



TECHNICAL REPORT

IN SITU ACTIVATED CARBON CASE STUDY REVIEW

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ACRONYMS AND ABBREVIATIONS

AC	activated carbon
AFB	Air Force Base
BAM	Bioavailable Absorbent Media
BDI	Bio-Dechlor Inoculum
CBGS	Colorado Basic Groundwater Standard
COC	constituent of concern
COD	chemical oxygen demand
CSIA	compound specific isotope analysis
CSM	conceptual site model
CT	carbon tetrachloride
cVOC	chlorinated volatile organic compound
DCE	dichloroethylene
DHC	<i>Dehalococcoides</i>
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DPT	direct push technology
FTF	Former Tank Farm
GAC	granular activated carbon
HRC	hydrogen release compound
ISCO	in situ chemical oxidation
LMTF	Little Mountain Test Facility
LNAPL	light non-aqueous phase liquid
MNA	monitored natural attenuation
MPE	multi-phase extraction
NIROP	Naval Industrial Reserve Ordnance Plant
nm	nanometer
ORP	oxidation reduction potential
OU	Operable Unit
PAC	powder activated carbon
PFAS	per- and polyfluoroalkyl substances

ROD	Record of Decision
TCE	trichloroethene
TMB	1,2,4-trimethylbenzene
TOC	total organic carbon
VC	vinyl chloride
VFA	volatile fatty acid
VOC	volatile organic compound
ZVI	zero valent iron

1.0 INTRODUCTION

Activated carbon (AC)-based amendments are being applied for the in situ remediation of a wide range of organic contaminants in groundwater. These amendments typically combine AC for enhanced contaminant sequestration, along with chemical or biological additives to further facilitate in situ contaminant destruction. Rapid contaminant removal and limited rebound have been reported during field applications, which suggests a potential role for the technology in addressing back diffusion from residual sources in low permeability zones. This white paper describes the types of amendments available and the contaminants treated. Three Department of Defense (DoD) case studies illustrate various application approaches and provide results and lessons learned for this innovative technology.

2.0 WHAT ARE ACTIVATED CARBON-BASED AMENDMENTS AND HOW DO THEY WORK?

Several AC-based amendments are commercially-available for full-scale application. Table 1 summarizes available AC formulations, along with their properties, removal mechanisms, and the contaminants targeted for treatment. Each type of amendment contains a form of organic carbon and one or more additives (e.g., zero valent iron [ZVI]), sodium persulfate, electron donor, electron acceptor, bacteria, and/or nutrients).

Table 1. Properties of Commercially Available AC-based Amendments for In Situ Remediation

Amendment	Manufacturer	Property	Removal Mechanisms	Contaminants Treated
PlumeStop®	Regenesis	Colloidal AC suspension with an organic stabilizer	Enhanced biotic reductive dechlorination for chlorinated solvents and aerobic and anaerobic biodegradation for petroleum hydrocarbons	Chlorinated solvents or petroleum hydrocarbons
Petrofix®		Colloidal AC suspension with slow- and quick-release inorganic electron acceptors including sulfate and/or nitrate	Aerobic and anaerobic biodegradation enhanced via biostimulation	Petroleum hydrocarbons
BOS 100®	RPI	Granular activated carbon (GAC) impregnated with ZVI	Abiotic reductive dechlorination	Chlorinated solvents
BOS 200®		Powder activated carbon (PAC) mixed with nutrients, electron acceptors, and bacteria	Aerobic and anaerobic biodegradation enhanced via biostimulation and bioaugmentation	Petroleum hydrocarbons

Table 1 (continued). Properties of Commercially Available AC-based Amendments for In Situ Remediation

Amendment	Manufacturer	Property	Removal Mechanisms	Contaminants Treated
COGAC™	Remington Technologies	GAC mixed with calcium peroxide and sodium persulfate	Chemical oxidation, aerobic and anaerobic biodegradation enhanced via biostimulation	Chlorinated solvents or petroleum hydrocarbons
Bioavailable Absorbent Media (BAM)	Orin Technologies	Pyrolyzed, cellulosic biomass product (>80% fixed carbon) derived from a proprietary blend of recycled organic materials	Aerobic and anaerobic biodegradation enhanced via biostimulation	Chlorinated solvents or petroleum hydrocarbons

AC-based amendments typically rely upon both adsorption and degradation mechanisms as shown in Figure 1 (Fan et al., 2017). Adsorption onto the AC results in the rapid initial removal of contaminants from the aqueous phase, while the reactive portion of the amendment subsequently destroys the contaminants in place (such as ZVI in Figure 1).

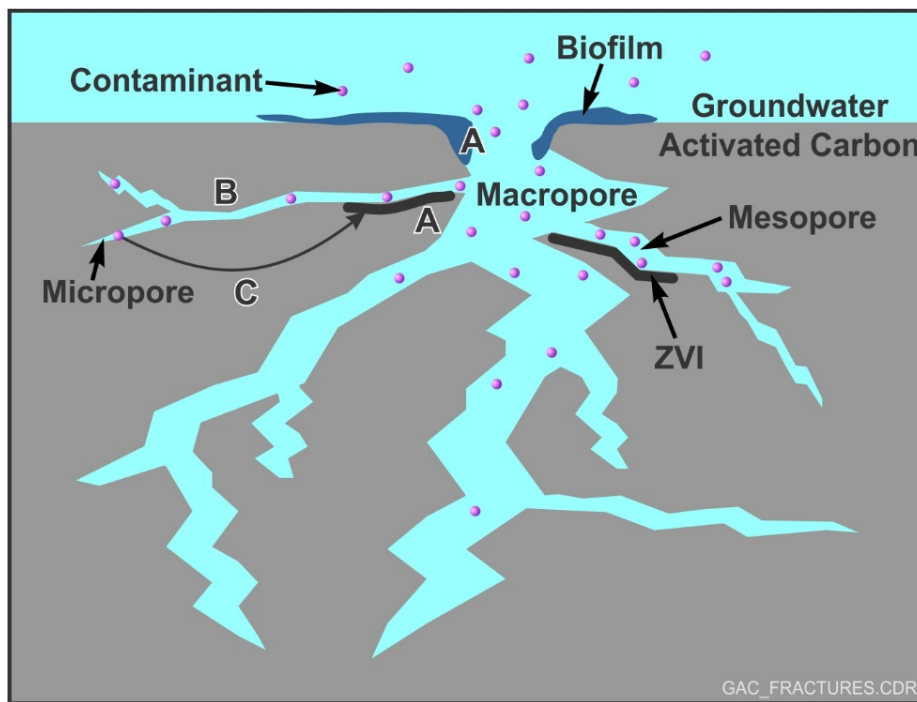


Figure 1. Conceptual Diagram of AC-Based Contaminant Removal Process

Illustrates the following processes: (A) direct adsorption and/or degradation by reactive amendment, (B) micropore adsorption, and (C) desorption/diffusion form micropore followed by degradation via reactive amendment

(Modified from Fan et al., 2017 and reproduced with permission from Journal of Environmental Management)

Physical adsorption is the dominant removal mechanism under typical subsurface conditions. Adsorption onto the AC matrix is enhanced by its highly porous internal structure ranging in size from the largest macropores (>50 nanometer [nm]) down to the smallest micropores (<2 nm). The micropores tend to serve as adsorption sites for contaminants such as trichloroethene (TCE) and benzene due to their similar dimensions. Different AC products will have varying adsorption capacities based on several factors. The saturation adsorption capacity of a given AC media is based on the contaminant properties, site-specific environmental factors, as well as being a function of the media's microporosity and surface acidity (Fan et al., 2017).

