Base Catalyzed Decomposition (BCD) of PCB and Dioxin Contaminated Condensate Oil from the Remediation of the Warren County Landfill, NC

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Base Catalyzed Decomposition

- The BCD process was developed and patented by the EPA Risk Reduction Laboratory (RREL) in Cincinnati, Ohio, following initial research on the APEG and KPEG dehalogenation processes
- The BCD process detoxifies and chemically decomposes contaminants by catalytic hydrogenation.
- A hydrogen donor oil supplies hydrogen atoms which displace chlorine atoms from a halogenated organic contaminant.
- The chlorinated contaminant is reduced to less toxic unchlorinated compound

Base Catalyzed Decomposition

$$\text{R-(Cl)} + \text{R'} + \text{Catalyst} + \text{Na}^{+} \xrightarrow{620 - 650^{\circ}\text{F}} \text{R-H}^{+} + \text{R''} + \text{NaCl}$$

- R-(Cl) as shown can be any halogenated compound such as PCDDs, PCDFs, PCBs, 2,4-D, or 2,4,5-T
- R' is a hydrogen donor oil whose oxidation potential is sufficiently low to generate nucleophilic hydrogen in the presence of base Na+ (sodium hydroxide) and at temperatures between 250˚ - 350˚C
- Under these conditions, chlorine on R-Cl is replaced by H+ to produce R-H with loss of hydrogen from R' to R" and the formation of sodium chlolride. This reaction achieves complete dechlorination of chlorinated compounds

Base Catalyzed Decomposition

- **The process uses sodium base material, a hydrogen donor, and elevated heat (650˚ - 800˚F) to replace the halogen atoms from a heavy halogenated organic molecule with hydrogen radicals**
- **Remediation of contaminated soil, sludge, or sediment with the BCD process is a two stage process beginning with thermal desorption**
- **The first stage, the modified thermal desorption phase may include mixing contaminated material with 1- 5% sodium bicarbonate**
- **Sodium bicarbonate was not utilized at Warren Co.**

Base Catalyzed Decomposition

- The recovered contaminated condensate oil from the APCD is transferred into a heated, stirred liquid tank reactor for dehalogenation
- High boiling point oil, NaOH, and proprietary reagents are added to the reactor
- After reaching temperature the material is cooked approximately 1 - 4 hours (depending on treatability testing)
- The resulting dechlorinated hydrocarbon can be recycled as a fuel supplement in any industrial boiler

Warren County Landfill

- In the late 1970s thousands of gallons of transformer fluid contaminated with polychlorinated bi-phenyls (PCBs) were illegally disposed of in North Carolina. They were sprayed alongside approximately 210 miles of the state of roadways
- Listed as a Superfund site the roadway berms were removed while a study was undertaken to identify the best and most secure location to construct a TOSCA approved landfill for the PCB contaminated soils
- After a statewide evaluation of geology, geography, accessibility; the decision was made to build the landfill in a remote location in Warren County, NC.

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Warren County Landfill

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- Listed as a Superfund site the

Warren County Landfill

There was much opposition to the landfill from the local community. The extent of that uproar was the start of the Environmental Justice movement.

Warren County Landfill

- In 1982, Governor James Hunt Jr. made a commitment to the people of Warren County that if appropriate and feasible technology other than incineration became available, the state would explore detoxification and removal of the landfill

- The landfill was built on approximately 170 acres of state land. The landfill was a monofill about 15 feet high. It was vegetated and well maintained. Samples from around the area showed no signs of PCB release.

