Study of a Reactive Barrier for the Biodegradation of Chlorobenzene Contaminants in Groundwater

National Institute of Environmental Health Sciences
Superfund Research Program

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Background

Chlorobenzenes are organic solvents used primarily as chemical intermediates in the production of numerous widely-used goods, such as pesticides, deodorant, rubber, and disinfectants. Historically, thousands of tons have been released into the environment both intentionally and accidentally. Due to their limited solubility in water and resistance to environmental chemical reactions, spills create a pollutant source that can persist for decades. In terms of human health, long-term exposure to these compounds is known to affect the central nervous system, with extreme chronic effects including neurotoxicity and kidney and liver damage.

The ultimate goal of this research is to study how a reactive barrier will sequester and degrade chlorobenzenes using the sorptive capacity of activated carbon and the biodegradation capacity of specialized microorganisms. Specifically, we are using the conditions found in a contaminated wetland adjacent to a Superfund site in Delaware, where numerous spills have led to chlorobenzene contamination in the groundwater and soils, where removal is extremely difficult.

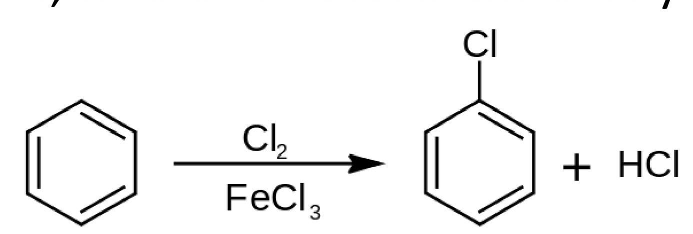


Figure 1. The chlorination of benzene. Image from Wikipedia: "Chlorobenzene." 2016

In-Situ Remediation

The high concentrations of chlorobenzenes in the groundwater around the Superfund site call for an effective solution to avoid permanent contamination of the surrounding ecosystems. Known biodegradation pathways for chlorobenzenes involve aerobic and anaerobic bacterial breakdown.

Our proposed solution is a reactive barrier that would employ abiotic sorption using granular activated carbon (GAC) and microbial biodegradation using both aerobic and anaerobic cultures. The barrier would be divided into aerobic and anaerobic zones; groundwater would then flow from the bottom anaerobic zone up through the aerobic zone. Also packed throughout the barrier are sand, GAC, and chitin, a source of carbon for the microbes.

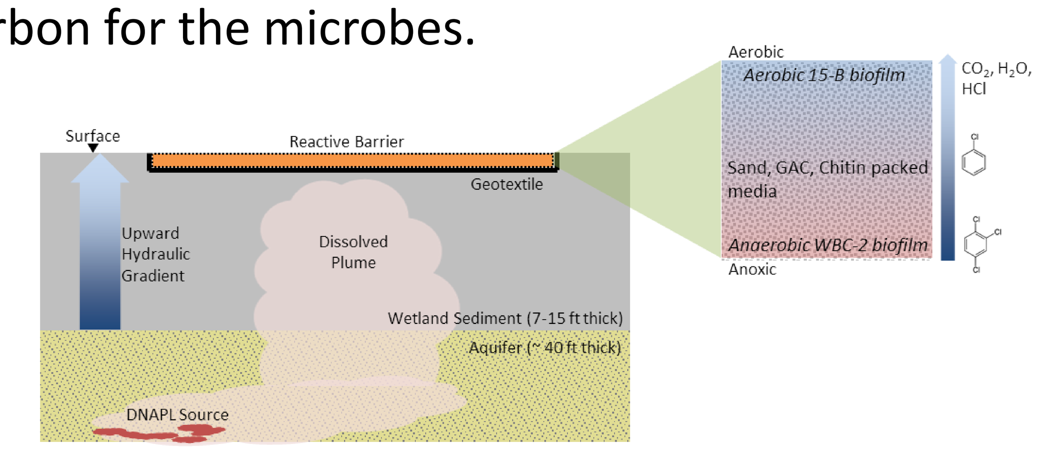
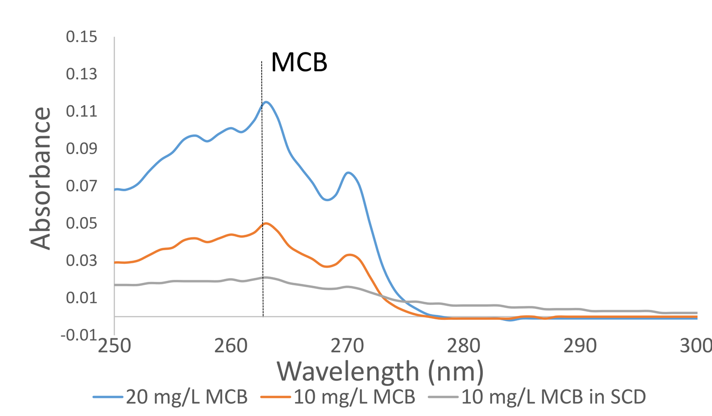