For the reactive component of the AC amendments, similar processes are relied upon as utilized by other remedial techniques including chemical reduction, chemical oxidation, and biodegradation. Manufacturer's proprietary and/or patented formulations include the addition of reductants, oxidants, or a targeted selection of electron acceptors, electron donors, nutrients, or microbes to stimulate a specific biodegradation pathway. As contaminants are absorbed into the macropores and mesopores within the AC, they come into direct contact with the reactive material and are then degraded (e.g., as shown in Figure 1 for ZVI). However, contaminants sorbed deeper into the micropores of the AC are not directly degraded, but may back diffuse over time in to the mesopores and/or macropores. The contaminant then comes into contact with the reactive component of the AC amendment and is further degraded.

3.0 WHERE HAVE ACTIVATED CARBON AMENDMENTS BEEN APPLIED?

Table 2 summarizes 26 case studies compiled from a literature search, as well as from case studies provided by remediation practitioners and manufacturers. The majority of the sites (19) were private sites related to underground storage tank sites and manufacturing plants. Three of the sites were DoD sites. A detailed description and evaluation of the AC-based amendments at the DoD sites are presented in the sections that follow.

The primary groups of contaminants that have been treated include petroleum hydrocarbons and chlorinated solvents. However, research currently is being conducted to evaluate treatment efficacy for emerging contaminants such as per- and polyfluoroalkyl substances (PFAS). As shown in Table 2, most of the applications successfully achieved a reduction of contaminant concentrations.

The case studies illustrate the application of AC amendments in a variety of ways - in situ mixing, injection using direct push technology (DPT), packer auger system, and permeable reactive barrier. However, the majority of the case studies involve the use of DPT for amendment emplacement. In some cases, temporary injection wells were used to deliver the amendment. Other applications used grid injection that targeted a well-defined contaminated area.

Table 2. Summary of Activated Carbon-Based Amendment Case Studies

No.	Site Name	Amendments Applied	Contaminants	Target treatment Area or Volume ^(a)	Treatment Zone Depth (ft bgs)	% degradation
1	Gas Station, Daly City, CA	Plume Stop® ORC- A	Petroleum hydrocarbons	~400 ft ²	32 to 37	65% reduction of MTBE; 81% TBA.
2	Former Gas Station, Long Island, NY	BOS 200®	Petroleum hydrocarbons	~82,500 ft ³	NA	Injections were performed at 9 former and active gasoline service stations in the northeastern US (NY, NJ and PA) between 2015 and 2017. 66 to 99 % reduction post 1 year.
3	PCF Site I42706505, Boulder, CO	COGAC™	Petroleum hydrocarbons	NA	NA	Several other products (persulfate, phosphate, potassium, calcium nitrate, ferrous sulfate, ORC-A) were injected at the site at various points.
4	Remington Site 1-UST, Washington	COGAC™	Petroleum hydrocarbons	NA	NA	93% reduction of benzene; ~97% reduction of total petroleum hydrocarbons. Met regulatory standards.
5	Remington Site 2-UST, Denver, Colorado	COGAC™	Petroleum hydrocarbons	NA	5 to 10	Concentrations below regulatory levels.
6	Remington Site 3-UST, Colorado	COGAC™	Petroleum hydrocarbons	1,800 ft ²	8 to 23	Reached < 5 ug/l for benzene at well; achieved regulatory remedial goals for no further action.
7	Remington Site 4-UST, Colorado	COGAC™	Petroleum hydrocarbons	1,700 ft ²	12 to 15	Achieved regulatory remedial goals.
8	Remington Site 5-Pipeline release site, Weld County, Colorado	BOS 200® followed by COGAC™	Petroleum hydrocarbons	NA	NA	Achieved regulatory remedial goals.
9	Remington Site-6 UST, Colorado	COGAC™	Petroleum hydrocarbons	300 ft ²	15	Site closure pending; reached regulatory levels.
10	Remington, Norman, OK	COGAC™	Petroleum hydrocarbons	NA	NA	Reached below site-specific target level of 5.576 mg/L for benzene.

Table 2 (continued). Summary of Activated Carbon-Based Amendment Case Studies

No.	Site Name	Amendments Applied	Contaminants	Target treatment Area or Volume ^(a)	Treatment Zone Depth (ft bgs)	% degradation
11	Naval Industrial Reserve Ordnance Plant (NIROP), Fridley, MN	Plume Stop [®] HRC BDI	NA	640 ft ^{2(b)}	61 to 66 72 to 77	Test area 1- 100% reduction. Test area 2- 70%; Completed reduction not accomplished in test area 2 due to groundwater extraction system turned on-hydraulic zones affecting the distribution.
12	Industrial site, Canada	Plume Stop [®] ORC	Petroleum hydrocarbons	NA	NA	Reached below guidelines.
13	Private School, Midwest	Plume Stop [®] ORC-advanced	Petroleum hydrocarbons	NA	NA	99.90% reduction.
14	Electronics Site, Midwest	Plume Stop [®] HRC	Chlorinated ethenes	NA	9 to 21	99% reduction.
15	Gas Station, Taylor County, Florida	Regenox PlumeStop [®] ORC-advanced	Petroleum hydrocarbons	NA	NA	Successful reduction. 99%- B; T- 80%; E-97%; X-94%; Naphthalene-99%
16	Former Plating Facility, Michigan	3DME PlumeStop [®] HRC BDI	Chlorinated ethenes	NA	2 to 5	95% reduction. Other products were also used at the site.
17	Manufacturing Facility, Santa Barbara, CA	Plume Stop [®] HRC BDI	Chlorinated ethenes	4,100 ft ²	6 to 15	Met state-specific standards; site closure requested.
18	Landfill, Ann Arbor, MI	BAM	Chlorinated ethenes	625 ft ²	11 to 20	80% reduction.
19	Former Manufacturing Plant, Moultrie, GA	BAM	Chlorinated ethenes	NA	10 to 30	100% reduction.
20	Former Asphalt Plant, Jackson, MS	BAM	Chlorinated ethenes and Petroleum hydrocarbons	2,260 ft ²	22 to 34	100% reduction.

