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PCE Plume Fringe Attenuation Dynamics in Hyporheic Groundwater Reflect Remediation Success – 23477

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ABSTRACT

The recent first-time detection that Savannah River Site (SRS) CMP Pits perchloroethylene (PCE) groundwater plume had impacted a Gordon aquifer-well above the maximum contaminant level (MCL) highlights the importance of our project to the DOE Mission at SRS. Protecting this regional aquifer and others from plume impacts is a key DOE Mission remediation goal; advanced by S.C. State University (SCSU) DOE-Minority Serving Institutions Participation Program (MSIPP) collaborative efforts with Savannah River National Laboratory (SRNL), Pacific Northwest National Laboratory (PNNL) and Savannah River Nuclear Solutions (SRNS). The added MSIPP benefit of preparing minority students for environmental employment pipelines is also being achieved with unique collaborations with SRNS, SRNL, and PNNL. By applying comprehensive plume assessment methodologies for natural attenuation (NA) to Pen Branch, SCSU faculty and students merged field research/sampling experiences at SRS with microbial biotechnology to better assess NA pathways in hyporheic sediments. These efforts included microbial 16S rRNA gene sequencing with qPCR and gas chromatography-mass spectrometry (GCMS); and GC-isotope ratio mass spectrometry (GC-IRMS) with compound- specific isotope analysis (CSIA). Results yielded more decisive evidence for biotic NA pathways in Pen Branch.

These collaborative efforts should enable documentation of expected plume final-stage NA at SRS; potentially generating significant cost-savings with EPA fully accepting the SRNS Effectiveness Monitoring Report (EMR) plan. Our detection of dechlorinating bacteria has strengthened the Record of Decision for SRS. Both Pen Branch hyporheic sediments and groundwater and surface water samples were collected for analysis. Hyporheic sampling inserted a PVC piezometer beneath the stream bottom; bailing enclosed water; and hand-augering to reach the confining layer (up to 80 cm below stream bottom). Sediment samples were collected from several strata on replicate sampling dates; providing detection of cVOC spatial and temporal variability. Piezometer bottom-water sampling used both hole-water grab samples and passive diffusion bag (PDB) methods. All water and sediment samples were immediately stored on ice until chain-of-custody transport to the analytical lab. Microbial samples were immediately frozen/stored on dry ice. Our previous sampling determined the CMP Pits plume main Pen Branch impact area was along a 20 m stream-reach. We installed piezometers at these hot-spot stations along with upstream and downstream sentinel stations. Concentrations of cVOC were determined at the EPA- certified Pace Labs, Inc. All GC-IRMS and CSIA results were conducted at PNNL. Similarly, microbial analyses (16S rRNA gene sequencing with qPCR) were conducted at SCSU with more expansive microbial results conducted at PNNL to address NA. It is important to partition NA actions between microbial or abiotic degradation versus contaminant physical dilution or dispersion. Stream flow hydrology at SRS displays temporal variability and can therefore impact NA. Hydrological, geological, and microbial conditions in hyporheic zones are often heterogeneous. For this reason, we conducted observations of antecedent precipitation along with chemical analyses of hyporheic zone and surface waters. The high value of these MSIPP collaborations between SCSU faculty and students with SRNL and PNNL is that SRS Mission goals are being achieved by validating NA actions at Pen Branch while expanding the pool of HBCU students trained in higher-technology environmental remediation. As an HBCU, S.C. State University STEM-majors continued to advance their careers and enrich the DOE employment pipeline. This research developed the professional skills of SCSU students and faculty in multiple dimensions. At SRS, close interactions with SRNS professional engineers and scientists exposed our students to required job skills of project managers, engineers, safety officers, and researchers.

MSIPP experiences covered the full range of environmental management tasks from field sampling at SRS to high-tech laboratory experiences. Students achieved a full understanding of the scope of environmental operations ranging from safety protocol to chain of custody security. With regards to graduate school preparation, faculty-student mentoring also prepared MSIPP students for advanced degrees by training them in literature search and critical review skills; assisting manuscript preparations. . Our results quantified apparent NA progress for this plume; discovering levels of PCE, TCE, cis-DCE and VC declining by nearly 90% at piezometer 5DB80 from 2015 to 2022. Additionally, sediment sampling at different strata provided evidence of hydrological plume entry depths and relative NA activity. Since evidence of lowered cVOC concentration alone is inconclusive as to whether declines are caused by biotic microbial NA, our sediment microbial and CSIA results provided SRS with more comprehensive evidence that biotic NA is occurring and the cis-DCE and VC levels are not degradative "stalls" as hypothesized in some literature. Potential matchups between carbon-13 enrichment; indicating PCE degradation, and higher abundance of Dehalogenimonas in our piezometer hyporheic sediments were detected. Dehalogenimonas has been shown to reductively dechlorinate PCE to TCE and TCE to cis-DCE anaerobically.