Figure 2. Diagram of the proposed reactive barrier

Analysis Methods

UV-Vis Peak Wavelengths:

We constructed spectrum scans for different solutions to determine at what wavelength to detect each chlorobenzene. In a clean system, individual chlorobenzenes can be easily detected using absorbance measurements. However, in more complex systems with multiple chlorobenzenes, we have to use gas chromatography to separate the chlorobenzenes based on retention times, then detect them with mass spectrometry.



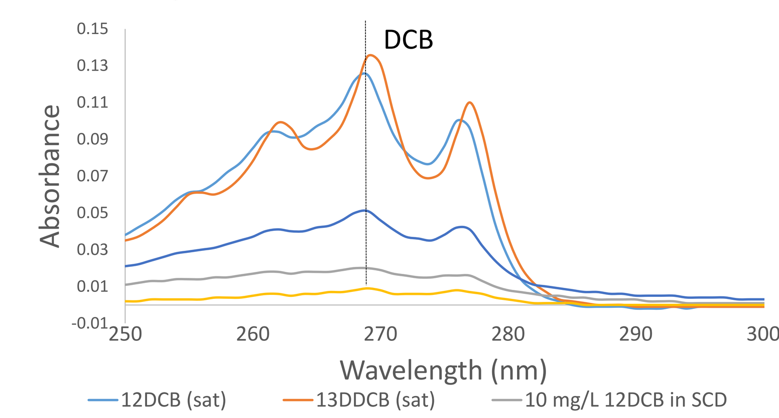
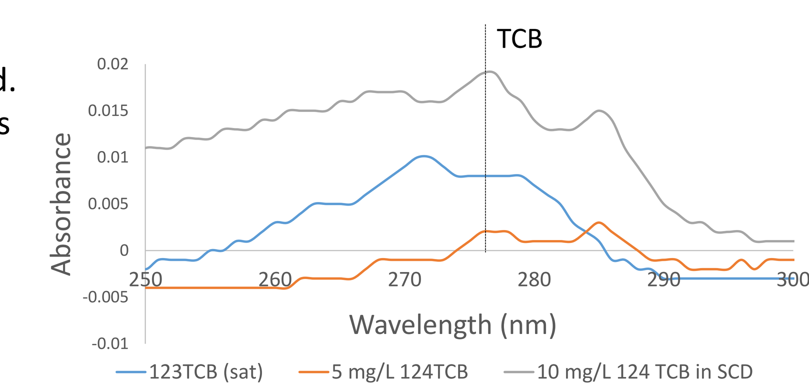


Figure 3. Spectra plots with peak absorbances identified. **Below:** table of chosen and published peak absorbances (Source: Carbon Adsorption Isotherm Study, 1980).