Table 2 (continued). Summary of Activated Carbon-Based Amendment Case Studies

No.	Site Name	Amendments Applied	Contaminants	Target treatment Area or Volume ^(a)	Treatment Zone Depth (ft bgs)	% degradation
21	Unnamed Site	BAM	Chlorinated ethenes	1,800 ft ²	25 to 40	65% reduction.
22	Manufacturing Facility, Dalton, GA	BAM	Chlorinated ethenes	3,000 ft ²	15 to 30	100% reduction.
23	Former Gas Station, Otwell, IN	BAM	Petroleum hydrocarbons	5,750 ft ²	5 to 15	71% reduction.
24	OU 5 Former Lowry Air Force Base	BOS 200 [®]	Chlorinated ethenes	8,000 ft ²	12 to 16 24 to 39	99% reduction for CT; 98% reduction for TCE.
25	Hill Air Force Base	COGAC [™]	LNAPL and residual sorbed mass; BTEX, trimethylbenzene compounds and methylene chloride	40,000 ft ²	15 to 25	Concentrations of 1,2,4-TMB are below the ROD preliminary action level of 2,800 micrograms per liter (µg/L). Benzene concentrations in groundwater are still above the ROD remedial action goal of 5 µg/L, but overall trends in benzene concentrations are decreasing.
26	Vandenberg AFB	BOS 100 [®]	Chlorinated ethenes	2,200 ft ² (vertical) ^(c)	71 ft 50 ft	Not available.

a. Area units are square feet (ft²) and volumes are in cubic ft (ft³)

b. Two treatment areas, each approximately 320 ft²

c. Installed as a biobarrier (2 barriers)

3DME – 3-D Microemulsion[®]

BDI - Bio-Dechlor INOCULUM[®] Plus

HRC – Hydrogen Release Compound

NA- Not Available

3.1 PLUMESTOP® DEMONSTRATION AT THE NAVAL INDUSTRIAL ORDINANCE PLANT, FRIDLEY

3.1.1 Background

The United States Naval Industrial Reserve Ordnance Plant (NIROP) in Fridley, Minnesota consists of 83 acres located approximately 700 feet east of the Mississippi River in Fridley, Minnesota. Groundwater and soil at the facility are contaminated with chlorinated volatile organic compounds (cVOCs) including TCE and its daughter products dichloroethylene (DCE) and vinyl chloride (VC). The selected remedy is a groundwater extraction and treatment system, which has been in operation from September 1992 to present. Through the end of 2014, the system had treated approximately 5.1 billion gallons of groundwater and extracted approximately 39,713 pounds of TCE and other volatile organic compounds (VOCs).

In July 2013, the Navy performed an investigation to evaluate potential sources of TCE contamination (NAVFAC, 2017). Results of the investigation indicated that the East Plating Shop, 8th Avenue Area south of the East Plating Shop, and 7th and Broadway area are the primary areas contributing TCE to groundwater. All three areas had elevated levels of TCE, with the highest concentration, about 1,200 mg/L [indicative of the presence of dense non-aqueous phase liquid (DNAPL)], measured at the 7th and Broadway area.

The groundwater treatment system continues to operate in accordance with the Record of Decision (ROD) for the site. However, given the discovery of the three source areas and the Navy's mandate to periodically evaluate new remedies and optimize cleanup to achieve site closure faster and reduce life-cycle remediation costs, the Navy elected to perform a demonstration of colloidal activated carbon (PlumeStop®) to treat cVOCs in subsurface soil and groundwater.

3.1.2 Design and Application

Two areas were selected for the demonstration. Each was approximately 20 feet long by 16 feet wide. Area 1 was located near 7th and Broadway near the area where the highest concentration of TCE was measured. Area 2 was located in a portion of the downgradient plume coinciding with 10,000 µg/L contour lines as determined by previous vertical profile sampling.

Three reagents, including PlumeStop®, Hydrogen Release Compound (HRC®), and Bio-Dechlor Inoculum® Plus (BDI), were introduced into each of the demonstration areas. PlumeStop®, a colloidal groundwater remediation agent, absorbs contaminants and is easily colonized by contaminant-degrading bacteria. The intended result of a PlumeStop® application is to enhance biodegradation of site contaminants and to sorb contaminants from groundwater in a treatment zone, thus controlling the plume migration and accelerating cVOC degradation. The other two amendments were used to enhance biodegradation to ensure complete breakdown of chlorinated solvents to non-toxic byproducts such as water and carbon dioxide and reduce accumulation of TCE and its degradation products on the activated carbon. HRC® is a polylactate ester material that, when hydrated, is subject to microbial breakdown producing a controlled release of hydrogen to enhance anaerobic bioremediation. BDI is a consortium of bacteria that have been shown to be effective in the dechlorination of chlorinated ethenes and ethanes.

The conceptual layout of the application design is shown in Figure 2 and Table 3 summarizes key design information for each of the demonstration areas. PlumeStop[®] and BDI were injected under pressure using DPT into 10 points into the intermediate zone of the aquifer in each demonstration area. Injections were performed in 2-foot-long increments using a bottom-up approach, which consisted of driving the probes to the lowest depths, injecting the fluid, and then raising the probe to the next injection interval. About 290 and 240 gallons of PlumeStop[®] were injected into each location in Areas 1 and 2, respectively. HRC[®] was injected into four points in each demonstration area, which were advanced in a row along the northeastern (upgradient) portion of the area. Approximately 4.8 gallons was injected at each location.

Two 2-inch-diameter wells equipped with 5-foot-long screens were installed in each demonstration area for the purpose of monitoring the application and evaluating its impact on constituents of concern (COCs) in the aquifer. In addition, four boreholes (three in Area 1 and one in Area 2) were advanced and the resulting cores were visually inspected and sampled to evaluate the distribution of PlumeStop[™], which is easily identified due to its distinct black coloration (in contrast to the native brown sand/silty sand).

Groundwater monitoring was performed in Areas 1 and 2 prior to injection activities and approximately one to six months after the initial injection events. Monitoring included field measurements of groundwater quality parameters and collection of groundwater samples for laboratory analysis of cVOCs, ethane, ethane, methane, total iron, dissolved iron, sulfate, carbon dioxide, total alkalinity, sulfide, nitrogen, chemical oxygen demand (COD), total organic carbon (TOC), compound specific isotope analysis (CSIA), microorganisms, and volatile fatty acids (VFAs).

