

SIAD

Nano-Photonics

PCB Reduction Treatment Study

PCB Recent History:

In 1973, the use of PCBs (polychlorinated biphenyls) was banned in "open" or "dissipative" sources.

PCB production and export in the U.S. was halted in October 1977 under the auspices of the Toxic Substances Control Act (TSCA). Use and import of PCBs were banned in Japan in 1972. In addition to the production ban instituted under TSCA, EPA regulates PCBs, as Aroclors, under a wide range of environmental statutes. For example, Aroclors are regulated in effluent guidelines developed under the Clean Water Act and administered through the National Pollutant Discharge Elimination System (NPDES). The Office of Water has established water quality criteria (WQC)

Concern over the toxicity and persistence (chemical stability) of PCBs in the environment led the United States Congress to ban their domestic production in 1979, although some use continues in closed systems such as capacitors and transformers. "Enclosed uses" of PCBs include capacitors, insulating fluids in transformers, vacuum pump fluids, and hydraulic fluids.

Estimates have put the total global production of PCBs on the order of 1.5 million tons. The United States was the single largest producer with over 600,000 tons produced between 1930 and 1977. The European region follows with nearly 450,000 tons through 1984. It is unlikely that a full inventory of global PCB production will ever be accurately tallied, as there were factories in Poland, East Germany, and Austria that produced unknown amounts of PCBs.

PCBs are the focus of one of the largest environmental cleanup projects in the United States. From 1947 to 1977, about 1.1 million pounds of PCBs were deposited in the bed of the upper Hudson River by two General Electric Co. capacitor manufacturing plants. GE is now bearing most of the estimated \$750 million cost of dredging PCBs out of a number of "hot spots" in the riverbed.

Current Reduction Methods:

These can be separated into three distinct categories: physical, microbial and chemical reduction. Included are incineration, ultrasound, irradiation, pyrolysis, microbial, nucleophilic aromatic substitution, reducing agents, photochemistry and organometallic. All have advantages and disadvantages (attachment)

Regulatory Criteria (EPA);

The EPA has established maximum contaminant level (MCL) for each contaminant. Maximum contaminant level is defined as "the maximum permissible level of a contaminant in water which is delivered to any user of a public water system". The Safe Drinking Water Act (SDWA) Amendments of 1996 contain a provision which amended Section 1401(4) regarding the definition of a public water system (PWS).

"A public water system (PWS) is a system for the provision to the public of water for human consumption through pipes or other constructed conveyances".

EPA has set an enforceable regulation for MCL (maximum contaminant limit) of polychlorinated biphenyls. Under the Safe Drinking Water Act, EPA has established a MCL for total Aroclor at 0.0005 mg/l or 500 ppt. (NOTE: 0.0005 mg/l = 0.50 ug/l). MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. Any water with all contaminant levels below MCL is officially *safe*

Under the auspices of the Resource Conservation and Recovery Act (RCRA) EPA has placed Aroclors on Appendix VIII (hazardous substances) and Appendix IX (groundwater monitoring), and has established a Universal Treatment Standard (UTS) of 1 mg/kg of Aroclors in non-wastewaters and 0.10 mg/l in wastewaters. PCBs are included in the Toxics Release Inventory (TRI) developed under the Emergency Planning and Community Right to Know Act (EPCRA).

Methodology;

Ten quarts (2.5 gal.) of PCB (Aroclor 1254 & 1260) contaminated, industrial water was obtained from a single facility and contained in a five gallon sealed container. Each sample for testing, including the control sample, was removed from the five gallon sealed container preceded by stirring the contaminated water prior to extracting contents for each sample. The control sample and each subsequent SIAD processed sample was placed into a one liter, labeled, glass sampling jars supplied by Waste Stream Technologies. All samples were placed in a thermal chest and transported to Waste Stream Technologies for analysis within one hour from SIAD processing.

