CAT 100: IN SITU CHEMICAL REMEDIATION WITHOUT DEPLETION OF METALLIC IRON

INTRODUCTION

CAT 100 was introduced into the marketplace over six years ago. It was based on the synergy discovered between microorganisms capable of degrading CVOC's (enhanced reductive dechlorination) and RPI's BOS100® granular activated carbon that has been impregnated with metallic iron. BOS 100 was engineered for abiotic degradation of halogenated organic compounds, and its main limitation is the fact that in abiotic dechlorination of these compounds, the metallic iron is oxidized and depleted over time.

The metabolic (biological process) process involves both electron donors and acceptors. There is a transfer of electrons during degradation or respiration of these halogenated compounds and the carbon and iron can facilitate this process. Recent work has shown that activated carbon (a conductor) can effectively shuttle electrons to absorbed compounds. The iron impregnated carbon provides an even more effective platform for the shuttling of electrons.

The origin of these electrons in conventional technology stems from fermentation of substrates like sodium lactate and emulsified oils, and these are not well suited to support degradation over an extended period in an efficient manner. Simple addition of a complex carbohydrate is not enough as those microorganisms adept at degrading halogenated compounds are not typically suited to the breakdown or fermentation of such materials. The key is to add organisms whose main function is degradation of complex carbohydrates because the large molecules are broken down into small pieces that are directly usable for beneficial degradation of halogenated compounds.

Of all the materials tested, starch produced the best overall results. Food-grade starch is readily available and inexpensive. Starch is slightly soluble in water and is readily fermented by a range of non-pathogenic organisms. We now have a system that rapidly adsorbs chlorinated solvents; adsorption results in a much higher concentration within the pore structure of the activated carbon where metallic iron resides and degrades the contaminants; added microorganisms breakdown the starch producing electrons which are shuttled by the carbon to metallic iron within in the activated carbon, preventing oxidation of the iron; and finally the overall process is enhanced by microorganisms capable of degrading CVOCs inhabiting the macropore and mesopores and exploiting generated sugars and other small organic molecules produced through degradation of the starch to generate additional electrons and assist with degradation of adsorbed CVOCs. The metallic iron is now playing a catalytic role in the degradation of CVOCs.

Data from four different sites where RPI's CAT 100 has been installed are discussed. These are DNAPL sites and range from having nearly 0.5 meters of free phase DNAPL to sites where soil impacts exceed generally accepted Csat values. Data summarized encompass results over extended periods of time from 1 to 5 years post injection. Key chemical data is presented along with metagenomic sequencing and biomass results to identify microbes thriving in heavily impacted areas and comparison with baseline controls so changes in the microbial community stemming from installation of CAT 100 are clearly illustrated.

SITE DATA

CAT 100 was developed for remediation of sites heavily impacted with CVOCVs in soil and groundwater (GW). The first example is a TCE DNAPL site in Kentucky. Initial TCE concentrations at many wells were in the hundreds of ppm. Figure 1 shows data from MW-18 which initially had right at 50 ppm TCE and just over 1 ppm cis-DCE. The product was injected late April 2020. Within a couple of months, TCE had nearly vanished, and the classic ERD signature emerged with rapid generation of cis-DCE and then vinyl chloride (VC). The cis-DCE topped out at just under 75 ppm, then began to fall and this all happened within the first six months, post injection. By the fall of 2021, only low levels of DCE and VC remain, and they are continuing to fall.

Figure 2 tracks generation of degradation byproducts and evidence of continued biological activity. Ethylene is one of the major byproducts of complete dechlorination of chloroethenes. The CAT 100 consortia have over one hundred different microorganisms. Some dedicated to degradation of the starch and others targeting specific chlorinated compounds and others providing metabolic support to the overall process. The CAT "signature" often contains low molecular weight volatile fatty acids like acetic, propionic, and butyric acids, in addition to gases including ethylene, methane, and carbon dioxide.

It is clear from the graph that methane and ethylene continued to increase well beyond the point where dissolved CVOCs remained. After two years, the ethylene concentration is over 1200 ppb, down from a high of 1700 ppb. Initial spikes in acetate, carbon dioxide, ethylene, and methane coincide with the onset of vigorous biological activity stemming from installation of CAT 100. Prior to installation of CAT 100, only trace amounts of ethylene and carbon dioxide were present, an indication that little naturally occurring degradation was taking place. Within a few months, CO2 had risen to roughly 50% of saturation and after two years, generation continues, and the concentration is over five times the original level. Acetate rose rapidly and then began to fall. Within the first nine months it essentially was non-detect. This does not mean it was not being generated, it more than likely is but it is being consumed as quickly as it is formed.