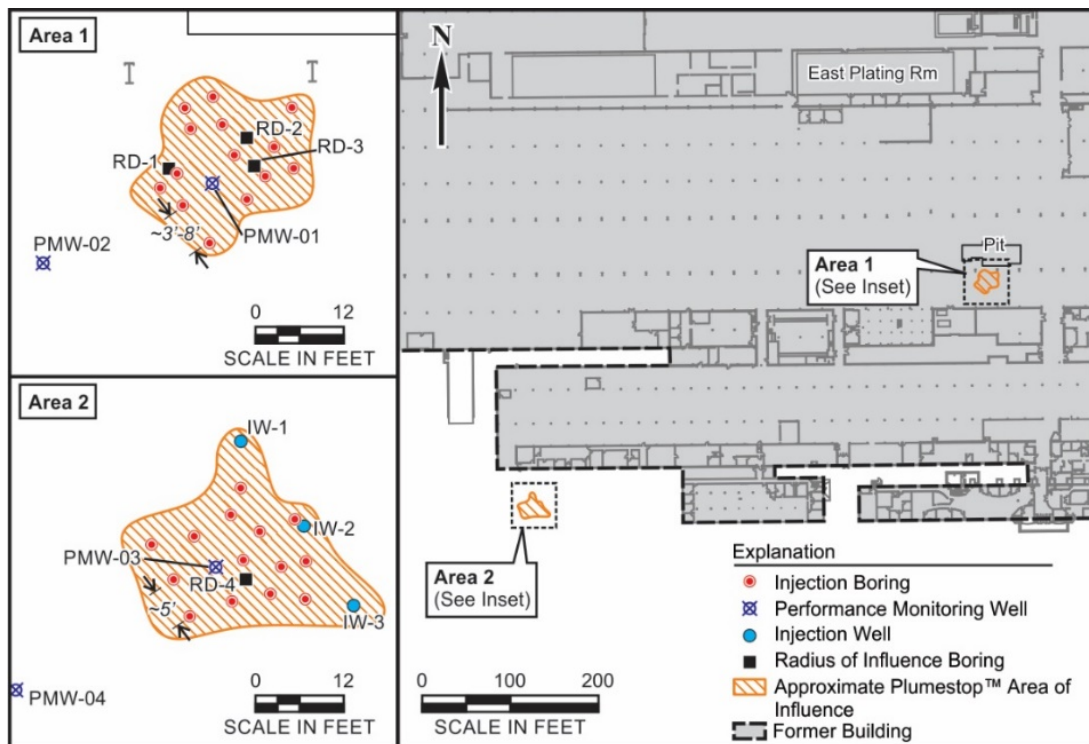


Figure 2. Conceptual Layout of the NIROP Fridley PlumeStop[™] Demonstration (Source: NAVFAC)

Table 3. Design Summary for NIROP Fridley PlumeStop™ Demonstration

Design Feature	Area 1	Area 2	
		Event 1	Event 2
Primary COC and Maximum Detected Concentration (µg/L)	TCE (100,000)	TCE (12,000)	
Predominant Geology in Treatment Zone	Silty sand	Fine to medium sand	
Reagents and (Quantity) Applied	PlumeStop™ (2,900 gallons) HRC (210 lbs) BDI (9 L)	PlumeStop™ (2,400 gallons) HRC (210 lbs) BDI (9 L)	PlumeStop™ (2,000 lbs)
Target Treatment Area (ft²)	320	320	320
Target Treatment Volume (ft³)	1,600	1,600	1,600
Number of DPT Injection Locations	14	14	0
Number of Injection Wells	0	4 ⁽¹⁾	3
Vertical Injection Interval (ft bgs)	61 to 66	72 to 77	71 to 76
Injection Spacing (ft)	~3 to 8	~5	~15
Application Timeframe (days)	5	5	1

(1) A second injection event was performed in Area 2 into which amendments were introduced into four newly installed wells.

A second injection event was performed in Area 2 to introduce an additional 2,000 pounds of PlumeStop™ in the upgradient portion of the treatment area. Three 2-inch-diameter wells, screened from 71 to 76 feet, were installed to introduce the PlumeStop™ into the aquifer. HRC® and BDI were not introduced during the second injection event.

3.1.3 Results

In Area 1, a decrease in cVOC concentrations was observed in well PMW-1 during the one-month post-application monitoring event and remained below the method detection limit during the remainder of the post-injection sampling events. The project team inferred that sorption was the primary mechanism for the decrease in cVOCs as opposed to biodegradation since 1) the change in concentration was rapid (changes due to biodegradation generally require several months), and

2) the presence of PlumeStop™ was observed in this well and soil boring RD-3, located to the northeast of this monitoring well. However, several lines of evidence indicated that biodegradation was occurring within the treatment area to some extent, including:

- Oxidation reduction potential (ORP) decreased and TOC increased, while pH remained neutral, indicating that the necessary conditions for biodegradation to occur were present after the amendments were introduced into the aquifer.
- The concentration of *Dehalococcoides* (DHC) increased by an order of magnitude.
- The concentrations of dissolved iron and methane increased, while the concentration of sulfate decreased consistent with the occurrence of biological reactions.
- The concentration of volatile fatty acids increased, indicating that the HRC® was being metabolized by bacteria.

Monitoring well PMW-2, located approximately 30 feet downgradient of the treatment area, did not exhibit reduction in cVOC concentrations, possibly because of the flat hydraulic gradient between the treatment area and PMW-2 and the relatively short monitoring period (i.e., 6 months).

The PlumeStop™ application was less effective in Area 2 than Area 1. There was no evidence that PlumeStop™ reached well PMW-3, located within 5 feet or less of at least four injection points, after the first injection event. The second set of injections also did not appear to result in immediate evidence of PlumeStop™ in well PMW-3 after injection, although some change in groundwater color was noted during the last monitoring event, possibly indicating that PlumeStop™ reached this location, although an increase in TOC was not measured. It was hypothesized that the amendments introduced into Area 2 may have migrated to a more permeable gravel zone beneath the target treatment interval. Also, Area 2 is impacted by the groundwater extraction and treatment system and regulatory requirements mandated that the system be restarted shortly after completing the injections; hence, the amendments may have been relatively quickly dispersed from the treatment area by the hydraulic gradient generated by the extraction system.

Although distribution of PlumeStop™ was less effective than expected, a rapid decrease in TCE (from about 520 to 21 µg/L) was measured in PMW-03 one month after the first injection and remained between 10 and 21 µg/L during the remainder of the monitoring events. Concentrations of DCE and VC exhibited slight increases, possibly indicating that degradation of TCE was occurring through reductive dechlorination to form these daughter products. An order of magnitude increase in *DHC* concentration and an enrichment in the TCE carbon 13 (¹³C) isotope provide additional lines of evidence that TCE was degrading through reductive dechlorination. However, other known degradation reaction products including dissolved hydrocarbon gases (i.e., methane, ethane, and ethene) were not observed to increase, sulfate levels were not observed to decrease, and VFAs were not detected. No meaningful changes were noted in monitoring well PMW-4, located approximately 35 feet downgradient of the treatment area indicating that this well was located too far downgradient from the treatment area to be impacted during the monitoring period allotted for this study.

