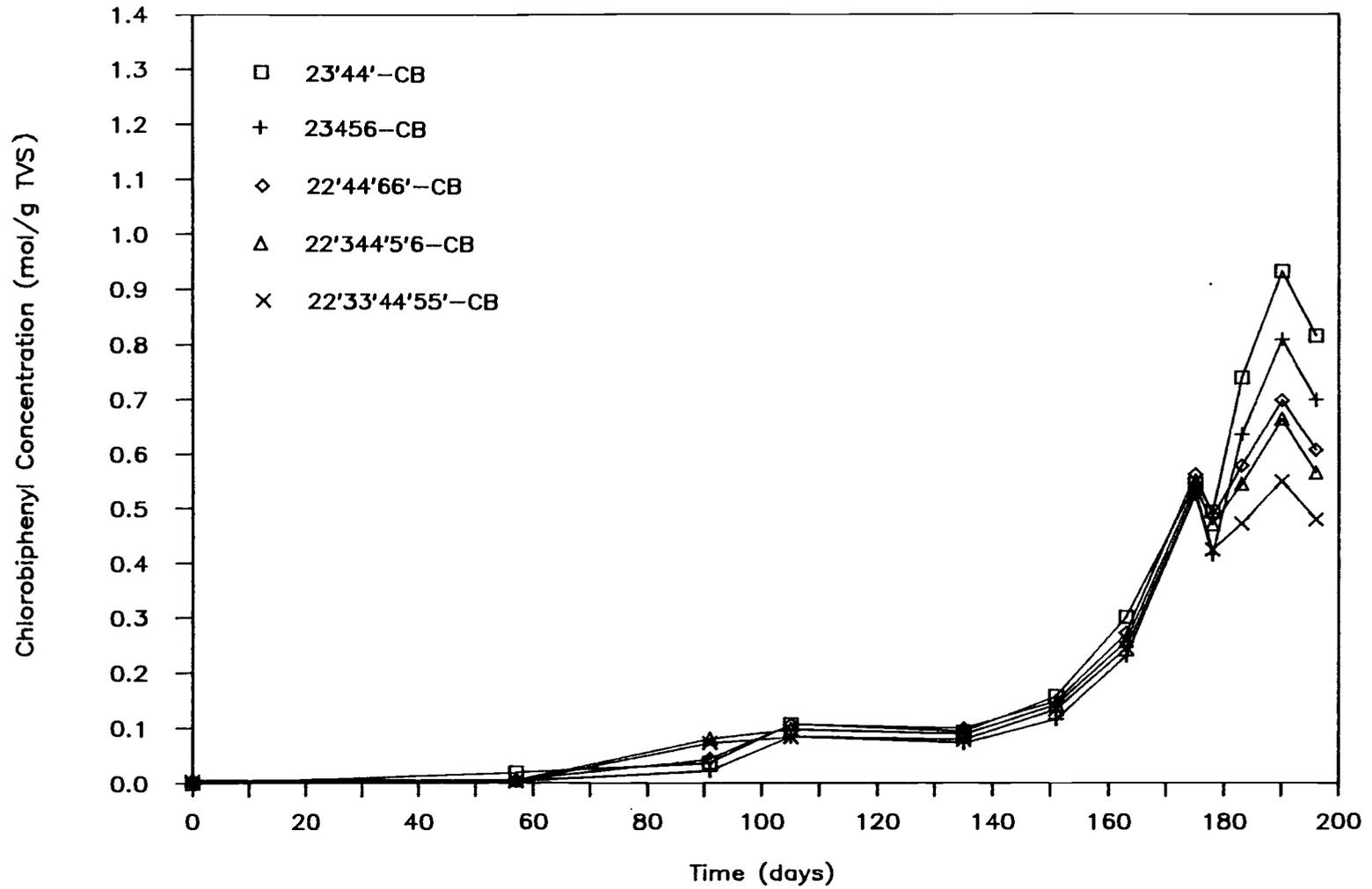


Figure C-10. Reactor No.2 Sediment PCB Concentration.