The next example is an industrial site in Europe involving PCE. In 2003/2004, excavation of accessible soil was completed, and mechanical systems operated for over five years. As indicated by the heat map in Figure 3, extensive DNAPL remained. Two km downgradient, private homeowners were forced to discontinue pumping wells in their gardens. Over 40 cm of free-phase DNAPL was present in monitor wells just outside the building footprint to the north. Multiple wells exhibited lesser amounts and soil impacts over 50,000 ppm were identified.

In the second quarter of 2017, CAT 100 was installed. Four years later, measurable free-phase DNAPL has been eliminated and concentrations have fallen dramatically as shown in Figure 4. Figure 5 depicts dissolved ethene in May of 2017. Little evidence of degradation existed prior to installation of the CAT 100. No or very low concentrations of daughter products and only trace amounts of ethylene were detected in early 2017. Animation of the changes in PCE and ethylene concentrations over the four years since installation of CAT 100 is available – just ask to see it.

Figure 6 shows ethylene generation is active throughout nearly the entire plume. Concentrations in the hundreds of ppb are evident and steady increases in ethylene production was evident over the four years since treatment commenced. It is important to keep in mind that 100% of all contaminant mass removal has resulted from a single installation event over the second quarter of 2017. No additional injections have been completed and no supplemental substrate, nutrients, or microorganisms have been added.

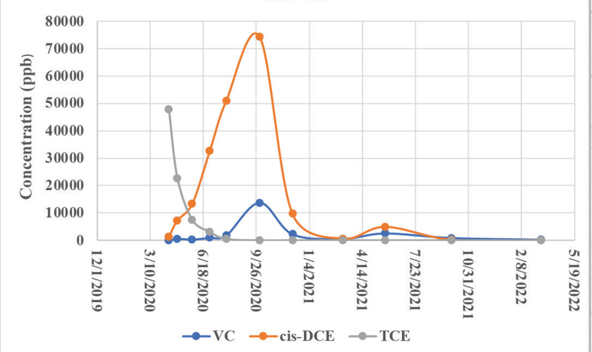
BIOLOGICAL DATA

This next site is unique in that CVOC remediation was implanted over several years. The first step eliminated off-site impacts and included installation of a PRB to prevent future migration of contamination off-site. The initial plan was to simply manage on-site contamination with minimal active remediation. However, with the advent of CAT 100, a decision was made to test the technology in one of the source areas. Results were good enough to motivate the owner to expand treatment. The expansion was implemented over a couple of years: each year expansion of treatment into a new region was completed with the scope tailored to financial constraints to mitigate the impact on cash flow. The largest plume consisted of PCE and daughters while a smaller area was impacted with carbon tetrachloride (CT). The CT plume comingled with the larger PCE plume making for an interesting mix of COCs.

Samples of GW was collected from several wells at the site and sent to Microbac in TN for biomass and metagenomic sequencing (MGS) to identify microbes thriving in various environments across the site. This included an up-gradient control where chloroethene impacts are low, an area where CAT 100 had been installed roughly two to three years ago, and a well where CAT 100 had been installed a year ago.

Figure 7 details those microbes identified in the up-gradient control. Microbes present in this well are identified on the far left and values in the orange column are the relevant abundance of each organism, going from the most to least abundant. Values below 1% are typically not included. There are three columns: the first is our control, the second is well number PDC-15 and is the location where CAT 100 had been in the ground for over two years, and the third is PDC-16A which is where CAT 100 was installed a year ago. Values listed under PDC-15 and PDC-16A indicate whether microbes observed in the control were also found in the other two wells. It is apparent that they are not to any significant extent. Microbes present in the control are predominantly associated with metabolism of methane.

FIG 1.