3.1.4 Conclusion and Lessons Learned

The following conclusions and lessons were learned as a result of this demonstration:

- Injection of PlumeStop™ resulted in complete removal of cVOCs in well PMW-1 in Area 1 and an order of magnitude decrease in Area 2.
- Sorption of cVOC in groundwater onto the AC was a primary and rapid removal mechanism as evidence by the sharp decreases in cVOC concentrations measured during the first post-injection monitoring event performed at each location.
- Lines of evidence including an increase in DHC concentration, an increase in cVOC daughter products, and/or an enrichment of the ¹³C isotope indicate that biodegradation of COCs was occurring to some extent in both demonstration areas.
- Performance monitoring wells PMW-3 and -4 were located too far downgradient of the treatment area to provide meaningful results during the duration of the demonstration.
- Operation of the existing extraction and treatment system may have biased the study results, primarily in Area 2, in which groundwater flow is influenced by its operation.
- The PlumeStop™ application in Area 2 maintained >70% reduction, but the results indicate a gradual and steady increasing concentration trend of TCE daughter products, DCE and VC. Final dechlorination end products including ethene and ethane were not measured, indicating that DCE and/or VC stall may be occurring or these gases were absorbed by the PlumeStop™.
- Amendments injected into Area 2 may have migrated into the gravelly layer located below well PMW-3.
- The baseline concentrations of cVOCs were orders of magnitude lower than those expected for the PlumeStop™ study. Hence, the effectiveness of PlumeStop™ to treat high concentration hot-spots could not be evaluated.
- Due to local geological and hydrogeological features, a greater mass of amendments than used, especially HRC® and bioaugmentation culture, are likely required to improve distribution and performance within the targeted treatment areas.

3.2 APPLICATION OF COGAC™ AT HILL AIR FORCE BASE, UTAH

3.2.1 Background

Hill Air Force Base (AFB) Little Mountain Test Facility (LMTF) is a 740-acre complex located in Weber County, Utah at the southwest end of Little Mountain along the north side of the Ogden Bay Waterfowl Management Area (Air Force, 2019). Past activities at the LMTF have resulted in the release of petroleum products into soil and groundwater at the Former Tank Farm (FTF), one of three sites that comprise Operable Unit (OU) A. The resulting light non-aqueous phase liquid (LNAPL) acts as a continuing source of dissolved-phase contamination to groundwater, which poses an unacceptable risk to human health and the environment due to the presence of 1,2,4-trimethylbenzene (TMB). In addition, because regulations require that groundwater be protected for future use, cleanup goals for 1,2-dichloroethane, arsenic, benzene, chlorobenzene, nitrate, selenium, toluene, TCE, and bis(2-ethylhexyl)phthalate have been established. As specified in the ROD (Air Force, 2015) these COCs and associated risks are being addressed using land use controls (LUCs) to prevent worker exposure, monitored natural attenuation (MNA) to address the dissolved-phase plume, and excavation to address the LNAPL source area.

To facilitate treatment of the source area, the Air Force elected to apply COGAC™ to the excavation pit to absorb and oxidize the remaining COCs. In addition, a treatability study consisting of the injection of COGAC™ combined with multi-phase extraction (MPE) was performed to address a larger area of the site at which petroleum-impacted soil and groundwater were present at lower levels.

3.2.2 Design and Application

The remedial action consisted of applying a carbon-based amendment in two portions of the site using two different application methods. COGAC™ was selected based on successful results of a bench-scale treatability study for the site COCs.

COGAC™ combines three common mechanisms for remediation of subsurface hydrocarbons and chlorinated compounds including: in situ chemical oxidation (ISCO), biostimulation, and carbon adsorption. COGAC™ contains sodium persulfate and calcium peroxide that react to produce persulfate radicals, which can persist for several weeks in the aquifer. Biostimulation is promoted by the nutrients that are made bioavailable during ISCO. The calcium peroxide is converted to hydrogen peroxide, which liberates oxygen that is used by bacteria to aerobically degrade petroleum hydrocarbons and other COCs. Lastly, the AC provides adsorption sites for organic contaminants that can quickly reduce the concentrations of COCs and minimize rebound. It also provides a substrate for the growth of contaminant-degrading bacteria.

Two methods were used to apply the COGAC™. One consisted of excavating the LNAPL source area hot spots to a depth of about 18 feet below ground surface (bgs) and emplacing a total of 2,386 lbs of COGAC™ into three treatment cells (about 954 lbs into one cell and 716 lbs into each of the other two cells). The excavation was then backfilled with sand and clean native soil.

The second application consisted of in situ injection of COGAC™ combined with MPE to recover LNAPL and enhance distribution of the COGAC™ throughout the target treatment zone. Table 4 summarizes key design information for each of the applications. Treatment areas and injection and extraction locations are shown in Figure 3.

The in situ application of COGAC™ consisted of installing 118 direct push points through which approximately 22,000 gallons of a 12% solution of COGAC™ in groundwater was introduced. The DPT points were advanced 18 to 25 feet bgs and the COGAC™ solution was introduced through a 5-foot-long screen. The injection depths varied slightly across the site based on the degree of LNAPL and soil contamination as evidenced by nearby soil cores. At several locations, the injected COGAC™ solution would surface at a nearby temporary injection point or within an active extraction point. When this occurred, injection was ceased at its current location and was performed at the next location.

Table 4. Design Summary for the COGAC™ Treatability Study at the FTF, Hill AFB LMTF

Design Feature	Treatability Study	Excavation
Primary COC and Maximum Detected Concentration (µg/L)	LNAPL (1.2 ft), 1,2,4-TNB (NA), and benzene (NA)	
Predominant Geology in Treatment Zone	Sand/silt	
Reagents and (Quantity) Applied	COGAC™ (22,058 lbs in a 12% solution) ⁽¹⁾	COGAC™ (2,386 lbs)
Target Treatment Area (ft²)	~40,000	Three 2,000 to 2,500 ft ² cells
Target Treatment Volume (ft³)	~200,000	~14,000 ⁽²⁾
Number of DPT Injection Locations	118	NA
Number of Extraction Wells	48	NA
Number of Injection Wells	NA	NA
Vertical Injection Interval (ft bgs)	15 to 25 ⁽³⁾	~18 ⁽⁴⁾
Injection Spacing (ft)	~10	NA
Application Timeframe (days)	18	<1 ⁽⁵⁾

- (1) About 16.6 lbs. of COGAC™ per pound of contaminant was injected, which exceeded the calculated design dosage of 15 lbs./lb.
 - (2) Assumes an average of 2,250 ft² treatment area and a two-foot-long treatment interval.
 - (3) Injection interval varied based on location of soil contamination. Reagents generally were introduced across a 5-foot-long interval.
 - (4) Amendments placed at bottom of open trench
 - (5) Does not include time to perform excavations.
- NA – Not applicable

An MPE system was used to extract groundwater and LNAPL through 48 temporary 1-inch-diameter DPT points. These points were installed in a configuration to facilitate recovery of LNAPL and enhance distribution of the COGAC™ solution. They were installed at depths ranged from 15 to 20 ft bgs to 20 to 25 ft bgs, corresponding to the highest concentrations of LNAPL and soil contamination as evidenced by soil cores. A 5-foot-long screen was used at most locations.

