

# CAT 100: Aggressive Formulation for Application to DNAPL, Persistent Organic Pollutants, and Complex Sites

Scott Noland - RPI



## Pentachlorophenol (PCP)

### Physical characteristics of chlorophenols

Most of these compounds are solids at room temperature. Solubility in water at 25 deg C ranges from 28 gms/L for 2-chlorophenol to 12 ppm for pentachlorophenol (PCP) and solutions are typically acidic. Solubility is significantly increased at high pH so PCP concentrations in groundwater can easily reach hundreds of ppm under such conditions. High pH conditions were not evaluated in this bench test.

A test protocol was developed and the bench commenced on February 19, 2025. In addition to PCP, 2,3,4,6-tetrachlorophenol (Tetra-CP), and 2,4,6-trichlorophenol (Tri-TCP) were included in the bench. The cleanest indicator of degradation is generation of chloride. The original plan included monitoring for chloride along with tracking changes in concentrations of chlorophenols, detection of partially dechlorinated phenols, and monitoring for evidence of biological activity.



## Evaluation of Toxicity

Chlorophenols are common environmental contaminants originating from their use as wide-spectrum biocides in industry and agriculture and their formation during pulp bleaching. CAT 100 functionality relies on bacterial activity so the potential for biocidal concentrations to be present in groundwater was a concern. 2,4,6-trichlorophenol (2,4,6-TCP) was chosen to evaluate this question. Solutions were prepared at 0.5 ppm, 5 ppm, 50 ppm, and 100 ppm. Evidence of biological activity is the only focus, so testing was limited to Standard Methods 300.1 for anions and RSK 175 for gases.

In this case, the Chloride Control becomes the optimal signature for expected biological activity for comparison with each of the four Tri-CP concentrations. Evidence of biological activity in the Control is shown by depletion of nitrate and generation of carbon dioxide. At time zero, 300 ppm of nitrate is present.

	Carbon Dioxide (ppm)		
	3/20/2025	4/15/2025	7/23/2025
CI-Control	203	311	163
0.5 ppm		119	133
5 ppm		274	35
50 ppm		238	227
100 ppm		1320	817

Clear evidence of biological activity is seen in the above photo of the 100 ppm Tri-CP vial where foaming and pressure has nearly burst the septa. Instead of suppressing the bacteria, it appears increasing the concentration stimulates activity.

	Nitrate (ppm)		
	3/20/2025	4/15/2025	7/23/2025
CI-Control	93	69.5	92.1
0.5 ppm	106		119
5 ppm	104	106	113
50 ppm	7.8		13
100 ppm	7.5	10.9	11.7

Most of the nitrate depletion occurs within the first month. The control dropped 69% which mirrors the two low Tri-CP concentrations while the higher concentrations nearly consumed 100% in that same time.

	Acetate (ppm)		
	3/20/2025	4/15/2025	7/23/2025
CI-Control	9	18.6	ND
0.5 ppm	10.8		33
5 ppm	16.7	16.3	38
50 ppm	1290		513
100 ppm	1570	644	670

Generation of acetate likely occurs from fermentation of added amendments. As with other indicators, significantly more is generated as the Tri-CP concentration increases. It is very possible we are seeing evidence of biological degradation of the Tri-CP in the 50 and 100 ppm vials.

## Discussion of Results

	Acetate Generation (ppm)			
	3/5/2025	3/20/2025	4/15/2025	7/23/2025
BOS 100 PCP	5.9	6.9	12.2	2.3
CAT 100 PCP	55.6	93.3	137	97.6
CAT Tetra-CP	56.5	97.7	80.8	96
CAT Tri-CP	97	79.4	90.1	104

Toxicity evaluation data should mirror chlorophenol test data as the only difference is now the BOS 100 is added. It should be kept in mind that the BOS 100 is made from granular activated carbon, and this will tend to adsorb organic compounds like acetic acid. Also, the PCP loaded BOS 100 treatment strictly abiotic with DI water, so it is not surprising to see no real evidence of biological activity in this treatment with very little generation of acetate or methane. Fermentation of the starch generates hydrogen, sugars, and electrons. Activated carbon is a conductor and shuttles electrons to the metallic iron within the microporous structure. This protects the iron from oxidation and catalyzes the reductive dechlorination of target contaminants. The fact that activated carbon absorbs many of the organics added or generated is a positive feature as significant contaminant mass will reside on the carbon and having the resources to degrade these compounds in contact or proximity to where they are needed is a perfect scenario.

