

The in situ treatment of TCE and PFAS in groundwater within a silty sand aquifer

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Abstract

Chlorinated ethenes such as trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), and vinyl chloride along with per- and polyfluoroalkyl substances (PFAS) have been identified as chemicals of concern in groundwater; with many of the compounds being confirmed as being carcinogens or suspected carcinogens. While there are a variety of demonstrated in-situ technologies for the treatment of chlorinated ethenes, there are limited technologies available to treat PFAS in groundwater. At a former industrial site shallow groundwater was impacted with TCE, *cis*-1,2-DCE, and vinyl chloride at concentrations up to 985, 258, and 54 µg/L, respectively. The groundwater also contained maximum concentrations of the following PFAS: 12,800 ng/L of perfluoropentanoic acid, 3240 ng/L of perfluorohexanoic acid, 795 ng/L of perfluorobutanoic acid, 950 ng/L of perfluorooctanoic acid, and 2140 ng/L of perfluorooctanesulfonic acid. Using a combination of adsorption, biotic, and abiotic degradation in situ remedial approaches, the chemicals of concern were targeted for removal from the groundwater with adsorption being utilized for PFAS whereas adsorption, chemical reduction, and anaerobic biodegradation were used for the chlorinated ethenes. Sampling of the groundwater over a 24-month period indicated that the detected PFAS were treated to either their detection, or below the analytical detection limit over the monitoring period. Postinjection results for TCE, *cis*-1,2-DCE, and vinyl chloride indicated that the concentrations of the three compounds decreased by an order of magnitude within 4 months of injection, with TCE decreasing to below the analytical detection limit over the 24-month monitoring period. *Cis*-1,2-DCE, and vinyl chloride concentrations decreased by over 99% within 8 months of injections, remaining at or below these concentrations during the 24-month monitoring period. Analyses of *Dehalococcoides*, ethene, and acetylene over time suggest that microbiological and reductive dechlorination were occurring in conjunction with adsorption to attenuate the chlorinated ethenes and PFAS within the aquifer. Analysis of soil cores collected pre- and post-injection, indicated that the distribution of the colloidal activated carbon was influenced by small scale heterogeneities within the aquifer. However, all aquifer samples collected within the targeted injection zone contained total organic carbon at concentrations at least one order of magnitude greater than the preinjection total organic carbon concentrations.

KEYWORDS

colloidal activated carbon, in situ, PFAS, synthetic dye, trichloroethene

1 | INTRODUCTION

In situ treatment of groundwater impacted by petroleum hydrocarbons and chlorinated solvents is well established (Huling & Pivetz, 2006; Interstate Technology & Regulatory Council [ITRC], 2005; Kashir & McGregor, 2015; Petri et al., 2011; Sra et al., 2013; Usman et al., 2012) with in situ chemical oxidation, in situ chemical reduction, and enhanced bioremediation being the most commonly applied. The emergence of per- and polyfluoroalkyl substances (PFAS) and the associated environmental issues associated with PFAS, has led to increased studies of the fate, transport, and remediation of PFAS in soil, surface water, wastewater, and groundwater. The majority of studies for the treatment of PFAS have been associated with aboveground treatment of PFAS-impacted soil and water with the in-situ treatment of PFAS just emerging (Darlington et al., 2018; ITRC, 2018; Ross et al., 2018). The remediation of PFAS-impacted groundwater is complex due to numerous factors including, that PFAS are highly recalcitrant to biological and chemical degradation due to the strong carbon-fluoride bonding (National Ground Water Association [NGWA], 2017); low regulatory guidelines; complicated environmental fate; and limited proven remedial approaches (Simon et al., 2019). Simon (2020) estimated that there may be greater than 42,000 PFAS-impacted sites which could cost over \$80 billion to address.

The most applied technologies for the treatment of PFAS in water treated above ground are systems utilize activated carbon and ion-exchange resin. Limited laboratory and field studies have been conducted looking at the possibility of using in situ methods to address PFAS-impacted groundwater (Aly et al., 2019; Barajas, 2019; Bruton & Sedlak, 2017; Carey & McGregor, 2019; Dombrowski et al., 2018; Eberle et al., 2017; Liu et al., 2020; McGregor, 2018; McGregor, 2020; Park et al., 2016). The use of in situ methods for the treatment of PFAS offers several advantages over extraction technologies including lower costs and flexibility. However, there are limitations on the effectiveness of using in situ approaches for PFAS including, their recalcitrance in the subsurface, treatment effectiveness (Dombrowski et al., 2018; McGregor, 2020) delivery and distribution of the remedial reagents (McGregor, 2020b); inefficient consumption of the reagents by scavenging compounds (McGregor, 2020a; Saeed, 2011); and matrix-diffusion and desorption issues in heterogeneous geologic materials (Carey et al., 2015).

