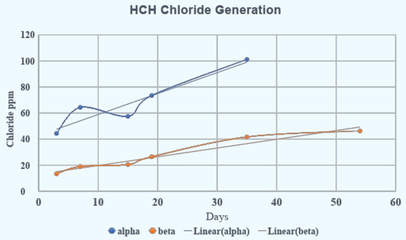
Plagued by POPs (Persistent Organic Contaminants): CAT 100 may be the Answer

BENCH TEST: Can BOS 100® degrade Lindane?

Batch Reactor – 150 ml Serum Vial
Dissolve Lindane in anhydrous ethanol
Load 54 mg onto 5 gms BOS 100 in Glove Box
Add 150 ml DI Water
Continuous Mixing – Contact Time 60 days
Extract 100 mg of BOS 100 and Analyze the Extract for VOCs

Lindane	Conc in Extract (ug/L)	Mass on Carbon (mg)	Percent Degrad.
Benzene	24975	12.488	86
Chlorobenzene	643	0.322	1.5
Lindane Mass	54 mg		
% Chloride	73%		
100 % Conv to Bz	14.5 mg		

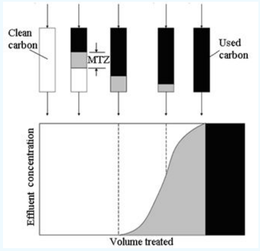
The 10 ml extract was analyzed using method 8260B. As shown in the table above, benzene and chlorobenzene were detected. After 60 days of contact, 86% of the original Lindane had been completely dechlorinated. A second test was conducted to demonstrate the alpha and beta isomers of HCH could also be degraded. In this case 25 mg of HCH was loaded onto 5 gms of BOS 100.



If 25 mg of α-HCH is 100 percent degraded, 18.29 mg of chloride will be generated, and the theoretical generation of benzene is 6.725 mg. Analysis showed that after 35 days of contact, 15.18 mg of chloride and 3.148 mg of benzene had been generated. The chloride generated represents 83% of the total possible and that of benzene represents 46.8% of the theoretical amount. The 3.148 mg-benzene generated within the pore structure of 5 gms BOS100® is a concentration equal to 630 ppm benzene in the carbon, and this amount resulted in only **1.5 ppb** of benzene detected in the water.

The 3.148 mg of benzene accounts for complete dechlorination of 11.7 mg of HCH and that equates to 8.56 mg of the measured 15.18 mg chloride. This means 6.62 mg of chloride is not accounted for, suggesting partially degraded intermediates are present. Using chloride data to estimate degradation rates: the α-HCH is 1.606 mg-chloride per day while that of the beta isomer is 0.671 mg-chloride per day. Degradation rate for the alpha isomer is about 2.4 times faster than the beta isomer.

The Column Test: Evaluation for PRB Design



Performance of an activated carbon treatment bed is a function of the organic compound, its concentration in the water to be treated, and residence time within the bed. At some point, the carbon becomes saturated, and the organic compound begins to break through the bed and escape with discharged water. Typically, adsorption by the carbon is the sole basis for design and no other mechanisms for elimination of the organic compound such as biotic or abiotic degradation are significant.

The bench test included:

- One column packed with the same activated carbon used in the P&T system currently in operation at the site.
- A second column was packed with RPI's BOS 100.

Pretest Expectations

The carbon packed column was expected to perform very much like the commercial beds in operation in the P&T system. No degradation of HCH contaminants was expected to occur nor were any chemical reactions anticipated. Simple adsorption would be the only significant contamination removal mechanism, followed by breakthrough.

Regarding BOS 100, preliminary bench testing confirmed evidence of degradation of HCH isomers through detection of byproducts including chloride, benzene, and chlorobenzene. The performance of the column packed with BOS 100 was expected to be quite different from that of the carbon only column. BOS 100 was expected to adsorb the HCH contaminants. However, abiotic degradation of the HCH isomers would occur and result in treatment of significantly more groundwater before measurable breakthrough would be observed.

No biological activity was expected.