	Methane Generation (ppb)			
	3/5/2025	3/20/2025	4/15/2025	7/23/2025
BOS 100 PCP	6.2		ND	ND
CAT 100 PCP	18.3	223	340	184
CAT Tetra-CP	18.9	52.3	219	78
CAT Tri-CP	26.3	41.6	264	84

Measuring changes in chloride concentration is the most direct means for demonstrating degradation of the chlorophenols. Chloride generation across treatments is provided in the following table. Using the BOS 100 PCP data as an example, the percent chloride composition for PCP is 66.2. Five grams of BOS 100 containing 3 mg PCP/gm-carbon is present in the serum vial, so we start with 15 mg of PCP. The amount of chloride will be  $15 * 0.662 = 9.93$  mg. This mass of chloride is dissolved in 150 ml of reagent water so the concentration at 100 percent degradation will be  $9.93 \text{ mg} / 0.15 \text{ liters} = 66.2$  ppm. As shown, 38.1 ppm chloride was generated in the BOS 100 control, so the percentage degraded is  $38.1 / 66.2 = 0.576$  or 57.6%.

	Chloride Generation (ppm)			
	3/5/2025	3/20/2025	4/15/2025	7/23/2025
BOS 100 PCP	7.5	ND	11.4	38.1
CAT 100 PCP	15.1	6.1	21.7	32.9
CAT Tetra-CP	15.1	5.7	15.5	28.8
CAT Tri-CP	14.7	6.8	36.3	19.7

	Mass % Cl	5-month Cl	% Degrad.
BOS 100 PCP	66.2	38.1	57.6
CAT 100 PCP	66.2	32.9	50
CAT Tetra-CP	61.1	28.8	47
CAT Tri-CP	53.9	extraction	NC

## Mass Balance

A rigorous mass balance requires all demands on the original mass must be included and ideally account for exactly 100% of the starting mass. This means we need to include the mass dissolved in the aqueous phase, mass adsorbed within the BOS 100, and mass degraded. The BOS 100 dose will basically adsorb 100 percent of the dissolved chlorophenol. So, there is no significant contribution from the dissolved phase.

The five-gram dose of BOS 100 is a dry wight and when the carbon is recovered it is saturated with water. In addition, it is contaminated with residual starch and other sludge stemming from biological activity. When the serum vials are sacrificed, those samples from the aqueous phase are collected and then the vial is shaken to suspend solids. The BOS 100 is allowed to settle and excess liquid carefully decanted. Additional water can be added and the process repeated to eliminate most of the residual solids contaminating the BOS 100. The BOS 100 is then washed from the vial onto a Buchner funnel and washed with reagent water and sucked dry.

BOS 100 saturated with water gains about 60% in weight so 1 gm dry becomes 1.6 gms saturated. Our example is data from the April sampling and extraction of the CAT 100 2,4,6-TCP treatment.