McGregor (2018, 2020) demonstrated that colloidal activated carbon could be injected and attenuate select PFAS in dilute mixed PFAS-petroleum hydrocarbon plumes at two sites with varying geology and hydrogeology. However, the use of colloidal activated carbon to treat a PFAS plume comingled with chlorinated ethenes such as trichloroethene (TCE) and its dechlorination daughter products *cis*-1,2-dichloroethene (*cis* 1,2-DCE) and vinyl chloride has not been demonstrated to date.

A study was undertaken at a site near Shanghai, China to evaluate the effectiveness of using colloidal activated carbon combined with micro-sulfidated zero-valent iron (micro-SZVI) to treat

groundwater in a residue source area impacted by various PFAS and chlorinated ethenes.

2 | SITE DESCRIPTION

The site is a former industrial facility where various mechanical components were manufactured over the past four decades. The shallow geology of the site consists of a thin layer of sandy fill which is underlain by a silty sand unconfined aquifer. The water table occurs at a depth of approximately 3.2 m below ground surface (mbgs) and flows at an estimated velocity of 9 m/year. Measurements of the horizontal hydraulic conductivity of the silty sand aquifer provided a range of 4.8×10^{-6} to 6.3×10^{-4} m/s (Figure 1).

The shallow groundwater is impacted with PFAS along with TCE, *cis*-1,2-DCE, and vinyl chloride. Sampling of the groundwater indicated that the concentrations of TCE, *cis*-1,2-DCE, and vinyl chloride ranged up to 985 $\mu\text{g/L}$, 258 $\mu\text{g/L}$, and 54 $\mu\text{g/L}$, respectively. Maximum concentrations of the PFAS detected within the groundwater included 12,800 ng/L for perfluoropentanoic acid (PFPeA), 3240 ng/L for perfluorohexanoic acid (PFHxA), up to 795 ng/L for perfluorobutanoic acid (PFBA), up to 950 ng/L for perfluorooctanoic acid (PFOA), and up to 2,140 ng/L for perfluorooctanesulfonic acid (PFOS).

3 | METHODOLOGY

The reagents used in this study were injected using a series of injection wells installed on a 4 m grid with a total of 10 injection wells being installed within the study area. The injection wells consisted of 0.1-m diameter Schedule 40 polyvinyl chloride (PVC) riser and screens with the screens being 3.0 m in length and having a slot 30 opening (Figure 2). The reagents were mixed and injected separately at ground surface using a mechanical mixer. Both reagents were mixed with potable water and injected at pressures ranging from 15 to 45 pounds per square inch (psi) with the colloidal activated carbon being injected before the micro-SZVI. The volume of reagent solution was determined by targeting approximately 30% of the effective pore volume of injection area.

The reagents used in this study were purchased from Regenesis. These reagents included concentrated colloidal activated carbon sold under the brand name PlumeStop™, micro-SZVI iron sold under the brand name Aqua ZVI™, and lactic acid sold under the brand name Hydrogen Release Compound (HRC™). PlumeStop™ is a mixture of 1–2-micron diameter colloidal activated carbon suspended in an organic carbon matrix, while Aqua ZVI™ contains zero-valent iron (ZVI) at diameters up to 5 microns suspended in an organic carbon mixture. HRC™ is a lactic acid slurry. A total of approximately 470 kg of PlumeStop™, 50 kg of Aqua ZVI™, and 50 kg of HRC™ was injected into the test area with the applied mass of reagents being calculated based on a pore volume estimate. The volume of reagent solution