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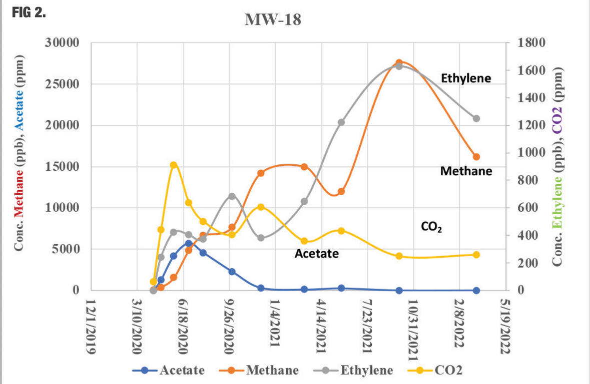

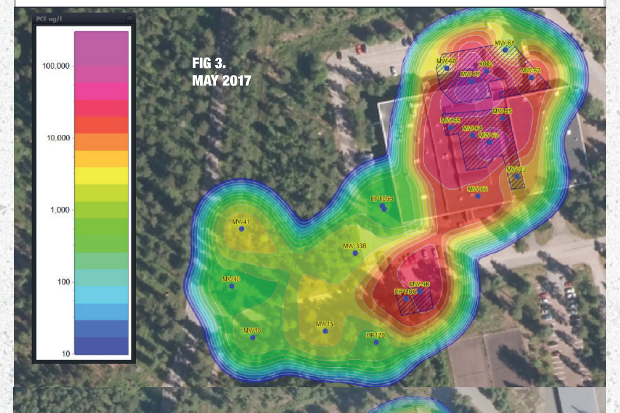

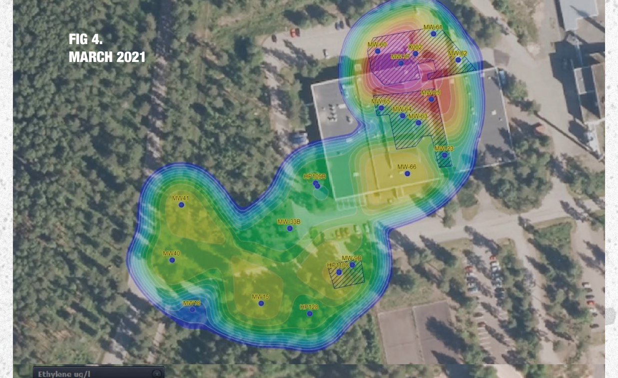

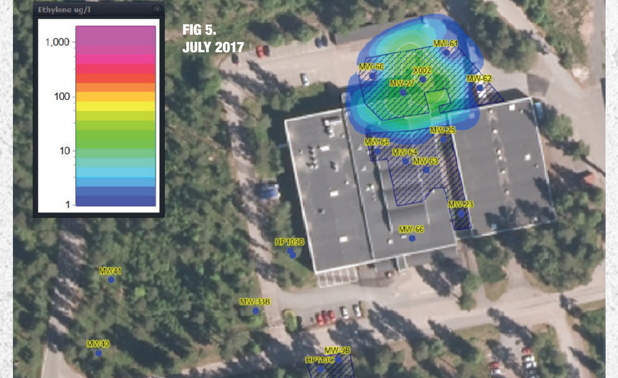

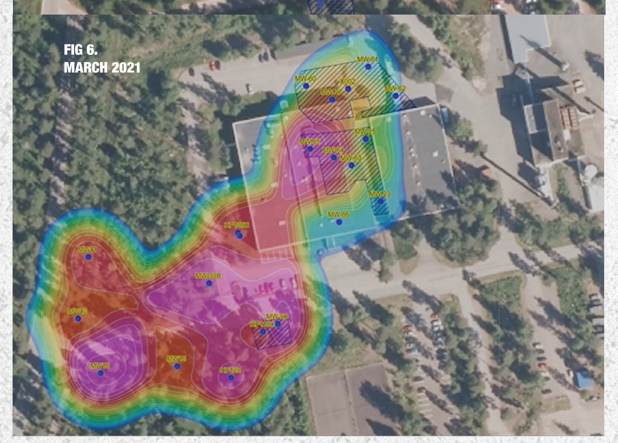

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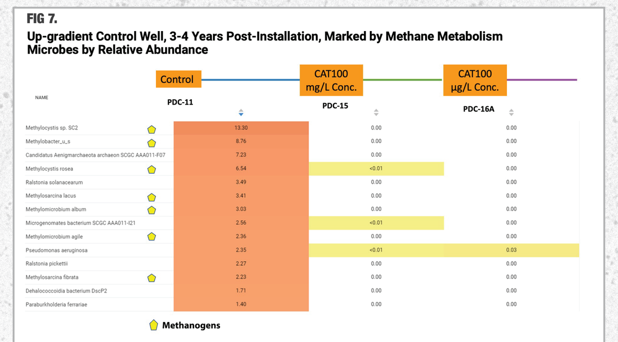