INTRODUCTION

Now largely focused on environmental remediation efforts, the US Department of Energy (DOE) Savannah River Site (SRS) is committed to a clean environmental legacy. Among these commitments is preventing off-site migration of contaminants to the adjacent Savannah River (Fig. 1). The recent first-time detection that the SRS CMP Pits perchloroethylene (PCE) groundwater plume had impacted a Gordon aquifer-well above the maximum contaminant level (MCL) highlights the importance of this MSIPP project by SCSU to the DOE Mission at SRS.

In common with other EPA CERCLA (Superfund) sites [7], SRS contaminants impacting groundwater are chlorinated volatile organic compounds (cVOC); producing plumes of PCE and TCE.

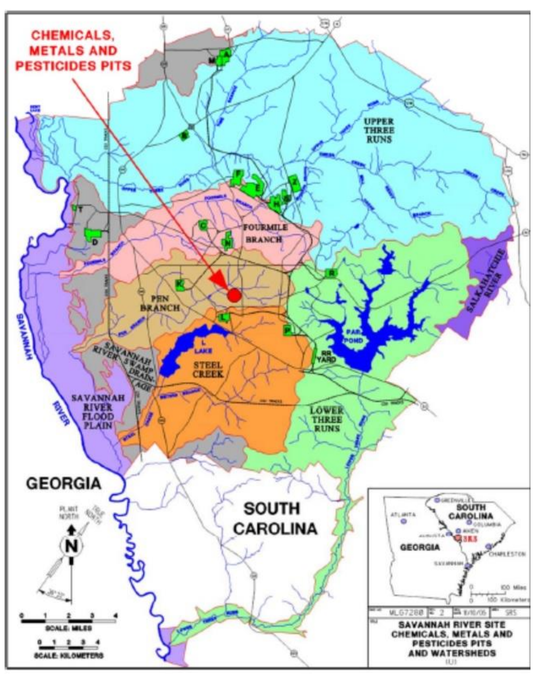

Fig. 1. US Department of Energy (DOE) Savannah River Site (SRS) showing location of CMP Pits and Pen Branch watershed drainage and flow to Savannah River (from [14]).

One CERCLA Operable Unit (OU), at SRS impacted heavily through the 1970's by cVOC disposal into pit trenches was the Chemical, Metals, and Pesticides (CMP) Pits [14]. All remediation categories detailed by EPA [8] ranging from: excavation of waste source soils; pump and treat of Dense Non-Aqueous Phase Liquids (DNAPL); *In Situ* Thermal Treatment (ISTT); and Soil Vapor Extraction (SVE) to more localized *in-situ* biogeochemical remedies collectively labeled: natural attenuation [9, 18, 20] were sequentially-implemented at CMP Pits following closure of these unlined pits in 1979 [14]. Soil-excavation implemented in 1984 and successive efforts [14], could not eliminate contaminated soil-remnants and deep-seepage of cVOC to underlying aquifers; producing a primarily PCE plume moving downslope to the nearby Pen Branch stream valley (Fig. 2) [14]. PCE and TCE were recognized as contaminants of concern (COC) for this plume, however, EPA determined that previous treatments of plume source materials were successful enough to designate natural attenuation as the remedial Record of Decision (ROD) [14, 15].