Each SIAD sample (A – D) was processed independently. Two quarts of the PCB contaminated water was poured into the SIAD holding tank. The gas extraction fan was fastened to the top of the SIAD processing tank and plumbed into a gas extraction catch container. The mixer started and continued through each processing at 600 rpm. The SIAD lamp was ignited and the oxygen valve turned on. Oxygen bled into the system at a very low rate. Due to the size of the oxygen bottles (in all trials except the initial 5 minute trial) the contents of the oxygen bottle was consumed prior to completion of each trial (four oxygen bottles were used – one each for samples A & B and two bottles for sample C). It should be noted that an oxygen generator would be more efficient and utilized in future SIAD systems.

Each independent SIAD sampling process timing began when the SIAD lamp reached peak voltage (144VAC). Lamp warm-up time (0 to 144VAC) took approximately 2 minutes. After each process time elapsed, the SIAD system was turned off and the processed water was emptied into the labeled sampling jar from the drain valve on the SIAD processing tank. The labeled sample jar was immediately sealed. The tank was drained completely. The excess processed water from the tank was placed in a separate 2.5 gallon container for disposal. The SIAD processing system and tank were completely wiped clean prior to beginning the next sample's SIAD processing. Each sampling (A – C) was processed independently in accordance with the preceding format except for the processing time differences. Sample D was processed the same as sample B except oxygen was not supplied. Sample D was utilized to compare SIAD processing with and without oxygen.

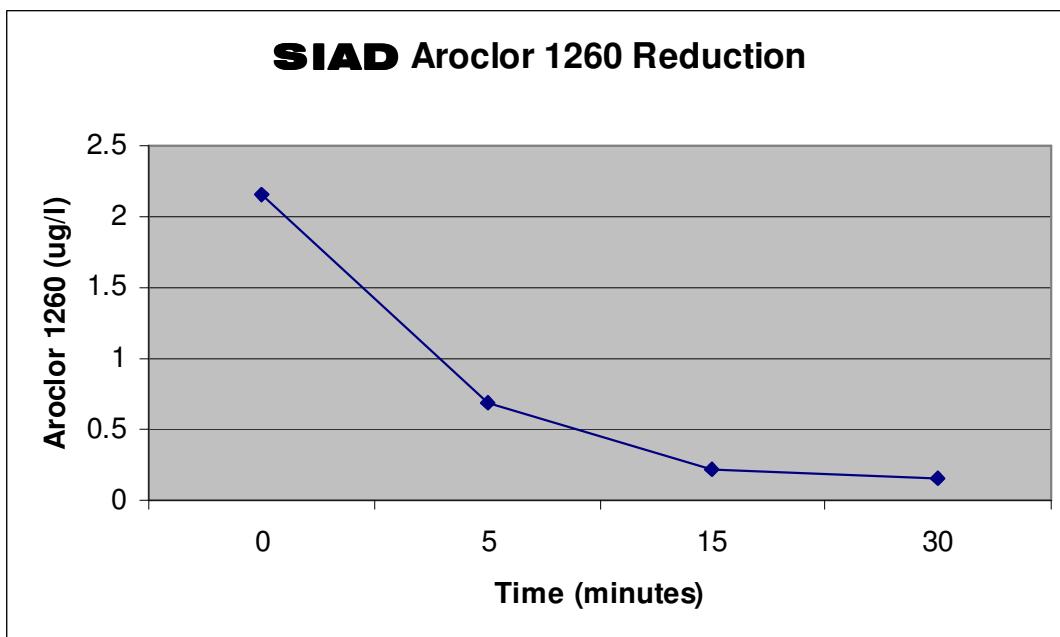
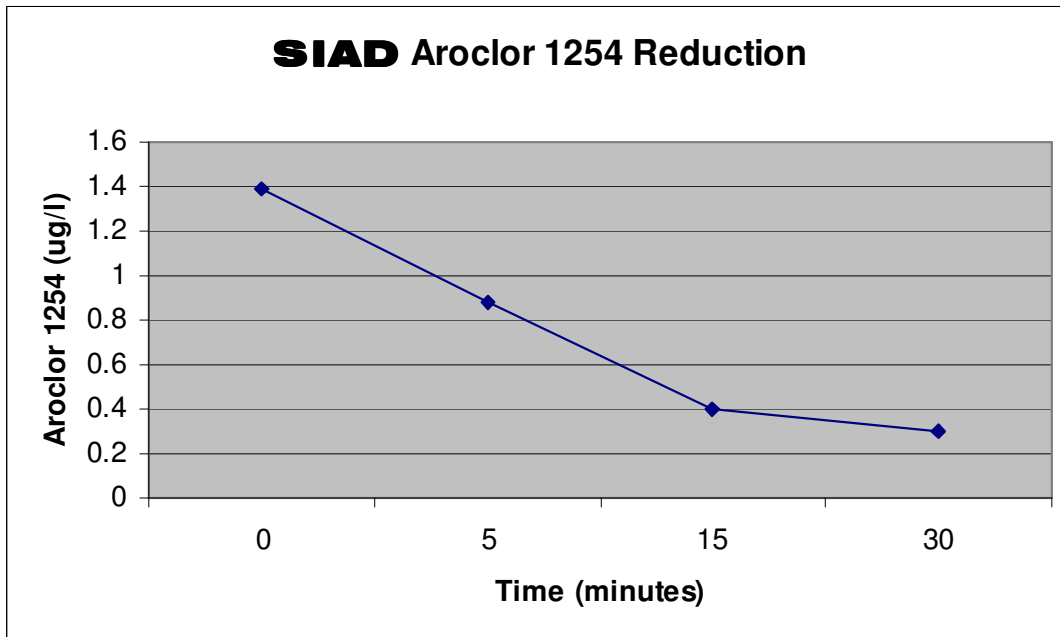
Following completion of the SIAD process trials, all excess PCB contaminated water was placed in a single, sealed container and returned to the parent facility (facility of original origin). All the SIAD processing equipment, pails, instrument, etc. were cleaned completely and stored.