This is not what happened. Instead:

- Extensive biological activity occurred on both the BOS 100 and activated carbon column. The biological activity resulted in degradation of numerous organic compounds and contaminants on the activated carbon as well as the BOS 100.
- Breakthrough of HCH isomers occurred on both columns at essentially the same time.
- Breakdown products of HCH degradation were also degraded.
- Additional CVOCs such as carbon tetrachloride, TCE, PCE, chloroform, 1,2-DCA, and 1,1,2-TCA were found on the columns.

Highlights of Column Test Operation

The most common model for how carbon beds work is a thin section or zone in the bed slowly moves from the top to the bottom. This is called the mass transfer zone (MTZ). Above the MTZ the carbon is saturated and the contaminant concentration there is the same as that entering the top of the bed. Below the MTZ, the contaminant concentration is zero or lower than applicable maximum contaminant levels (MCLs). Over time, the MTZ slowly moves down the bed until it breaks through the bed and measurable concentration of contaminants begin to increase.

Increasing the flow rate increases the length or thickness of the MTZ. There will be a flow rate where the thickness of the MTZ that develops is larger than the depth of the bed. Should this happen, there would be instant breakthrough of contaminants discharging from the bed.

As indicated, due to column test objectives, a highly specific column design was adopted:

- 7.8 mm column diameter
- 250 mm packed length
- 6.2 gms of activated carbon or BOS 100
- Targeted flow rate is 10 ml/min. This translates to a groundwater seep velocity of 360 meters/day
- Residence time: roughly one of order of magnitude shorter than that of commercial beds

To save time, the BOS 100 column and the activated carbon column were run in parallel. Based on method development using distilled water, transient pressure changes over the first couple of days were expected and adjustments would be required as the system stabilized.

As the test progressed the following issues were observed:

- Although liquid flow control valves were installed in front of each column, the two columns did not perform in the same way and pressure changes in either column adversely affected the other. This necessitated continual monitoring and complicated running of the test.
- Upon sacrificing the columns and analyzing for organic compounds adsorbed to the carbon and BOS 100, numerous volatile chlorinated solvents were found.
- Accumulation of biodegradable organic matter on the limited amount of carbon and the presence of microorganisms in the site groundwater resulted in significant biological activity. This activity was enhanced by dissolved oxygen (DO) and warm temperature (25^0 C).
- Associated formation of biofilm plugged both columns to the point where even a couple ml/per minute of flow required pressures between 2,000 and 3,000 psi.

Column Test Results

Degradation Byproducts found on the BOS 100				
Benzene	Cl-benz	1,2-DCB	1,3-DCB	1.2.4-TCB
0.016	0.0532	0.156	0.0779	0.1193
mg-HCH	mg-HCH	mg-HCH	mg-HCH	mg-HCH

Degradation Byproducts found on the Site Carbon				
Benzene	Cl-benz	1,2-DCB	1,3-DCB	1.2.4-TCB
0.0397	0.0537	0.2655	0.1	0.2169
mg-HCH	mg-HCH	mg-HCH	mg-HCH	mg-HCH

Biotic and abiotic degradation of HCH isomers can follow many different pathways and result in a variety of byproducts. Surprisingly, many of the benzene related byproducts typical of biotic degradation were detected in both the BOS 100 and the carbon only column. The five main compounds associated with dechlorination of HCH that were found on carbons in both columns are identified in the above table. The upper data set is associated with BOS 100 while the lower data set is the carbon only column. The yellow highlighting designates anaerobic pathways, and the blue is aerobic pathways.

For each compound, there is a relationship defining the mass of HCH required to produce a given mass of the degradation byproduct. Using benzene as an example: 3.78 mg of HCH are required to produce 1 mg of benzene. The total mass of each byproduct on the BOS 100 or the carbon packed into each column was determined and, using the relevant factor, the mass of HCH required to produce that byproduct was calculated. These are the values reported in the table and the units are mg of HCH.