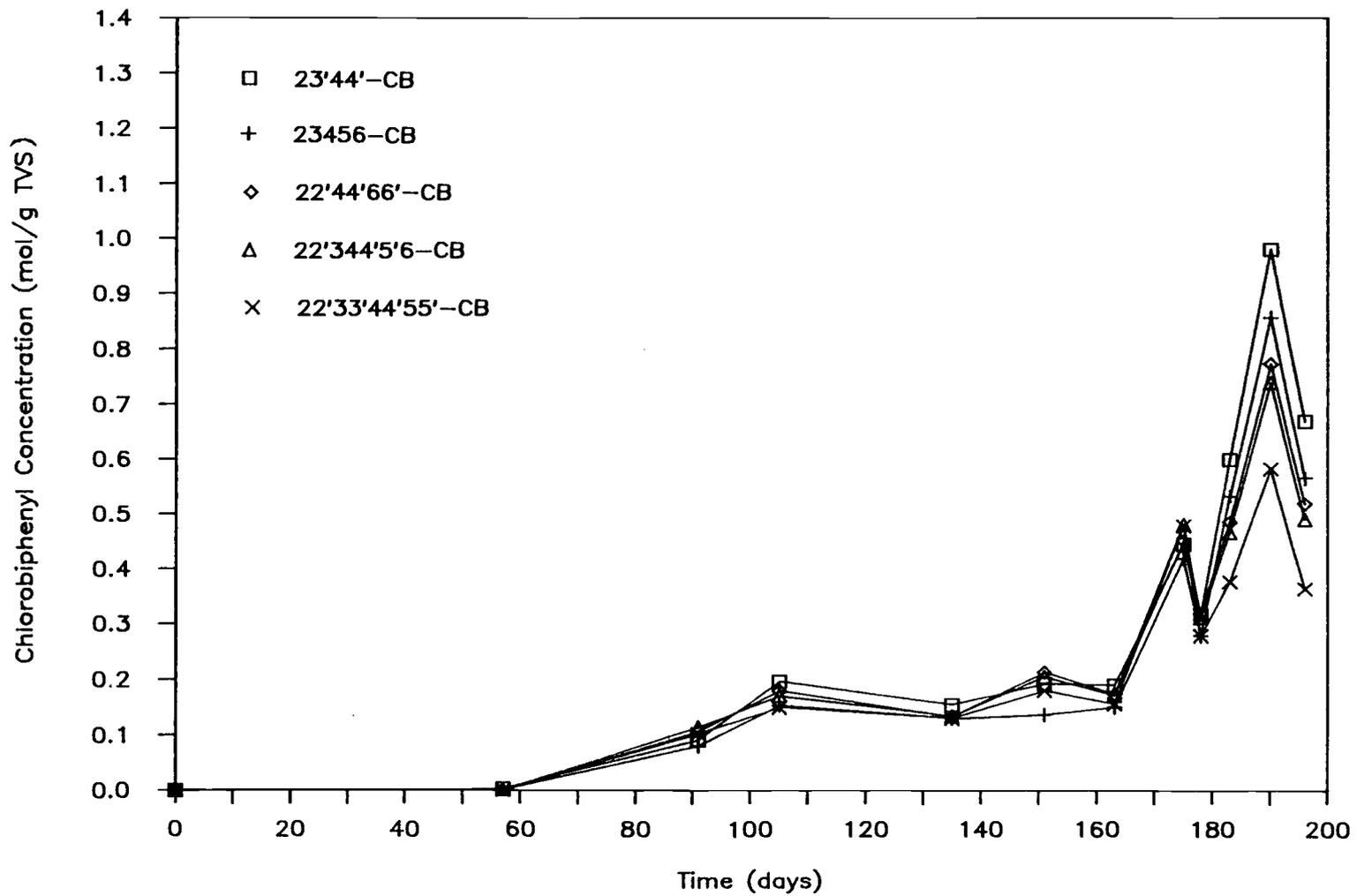


Figure C-11. Reactor No.3 Sediment PCB Concentration.