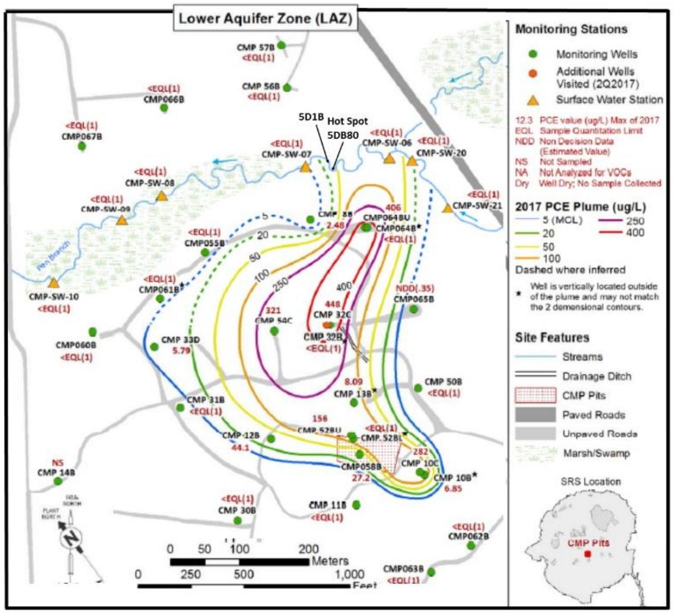

Fig. 2. Modeled PCE plume flow downslope from CMP Pits towards Pen at SRS (From [14]).

A key component of the SRS remediation mission was to fully document to EPA that natural attenuation was consistent and progressive for the CMP Pits plume as a sustained ROD. Our investigation sought to relate cVOC concentration differences and carbon isotopic enrichment within hyporheic zone strata to microbial community differences as well as groundwater elevation fluctuations. Another primary objective was to determine the extent of plume fringe penetration into the Pen Branch hyporheic zone. This would help achieve two important remediation objectives: 1). Plume movement and attenuation ground-truthing would yield more accurate model forecasting. 2) Delimiting actual plume hyporheic entry level will better assist any future efforts utilizing augmented or bioenhanced remediation approaches. Applying comprehensive plume assessment technologies to Pen Branch, MSIPP faculty and students acquired advanced research experiences including: training with PNNL and SCSU for microbial biotechnology ((16S rRNA gene sequencing with qPCR) and gas chromatography-isotope ratio mass spectrometry (GC-IRMS) with compound specific isotope analysis (CSIA). (Technologies described by Weatherill *et al.* (2018) as decisive evidence for biotic NA pathways.) Results of this PNNL collaboration will enable documentation of expected plume final stage (Bradley and Chapelle, 2011) natural attenuation (NA) at SRS; potentially generating significant cost-savings via EPA accepting SRNS NA plans with technology-transfer to other SRS plumes. A priority objective of this DOE-MSIPP research was the training and professional development of minority students, who conducted the bulk of field sampling and laboratory sample preparations (Fig. 3).

Fig. 3. SCSU MSIPP team with SRNS safety engineers planning for hazard-prevention in Pen Branch field sampling.

DESCRIPTION

Pen Branch cVOC plume fringe upwelling zone was determined from extensive longer-term hyporheic sampling that included an initial array of fifty-six piezometers sampled from 2009 to 2011. Annual revisions of piezometer placement eventually determined a primary plume impact stream reach of 30-40m which included hot spot stations 5DB80, 5DZ3, and 5D1B. Recent sampling years focused on this Pen Branch stream-reach with piezometers 5 to 10m apart, however sentinel stations were maintained above and below this reach to detect any plume migrations.

Seasonal variability was addressed in 2017-2022 by repeating piezometer insertions in winter and summer. Piezometers were installed by manually-driving a 10.2 cm diameter polyvinyl chloride (PVC) pipe through compacted substrata with no annular space to a depth of ca. 0.7 to 0.75 m below stream bottom. After residual stream water in the pipe was bailed out, a stainless steel 8.25 cm diameter auger was used to core through sediment layers to a hole-depth of 70 to 80 cm below the surrounding stream bottom. The PVC hole-liner was solid with no screened intervals. The SCSU team (Fig. 4) sampled

Fig. 4 SCSU MSIPP students played a key role in field sampling technologies and chain of custody protocols.

water from hyporheic upwellings into the pipe, while sediment core cVOC samples from the piezometers were collected at different depths as the hole progressed. South Carolina Department of Health & Environmental Control (DHEC) permit approvals were obtained prior to installing any piezometers. Surface water stations were also established along the Pen Branch study reach and sampled seasonally to detect any cVOC discharges (All surface water cVOC results were not-detected (ND).).