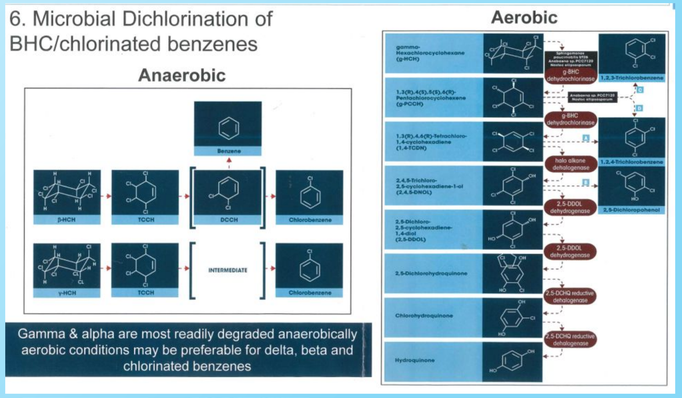
BOS 100				**Site Carbon**			
(mg)	β-HCH	α-HCH	γ-HCH	**(mg)**	β-HCH	α-HCH	γ-HCH
in:	3.188	0.013	0.0196	**in:**	2.856	0.0117	0.0176
out:	0.088			**out:**	0.082		
on Carbon	1.27	0.0105	0.0105	**on Carbon**	1.272	0.0096	0.0284
Degraded	0.422			**Degraded**	0.676		
Sum	1.78			**Sum**	2.03		

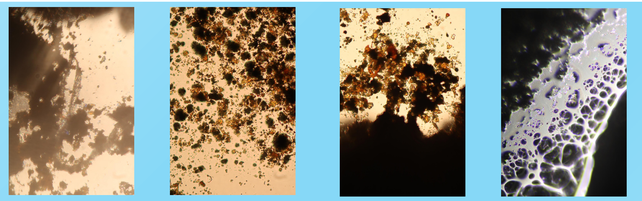
BOS 100 column

- 3.188 mg of beta-HCH entered the column,
- 1.78 mg is the sum of beta-HCH exiting in the discharge, mass recovered from the BOS 100, and that degraded,
- Hence only 55.8% of the total beta-HCH that entered the column is accounted for

Activated Carbon column:

- 2.856 mg of beta-HCH entered the column,
- 2.094 mg is the sum of beta-HCH exiting in the discharge, mass recovered from the carbon, and that degraded,
- Hence 71.1% of the total beta-HCH that entered the column is accounted for





Following the observation of bioaccumulation on both columns, several samples of groundwater to be analyzed for metagenomic sequencing and biomass were collected. In addition, a sample of GAC was collected from the top of the carbon bed in the P&T system on site for the same analytical.

- Total biomass in the monitor wells ranges from 2x10^8 to 1 x 10^9 gene copies per liter.
- Biomass on the carbon was 3.3 x 10^9 gc/gm-carbon, considerably higher than what is in groundwater.

The following summarizes some characteristics of the most abundant microbes

- All the samples contain Pseudomonas fluorescens BBc6R8. No publication has specifically identified Pseudomonas fluorescens BBc6R8 as a degrader of benzene or chlorobenzenes. However, when its KEGG-documented pathways are examined, some essential enzymes in the degradation of benzene and chlorobenzenes are present. For example, the catechol 1,2-dioxygenase is present. This enzyme is capable of chlorobenzene degradation (1,2-dichlorobenzene) (Alfreider, 2003) (Haigler, 1988). Note that Pseudomonas sp. NC02 and Pseudomonas aeruginosa have the same enzymes and are also present. Rugamonas rubra lacks 1,2-dioxygenase but produces many enzymes supporting downstream reactions post-ring breakage.
- Rugosibacter aromaticivorans, Janthinobacterium sp. BJB412, and Sulfuricaulis limicola have catechol 2,3-dioxygenase and the phenol 2-monooxygenases to degrade chlorobenzenes and benzene.
- Pseudomonas veroni has both catechol 1,2-dioxygenase and catechol 2,3-dioxygenase as does Sphingomonas sp. YL-JM2C and Sphingomonas wittichii RW1. Sphingomonas sp. MEA3-1 contains all the enzymes discussed above.