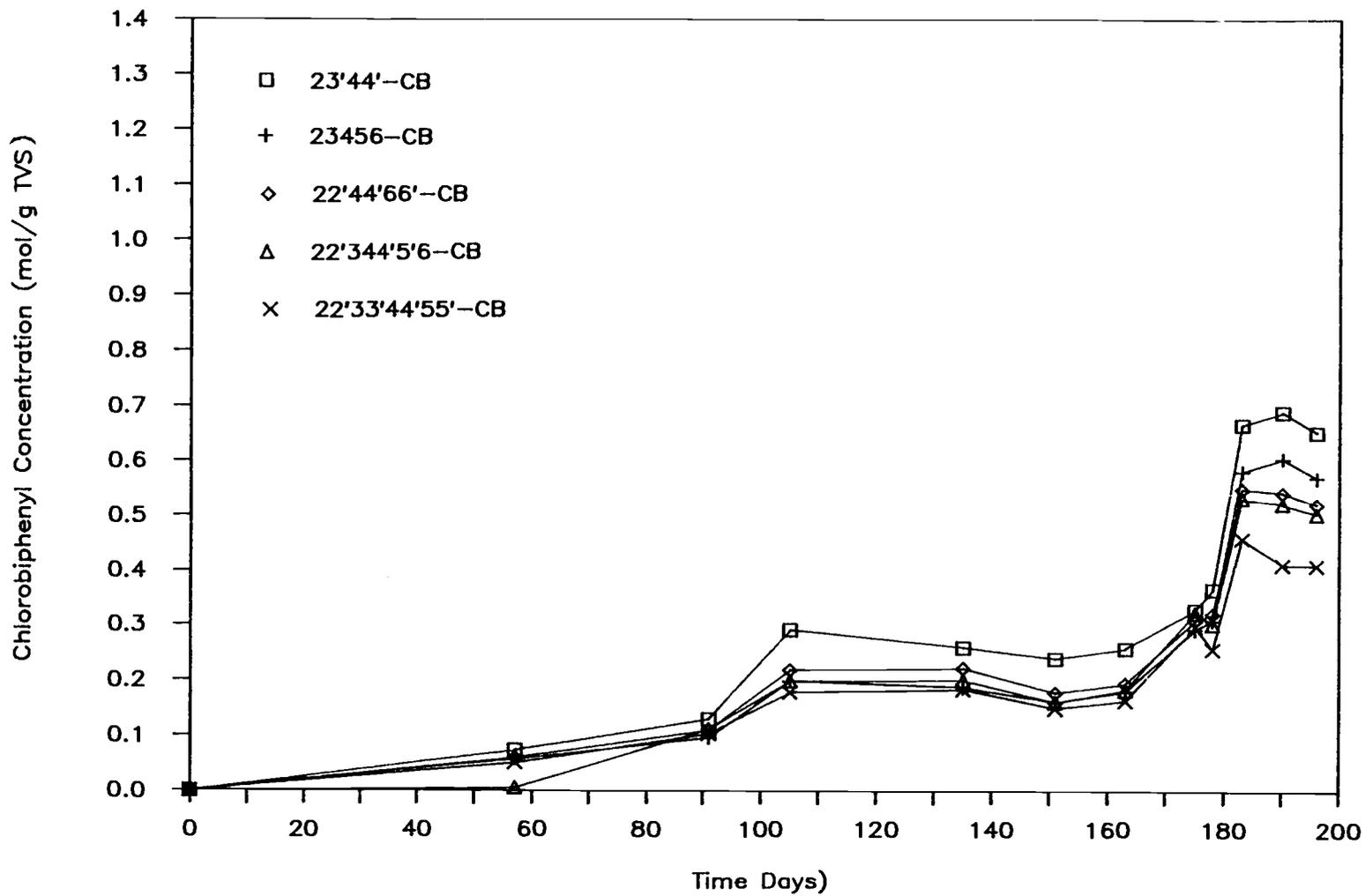


Figure C-12. Reactor No.4 Sediment PCB Concentration.

APPENDIX D

Mass Spectra for 2,3,5,6-tetrachlorobiphenyl

Sediment samples from reactors no.1, no.2, no.3 and no.4 were taken during Phases I, II and III and extracted with acetone and hexane. The extract was analyzed by GC/ECD, and the unknown metabolite was tentatively identified based on its retention time relative to the internal standard. The hexane extract was concentrated from 900 ul down to 25ul and analyzed by GC/MS using the procedure outlined in Chapter one (materials and methods). The tetrachlorobiphenyl was identified based on the comparison between a library of mass spectra of known PCBs and the mass spectra of the unknown metabolite. The metabolite was in sufficient concentration above the background existing PCB contaminants to make a positive identification as a tetrachlorobiphenyl.

The results of the analysis are presented in the following tables and figures.