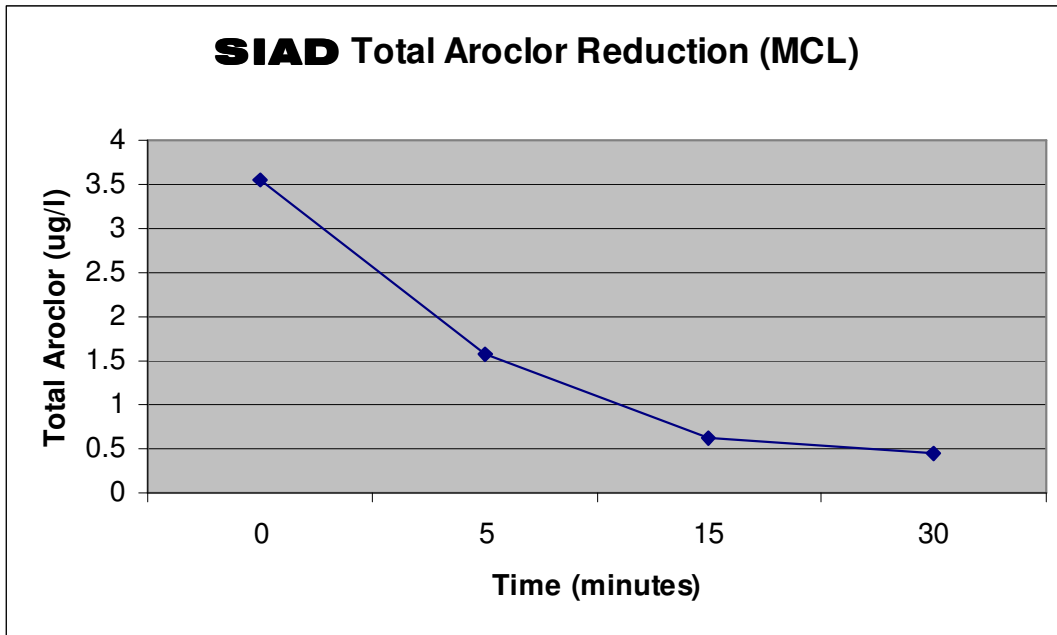
Results:

SIAD PCB Reduction Trials (May 9, 2011)

Trial	Sample	Amt (Ots)	8082 (l)	Time (min)	Initial (F)	Final (F)	VAC	Watts	RPM	Oxygen	Aroclor 1254 (ug/l)	Aroclor 1260 (ug/l)	Total (ug/l)
0	Control	0	1	0	52	52	0	0	0	No	1.39	2.15	3.54
1	A	2	1	5	53	199	144	400	610	Yes	0.882	0.684	1.566
2	B	2	1	15	51	140	144	400	610	Yes	0.405	0.224	0.629
3	C	2	1	30	52	192	144	400	610	Yes	0.303	0.152	0.455
4	D	2	1	15	55	140	144	400	610	No	0.462	0.301	0.763

(Attached is the Waste Stream Technology certified report.)