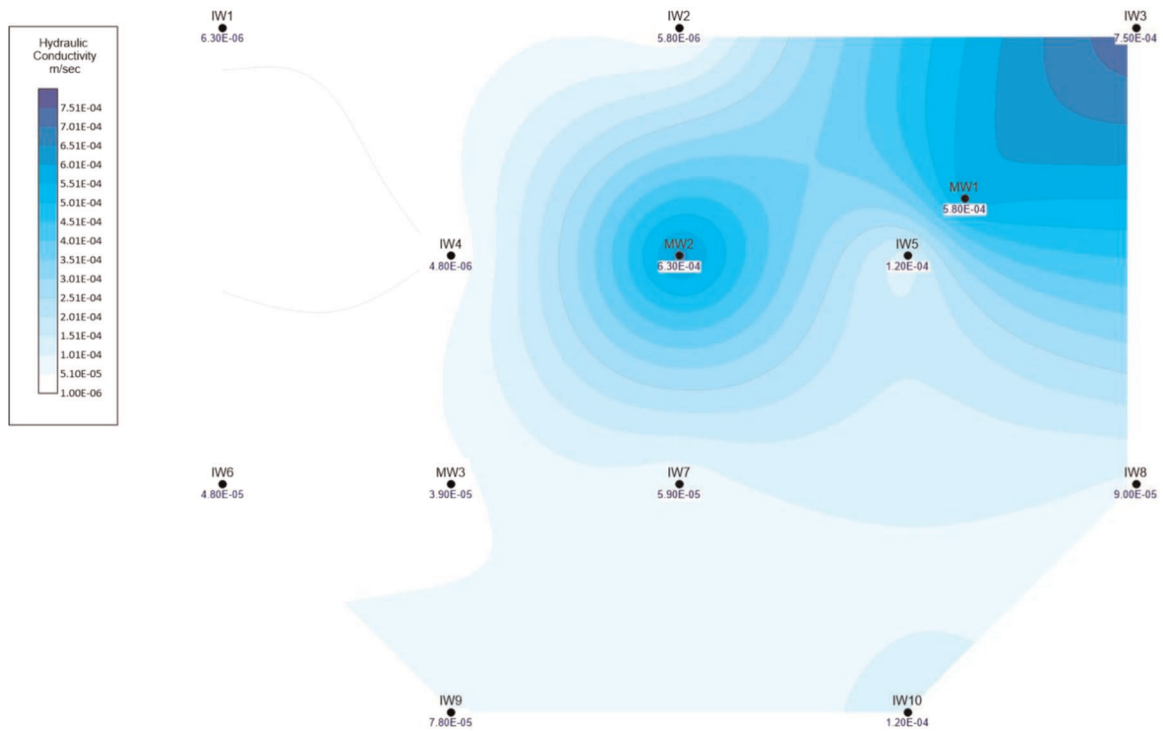


FIGURE 1 Horizontal hydraulic conductivity values distribution for injection area [Color figure can be viewed at wileyonlinelibrary.com]

injected was based on replacing approximately 33% of the impacted aquifer volume with the reagent solution.

The mixture of reagents used a combination of adsorption, abiotic, and biotic processes to attenuate the chemicals of concern within the groundwater. The PlumeStop™ was used to promote the adsorption/absorption of the compounds of concern whereas the AquaZVI was used to enhance the abiotic and biotic degradation of the compounds of concern. The HRC™ along with the carrier organic carbon based fluids within the PlumeStop™ and AquaZVI were injected to enhance biotic

degradation of the compounds of concern. The removal of PFAS was proposed by adsorption whereas the chlorinated ethenes were targeted for removal from the groundwater by anaerobic bioremediation, chemical reduction, and adsorption.

To evaluate the effectiveness of the reagents for the treatment of the chlorinated ethenes and PFAS, groundwater samples were collected on seven occasions from three monitoring wells (MW1, MW2, and MW3) within the injection area. Samples were collected twice before injection of the reagents to establish baseline concentrations and five