Thirteen tetrachlorobiphenyls were matched to the unknown peak at RT 24.15 (GC/ECD). The GC/MS RT for this peak was 18.92 minutes and is shown in Table D-1. The total ion chromatograph for the unknown tetra-CB at RT 18.92 minutes (peak no. 5) and the internal standard at RT 18.85 minutes (peak no.4) in the reactor extract is shown in Figure D-1. The total ion chromatograph for the major PCB contaminants and the five parent PCBs, 23'44'-CB (peak no.16), 23456-CB (peak no.18), 22'44'66'-CB (peak no.17), 22'344'5'6-CB (peak no.19) and 22'33'44'55'-CB (peak no.21) are shown in Figure D-2.

Table D-1. PCBs and Their Retention Times in GC/MS Analysis

Compound	R. T.	Scan#	Area	Conc	Units	q
1) *TETRA CHLORO NAPHTHALENE	18.85	970	970	1.00	PPM	83
2) 2-CHLORO BIPHENYL	9.60	437	16705	16705.00	NO CALIB	82
2)D 2-CHLORO BIPHENYL	10.43	485	4508	4508.00	NO CALIB	81
2)D 2-CHLORO BIPHENYL	12.84	624	3009^	3009.00	NO CALIB	40
2)D 2-CHLORO BIPHENYL	14.23	704	1655^	1655.00	NO CALIB	39
3) 4-CHLORO BIPHENYL	9.60	437	16705	16705.00	NO CALIB	86
3)D 4-CHLORO BIPHENYL	10.43	485	4508	4508.00	NO CALIB	85
3)D 4-CHLORO BIPHENYL	12.84	624	3009^	3009.00	NO CALIB	43
3)D 4-CHLORO BIPHENYL	14.23	704	1655^	1655.00	NO CALIB	42
3)D 4-CHLORO BIPHENYL	14.67	729	632	632.00	NO CALIB	45
4)D 4,4,'-DICHLORO BIPHENYL	7.25	302	198	198.00	NO CALIB	27
4)D 4,4,'-DICHLORO BIPHENYL	10.43	485	2003^	2003.00	NO CALIB	14
4) 4,4,'-DICHLORO BIPHENYL	10.95	515	28820	28820.00	NO CALIB	98
4)D 4,4,'-DICHLORO BIPHENYL	11.02	519	205^	205.00	NO CALIB	73
4)D 4,4,'-DICHLORO BIPHENYL	13.64	670	704	704.00	NO CALIB	14
5)D 2,2'-DICHLORO BIPHENYL	7.25	302	198	198.00	NO CALIB	59
5)D 2,2'-DICHLORO BIPHENYL	10.43	485	2003^	2003.00	NO CALIB	38
5)D 2,2'-DICHLORO BIPHENYL	10.95	515	28820	28820.00	NO CALIB	59
5) 2,2'-DICHLORO BIPHENYL	11.02	519	205^	205.00	NO CALIB	73
6)D 2,6'-DICHLORO BIPHENYL	7.25	302	198	198.00	NO CALIB	28
6)D 2,6'-DICHLORO BIPHENYL	10.43	485	2003^	2003.00	NO CALIB	15
6) 2,6'-DICHLORO BIPHENYL	10.95	515	28820	28820.00	NO CALIB	94
6)D 2,6'-DICHLORO BIPHENYL	11.02	519	205^	205.00	NO CALIB	73
6)D 2,6'-DICHLORO BIPHENYL	13.64	670	704	704.00	NO CALIB	10
7)D 2,4'-DICHLORO BIPHENYL	7.25	302	198	198.00	NO CALIB	31
7)D 2,4'-DICHLORO BIPHENYL	10.43	485	2003^	2003.00	NO CALIB	17
7) 2,4'-DICHLORO BIPHENYL	10.95	515	28820	28820.00	NO CALIB	90
7)D 2,4'-DICHLORO BIPHENYL	11.02	519	205^	205.00	NO CALIB	76
7)D 2,4'-DICHLORO BIPHENYL	13.64	670	704	704.00	NO CALIB	3
8) TRICHLORO BIPHENYL	21.75	1137	916	916.00	NO CALIB	27
9)D 2,3'5,5' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	90
9) 2,3'5,5' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	94
9)D 2,3'5,5' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	90
9)D 2,3'5,5' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	89
9)D 2,3'5,5' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	90
10)D 2,3'4'5 TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	94
10) 2,3'4'5 TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	97
10)D 2,3'4'5 TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	93
10)D 2,3'4'5 TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	90
10)D 2,3'4'5 TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	93
11)D 2,3,5,6 TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	94
11) 2,3,5,6 TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	95
11)D 2,3,5,6 TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	93
11)D 2,3,5,6 TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	89
12) 2,3,4,5 TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	95
12)D 2,3,4,5 TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	94
12)D 2,3,4,5 TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	93
12)D 2,3,4,5 TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	87
12)D 2,3,4,5 TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	91
13) 2,2'6,6' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	97
13)D 2,2'6,6' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	93
13)D 2,2'6,6' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	91
13)D 2,2'6,6' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	85
13)D 2,2'6,6' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	89
14) 2,2'5,5' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	86
14)D 2,2'5,5' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	79
14)D 2,2'5,5' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	74
14)D 2,2'5,5' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	67
14)D 2,2'5,5' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	69
15) 2,2'4,5' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	87
15)D 2,2'4,5' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	81