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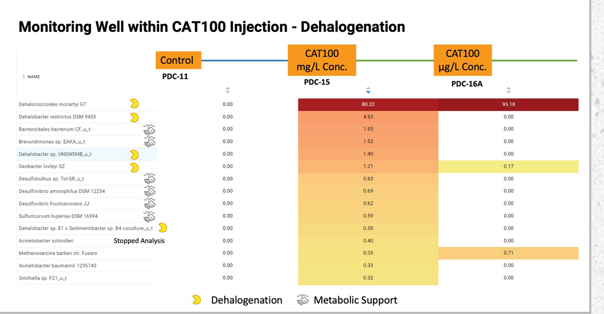

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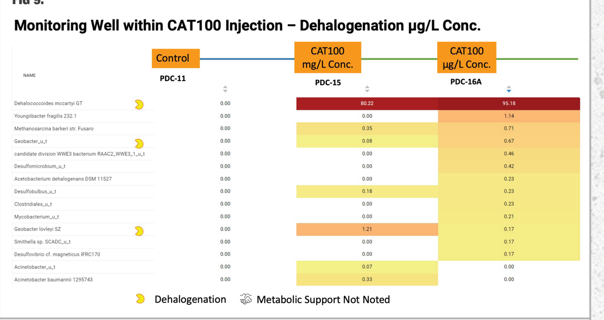

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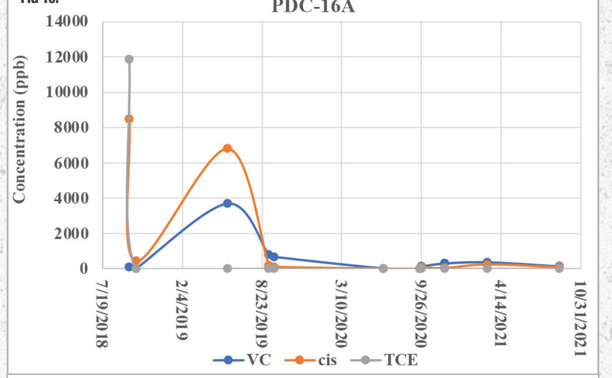

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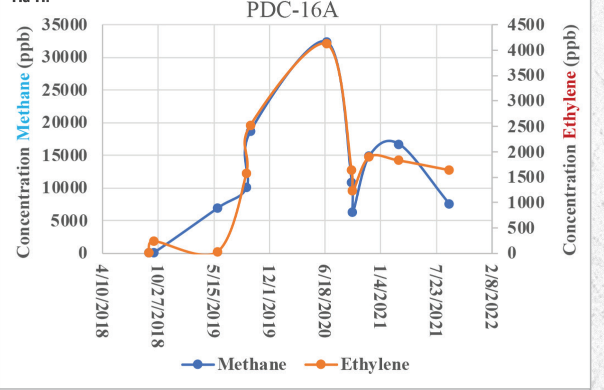

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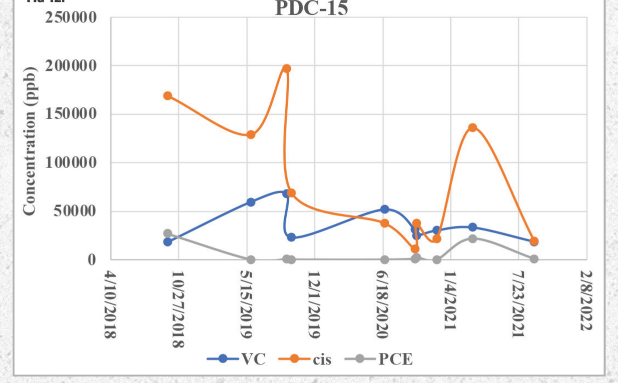

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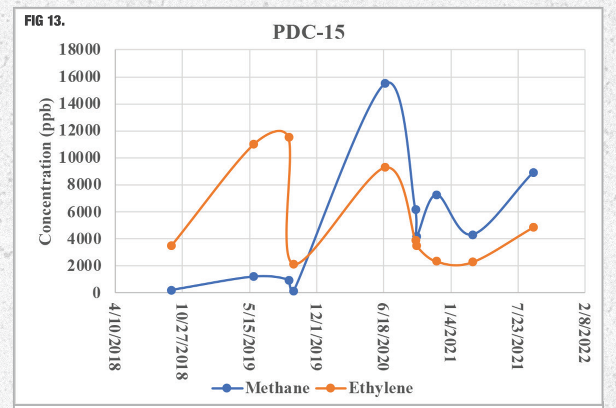
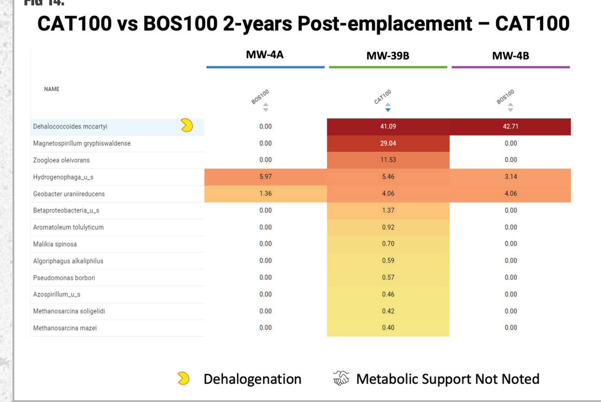