The MPE system was operated prior and during the injection of the COGAC™ to remove as much LNAPL as possible and to increase the radius of influence and facilitate distribution of the COGAC™. Approximately 100 gallons of LNAPL was recovered by the MPE system.

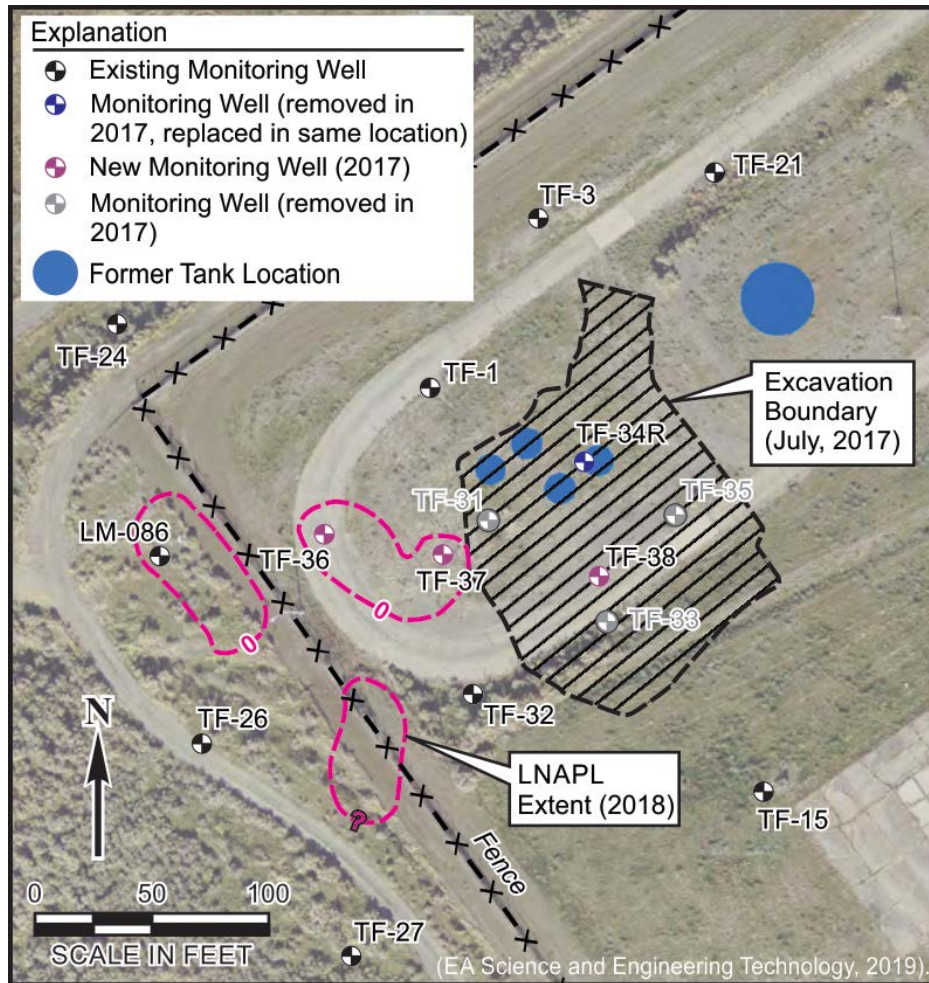


Figure 3. LNAPL Extent Pre- and Post-Excavation and COGAC™ Application (Source: U.S. Air Force)

Groundwater monitoring to track progress of the COGAC™ remedy toward achieving remedial goals included laboratory analyses of VOCs and alkalinity and field analyses of dissolved oxygen (DO), ORP, pH, specific conductance, and turbidity. The first round of groundwater monitoring took place in the Fall of 2018, a little more than one year after application of the COGAC™. In addition, measurement of LNAPL thickness in site wells was performed monthly after the COGAC™ application and a LNAPL transmissivity test was performed approximately 3 months after implementing the remedy. Monitoring continues to be performed annually.

3.2.3 Results

A small amount of LNAPL (less than 0.5 ft during the three most recent monitoring events) continues to persist in three of the monitoring wells. Results of a transmissivity test performed using the baildown method (ASTM, 2013) indicate that very little LNAPL remains and is not easily recoverable. DO measurements indicate that the aquifer has remained aerobic after the applications and ORP measurements indicate it is not as highly reducing compared to baseline (pre-injection) values, which are conducive to aerobic degradation of the remaining benzene and 1,2,4-TMB.

Concentrations of benzene and 1,2,4-TMB in groundwater were lower several months after the remedy was applied compared to pre-injection concentrations. However, additional long-term data are needed to assess the potential for rebound. Measured concentrations of 1,2,4-TMB are well below the ROD preliminary action level of 2,800 micrograms per liter ($\mu\text{g/L}$). Benzene concentrations in groundwater remain above their remedial action goal of 5 $\mu\text{g/L}$, but have decreased by close to an order of magnitude at some locations.

3.2.4 Conclusions and Lessons Learned

The following conclusions and lessons were learned as a result of this demonstration:

- Simultaneous application of MPE and COGAC™ appears to have reduced LNAPL and associated COCs including benzene and 1,2,4-TMB. However, additional long-term monitoring data are required to fully assess remedial performance.
- Surfacing of the COGAC™ solution was problematic at about 15% of the injection locations.
- Operation of the MPE system facilitated distribution of the COGAC™ solution and likely helped to minimize the frequency and severity of surfacing.
- Field monitoring performed close to one year after introducing COGAC™ into the aquifer indicates that sufficient oxygen (e.g., >2 mg/L) remains in the aquifer to support biodegradation of petroleum COCs.

3.3 BOS® 100 INJECTIONS AT FORMER LOWRY AIR FORCE BASE

3.3.1 Background

Lowry Air Force Base is a 1,866-acre facility located about 6 miles southeast of downtown Denver, Colorado. The base was in operation from 1937 through 1994. Base-wide groundwater, designated as OU 5, contains three TCE plumes, the largest of which is commingled with a carbon tetrachloride (CT) plume. The CT plume, which is the focus of this case study, likely resulted from CT used to clean mechanical parts. Historical photos indicate possible localized dumping activities occurred at the site during the 1940s. The volume of product released at the site is unknown.