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Warren County Landfill

Warren County Landfill

- **Beginning in 1996 the science advisors for the Warren County PCB Working Group along with the Division of Waste Management (division of NC DENR) conducted a technology screening of twelve different technologies. All but two were screened out: Base Catalyzed Decomposition (BCD) and Gas Phase Chemical Reduction technology**

- **After bench scale treatability studies were conducted, the Work Group selected BCD as the preferred technology**

- **In May of 2000 the EPA Administrator received a request from NC's 1st District Congressional Representative for support and funding to help the state complete the project**

Warren County Landfill

- **ORD/NRMRL determined that the planned use of BCD at the Warren County Landfill qualified as an innovative technology under the definition of 311b of CERCLA and our support could be conducted under the SITE program**

- **Over 72,000 tons of PCB contaminated soil were excavated and treated with an indirect fire thermal desorption unit**

- **Resulting in over 5,000 gallons of highly contaminated condensate oil – approximately .07 gallons/ton**

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BCD Bench Scale Testing

- **Since only 5000 gallons of contaminated oil was collected, the state with the approval of the TAG group determined it would be more convenient to ship the waste oil for incineration in Kansas**

- **Prior to shipment, ORD collected aliquot samples of the contaminated APCD oil for analysis and bench scale study**

BCD Bench Scale Testing

Initial characterization of the site oil exhibited:

Untreated Site Oil Analysis

TESTING PARAMETER	UNITS	RESULTS
Total PCBs		
Aroclor 1016	mg/kg	< 4,200
Aroclor 1221	mg/kg	< 4,200
Aroclor 1232	mg/kg	< 4,200
Aroclor 1242	mg/kg	**53,000**
Aroclor 1248	mg/kg	< 4,200
Aroclor 1254	mg/kg	< 4,200
Aroclor 1260	mg/kg	**38,000**

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BCD Bench Scale Testing

Untreated Site Oil Analysis

TESTING PARAMETER	UNITS	RESULTS
2,3,7,8-TCDF	ng/kg	290,000
Total TCDF	ng/kg	1,000,000
2,3,7,8-TCDD	ng/kg	370 (1)
Total TCDD	ng/kg	5,800
1,2,3,7,8-PeCDF	ng/kg	110,000
2,3,4,7,8-PeCDF	ng/kg	36,000
Total PeCDF	ng/kg	290,000
1,2,3,7,8-PeCDD	ng/kg	3,500
Total PeCDD	ng/kg	25,000
1,2,3,4,7,8-HxCDF	ng/kg	89,000
1,2,3,6,7,8-HxCDF	ng/kg	38,000
2,3,4,6,7,8-HxCDF	ng/kg	4,800
1,2,3,7,8,9-HxCDF	ng/kg	3,600
Total HxCDF	ng/kg	270,000
1,2,3,4,7,8-HxCDD	ng/kg	1,200
1,2,3,6,7,8-HxCDD	ng/kg	1,900
1,2,3,7,8,9-HxCDD	ng/kg	2,800
Total HxCDD	ng/kg	24,000
1,2,3,4,6,7,8-HpCDF	ng/kg	44,000
1,2,3,4,7,8,9-HpCDF	ng/kg	7,700
Total HpCDF	ng/kg	77,000
1,2,3,4,6,7,8-HpCDD	ng/kg	13,000
Total HpCDD	ng/kg	37,000
OCDF	ng/kg	28,000
OCDD	ng/kg	39,000

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BCD Bench Scale Testing Test #1

BCD Bench Scale Testing Test #1

- **Once the reactor and reagents reached 225˚C, 250 ml site oil (heated to 100˚C) was added over a 12 minute period**
  - This depressed the reactor temperature to 134 ˚C
- **Reactor was then heated to 330˚C**
- **Sample continued heating for 2 hours**