Hole-water and Pen Branch surface water were sampled using passive diffusion bags (PDB) [16] as well as pumped hole-water grab samples. PDB deployment at each station always exceeded the recommended 14-day minimum equilibration time [11] before transferal to an EPA-certified laboratory (Shealy Environmental Services, 106 Vantage Point Drive, West Columbia, SC 29172 (SES)) for purge and trap gas chromatograph mass spectrometer (GC/MS) analysis. Sediment vial samples were collected according to EPA Method 5035A protocol and both water and sediment samples were analyzed using EPA Method 8260B for purge and trap GC/MS.

Sediment core samples for microbial analyses were sent to the laboratory overnight in dry ice and stored at -80C until analysis. Microbial qPCR assays were conducted using extraction and sequencing methods similar to Atashgahi, *et al.* [2]. Parallel analyses were conducted at PNNL and SCSU. SCSU students gained much hands-on experience in these methodologies from Drs. Knowell and Brown (Fig. 5).

Fig. 5. SCSU faculty Drs. Brown and Knowell trained MSIPP students in microbial RNA extraction and qPCR assays similar to parallel analyses on the same sediment samples by PNNL.

DISCUSSION

Screening samples from 2009 to 2015 clearly identified the main Pen Branch stream reach impacted by CMP Pits cVOC plume hyporheic upwelling. As stated previously, this impacted reach extended along *ca.* 30-40 m between upstream station 5B and downstream station 5D1B. Hot spot station 5DB80, consistently highest in cVOC throughout the 2009 to 2015 screening period (Fig. 6), continued to be the main plume influx location. Impacts of plume source-reduction by ERH and SVE in the upslope vadose zone during 2008 to 2009 [14] were dramatically seen as an over sixty-percent reduction in total cVOC levels from 2009 to 2014 at Station 5DB80 along the plume-fringe (Fig. 6). However, this trend was reversed with the extreme cVOC rise at station 5DB80 in December 2015 (Fig. 6). This peak was likely connected to elevated aquifers beneath the CMP Pits plume pathway resulting from much higher rainfall during October to December in 2015 [19]. Rainfall at SRS for fall 2015 and 2016 was greatly elevated over the 20-year average [14]. For October and November 2015, it was nearly 250% higher than the 20-year average [19]. Elevated aquifer levels resulting from these hydrological events continued at SRNS monitoring wells into 2017 [14]; potentially raising plume cVOC concentrations with new mobilization of adsorbed PCE. Increased soil moisture content [5] and soil pore-space humidity [10] were shown to displace adsorbed PCE and chlorinated benzene compounds respectively.

Main plume hyporheic inflow appears to be channeled into a narrow entry reach at station 5DB80. Plume fringe hydrology can be inferred from the repeated patterns of relative cVOC concentrations at the hot spot stations 5DB80, 5DZ3, and 5D1B (Fig. 6). (Note: Data for 2021-2022 were hole-water grab samples while all other years were PDB samples.) Longitudinal plume movement within the hyporheic zone could then move successively to downgradient stations 5DZ3 and 5D1B. This hypothesis is supported by apparent movement of the pulse of increased cVOC with elevated PCE at station 5DB80 to downstream station 5D1B in 2016 (Fig.6). Dynamic natural attenuation actions on plume cVOC along this pathway are also demonstrated by the higher occurrence of VC at stations 5DZ3 and 5D1B which are further from the plume source; allowing more time for hyporheic microbial attenuation (Fig. 6). However, the appearance of new PCE at station 5D1B in 2021 and not at intervening station 5DZ3 implies a new source of plume entry.