	Chosen	EPA
MCB	263	209
DCB	269	214
TCB	276	227

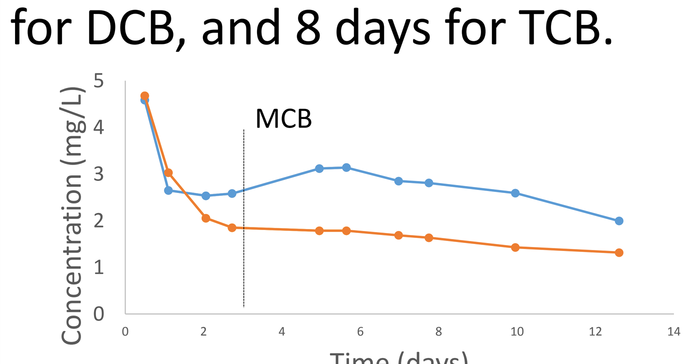


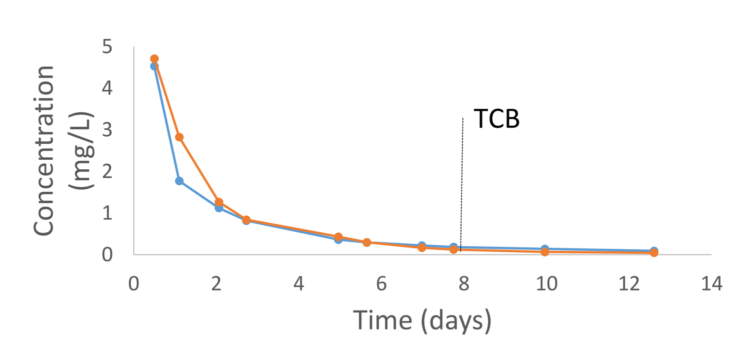
CB Sorption to Activated Carbon

Sorption, the process of binding molecules together, is used in this remediation process to adhere different chlorobenzene compounds to granulated active carbon and therefore remove it from the surrounding environment. In theory, GAC will absorb chlorobenzenes over time until an equilibrium concentration is reached, in which the GAC is at sorption capacity. Such is how sorption is used in cleanup of contaminants.

Kinetic Stir Bar Experiment:

We conducted this experiment to show how GAC takes up a mixture of different chlorobenzenes at different rates over time. Because it requires more energy to cut off more Cl- molecules, it should take the longest for TCB to reach equilibrium sorption, and MCB the shortest. We found that the time to equilibrium sorption was approximately 3 days for MCB, 5 days for DCB, and 8 days for TCB.





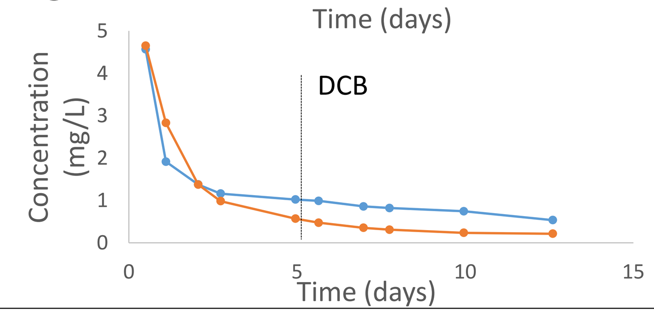


Figure 4. Change in concentration plots for (top left) MCB, (bottom left) DCB, and (above) TCB in solutions with **50 mg/L GAC** over a period of two weeks. With **5 mg/L** of each of MCB, 1,2-, 1,3-, and 1,4-DCB, and 1,2,3- and 1,2,4-TCB added, the concentration of chlorobenzenes totaled **30 mg/L**. The two experimental replicates are indicated by the two different-colored lines.