FIG 14.



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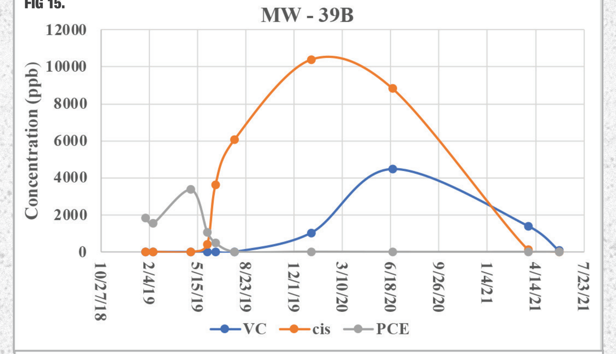


FIG 16.

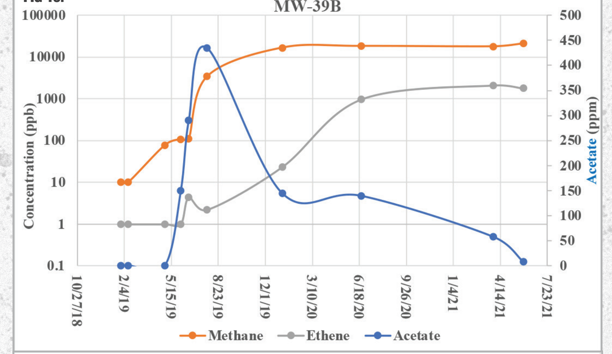
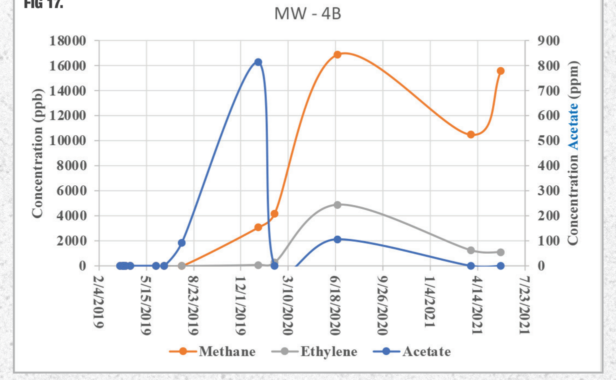


FIG 17.



BIOLOGICAL DATA CONT.

1. Methylocystis sp. SC2, 13.30%, Reduces methane to methanol attenuating methane release.
2. Methylobacter, 8.76%, Identified at the genus level, it is the most abundant methanotrophs in wetlands. Reduces methane to methanol.
3. Candidatus Aenigmarchaeota archaeon SCGC AAA011-F07, 7.23%, Limited metabolic capacity, committed symbiotic lifestyle, meaning that it is dependent on other microbes to live. It cannot produce its own amino acids, etc. Symbiosis marker.
4. Methylocystis rosea SV97, 6.54%, Grows on methane.
5. Methylosarcina lacus LW14, 3.41%, Grows on methane and methanol.
6. Methylomicrobium agile, 2.36%, Grows on methane and methanol.

Figure 8 is set up just like the previous except that now we are looking at the microbes found in the older CAT 100 installation. The first thing to notice is that the microbial community has completely changed. Not one of the microbes found here are found in the control. A diverse community is now present with several microbes known for dehalogenation and even more microbes that provide metabolic support. For example, the starch provides a carbon source and Bacteroidales ferments this to form ethanol. Desulfobulbus uses starch to form propionate and desulfovibrio generates formate. These intermediate compounds in turn are used to produce acetate, CO2, H2, and electrons. D mccartyi needs acetate for complete dechlorination of the chloroethenes. These microbes are consistent with a dechlorinating syntrophy, working as a team with the goal of degrading these CVOCs.