- This compound is 53.9% chlorine so 100 % degradation would produce 8.09 mg chloride.  $15 \text{ mg } 2,4,6\text{-TCP} * 0.539 = 8.09$ .
- 36.3 ppm chloride was present in the serum vial and baseline was 7.1 ppm so 29.2 ppm of chloride was generated.
- In 150 ml this 29.2 ppm equates to 4.38 mg of chloride generation or 54.2% degradation.  $(4.38 / 8.09) * 100 = 54.2$ .
- 0.2963 gms of wet carbon was extracted with 10 ml of solvent and the 2,4,6-TCP concentration in the extract was 26.9 ppm.
- The dry wt. will be  $0.2963 / 1.6 = 0.1852$  gms and the mass factor will be 5 gm-carbon / 0.1852 gm extracted = 27
- Recovered mass will be:  $(26.9 * 0.01) * 27 = 7.263$  mg
- Chloride recovered:  $7.263 * 0.539 = 3.915$  mg
- Total chloride recovered =  $3.915 + 4.38 = 8.295$ . We started with 8.09:  $8.295 / 8.09 = 1.03$  or 103% recovery.

## Conclusions

- Unless dissolved concentrations of chlorophenols significantly exceed 100 ppm, there should not be any suppression of the CAT 100 technology, and the microcosm should develop diversity and thrive. Biocidal activity should not be an issue.
- Adsorption capacity of BOS 100 for site COCs is high so a large drop in dissolved concentrations will be rapidly observed. Most of the contaminant mass will quickly reside on the BOS 100.
- Multiple lines of evidence support the ability of CAT 100 to degrade PCP. Further all other chlorophenols that are either present or created through degradation of parent contaminants can also be degraded by CAT 100.

For the trichlorophenol and tetrachlorophenol treatments, 100 ppm solutions were prepared in reagent water to fill the vials after addition of other amendments including trace metals, micro and macro nutrients, bacteria, starch, yeast extract, soy fiber, and BOS 100. 150 ml serum vials were filled with the solutions resulting in 15 mg of chlorophenol in each test vial. Because of the low solubility of PCP, a 100 ppm solution was not possible. PCP was dissolved in anhydrous 200 proof ethyl alcohol and this solution was uniformly loaded onto BOS 100 in a glove box under an atmosphere of nitrogen. Since 5 gms of BOS 100 was added to each test vial, the alcohol solution was adjusted to result in 3 mg of PCP per gram BOS 100, matching the 15 mg dose/vial from 100 ppm solutions.

The following tests were included

- Chloride control – Contained all amendments except no BOS 100 or chlorophenols were added. This control tracks baseline chloride throughout the 5-month bench test.
- BOS 100 PCP – This treatment contains only BOS 100 loaded with PCP and DI water. Purpose is to track performance of abiotic dechlorination of PCP by BOS 100 alone.
- CAT 100 PCP – Contains BOS 100 loaded with PCP and all amendments and bacteria to create CAT 100.
- CAT 100 Tetra-CP – CAT 100 with all amendments and 150 ml of 100 ppm Tetra-CP solution.
- CAT 100 Tri-CP – CAT 100 with all amendments and 150 ml of 100 ppm Tri-CP solution.
- Toxicity Tri-CP included all amendments and bacteria along with Tri-CP at four different concentrations to evaluate possible biocidal effects. No BOS 100 was included.

The plan included a set of seven serum vials for each treatment in the bench which was proposed to run for five months. Over that time, serum vials from each set were to be sacrificed and analytical testing performed on the water and recovered BOS 100. Proposed testing included inorganic and organic anions, low molecular weight hydrocarbon gases such as methane and carbon dioxide, and GC/MS determination of volatile and semi-volatile organic compounds.

## Amendments

The purpose of adding starch, yeast extract, and plant fiber such as soy or pea is two-fold. Fermentation of starch and fiber produces hydrogen and electrons that participate in reductive dechlorination and prevent oxidation of the metallic iron residing in the microporous structure of the BOS 100. This enables degradation of chlorophenols through a sustainable process. In addition, these amendments provide a source of amino acids, vitamins, and protein to support microbial growth and diversity.

## Analytical Testing

- Standard Methods 300.1 - Inorganic and Organic anions
- RSK 175 - Low molecular weight hydrocarbon gases and carbon dioxide
- Method 8270 – Semivolatle Organic Compounds
- Method 8260B – Volatile Organic Compounds