Groundwater-bearing units at the site include alluvium (consisting of sands and silt) and bedrock (weathered and fractured claystone). The conceptual site model (CSM) suggests that CT has infiltrated through the saturated alluvium sorbing to sediment grains and into the water-bearing zones in bedrock. The lack of lateral continuity of water-bearing zones has prevented the higher concentrations of CT in bedrock from migrating away from the source area. Historical information indicates that the CT is confined to approximately 28 to 36 feet bgs with the top of bedrock encountered between approximately 20 and 23 feet bgs.

ISCO using activated sodium persulfate was selected as the preliminary remedy to address the CT source area and bedrock plume. It was applied as an interim remedial action in 2006. Approximately 34,750 gallons of 4.74 percent Klosur and 1.44 percent sodium hydroxide was introduced through 55 locations into the bedrock aquifer. However, post-injection monitoring indicated that the application did not effectively reduce the CT concentrations and additional treatment would be required.

The Air Force elected to apply BOS 100[®] - an innovative carbon-based amendment to sequester the CT and enhance reductive dechlorination. A full-scale application in the CT source area was performed in 2008, followed by a smaller-scale localized application in 2010 to treat hot spot areas in the vicinity of Well MWCT08 that exceeded the Colorado Basic Groundwater Standard (CBGS) of 5 µg/L.

3.3.2 Design and Application

The remedial action consisted of an application of BOS 100[®] in the bedrock and alluvial aquifer to treat groundwater contaminated with CT and TCE. BOS 100[®] is a carbon-based amendment that is impregnated with iron at high temperature. It is particularly effective for treating chlorinated ethenes since it promotes chemical reduction in a similar manner as ZVI. However, unlike ZVI, the AC also provides a large surface area to facilitate sorption of COCs. Hence, an immediate reduction in COC concentrations can be realized upon emplacement, which is subsequently eliminated through chemical reduction.

The full-scale BOS 100[®] application was performed in two phases. The first phase was performed to evaluate the efficacy of two types of injection equipment to achieve the necessary injection depths and to introduce and distribute the amendments. Based on the results from the first phase, the second phase was completed with conventional DPT and injection pump technology. The most effective injection method to achieve the maximum design depth of about 40 ft bgs was to first advance a pilot hole through the alluvium and into the top 6 inches of bedrock using 2.5-inch-diameter rods, and then transition to 1.5-inch-diameter rods to complete the hole.

The second phase, which consisted of the full-scale application of BOS 100[®], is summarized in Table 5. It consisted of advancing 81 injection points into the bedrock interval and 83 points into the alluvial interval using a 10-foot grid spacing and 2-foot vertical spacing between injection intervals. The BOS 100[®] slurry was prepared by mixing 210 lbs of granular BOS 100[®] with approximately 365 gallons of water. The desired quantity of BOS 100[®] was then pumped into the bedrock interval using a top-down injection approach. A top-down injection approach also was planned for the alluvial aquifer; however, due to excessive surfacing of reagent, the application was modified to use a bottom-up approach beginning at a depth of 16 feet. The amendment was introduced into 30 locations using the top-down and 53 locations using the bottom-up approach. Design parameters for this application are summarized in the second column of Table 5.

Post-treatment groundwater samples were collected from the seven monitoring locations at 2 weeks, 1 month, 2 months and 4 months after completing the injections. All samples were analyzed for VOCs. Analyses for potential CT degradation daughter products (chloroform, methylene chloride, and chloromethane) were also included.

In 2010, a follow-up injection event, which consisted of injecting 600 pounds of BOS 100[®] into 17 bedrock points, was performed as a polishing step in the vicinity of Well MWCT03 to address remaining elevated levels in this localized area.

Table 5. Design Summary for the Application of BOS 100® at OU 5, Former Lowry Air Force Base

Design Feature	2008 Full-Scale Source Area Application
Primary COC and Maximum Detected Concentration (µg/L)	Carbon Tetrachloride (5,856) and TCE (289)
Predominant Geology in Treatment Zone	Fine-grained alluvial matrix consisting of interbedded silts and clays and underlying weathered/fractured bedrock
Reagents and (Quantity) Applied	BOS 100® [15,000 lbs ⁽¹⁾]
Target Treatment Area (ft²)	8,000
Target Treatment Volume (ft³)	NA
Number of DPT Injection Locations	164 (81 in bedrock and 83 in saturated alluvium)
Number of Injection Wells	0
Vertical Injection Interval (ft bgs)	4 ft below top of bedrock to 24 to 39 ft bgs in bedrock; 12 to 16 feet in alluvial zone
Injection Spacing (feet)	10
Application Timeframe (days)	~15

(1) Twenty-five lbs per injection point were introduced into each of 40 bedrock points located closest to Well ETMW03. The remaining 41 (downgradient) bedrock injection points received 15 lbs.
 NA – Not available.

3.3.3 Results

Post-injection monitoring event results indicated a substantial decline in CT concentrations in the source area bedrock monitoring wells. For instance, the CT concentration in well ETMW03, which had the highest CT concentration (5,856 µg/L) prior to the BOS 100® application, decreased to below detection within six months after completing the injections. Concentrations remained below detection for four consecutive monitoring events during a two-year period. Concentrations in other wells within the CT source area exhibited similar results, being stable, decreasing or below the remedial goal of 0.5 µg/L. Based on the four post-injection monitoring events, contaminant rebound has not been observed and the degradation of CT in the source area has been very successful.

3.3.4 Conclusions and Lessons Learned

The following conclusions and lessons were learned as a result of this demonstration:

- Performing the treatability study helped to address several issues that would have resulted in additional costs.
- Surfacing of reagents/groundwater occurred at several locations. The volume of water used to make up the BOS 100[®] slurry was reduced in an attempt to mitigate surfacing.
- Advancing the DPT points into the bedrock layer was challenging and refusal occurred at two locations requiring modifications to the volumes of amendments introduced.
- Groundwater monitoring was problematic during injection activities. Levels increased to the top of casing in several wells and in several instances monitoring well caps popped off the wells due to increased pressure inside the well.

4.0 WHAT ARE SEVERAL KEY FINDINGS PERTAINING TO THE APPLICATION OF IN SITU CARBON-BASED AMENDMENTS?

Several key findings have been identified from this review of AC-based amendments as follows:

Applicability

AC amendments are well-suited for application at a wide range of sites and geologic conditions. The amendments can be used to treat source areas and downgradient plumes. They can be installed in biobarriers either through direct injection or via trenching and emplacement. As demonstrated by the case studies described above, they can be effectively emplaced in silts and clays, as well as bedrock.

Short- and Long-Term Efficacy

As shown in the three case studies, AC-based amendments have been demonstrated to be an effective technology to address a range of dissolved-phase COCs in groundwater and possibly treat source areas containing residual NAPL. However, these amendments may not be as effective in source areas containing a large volume of NAPL due to the mass of amendments that would be required to provide sufficient sorption capacity, which could be cost-prohibitive and potentially result in adverse impacts to the aquifer (e.g., reduced hydraulic conductivity).