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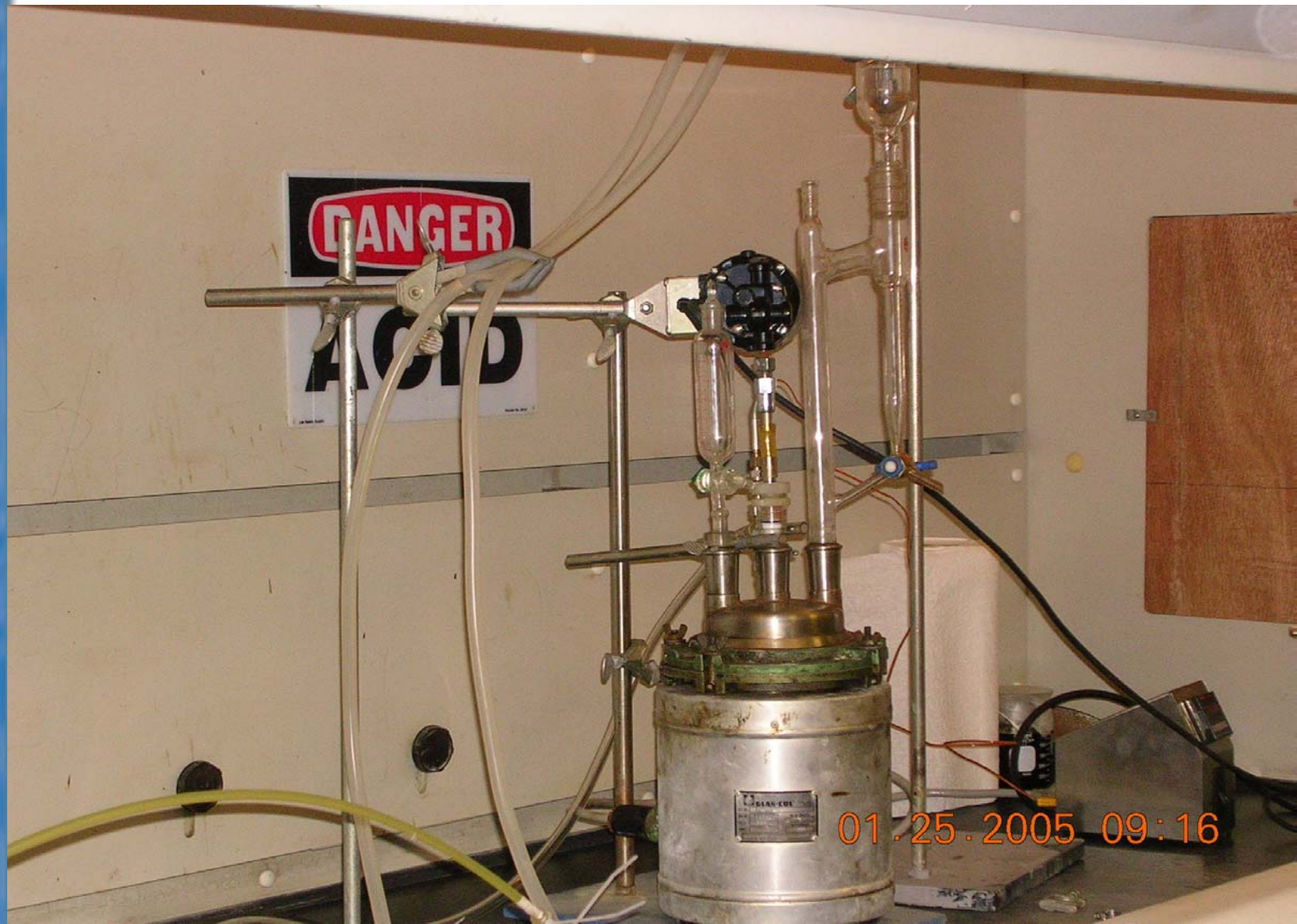
BCD Bench Scale Testing Test #2



BCD Bench Scale Testing Test #2

- **Once the reactor and reagents reached 336˚C, 250 ml site oil was added over a 255 minute period**
  - This kept reactor temperature at at least 320˚C
- **After all site oil added sample continued heating for one hour**

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BCD Bench Scale Testing PCB Results