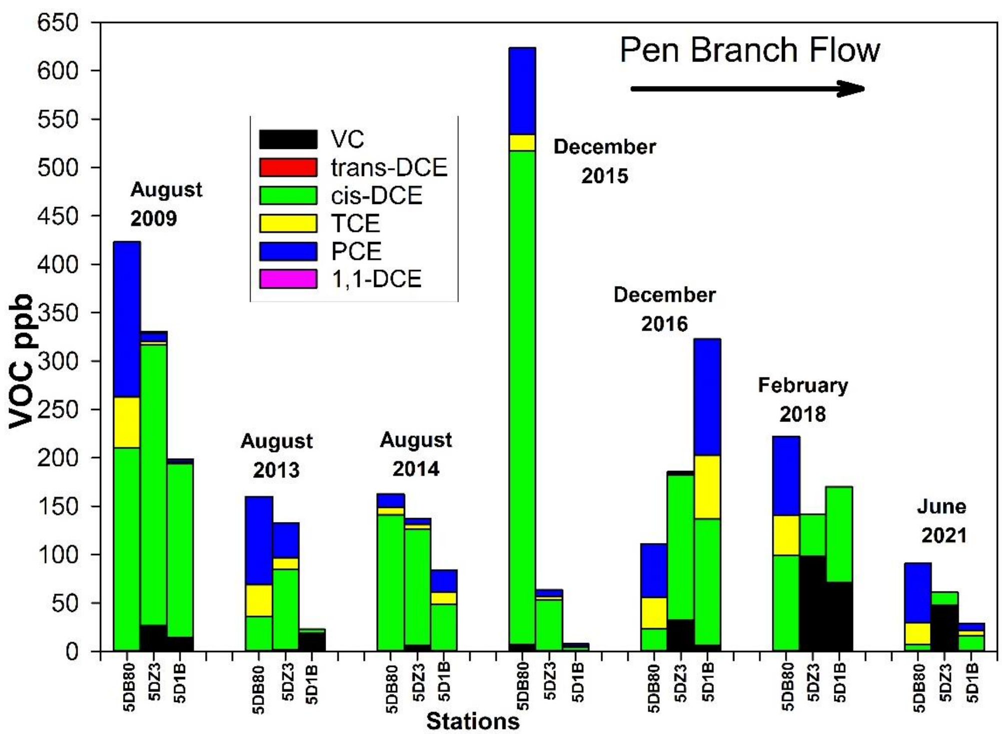

Fig. 6. Changes in cVOC from 2009 to 2021 for Pen Branch hot spot stations.

Comparisons of cVOC levels in sediment cores and hole-water for the same piezometer station in different years and between piezometers within the same year using Duncan's Multiple Range Test (DMRT) can determine the significance of graphical trends in Figs. 7 and 8; providing additional support for apparent groundwater plume movements and sediment natural attenuation interactions. Using DMRT for bottom sediment (65cm deep) cVOC, it was found that hotspot station 5DB80 had significantly higher PCE levels in sediments for 2018 than in 2017, 2020, or 2022 and that PCE levels did not significantly decline for these sediments between 2020 and 2022. In comparing hole-water cVOC for different stations during the same year with DMRT, different patterns emerged. PCE at station 5DB80 was significantly higher than both stations 5DZ3 and 5D1B, which were not significantly different from each other; helping to confirm station 5DB80 as the plume entry point. However, for cis-DCE, concentrations at station 5D1B were greater than at station 5DB80 which was significantly higher than cis-DCE levels at station 5DZ3. In contrast, station 5DZ3 had significantly higher concentrations of VC than either station 5DB80 or station 5D1B. These significant differences seem relevant to CSIA and microbial results discussed below.

Sediment cores collected beneath Pen Branch during piezometer installation from the upper 15 cm and from the hole bottom core were compared for stations 5DB80 and 5D1B (Fig. 7). Hole-water grab samples were collected at least 24 h after piezometer installation from the bottom water layer using a peristaltic pump and clear pvc tubing. CMP Pits plume trends observed for longer-term PDB hole water samples (Fig. 6) were reflected in sediment core samples (Fig. 7) and included: much higher cVOC with PCE at station 5DB80 compared to 5D1B and 5DZ3 (as indicated by DMRT results) and a continued decline in total cVOC over time; indicating the continued success of ERH and SVE at CMP Pits in 2008 [14].

For both stations, sediment cores from the hole bottom were a greater reflection of groundwater inflow; showing no degradation products at station 5DB80 and only small amounts of cis-DCE at station 5D1B for both dates (Fig. 7). In contrast, sediments from the top cores and piezometer hole-water at both stations showed more evidence of PCE degradation products, cis-DCE and VC (Fig. 7). Natural attenuation progress in these shallower sediment layers and hole-water may be related to exposure to more aerobic conditions [1, 6, 13].