Conclusion:

Premised on the certified test results, the SIAD process achieved PCB reduction in contaminated water to levels equivalent with EPA criteria for a public water system (PWS) of water for human consumption.

Attachment: Current Methods of PCB Reduction in Industry

These can be separated into three distinct categories: physical, microbial, and chemical destruction.

Physical

Incineration – Although PCBs do not ignite themselves, they can be combusted under extreme and carefully controlled conditions. The current regulations require that PCBs are burnt at a temperature of 1200 °C for at least two seconds, in the presence of fuel oil and excess oxygen. A lack of oxygen can result in the formation of PCDDs, PCDFs and dioxins, or the incomplete destruction of the PCBs. Such specific conditions mean that it is extremely expensive to destroy PCBs on a tonnage scale, and it can only be used on PCB-containing equipment and contaminated liquid. This method is not suitable for the decontamination of affected soils.

Ultrasound – In a similar process to combustion, high power ultrasonic waves are applied to water, generating cavitation bubbles. These then implode or fragment, creating microregions of extreme pressures and temperatures where the PCBs are destroyed. Water is thought to undergo thermolysis, oxidising the PCBs to CO, CO₂ and hydrocarbons such as biphenyl, and releasing chlorine. The scope of this method is limited to those congeners that are the most water-soluble, those isomers with the least chlorine substitution.

Irradiation – If a deoxygenated mixture of PCBs in isopropanol or mineral oil is subjected to irradiation with gamma rays then the PCBs will be dechlorinated to form biphenyl and inorganic chloride. The reaction works best in isopropanol if potassium hydroxide (*caustic potash*) is added. Solvated electrons are thought to be responsible for the reaction. If oxygen, nitrous oxide, sulfur hexafluoride, or nitrobenzene is present in the mixture then the reaction rate is reduced. This work has been done recently in the US often with used nuclear fuel as the radiation source.

Pyrolysis – Destruction of PCBs with pyrolysis using plasma arc processes, like incineration, uses heat. However, unlike incineration, there is no combustion. The long-chain molecules are broken with extreme temperature provided by an electric arc in an inert environment. Adequate post-pyrolysis treatment of the resultant products is required in order to prevent the risk of back reactions.

Microbial

Much recent work has centered on the study of micro-organisms that are able to decompose PCBs. In general, these organisms work in one of two ways: Either they use the PCB as a carbon source or destruction takes place through reductive dechlorination, with the replacement of chlorine with hydrogen on the biphenyl skeleton. However, there are significant problems with this approach. First, these microbes tend to be highly selective in their dechlorination, with lower chlorinated biphenyls being readily transformed, and with preference to dechlorination in the para and meta positions. Second, microbial dechlorination tends to be rather slow-acting on PCB as a soil contaminant in comparison to other methods. Last, while microbes work well in laboratory conditions, there is often a problem in transferring a successful laboratory strain to a natural system. This is because the microbes can access other sources of carbon, which they decompose in preference to PCBs.

Further recent developments have focused on testing enzymes and vitamins extracted from microbes that show PCB activity. Especially promising seems to be the use of vitamin B12, in which a cobalt ion is in

oxidation state (III) under normal redox conditions. Using titanium (III) citrate as a strong reductant converts the cobalt from Co(III) to Co(I), giving a new vitamin known as B12s, which is a powerful nucleophile and reducing catalyst. This can then be used on PCBs, which it dechlorinates in a rapid and selective manner.

Chemical

Many chemical methods are available to destroy or reduce the toxicity of PCBs.

Nucleophilic aromatic substitution is a method of destroying low-concentration PCB mixtures in oils, such as transformer oil. Substitution of chlorine by polyethylene glycols occurs in less than two hours under a blanket of nitrogen, to prevent oxidation of the oil, to produce aryl polyglycols, which are insoluble in the oil and precipitate out.