BCD TREATED MATERIAL

Summary of Total PCB Analyses

SAMPLE ID	RESULTS (mg/kg)							
	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1268
Untreated	<4,200	<4,200	<4,200	**52,000**	<4,200	<4,200	**38,000**	NA
Test #1								
Condensate	<42	<42	<42	**481**	<42	<42	<42	<42
243°C	<2,500	<2,500	<2,500	**48,700**	<2,500	<2,500	**32,400**	<2,500
Time 0 Minutes	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Time 30 Minutes	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Time 60 Minutes	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Time 90 Minutes	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Time 120 Minutes	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Test #2								
Condensate	<5.0	<5.0	<5.0	**2,260**	<5.0	<5.0	<5.0	<5.0
Time 0 Minutes	<5.0	<5.0	<5.0	**5,280**	<5.0	<5.0	<5.0	<5.0
Time 60 Minutes	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

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BCD Bench Scale Testing

TESTING PARAMETER	UNITS	RESULTS		
		Untreated	Test #1 Treated @ 120 Minutes	Test #2 Treated @ 60 Minutes
Total PCBs				
Aroclor 1016	mg/kg	< 4,200	< 5.0	< 5.0
Aroclor 1221	mg/kg	< 4,200	< 5.0	< 5.0
Aroclor 1232	mg/kg	< 4,200	< 5.0	< 5.0
Aroclor 1242	mg/kg	**52,000**	< 5.0	< 5.0
Aroclor 1248	mg/kg	< 4,200	< 5.0	< 5.0
Aroclor 1254	mg/kg	< 4,200	< 5.0	< 5.0
Aroclor 1260	mg/kg	**38,000**	< 5.0	< 5.0
Aroclor 1268	mg/kg	**NA**	< 5.0	< 5.0
Total Metals				
Arsenic	mg/kg	< 2.45	< 1.0	< 0.54
Barium	mg/kg	< 2.45	< 1.0	< 0.54
Cadmium	mg/kg	< 0.245	< 0.1	< 0.054
Chromium	mg/kg	< 2.45	< 1.0	**1.3**
Lead	mg/kg	**2.05**	< 0.63	< 0.33
Mercury	mg/kg	< 0.0194	< 0.021	< 0.021
Selenium	mg/kg	**4.06**	< 15.7	**1.6**
Silver	mg/kg	< 2.45	< 1.0	< 0.54
Sodium	mg/kg	**267**	**102,000**	**23,700**
Sulfide Content	mg/kg	**9.6**	**15.5**	**12.1**
TPH				
Gasoline Range Organics	mg/kg	**129,584**	**1,323**	**< 100**
Diesel Range Organics	mg/kg	**855,548**	**NA**	**340,000**
Chlorine Content	mg/kg	**77,350**	**4,690**	**2,667**
Initial Boiling Point	^{0}F	**301**	**473**	**410**
Oil and Grease Content	wt%	**43.69**	**31.62**	**34.22**
Heat of Combustion	Btu/lb	**16,396**	**19,079**	**18,894**

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BCD Bench Scale Testing Dioxin Results