Table D-1. PCBs and Their Retention Times in GC/MS Analysis

	Compound	R. T.	Scan#	Area	Conc	Units	q
15)D	2,2'4,5' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	77
15)D	2,2'4,5' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	70
15)D	2,2'4,5' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	71
16)D	2,2',4,4' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	86
16)D	2,2',4,4' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	92
16)D	2,2',4,4' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	85
16)D	2,2',4,4' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	97
16)	2,2',4,4' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	98
17)	2,2'3,5' TETRACHLORO BIPHENYL	16.82	853	2269	2269.00	NO CALIB	57
17)D	2,2'3,5' TETRACHLORO BIPHENYL	18.40	944	2315	2315.00	NO CALIB	48
17)D	2,2'3,5' TETRACHLORO BIPHENYL	18.62	957	1362	1362.00	NO CALIB	52
17)D	2,2'3,5' TETRACHLORO BIPHENYL	18.76	965	1520	1520.00	NO CALIB	39
17)D	2,2'3,5' TETRACHLORO BIPHENYL	22.87	1201	3895	3895.00	NO CALIB	53
18)	2,2'3,3' TETRACHLORO BIPHENYL	16.82	853	2269	2269.00	NO CALIB	63
18)D	2,2'3,3' TETRACHLORO BIPHENYL	18.40	944	2315	2315.00	NO CALIB	52
18)D	2,2'3,3' TETRACHLORO BIPHENYL	18.62	957	1362	1362.00	NO CALIB	57
18)D	2,2'3,3' TETRACHLORO BIPHENYL	18.76	965	1520	1520.00	NO CALIB	46
18)D	2,2'3,3' TETRACHLORO BIPHENYL	22.87	1201	3895	3895.00	NO CALIB	51
19)D	3,3'4,4' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	89
19)	3,3'4,4' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	96
19)D	3,3'4,4' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	87
19)D	3,3'4,4' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	93
19)D	3,3'4,4' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	93
20)	3,3',5,5' TETRACHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	96
20)D	3,3',5,5' TETRACHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	89
20)D	3,3',5,5' TETRACHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	88
20)D	3,3',5,5' TETRACHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	82
20)D	3,3',5,5' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	85
21)D	2,3',4,4' TETRACHLORO BIPHENYL	20.76	1080	215	215.00	NO CALIB	77
21)D	2,3',4,4' TETRACHLORO BIPHENYL	20.93	1090	593	593.00	NO CALIB	83
21)	2,3',4,4' TETRACHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	95
21)D	2,3',4,4' TETRACHLORO BIPHENYL	21.54	1125	262^	262.00	NO CALIB	87
22)	TETRA CHLORO BIPHENYL	16.84	854	3037	3037.00	NO CALIB	86
22)D	TETRA CHLORO BIPHENYL	18.40	944	3622	3622.00	NO CALIB	78
22)D	TETRA CHLORO BIPHENYL	18.76	965	2309	2309.00	NO CALIB	73
22)D	TETRA CHLORO BIPHENYL	18.92	974	11562	11562.00	NO CALIB	66
22)D	TETRA CHLORO BIPHENYL	21.25	1108	71658	71658.00	NO CALIB	68
23)D	2,3,4,5,6 PENTACHLORO BIPHENYL	22.43	1176	437	437.00	NO CALIB	83
23)	2,3,4,5,6 PENTACHLORO BIPHENYL	22.85	1200	32107^	32107.00	NO CALIB	96
23)D	2,3,4,5,6 PENTACHLORO BIPHENYL	22.94	1205	455^	455.00	NO CALIB	89
23)D	2,3,4,5,6 PENTACHLORO BIPHENYL	23.11	1215	1444	1444.00	NO CALIB	87
24)D	PENTA CHLORO BIPHENYL	20.83	1084	164	164.00	NO CALIB	81
24)D	PENTA CHLORO BIPHENYL	21.82	1141	585	585.00	NO CALIB	86
24)D	PENTA CHLORO BIPHENYL	22.03	1153	491	491.00	NO CALIB	89
24)	PENTA CHLORO BIPHENYL	22.85	1200	31997^	31997.00	NO CALIB	93
24)D	PENTA CHLORO BIPHENYL	23.11	1215	1444	1444.00	NO CALIB	82
25)	2,2'4,4'6,6'HEXACHLORO BIPHENYL	21.75	1137	46043	46043.00	NO CALIB	93
26)D	HEXA CHLORO BIPHENYL	21.75	1137	46043	46043.00	NO CALIB	82