Between 700 and 925 °C, H₂ cleaves the carbon-chlorine bond, and cleaves the biphenyl nucleus into benzene, yielding HCl without a catalyst. This can be performed at lower temperatures with a copper catalyst, and to yield biphenyl. However, since both of these routes require an atmosphere of hydrogen gas and relatively high temperatures, they are prohibitively expensive.

Reaction with highly electropositive metals, or strong reducing agents such as sodium naphthalide, in aprotic solvents results in a transfer of electrons to the PCB, the expulsion of a chloride ion, and a coupling of the PCBs. This is analogous to the Wurtz reaction for coupling halogenoalkanes. The effect is to polymerise many molecules, thereby reducing the volatility, solubility, and toxicity of the mixture. This methodology is most successful on low-strength PCB mixtures and can also be performed electrochemically in a partly aqueous bicontinuous microemulsion.

The solution photochemistry of PCBs is based on the transfer of an electron to a photochemically excited PCB from a species such as an amine, to give a radical anion. This either expels a chloride ion and the resulting aryl radical extracts a hydrogen atom from the solvent or immediately becomes protonated, leading to the loss of a chlorine atom. It is useful only for water-soluble PCBs.

The major pathway for atmospheric destruction of PCBs is via attack by OH radicals. Direct photolysis can occur in the upper atmosphere, but the ultraviolet wavelengths necessary to excite PCBs are shielded from the troposphere by the ozone layer. It has, however, been shown that higher wavelengths of light (> 300 nm) can degrade PCBs in the presence of a photosensitizer, such as acetone.

The Schwartz reaction is the subject of much study, and has significant benefits over other routes. It is advantageous since it proceeds via a reductive process, and thus yields no dioxins through oxidation. The proposed reaction scheme involves the electron transfer from a titanium (III) organometallic species to form a radical anion on the PCB molecule which expels chlorine to eventually form the relatively non-toxic biphenyl.

Attachment: Waste Stream Technology Analytical Data Report – PCB Reduction

WASTE STREAM TECHNOLOGY, INC.

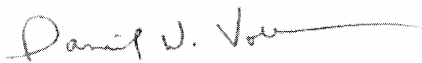
302 Grote Street
Buffalo, NY 14207
(716) 876-5290

Analytical Data Report
Report Date: 05/23/11
Work Order Number: 1E09005

Prepared For
Robert Duthie
Synergene, Inc.
155 Blake Hill Road
East Aurora, NY 14052
Fax: (716) 652-7073
Site: PCB Reduction

Enclosed are the results of analyses for samples received by the laboratory on 05/09/11. If you have any questions concerning this report, please feel free to contact me.

Sincerely,



Daniel W. Vollmer, Laboratory QA/QC Officer

ENVIRONMENTAL LABORATORY ACCREDITATION CERTIFICATION NUMBERS
NYSDOH ELAP #11179 NJDEPE #73977 PADEP #68757 CTDPH #PH-0306 MADEP #M-NY068 FLDOH #E87662



Waste Stream Technology

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.

Synergene, Inc.
155 Blake Hill Road
East Aurora NY, 14052

Project: Env. Projects - Aqueous
Project Number: PCB Reduction
Project Manager: Robert Duthie

Reported:
05/23/11 16:00

ANALYTICAL REPORT FOR SAMPLES

Sample ID	Laboratory ID	Matrix	Date Sampled	Date Received
Control	1E09005-01	Water	05/09/11 00:00	05/09/11 13:58
A	1E09005-02	Water	05/09/11 00:00	05/09/11 13:58
B	1E09005-03	Water	05/09/11 00:00	05/09/11 13:58
C	1E09005-04	Water	05/09/11 00:00	05/09/11 13:58
D	1E09005-05	Water	05/09/11 00:00	05/09/11 13:58

Synergina, Inc.
 155 Blake Hill Road
 East Aurora NY, 14052

Project: Env. Projects - Aqueous
 Project Number: PCB Reduction
 Project Manager: Robert Duthie