BCD TREATED MATERIAL
Summary of Dioxin / Furan Analyses

TESTING PARAMETER	RESULTS (ng/kg) Untreated Result	Untreated Lower Reporting Limit	Test #1 Treated @ 120 Minutes Result	Test #1 Treated @ 120 Minutes Lower Reporting Limit	Test #2 Treated @ 60 Minutes Result	Test #2 Treated @ 60 Minutes Lower Reporting Limit
PCDD/PCDF						
2,3,7,8-TCDF	**290,000**	310	-	14.0	-	18.0
Total TCDF	**1,000,000**	190	-	9.1	-	15.0
2,3,7,8-TCDD	**370**	340	-	14.0	-	27.0
Total TCDD	**5,800**	190	-	9.1	-	15.0
1,2,3,7,8-PeCDF	**110,000**	960	-	45.0	-	77.0
2,3,4,7,8-PeCDF	**36,000**	960	-	45.0	-	77.0
Total PeCDF	**290,000**	960	-	45.0	-	77.0
1,2,3,7,8-PeCDD	**3,500**	960	-	45.0	-	77.0
Total PeCDD	**25,000**	960	-	45.0	-	77.0
1,2,3,4,7,8-HxCDF	**89,000**	960	-	45.0	-	77.0
1,2,3,6,7,8-HxCDF	**38,000**	960	-	45.0	-	77.0
2,3,4,6,7,8-HxCDF	**4,800**	960	-	45.0	-	77.0
1,2,3,7,8,9-HxCDF	**3,600**	960	-	45.0	-	77.0
Total HxCDF	**270,000**	960	-	45.0	-	77.0
1,2,3,4,7,8-HxCDD	**1,200**	960	-	45.0	-	77.0
1,2,3,6,7,8-HxCDD	**1,900**	960	-	45.0	-	77.0
1,2,3,7,8,9-HxCDD	**2,800**	960	-	45.0	-	77.0
Total HxCDD	**24,000**	960	-	45.0	-	77.0
1,2,3,4,6,7,8-HpCDF	**44,000**	960	-	45.0	-	77.0
1,2,3,4,7,8,9-HpCDF	**7,700**	960	-	45.0	-	77.0
Total HpCDF	**77,000**	960	-	45.0	-	77.0
1,2,3,4,6,7,8-HpCDD	**13,000**	960	-	45.0	-	77.0
Total HpCDD	**37,000**	960	-	45.0	-	77.0
OCDF	**28,000**	1900	-	91.0	-	150.0
OCDD	**39,000**	1900	-	91.0	-	150.0

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BCD Bench Scale Testing
Volatile Results (ug/kg)

Total Volatiles	Untreated Result	Test #1 Result	Test #1 Result
Acetone	NA	-	-
Acrolein	NA	-	-
Acrylonitrile	NA	-	-
Allyl chloride	NA	-	-
Benzene	-	-	-
Bromobenzene	-	-	-
Bromochloromethane	-	-	-
Bromodichloromethane	-	-	-
Bromoform	-	-	-
Bromomethane	-	-	-
2-Butanone	NA	-	-
n-Butylbenzene	510,000	-	-
sec-Butylbenzene	-	-	-
tert-Butylbenzene	-	-	-
Carbon disulfide	NA	-	-
Carbon tetrachloride	-	-	-
Chlorobenzene	-	-	-
Chloroethane	-	-	-
2-Chloroethylvinyl ether	NA	-	-
Chloroform	-	-	-
Chloromethane	-	-	-
2-Chlorotoluene	-	-	-
4-Chlorotoluene	-	-	-
Cyclohexane	NA	-	-
1,2,-Dibromo-3-chloropr	-	-	-
Dibromochloromethane	-	-	-
1,2-Dibromoethane	-	-	-
Dibromomethane	-	-	-
1,2-Dichlorobenzene	-	-	-
1,3-Dichlorobenzene	-	-	-
1,4-Dichlorobenzene	600,000	-	-
trans-1,4-Dichloro-2-but	NA	-	-
Dichlorodifluoromethane	-	-	-
1,1-Dichloroethane	-	-	-
1,2-Dichloroethane	-	-	-
1,2-Dichloroethene (Tota	NA	-	-
1,1-Dichloroethene	-	-	-
cis-1,2-Dichloroethene	-	-	-
trans-1,2-Dichloroethene	-	-	-
Dichlorofluoromethane	NA	-	-
1,2-Dichloropropane	-	-	-