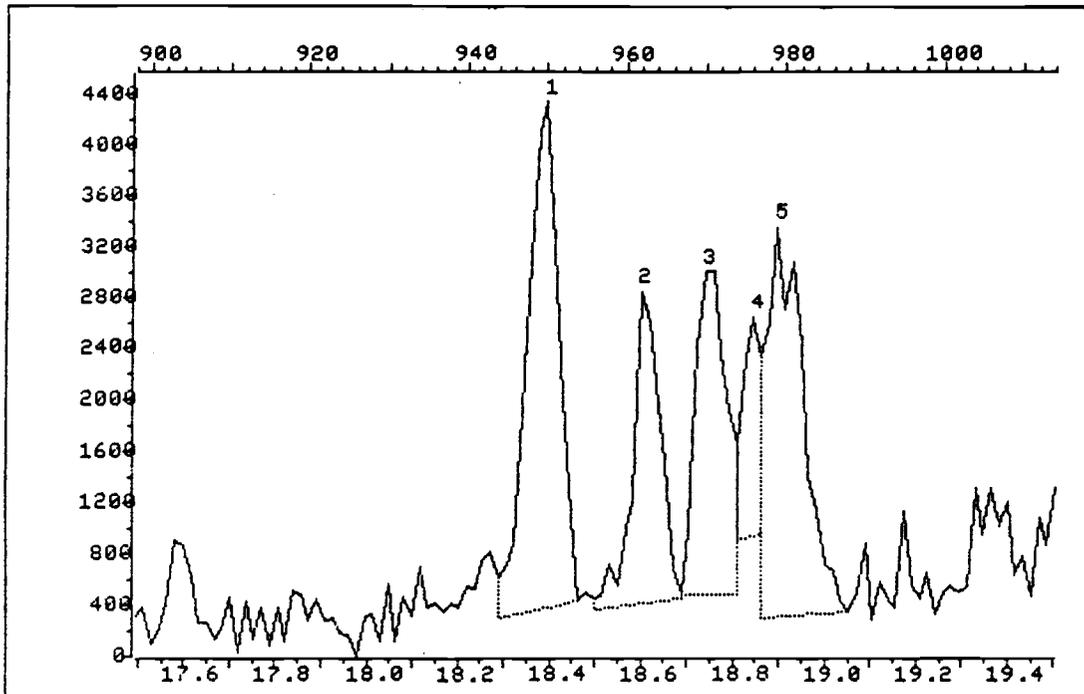


Figure D-1. Total Ion Chromatogram of the Unknown Tetra-CB at RT 18.92 Minutes (Peak No.5) and the Internal Standard, Tetrachloronaphthalene at RT 18.85 Minutes (Peak no.4)