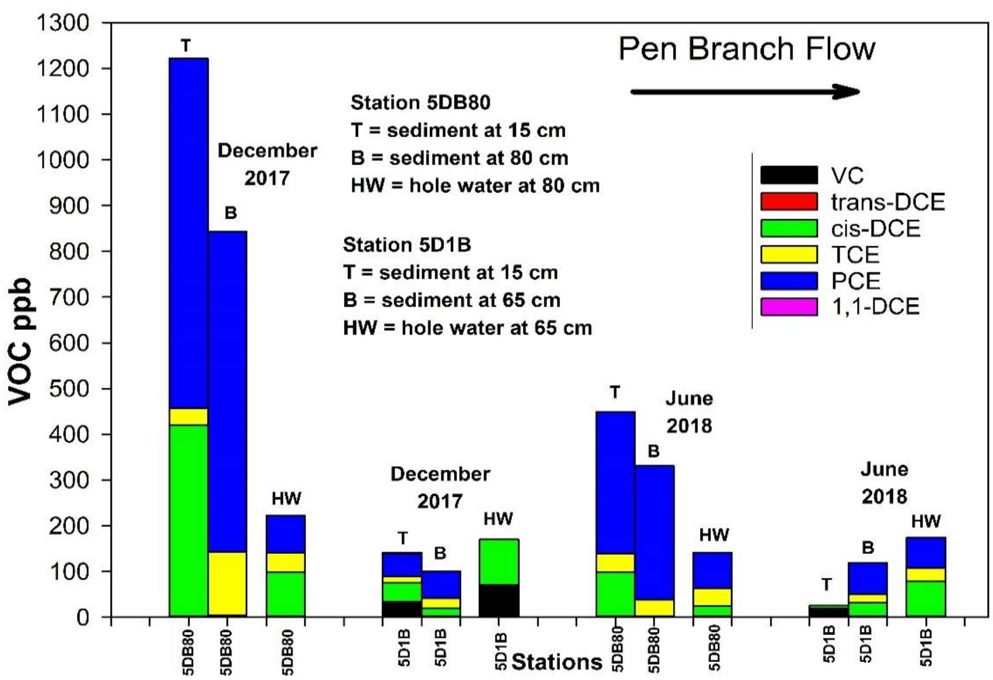

Fig. 7. Pen Branch hyporheic sediment core cVOC versus hole-water cVOC at stations 5DB80 and 5D1B for December 2017 and June 2018.

CMP plume impacts to different hyporheic sediment layers (Fig. 7) showed that the cVOC plume entering this reach of Pen Branch had a potential vertical flow of at least 65 to 80 cm in depth. In order to analyze these groundwater inputs more precisely, additional sediment cores (15, 40, 65, and 85 cm deep) were sampled for station 5DB80 in June 2018 (Fig. 8). Similar to patterns in Figure 7, samples from the shallow 15 cm core depth resembled cVOC in the hole-water (Fig. 8); reflecting more access to probable aerobic microbial dechlorination [1, 6, 13]. Deeper core cVOC (65 and 85 cm cores) displayed PCE plume cVOC without degradation products. Sediment cVOC for 65 cm and deeper clearly reflected groundwater plume flow with no natural attenuation. The lower concentrations of PCE and TCE for the 85 cm core (Fig. 8) likely indicate this layer is near the bottom of the plume inflow. Sediments in this 85 cm core were more compacted with a higher clay composition probably reflecting the Pen Branch semi-confining layer; likely reducing PCE flow rates [6]. Additionally, PCE levels at station 5DB80 for the 65 cm core were significantly higher than PCE in the 85 cm core using DMRT; further indicating this bottom core may be within the confining layer; restricting plume inflow due to more compacted clay inhibiting plume inflow from above.