Total Volatiles	Untreated Result	Test #1 Result	Test #1 Result
1,3-Dichloropropane	-	-	-
2,2-Dichloropropane	-	-	-
1,1-Dichloropropene	-	-	-
cis-1,3-Dichloropropene	-	-	-
trans-1,3-Dichloroproper	-	-	-
Diethyl ether	NA	-	-
Diisopropyl ether	NA	-	-
Ethylbenzene	290,000	-	-
Hexachloro-1,3-butadien	-	-	-
2-Hexanone	NA	-	-
Iodomethane	NA	-	-
Isopropylbenzene	-	-	-
p-Isopropyltoluene	250,000	-	-
Methylene chloride	-	-	-
2-Methylnaphthalene	NA	157,000	2,390,000
4-Methyl-2-pentanone	NA	-	-
Methyl-tert-butyl ether	NA	-	-
Naphthalene	2,100,000	NA	1,640,000
n-Propylbenzene	200,000	-	-
Styrene	580,000	-	-
1,1,1,2-Tetrachloroethan	-	-	-
1,1,2,2-Tetrachloroethan	-	-	-
Tetrachloroethene	-	-	-
Tetrahydrofuran	NA	-	-
Toluene	420,000	-	-
1,2,3-Trichlorobenzene	340,000	-	-
1,2,4-Trichlorobenzene	720,000	-	-
1,1,1-Trichloroethane	-	-	-
1,1,2-Trichloroethane	-	-	-
Trichloroethene	-	-	-
Trichlorofluoromethane	-	-	-
1,2,3-Trichloropropane	-	-	-
1,1,2-Trichlorotrifluoroe	NA	-	-
1,2,4-Trimethylbenzene	1,000,000	-	-
1,3,5-Trimethylbenzene	210,000	-	-
Vinyl acetate	NA	-	-
Vinyl chloride	-	-	-
Xylene (Total)	1,100,000		-

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BCD Bench Scale Testing Volatile Results

Total Volatiles (ug/kg)	Untreated Result		Test #1 Result		Test #1 Result
n-Butylbenzene	**510,000**		-		-
1,4-Dichlorobenzene	**600,000**		-		-
Ethylbenzene	**290,000**		-		-
p-Isopropyltoluene	**250,000**		-		-
2-Methylnaphthalene	**NA**		**157,000**		**2,390,000**
Naphthalene	**2,100,000**		**NA**		**1,640,000**
n-Propylbenzene	**200,000**		-		-
Styrene	**580,000**		-		-
Toluene	**420,000**		-		-
1,2,3-Trichlorobenzene	**340,000**		-		-
1,2,4-Trichlorobenzene	**720,000**		-		-
1,2,4-Trimethylbenzene	**1,000,000**		-		-
1,3,5-Trimethylbenzene	**210,000**		-		-
1,2,4-Trimethylbenzene	**1,000,000**		-		-
1,3,5-Trimethylbenzene	**210,000**		-		-

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BCD Bench Scale Testing
SemiVolatile Results (ug/kg)

TOTAL SEMIVOLATILE	Untreated Result	Test #1 Result	Test #2 Result
1,2,4-Trichlorobenzene	890,000	-	-
1,2-Dichlorobenzene	-	-	-
1,3-Dichlorobenzene	-	-	-
1,4-Dichlorobenzene	720,000	-	-
2,4,5-Trichlorophenol	-	-	-
2,4,6-Trichlorophenol	-	-	-
2,4-Dichlorophenol	-	-	-
2,4-Dimethylphenol	530,000	-	-
2,4-Dinitrophenol	-	-	-
2,4-Dinitrotoluene	-	-	-
2,6-Dinitrotoluene	-	-	-
2-Chloronaphthalene	-	-	-
2-Chlorophenol	-	-	-
2-Methylnaphthalene	4,000,000	561,000	1,330,000
2-Methylphenol	-	-	-
2-Nitroaniline	-	-	-
2-Nitrophenol	-	-	-
3&4-Methylphenol	NA	-	-
3,3'-Dichlorobenzidine	250,000	-	-
3-Nitroaniline	-	-	-
4,6-Dinitro-2-methylphenol	-	-	-
4-Bromophenylphenyl ether	-	-	-
4-Chloro-3-methylphenol	-	-	-
4-Chloroaniline	-	-	-
4-Chlorophenylphenyl ether	-	-	-
4-Nitroaniline	-	-	-
4-Nitrophenol	-	-	-
Acenaphthene	-	-	-
Acenaphthylene	590,000	-	-
Anthracene	450,000	180,000	-
Benzo(a)anthracene	210,000	-	-
Benzo(a)pyrene	-	-	-
Benzo(b)fluoranthene	230,000	-	-
Benzo(g,h,i)perylene	-	-	-