Figure 9 tabulates microbes found in the more recent CAT 100 installation. Although there are differences, the microbial communities intersect significantly. With the microbial communities in mind, changes in CVOC concentrations over time are shown in figures 10 and 11. Although not shown on the graph, PCE is initially 35 ppm. The initial drop in all CVOCs is due to adsorption by the activated carbon in CAT 100. This drop is followed by rapid generation of both cis-DCE and VC. These are also degraded and within roughly one year are reduced to values close to the MCLs. In less than 30 days, PCE vanishes and remains below the MCL.

The mass factor between ethylene and PCE is roughly six. This means 6 ppm of PCE, if fully degraded to ethylene, will result in 1 ppm of ethylene. Initially, methane and ethylene are present in only trace amounts, 55 ppb and 6 ppb, respectively. There is a lag of about two months before the onset of rapid rise stemming from degradation of CVOCs by the CAT 100. In less than a year, ethylene production has exceeded 4 ppm which accounts for over 24 ppm of PCE. Except for a scaling factor, the methane and ethylene generation depicted on Figure 11 track very closely. As total contaminant mass in soil and GW is consumed, methane and ethylene are falling. Although the site is not yet clean, the progress to date is good, has taken about two years and resulted from just a single installation of CAT 100. The site is not yet clean, but the progress after two years is good. This progress resulted from just a single installation of CAT 100.

The last data to be presented stems from a large redevelopment of a property that historically included a dry cleaner. Release of PCE over a long period had resulted in a long narrow plume that had gone off-site into a commercialized area. That portion of the plume on-site is over five hundred feet long. GW moving off-site contained double digit ppm PCE and impacts to soil in the upgradient source area runs into thousands of ppm PCE. CAT 100 was installed in the upgradient source area and a BOS 100® PRB at the downgradient property boundary were installed in the spring of 2019. Between the area where CAT 100 was installed and the BOS 100 PRB, there is roughly two hundred feet of untreated plume. As a result, declining COC concentrations entering the PRB would not be expected for some time.

Biologic data collected two years post injection in the source area and in the downgradient PRB is shown in Figure 14. The source area well exhibits a diverse microbial community with a strong presence of CVOC degraders. The more interesting data is that key microbes in the CAT 100 area are also present in the PRB well and at almost the same relative abundance. Well 4A is screened in the uppermost region of the water table while 4B is screened in a deeper zone. The shallow aquifer contains dissolved oxygen, so it is not surprising that dehalococcoides (DHC) is not present, being a strict anaerobe.

Chemical data is completely consistent with the biological microcosm. Figure 15 depicts the CVOC data within the source area. Initially, no VC was detectible and cis-DCE was less than 10 ppb. After two years, PCE is non-detect, cis-DCE is less than 10 ppb, and VC is declining but currently is above the MCL. Previously, cis-DCE had risen to above 10 ppm and VC had been above 4 ppm. Biomarkers are plotted in Figure 16 and demonstrate the lack of biological activity prior to installing CAT 100 and the rapid rise in acetate, ethene, and methane. Generation of ethylene has been consistent over the last year, persisting at a concentration exceeding 1000 ppb. The fact that acetate is declining is not alarming. In fact, it is known that DHC require acetate to completely dechlorinate CVOCs, producing ethene. The strong presence of DHC explains the loss of acetate over time.

A similar fingerprint is observed at the PRB-well screened in the deeper aquifer on Figure 17. No evidence of biological activity was noted prior to implementation of treatment, and no biological activity was expected at this location on site. After a lag of several months, rising acetate, followed by methane and then ethylene, was observed in the well. It is believed that degradation of starch in the upgradient CAT 100 area was carried by GW to the PRB area where BOS 100 provided an attractive platform, supporting establishment of a microbial community like that thriving in the source area. While VC and cis-DCE continue to enter the PRB, concentrations are slowly declining.

ESSENTIAL TAKEAWAYS

1. Microbial communities existing before installation of CAT 100 are completely altered by a combination of the BOS 100, substrates, nutrient, and microbes making up the CAT 100 technology.
2. Electrical connection between activated carbon and metallic iron residing in the microporous structure of BOS 100 promotes shuttling of electrons to iron and mitigates oxidation so that the iron increases the rate of CVOC degradation without being consumed.
3. Clean up of sites heavily impacted by CVOCs is possible with a single application of CAT 100.