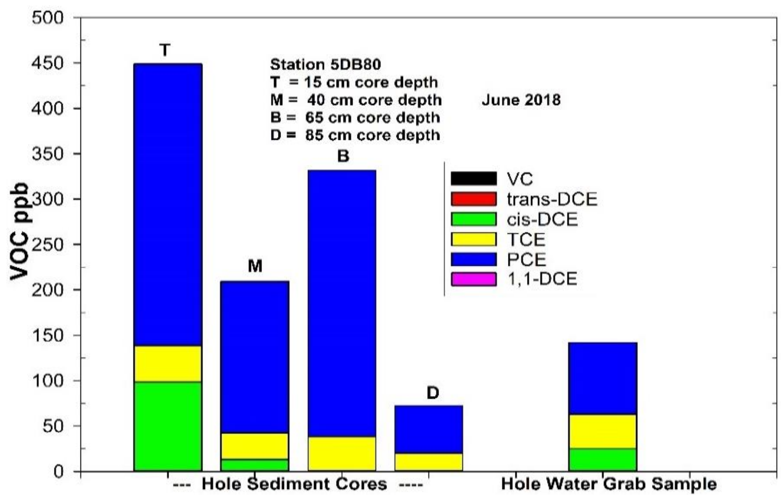

Fig. 8. Pen Branch hyporheic sediment core cVOC versus hole-water cVOC for station 5DB80 in June 2018.

PNNL efforts to better extract cVOC for CSIA analyses have improved over the course of our study. In general, results for stable carbon isotope ratios revealed bacterial fractionation in PCE becoming TCE and cis-DCE (TABLE I). C-13 enrichment levels were similar to ranges from previous microbial dechlorination research [12]. These C-13 enrichment patterns reflect bacterial fractionation and although bacterial taxa associated with dehalogenation activity did not show clear trends in abundance between stations 5DB80 and 5DZ3, VC, as a more final-stage degradation compound, was more abundant at 5DZ3. *Dehalococcoidaceae*, a family with known dehalogenation activity, had higher abundance at 5DZ3 than 5DB80. In contrast, *Dehalobacter* was more abundant in 5DB80 than in 5DZ3, while *Dehalogenimonas* was more abundant at 5DZ3. Additional microbial analyses detected higher abundance of *Dehalogenimonas* in some hyporheic sediments along the plume fringe. *Dehalogenimonas* has been shown to reductively dechlorinate PCE to TCE and TCE to cis-DCE anaerobically [13].

TABLE I. Stable carbon isotope ratios revealed bacterial fractionation in PCE becoming TCE and cis-DCE.

Station	Sample depth	Analyte	Ave. δ13C (‰)	Stan Dev. (‰)	n
5DB80	(25-35 cm)	DCE	-14.79	3.12	5
5DB80	(25-35 cm)	TCE	-21.43	3.73	5
5DB80	(25-35 cm)	PCE	-24.92	2.59	5
5DB80	(40-60 cm)	DCE	-22.01	0.48	4
5DB80	(40-60 cm)	TCE	-22.39	1.01	4
5DB80	(40-60 cm)	PCE	-28.27	2.69	4
5D3Z	(25-35 cm)	DCE	-20.16	3.52	3
5D3Z	(25-35 cm)	TCE	-28.09	n/a	1
5D3Z	(25-35 cm)	PCE	-27.78	6.18	2
5D3Z	(40-60 cm)	DCE	-21.83	1.82	5
5D3Z	(40-60 cm)	TCE	-23.23	n/a	1
5D3Z	(40-60 cm)	PCE	-30.52	3.62	5

CONCLUSIONS

Our results conclusively show natural attenuation is effectively reducing cVOC contaminant loads along the CMP Pits plume-fringe and the dynamic hyporheic biogeochemical pathways are playing a major role.

Groundwater elevation fluctuations along the Pen Branch valley vadose zone lower boundary may contribute to desorbing and transporting new source cVOCs into groundwater flows. Our previous 'hot spots' (stations 5DB80, 5DZ3, and 5D1B) displayed a progression of cVOC plume pulses; indicating introduction of new plume PCE followed by natural attenuation at downgradient stations.

Plume fringe depth and entry into the Pen Branch hyporheic zone are very limited vertically and longitudinally. Sediment core cVOC indicated the sandy-clay semi-confining layer is restricting plume groundwater penetration beneath Pen Branch and natural attenuation in the upper hyporheic sediments revealed a mixture of aerobic and anaerobic probable microbial degradation pathways.

CSIA results for stable carbon isotope ratios show apparent bacterial fractionation in PCE being dechlorinated to cis-DCE; becoming vinyl chloride. Microbial analyses also detected higher abundance of *Dehalogenimonas* in some hyporheic sediments along the plume fringe. *Dehalogenimonas* has been shown to reductively dechlorinate PCE to TCE and TCE to cis-DCE anaerobically [13]. Continued sampling of this microbial community may bring stronger support for microbial natural attenuation.

ACKNOWLEDGEMENTS

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