Degradation Experiment Results

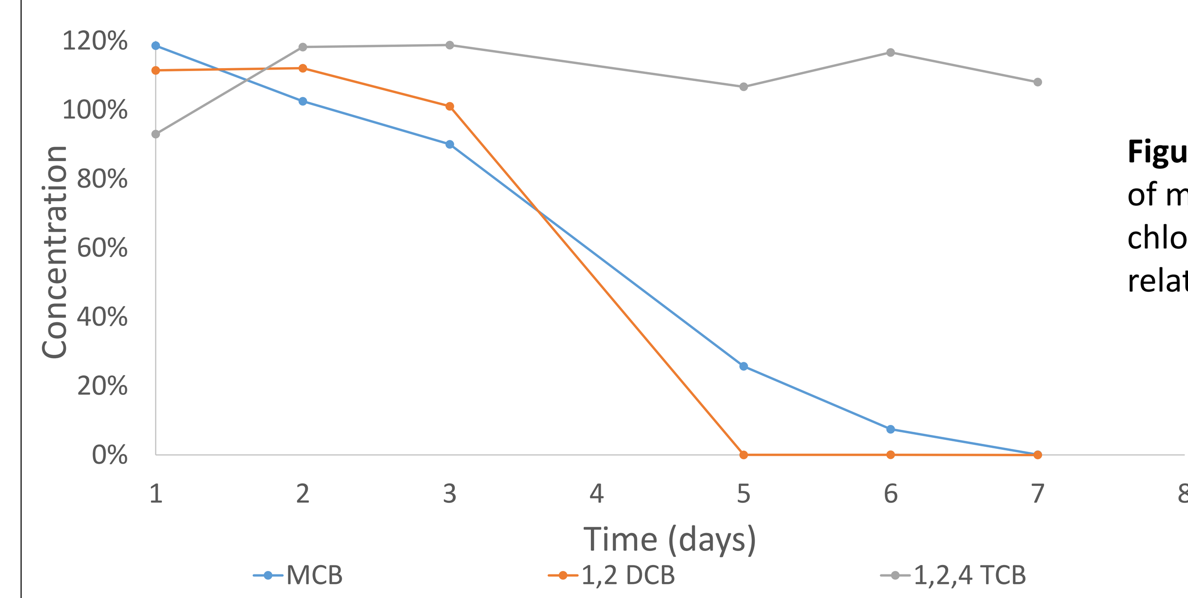


Figure 5. Aerobic degradation of mono-, di-, and tri-chlorobenzene compounds relative to controls.

This experiment compared how quickly each chlorobenzene mixture degraded in the presence of aerobic bacteria. By the end of the seven day period, MCB and DCB had completely exhausted, and TCB concentration was still slowly decreasing. This matched our predictions; TCB was expected to degrade at the slowest rate. However, in theory, DCB should have degraded at a noticeably slower rate than MCB, so experimental errors could have contributed to some skew in the results.

Column Study and Preparation

- Glass columns, each with different cultures and sand/GAC mixtures
- Influent feed bottle pumps a highly concentrated chlorobenzene solution through each of the columns
- Tracer test used to confirm that flow rates are as close as possible so that the columns are all packed similarly

Figure 6. Current column experiment

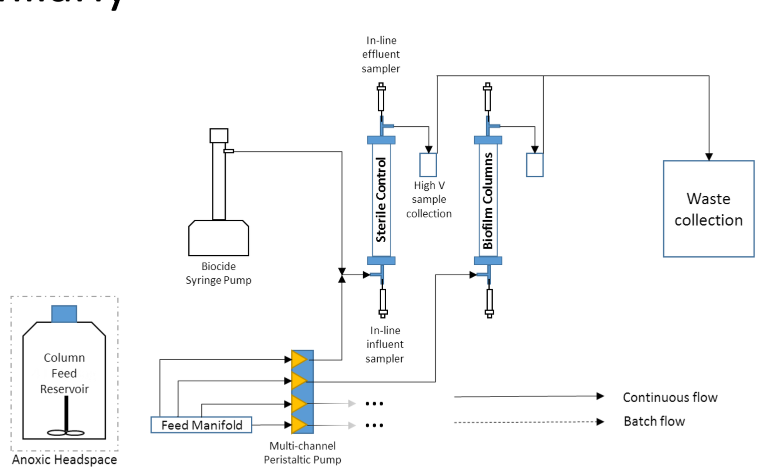


Figure 7. Column setup diagram

Conclusions and Outlook

For the past few months, we have explored the mechanisms of a reactive barrier that offers a solution for chlorobenzene contamination in groundwater. In reality, the site conditions will differ from the ideal ones we simulated in this study. In the long term, we will have to determine how the barrier would respond to factors such as the presence of different microbes, non-sterile groundwater, etc. Throughout the experiment, one specific difficulty that arose was that some compound was consistently lost during transfer from the feed bottle through the multi-channel pump, and then through a length of tubing into the columns. In the future, we will be able to work out challenges such as this one so that we can apply our findings more broadly.

Supporting Research Grant: "Dual-Biofilm Reactive Barrier for Treatment of Chlorinated Benzenes at Anaerobic-Aerobic Interfaces in Contaminated Groundwater and Sediments", National Institute of Environmental Health Sciences, September 10, 2014 to May 31, 2018; Dr. Michelle Lorah (USGS), Co-PI and Drs. Neal Durant and Amar Wadhawan (Geosyntec), Co-PIs