Reported:
 05/23/11 16:00

**Polychlorinated Biphenyls by EPA Method 8082
 Waste Stream Technology**

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
Control (1E09005-01RE1) Water Sampled: 05/09/11 00:00 Received: 05/09/11 13:58									
Aroclor 1016	ND	0.050	ug/l	1	AE11207	05/12/11	05/23/11	8082**	U
Aroclor 1221	ND	0.050	"	"	"	"	"	"	U
Aroclor 1232	ND	0.050	"	"	"	"	"	"	U
Aroclor 1242	ND	0.050	"	"	"	"	"	"	U
Aroclor 1248	ND	0.050	"	"	"	"	"	"	U
Aroclor 1254	1.39	0.050	"	"	"	"	"	"	
Aroclor 1260	2.15	0.050	"	"	"	"	"	"	
Aroclor 1262	ND	0.050	"	"	"	"	"	"	U
Aroclor 1268	ND	0.050	"	"	"	"	"	"	U
<i>Surrogate: Tetrachloro-meta-xylene</i>		70.6 %		45-135	"	"	"	"	
<i>Surrogate: Decachlorobiphenyl</i>		63.7 %		55-120	"	"	"	"	
A (1E09005-02RE1) Water Sampled: 05/09/11 00:00 Received: 05/09/11 13:58									
Aroclor 1016	ND	0.050	ug/l	1	AE11207	05/12/11	05/23/11	8082**	U
Aroclor 1221	ND	0.050	"	"	"	"	"	"	U
Aroclor 1232	ND	0.050	"	"	"	"	"	"	U
Aroclor 1242	ND	0.050	"	"	"	"	"	"	U
Aroclor 1248	ND	0.050	"	"	"	"	"	"	U
Aroclor 1254	0.882	0.050	"	"	"	"	"	"	
Aroclor 1260	0.684	0.050	"	"	"	"	"	"	
Aroclor 1262	ND	0.050	"	"	"	"	"	"	U
Aroclor 1268	ND	0.050	"	"	"	"	"	"	U
<i>Surrogate: Tetrachloro-meta-xylene</i>		83.5 %		45-135	"	"	"	"	
<i>Surrogate: Decachlorobiphenyl</i>		60.6 %		55-120	"	"	"	"	

Waste Stream Technology

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Synergene, Inc.
 155 Blake Hill Road
 East Aurora NY, 14052

Project: Env. Projects - Aqueous
 Project Number: PCB Reduction
 Project Manager: Robert Duthie

Reported:
 05/23/11 16:00

**Polychlorinated Biphenyls by EPA Method 8082
 Waste Stream Technology**

Analyte	Result	Reporting		Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
		Limit								
B (1E09005-03RE1) Water Sampled: 05/09/11 00:00 Received: 05/09/11 13:58										
Aroclor 1016	ND	0.050	ug/l	I	AE11207	05/12/11	05/23/11	8082**		U
Aroclor 1221	ND	0.050	"	"	"	"	"	"		U
Aroclor 1232	ND	0.050	"	"	"	"	"	"		U
Aroclor 1242	ND	0.050	"	"	"	"	"	"		U
Aroclor 1248	ND	0.050	"	"	"	"	"	"		U
Aroclor 1254	0.405	0.050	"	"	"	"	"	"		
Aroclor 1260	0.224	0.050	"	"	"	"	"	"		
Aroclor 1262	ND	0.050	"	"	"	"	"	"		U
Aroclor 1268	ND	0.050	"	"	"	"	"	"		U
<i>Surrogate: Tetrachloro-meta-xylene</i>		77.8 %		45-135	"	"	"	"		
<i>Surrogate: Decachlorobiphenyl</i>		51.0 %		55-120	"	"	"	"		L
C (1E09005-04RE1) Water Sampled: 05/09/11 00:00 Received: 05/09/11 13:58										
Aroclor 1016	ND	0.050	ug/l	I	AE11207	05/12/11	05/23/11	8082**		U
Aroclor 1221	ND	0.050	"	"	"	"	"	"		U
Aroclor 1232	ND	0.050	"	"	"	"	"	"		U
Aroclor 1242	ND	0.050	"	"	"	"	"	"		U
Aroclor 1248	ND	0.050	"	"	"	"	"	"		U
Aroclor 1254	0.303	0.050	"	"	"	"	"	"		
Aroclor 1260	0.152	0.050	"	"	"	"	"	"		
Aroclor 1262	ND	0.050	"	"	"	"	"	"		U
Aroclor 1268	ND	0.050	"	"	"	"	"	"		U
<i>Surrogate: Tetrachloro-meta-xylene</i>		83.9 %		45-135	"	"	"	"		
<i>Surrogate: Decachlorobiphenyl</i>		39.7 %		55-120	"	"	"	"		