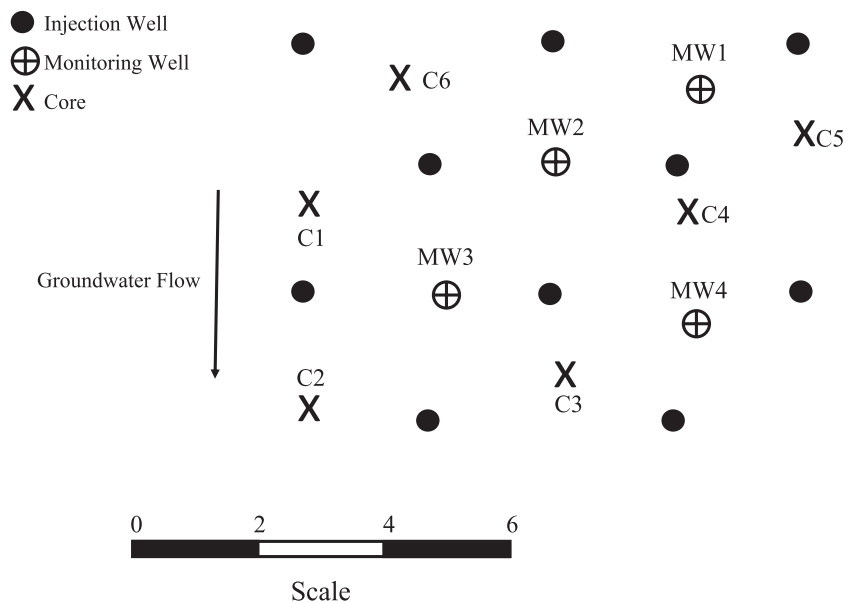


FIGURE 2 Layout of injection area showing monitoring and injection wells along with aquifer coring locations

times postinjection on Days 122, 248, 362, 547, and 724. The groundwater samples were collected using low-flow sampling methods (Puls & Barcelona, 1996) with selected field parameters being measured at the wellhead using a flow-through cell connected to a YSI Professional Plus hand-held multiparameter meter (YSI; Yellow Springs). The parameters measured at the wellhead included pH, oxidation–reduction potential (ORP), temperature, specific conductivity, turbidity, and dissolved oxygen (DO). The pH meter was calibrated to solutions of 4.0, 7.0, and 10.0 standard units before each sampling event. A calibration check was performed before collecting each sample. The ORP was checked with Zobell's solution (Nordstrom, 1977) before each sample measurement and electrical conductivity was calibrated to a National Institute of Standards and Technology (NIST) traceable standard solution.

Groundwater samples were collected for analysis of a variety of inorganic chemicals, chlorinated ethenes, and PFAS during the monitoring program. A total of 23 PFAS compounds consisting of the following were analyzed:

6:2 fluorotelomer sulfonic acid (6:2 FTS),
8:2 fluorotelomer sulfonic acid (8:2 FTS),
N-ethyl perfluorooctane sulfonamide (EtFOSA),
N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE),
N-methyl perfluorooctane sulfonamide (MeFOSA),
N-methyl perfluorooctane sulfamidoethanol (MeFOSE),
perfluorobutanesulfonic acid (PFBS),
perfluorobutanoic acid (PFBA),
perfluorodecanesulfonate (PFDS),
perfluorodecanoic acid (PFDA),
perfluorododecane sulfonic acid (PFDoDS),
perfluorododecanoic acid (PFDoA),
perfluorooctane sulfonamide (PFOSA),
perfluorohexanoic acid (PFHxA),
perfluoroheptanoic acid (PFHpA),
perfluorohexane sulfonate (PFHxS),
perfluorononanoic acid (PFNA),
perfluorooctanesulfonic acid (PFOS),
perfluorooctanoic acid (PFOA),
perfluoropentanoic acid (PFPeA),
perfluorotetradecanoic acid (PFTeDA),
perfluorotridecanoic acid (PFTTrDA), and
perfluoroundecanoic acid (PFUnA).

The PFAS samples were collected using high-density polyethylene (HDPE) containers, whereas the chlorinated ethene (TCE, *cis*- and *trans*-1,2-DCE, and vinyl chloride) samples were collected in 60-ml amber glass vials. Samples for dissolved ethene and acetylene were collected in 60-ml amber glass vials for analysis while samples for *Dehalococcoides* (Dhc) were collected in 0.5-L HDPE sample bottles. The PFAS, chlorinated ethene, acetylene, ethene, and Dhc samples were shipped to commercial laboratories for analyses.

Inorganic parameters, including chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), dissolved iron (Fe), dissolved manganese (Mn), and alkalinity, were also analyzed by a commercial laboratory.

The samples for SO_4^{2-} , NO_3^- , and Cl^- were not filtered, whereas the samples for alkalinity, dissolved Fe, and dissolved Mn were filtered with a 0.45-micron cellulose acetate membrane. The samples for dissolved Fe and Mn were acidified to pH below 2 with nitric acid (HNO_3).