TOTAL SEMIVOLATILE	Untreated Result	Test #1 Result	Test #2 Result
Benzo(k)fluoranthene	-	-	-
Benzoic acid	-	-	-
Benzyl alcohol	-	-	-
Butylbenzylphthalate	-	-	-
Chrysene	300,000	-	-
Di-n-butylphthalate	-	-	-
Di-n-octylphthalate	-	-	-
Dibenz(a,h)anthracene	-	-	-
Dibenzofuran	750,000	292,000	-
Diethylphthalate	-	-	-
Dimethylphthalate	-	-	-
Fluoranthene	-	290,000	-
Fluorene	1,800,000	514,000	-
Hexachloro-1,3-butadiene	-	-	-
Hexachlorobenzene	-	-	-
Hexachlorocyclopentadiene	-	-	-
Hexachloroethane	-	-	-
Ideno(1,2,3-cd)pyrene	-	-	-
Isophorone	-	-	-
N-Nitroso-di-n-propylamine	-	-	-
N-Nitrosodiphenylamine	-	-	-
Naphthalene	2,700,000	127,000	-
Nitrobenzene	-	-	-
Pentachlorophenol	-	-	-
Phenanthrene	500,000	890,000	-
Phenol	500,000	-	-
Pyrene	150,000	-	-
bis(2-Chloroethoxy)methane	-	-	-
bis(2-Chloroethyl) ether	-	-	-
bis(2-Chloroisopropyl) ether	-	-	-
bis(2-Ethylhexyl)phthalate	-	-	-

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BCD Bench Scale Testing SemiVolatile Results

TOTAL SEMIVOLATILE (ug/kg)	Untreated Result		Test #1 Result		Test #2 Result
1,2,4-Trichlorobenzene	**890,000**		**-**		**-**
1,4-Dichlorobenzene	**720,000**		**-**		**-**
2,4-Dimethylphenol	**530,000**		**-**		**-**
2-Methylnaphthalene	**4,000,000**		**561,000**		**1,330,000**
3,3'-Dichlorobenzidine	**250,000**		**-**		**-**
Acenaphthylene	**590,000**		**-**		**-**
Anthracene	**450,000**		**180,000**		**-**
Benzo(a)anthracene	**210,000**		**-**		**-**
Benzo(b)fluoranthene	**230,000**		**-**		**-**
Chrysene	**300,000**		**-**		**-**
Dibenzofuran	**750,000**		**292,000**		**-**
Fluoranthene	**-**		**290,000**		**-**
Fluorene	**1,800,000**		**514,000**		**-**
Naphthalene	**2,700,000**		**127,000**		**-**
Phenanthrene	**500,000**		**890,000**		**-**
Phenol	**500,000**		**-**		**-**
Pyrene	**150,000**		**-**		**-**

Summary

- BCD reduced all PCBs (Aroclor 1242 and 1260) from 52,000 and 38,000 mg/kg to ND (<5.0 mg/kg) in each test
- BCD reduced dioxins (i.e.Total TCDD/TCDF) from 5,800 and 1,000,000 ng/kg to ND (<9.1 and <15.0 ng/kg) in each test
- While both methods eliminated PCBs and Dioxins:
  - Test Method #1 resulted in lower concentration of PCBs in the aqueous condensate than Test Method #2
- Base Catalyzed Decontamination is an effective and inexpensive method of dechlorination halogenated contaminated soils, sediments, and oils