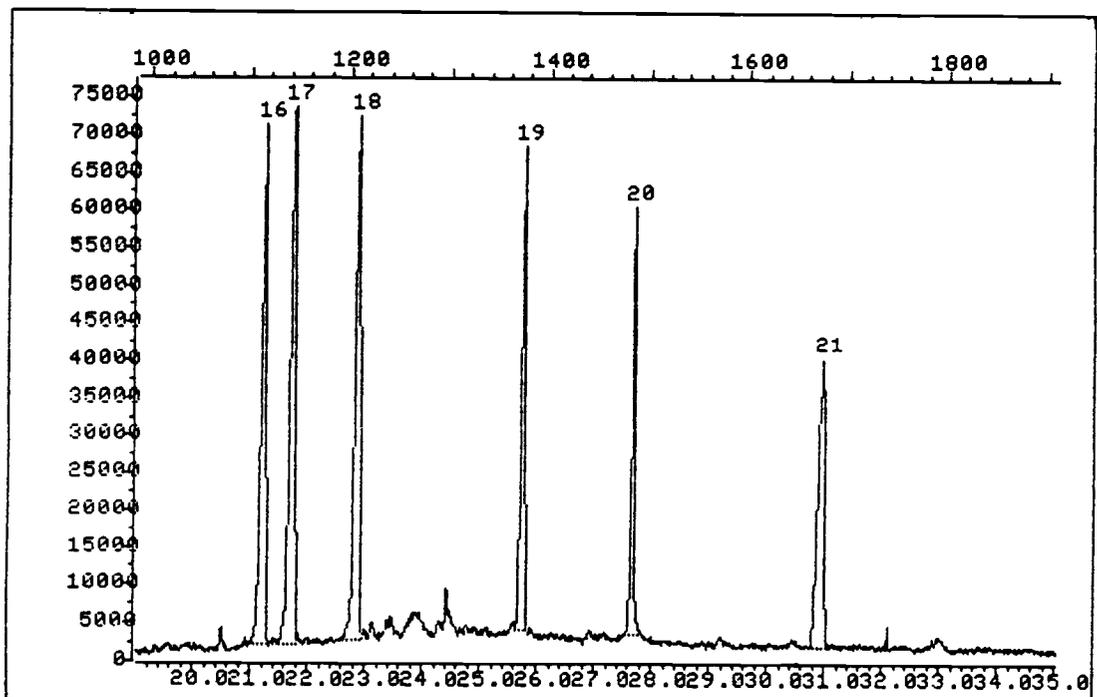
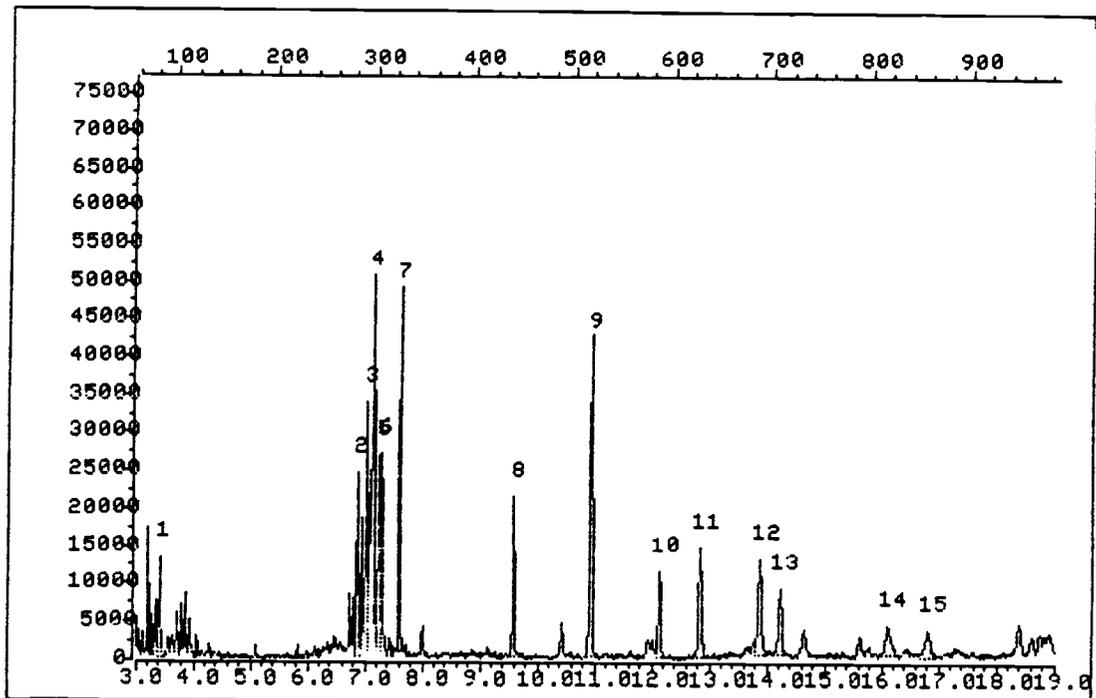


Figure D-2. Total Ion Chromatogram of the Sediment Extract Showing the Major Ions, and the Parent PCB Compounds at Peaks No. 16, No.17, No.18, No.19 and No.21.