Horizontal hydraulic conductivity (K_H) estimates were made by conducting falling and rising head tests within selected 0.05-m diameter monitoring wells screened within the silty sand aquifer. Aquifer solid cores were collected both prior and post-injection for analysis of the total organic carbon (TOC) content of the aquifer to determine the distribution of the colloidal activated carbon. The postinjection cores were collected following the injection of the colloidal activated carbon and before the injection of the micro-SZVI to not bias the TOC analysis with the organic carbon matrix that was used to suspend the micro-SZVI. The core samples were submitted to a commercial laboratory for TOC following the combustion methods outlined by the ASTM (2011, 2013).

4 | RESULTS AND DISCUSSION

4.1 | Reagent distribution

Cores of the aquifer material were collected prior- and post-injection to determine the changes in TOC concentration within the material following the injection of the colloidal activated carbon. Pre- and post-injection of the reagents, a total of nine continuous aquifer cores were collected, with three being collected preinjection and six being collected postinjection.

Before the injection of the reagents, the mean TOC concentration was 0.068 g/kg ($SD = 0.019$ g/kg) with TOC values ranging from the method detection limit (0.05 g/kg) to 0.11 g/kg (Core 2, depth 6.7 mbgs, Figure 3). Postinjection, the mean TOC concentrations within the target injection zone was 0.765 g/kg ($SD = 0.164$ g/kg) which represents an increase of 1025% compared to the preinjection TOC concentration (Figure 4). Outside of the target injection zone the mean postinjection TOC concentration was 0.063 g/kg ($SD = 0.034$ g/kg) which when compared to the pre-injection TOC concentration represented a slight decrease in the TOC concentrations. This decrease is attributed to heterogeneity within the aquifer, and not the removal of TOC from the aquifer itself.

A total of 36 aquifer samples were collected from within the targeted injection zone. Analysis of the TOC of these samples indicated that 100% of the samples had detectable TOC within them postinjection. Outside of the targeted injection zone, a total of 24 samples were collected with 13% of the samples analyzed having TOC concentrations greater than the method detection limit of 0.05 g/kg.

As with the vertical distribution of the activated carbon, the lateral distribution of the activated carbon is a key factor in the success of any in situ remedial program. For this program, a radius of influence of approximately 2 m was used for the design. Cores were collected from 0.75 m up to 2.00 m away from injection points to determine if the

FIGURE 3 Preinjection TOC profiles for aquifer solids collected within each of the injection area. mbgs, meters below ground surface; TOC, total organic carbon

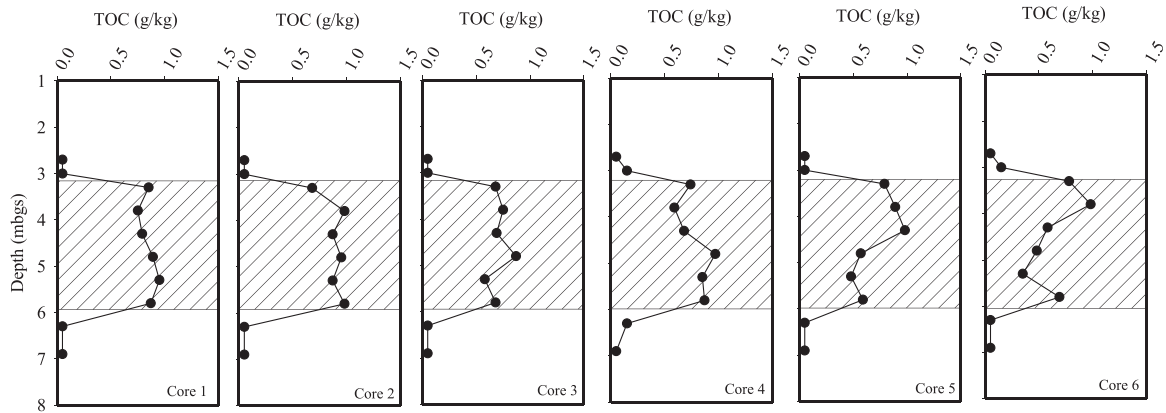
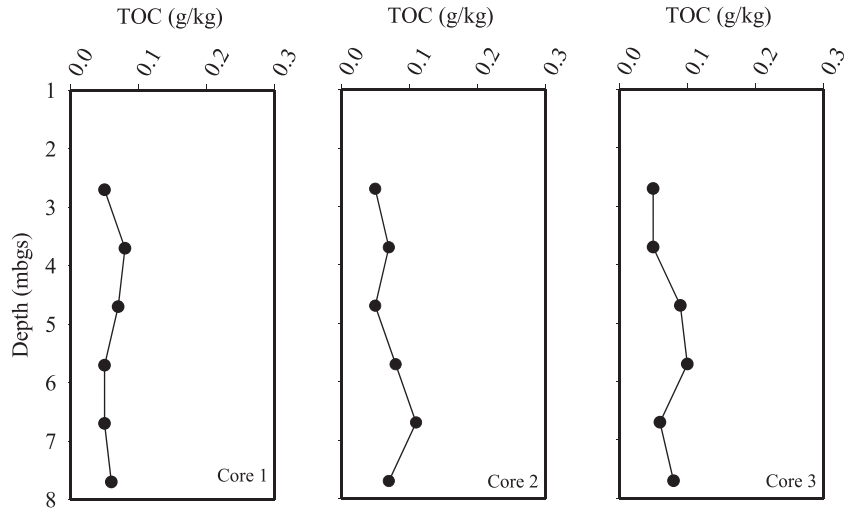