Concentrations of COCs in the aqueous phase appear to decrease rapidly after application presumably due to sorption processes provided that adequate distribution of the amendments throughout the target treatment zone is achieved. The contribution of secondary removal mechanisms such as biodegradation, ISCO, or in situ reduction is less certain and more difficult to quantify, but as shown by the Fridley case study, CSIA and other data can be collected to evaluate these other mechanisms.

Application of this technology can result in long-term reduction of COCs. All three case studies demonstrated that COC concentrations remained much lower than baseline values one or more

years after treatment was performed. Although some rebound was observed at the Fridley site, it is important to note that the evaluation performed at the site only targeted a limited portion of the plume and the continued operation of the groundwater recovery system generates a hydraulic gradient that may facilitate the movement of contaminated groundwater into and amendments away from the treatment area. In general, competitive adsorption may affect long-term effectiveness when the strongly sorbed compounds may displace weakly sorbed compounds, resulting in release of the latter and performance assessment data should be collected and evaluated to determine long-term effects.

Remedial Design and Application Considerations

As with any in situ remediation technology, effectiveness of the AC amendments is impacted by factors such as site geology and its degree of heterogeneity, the type, mass, and phase (i.e., dissolved, NAPL, sorbed to soil) of contaminants, and other site-specific factors, all of which must be considered when developing the design for the application. Hence, prior to finalizing the design, it is important that the CSM is accurate and up to date. A detailed CSM that accurately reflects site conditions is a powerful tool for designing various aspects of the remedy including selecting appropriate amendment(s) and suitable mass loading rates; identifying injection well/point spacing, injection intervals, and the need for recirculation; and determining appropriate design flowrates and solution concentrations, among others. As performed at the Hill AFB site, oftentimes it is necessary to perform bench-scale treatability studies to test one or more carbon-based amendments using site-specific soils and groundwater. In addition, small-scale field treatability testing, such as the treatment areas described at the Fridley site, may be performed to further evaluate dosages, injection methods, injection point spacing and impacts of site-specific conditions on other design parameters.

AC-based amendments are emplaced using methods that are commonly used to emplace other types of amendments such as permanganate and ZVI. Direct push injection is a commonly used delivery method, which can be applied in high or low permeability soils. Low pressure injection often is effective in moderate to high permeability soils; however, greater pressures may be needed in lower permeability formations. Hydraulic or pneumatic fracturing may be necessary to distribute amendments in lower permeability soils or bedrock. As with all in situ technologies that rely on the application of amendments, subsurface distribution can be difficult to predict and generally is not uniform.

Surfacing of reagents and groundwater is a known concern and was documented to have occurred during the applications at Hill and Lowry AFBs. However, the frequency and severity of surfacing can be minimized by reducing water flowrate, injecting at lower pressures, and using a recirculation approach where groundwater is extracted downgradient, amended with the AC and then injected into upgradient points or wells.

Application of the amendments can be particularly effective if the treatment areas are relatively small such as in a localized source area, whereas a biobarrier approach may be more appropriate to treat large dissolved-phase plumes. However, the specific configuration used should be based on a number of additional factors including remedial action objectives, site lithology, subsurface infrastructure, and treatment depth.

AC-based amendment vendors provide spreadsheets to calculate the loading rates of amendments based on estimated contaminant mass (or mass flux), adsorption capacity, remedial objectives, and the designed lifetime of the remedy. These calculations are largely empirical due to various uncertainties caused by subsurface heterogeneity, but can provide a useful starting point for the design.

Monitoring

Monitoring should be performed during amendment application (process monitoring) and after application (performance monitoring). The objective of process monitoring is to ensure that the amendments are introduced and distributed according to the design. Monitoring may consist of various on-site field measurements and visual observations. Groundwater levels may be measured to provide an indication of distribution of amendments and potential for surfacing to occur during application. Changes in groundwater quality parameters including ORP, pH, and conductivity can provide additional information regarding amendment distribution. For instance, application of BOS 100[®], which contains ZVI, a strong reductant, would be expected to result in a drop in ORP, whereas application of COGAC[™], which contains an oxidant, would be expected to increase ORP. Other parameters such as TOC, turbidity, and visual observations also may be measured to evaluate the presence of AC in monitoring wells and gauge how effectively the amendment is being distributed and to alter the injection strategy to improve distribution as necessary during application.

Performance monitoring is performed to evaluate the long-term effectiveness of the remedy, identify the need for additional application of amendments, assess progress toward achieving remedial goals and remedial action objectives, and determine if rebound is occurring. Oftentimes, performance monitoring is limited to sampling groundwater; however, soil sampling also can be performed to evaluate long-term distribution and persistence of amendments. The frequency of performance monitoring is site-specific and often depends on regulatory requirements. It could range from monthly to quarterly to yearly. It is generally performed more frequently immediately after application and less frequently as time-series data become available that provide a solid basis for predicting future changes.

The duration of performance monitoring is site-specific and oftentimes is based on agreements established with the regulatory agencies and other project stakeholders. Since AC can continue to function over a long time, it is usually necessary to monitor sites for several years after application to evaluate effectiveness of the amendments. Resulting data provide insight into rebound and longevity of the amendments and determine if/when additional applications may be required.

Performance monitoring consists of a variety of measurements that will be based on remedial goals, the types of contaminants present, and amendments used. In all cases, it should be conducted in monitoring wells and not in injection wells since data from injection wells may be biased due to the introduction of high concentrations of amendment. In general, it should consist of measuring concentrations of COCs along with groundwater quality parameters and water levels. Depending on the type of AC amendments applied and the expected removal mechanism (e.g., biodegradation, oxidation, reduction), parameters that are commonly monitored for those types of processes also may be measured. For instance, as performed at the Fridley site, the microbial

population can be assessed using 16s RNA or CENSUS analyses to understand changes in the concentration of microbes responsible for dechlorination.

Experience has shown that it can be difficult to distinguish contaminant removal from adsorption compared to degradation since these processes may occur simultaneously without the appearance of daughter products and the daughter products can be absorbed onto the AC media. However, environmental molecular diagnostic tools, such as CSIA, are powerful methods to provide lines of evidence to help to distinguish biodegradation from contaminant removal by other physical processes, such as adsorption or volatilization.

Regardless of the type of monitoring performed, a baseline set of data should be collected prior to introducing the amendments to which post-application performance monitoring data may be compared.

Additional research is needed to thoroughly understand the implications of long-term effects from emplacement of the AC-based amendments. As seen in some of the case studies, there currently is a lack of sufficient monitoring data beyond a year post implementation. Thus, long-term effectiveness and other hydraulic impacts need to be evaluated as data become available.

5.0 REFERENCES

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