APPENDIX E**Cochromatography Results**

Figure E-1 represents the results from cochromatography of a Reactor No.4 sediment extract (3/7/88) containing the unknown metabolite and a 2356-CB stock solution, respectively.

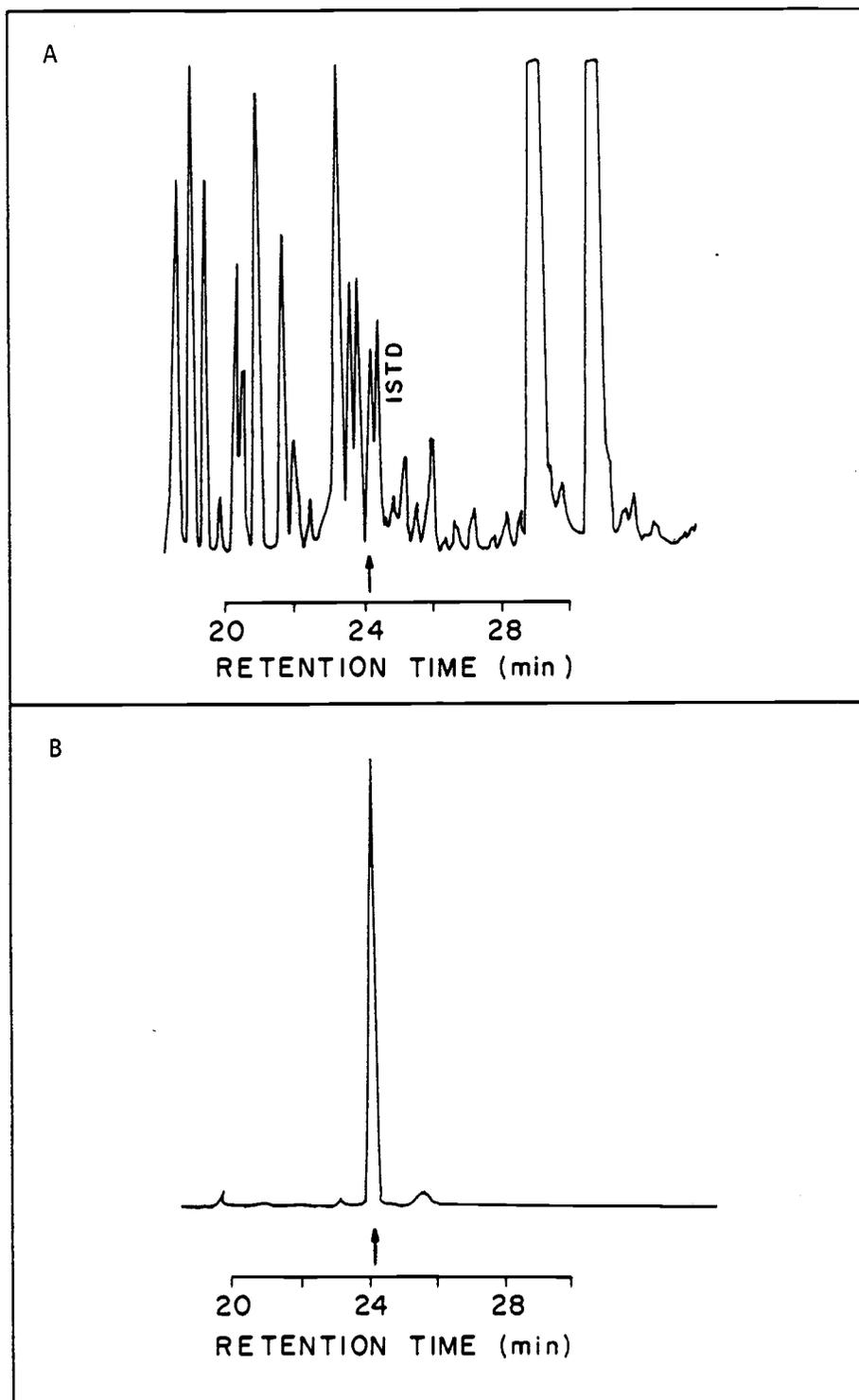


Figure E-1. DB-5 Chromatograph of the Unknown Peak at RT 24.15 Minutes and a 2356-tetrachlorobiphenyl. (A) Unknown Peak at RT 24.15 Minutes. (B) 2356-tetrachlorobiphenyl at RT 24.15 Minutes.