FIGURE 4 Postinjection TOC profiles for aquifer solids collected within the injection area. The hatched area represents the targeted injection zone. mbgs, meters below ground surface; TOC, total organic carbon

colloidal activated carbon content, as defined by TOC concentration, decreased with distance from the injection points. Figure 5 provides vertical cross-sections of five cores collected at distances of 0.75, 1.25, 1.50, 1.75, and 2.00 m away from injection points. Analyses of the TOC

content within the target injection zones indicates that the mean TOC concentration varied from 0.643 g/kg (Core 6) to 0.888 g/kg (Core 2) which are located 1.25 and 2.00 m away from injection points, respectively. The analyses of the TOC concentrations within the target

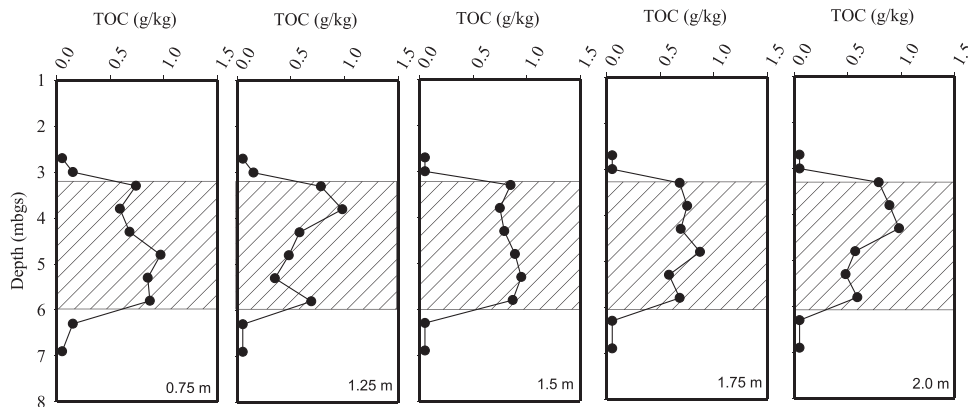


FIGURE 5 Postinjection TOC concentration profiles arranged based on distance from injection point. TOC, total organic carbon

injection zones from the five cores suggest that the colloidal activated carbon is uniformly distributed within the target injection zone within 2 m of the injection points confirming that the radius of influence used in the design of the remedial program was valid for this site.

A mass balance calculation was completed using the TOC analysis conducted on the six cores to compare the TOC mass measured with the mass of injected TOC. Additionally, the measured TOC was used to evaluate the vertical distribution of the colloidal activated carbon to determine if vertical heterogeneity within the aquifer influenced the distribution of the colloidal activated carbon over the injection area. The injection area was subdivided into 80 m² cells that were 0.5-m thick. The injection area was assumed to extend 0.5 m above and below the target injection zone which resulted in eight vertical layers. The results of the mass balance estimates determined that the TOC mass within the eight layers ranged from below the detection limit to an estimated 46.2 kg of TOC at a depth of 4.55–5.05 mbgs (Figure 6).