Waste Stream Technology

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Synergene, Inc.
 155 Blake Hill Road
 East Aurora NY, 14052

Project: Env. Projects - Aqueous
 Project Number: PCB Reduction
 Project Manager: Robert Duthie

Reported:
 05/23/11 16:00

Polychlorinated Biphenyls by EPA Method 8082
Waste Stream Technology

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
D (1E09005-05RE1) Water Sampled: 05/09/11 00:00 Received: 05/09/11 13:58									
Aroclor 1016	ND	0.050	ug/l	1	AE11207	05/12/11	05/23/11	8082**	U
Aroclor 1221	ND	0.050	"	"	"	"	"	"	U
Aroclor 1232	ND	0.050	"	"	"	"	"	"	U
Aroclor 1242	ND	0.050	"	"	"	"	"	"	U
Aroclor 1248	ND	0.050	"	"	"	"	"	"	U
Aroclor 1254	0.462	0.050	"	"	"	"	"	"	
Aroclor 1260	0.301	0.050	"	"	"	"	"	"	
Aroclor 1262	ND	0.050	"	"	"	"	"	"	U
Aroclor 1268	ND	0.050	"	"	"	"	"	"	U
<i>Surrogate: Tetrachloro-meta-xylene</i>		89.3 %		45-135	"	"	"	"	
<i>Surrogate: Decachlorobiphenyl</i>		52.6 %		55-120	"	"	"	"	L

Synergene, Inc.
155 Blake Hill Road
East Aurora NY, 14052

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Project Manager: Robert Duthie

Reported:
05/23/11 16:00

Notes and Definitions

- U Analyte included in the analysis, but not detected at or above the reporting limit.
- L L denotes analyte recovery is less than the lower quality control limit.
- DFT Analyte DETECTED
- ND Analyte NOT DETECTED at or above the reporting limit
- NR Not Reported
- dry Sample results reported on a dry weight basis
- RPD Relative Percent Difference
- ** Denotes a promulgated method, but not the most updated version.

CHAIN OF CUSTODY



Waste Stream Technology Inc.
 302 Grote Street, Buffalo, NY 14207
 (716) 876-5290 • FAX (716) 876-2412

OFFICE USE ONLY

GROUP # _____

DUE DATE _____

TURN AROUND TIME: _____

QUOTATION NUMBER: _____

PAGE _____ OF _____

ARE SPECIAL DETECTION LIMITS REQUIRED:
 YES NO
 If yes please attach requirements

Is a QC Package required:
 YES NO
 If yes please attach requirements

Is a QC Package required:
 YES NO
 If yes please attach requirements

- DW DRINKING WATER
- GW GROUND WATER
- SW SURFACE WATER
- WW WASTE WATER
- O OIL
- SL SLUDGE
- SO SOIL
- S SOLID
- W WIPE
- OTHER

ANALYSES TO BE PERFORMED

SAMPLE ID.	DATE SAMPLED	TIME OF SAMPLING	SAMPLE TYPE	TOTAL NO. OF CONTAINERS	ANALYSES TO BE PERFORMED										TYPE OF CONTAINER/ COMMENTS:	OFFICE USE ONLY WST. I.D.	
1																	
2																	
3																	
4																	
5																	
6																	
7																	
8																	
9																	
10																	

SAMPLER SIGNATURE _____

PROJECT DESCRIPTION _____

PO# _____

BILL TO: _____

FAX # () _____

PH. # () _____

CONTACT _____

REMARKS:

RELINQUISHED BY: _____

DATE: / /

TIME: _____

RECEIVED BY: _____

DATE: / /

TIME: _____

RELINQUISHED BY: _____

DATE: / /

TIME: _____

RECEIVED BY: _____

DATE: / /

TIME: _____