Comparison of the estimated TOC mass within each vertical layer of the targeted injection zone indicated that the maximum TOC mass within each layer was 46.2 kg compared to a minimum of 38.2 kg (Figure 6). This represents a maximum difference of 21% suggesting that the distribution of colloidal activated carbon within the targeted injection zone is affected by heterogeneity within the aquifer.

The total estimated mass within the target injection zone was 258 kg compared to less than 1 kg outside of the target injection zone. The total TOC injected was 362 kg suggesting that some of the TOC was not captured in the analysis of the aquifer cores. This is likely due to heterogeneity associated with sampling and analysis of the aquifer as well as the colloidal activated carbon migrating outside of the injection area.

4.2 | General groundwater geochemistry

Groundwater samples were analyzed for select inorganic parameters to gather information on the geochemical environment and processes occurring within the injection area before and post-injection. The mean pH of the groundwater within the injection area before the injection of the colloidal activated carbon and micro-SZVI was 7.87 ($n = 6$). On Day 122, the pH ranged from 6.89 to 7.63, averaging 7.14 ($n = 3$). The depressed pH within the injection area on Day 122 was attributed to an increase in microbiological activity associated with the organic carbon colloidal activated carbon and micro-SZVI matrices. On Day 362, the mean pH remained depressed compared to the preinjection pH with a mean pH of 7.58 ($n = 3$) being measured.

The mean alkalinity of the groundwater measured from six monitoring and injection wells before injection was 378 mg/L (as CaCO₃). On Day 122, the alkalinity increased to 519 mg/L (as CaCO₃), suggesting that carbonate buffering was occurring within the aquifer, most likely associated with the increased microbiological reactions associated with the degradation of the chlorinated ethenes.

The mean ORP of the groundwater before the injection of the colloidal activated carbon and micro-SZVI was -214 mV ($n = 6$).

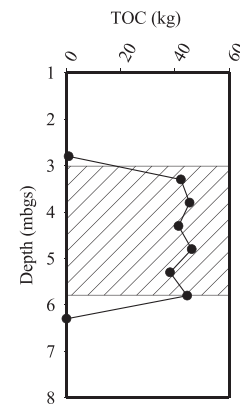


FIGURE 6 Calculated TOC mass with depth within injection area. Hatched area represents the target injection zone. mbgs, meters below ground surface; TOC, total organic carbon

The mean ORP of the groundwater sampled on Day 122 decreased to -315 mV ($n = 3$) suggesting that the additional of the organic carbon matrices associated with the colloidal activated carbon and micro-SZVI plus the micro-SZVI itself enhanced the reductive geochemical conditions within the plume. By Day 362, the ORP had increased to -278 mV ($n = 3$) indicating that reducing conditions were still present within the injection area. Corresponding with the low ORP values were low dissolved oxygen levels. Before the injection of the colloidal activated carbon and micro-SZVI, the dissolved oxygen averaged 1.1 mg/L ($n = 6$). Following the injection of colloidal activated carbon and micro-SZVI, the mean dissolved oxygen was 0.9 and 0.8 mg/L at Day 122 and 362, respectively.

Nitrate concentrations within the groundwater prior- and post-injection of the colloidal activated carbon and micro-SZVI remained below the method detection limit of 0.1 mg/L. Sulfate concentrations before the injection of the colloidal activated carbon and micro-SZVI averaged 10.5 mg/L, ranging from 9.5 to 12.7 mg/L. On Day 122, sulfate concentrations within the groundwater averaged 9.8 mg/L whereas on Day 362, the dissolved sulfate concentrations averaged 5.8 mg/L, suggesting that sulfate reduction occurred within the injection area.

Dissolved manganese and iron samples were collected from the monitoring wells and select injection wells before the injection of the colloidal activated carbon and micro-SZVI to aid in determining mass loadings of electron acceptors and donors as well as to determine the geochemical environment of the injection area. Dissolved manganese and iron concentrations before the injection event averaged 0.28 and 2.98 mg/L, suggesting that the plume was iron reducing before the injection of the colloidal activated carbon and micro-SZVI. Post-injection, the mean dissolved iron concentration increased to a mean 3.18 mg/L ($n = 3$) on Day 122 but decreased by Day 362 to a mean of 2.58 mg/L ($n = 3$). A similar trend was noted for the mean dissolved manganese concentrations in groundwater sampled from the three monitoring wells postinjection on Day 122 and 362 with mean concentrations of 0.32 and 0.29 mg/L.

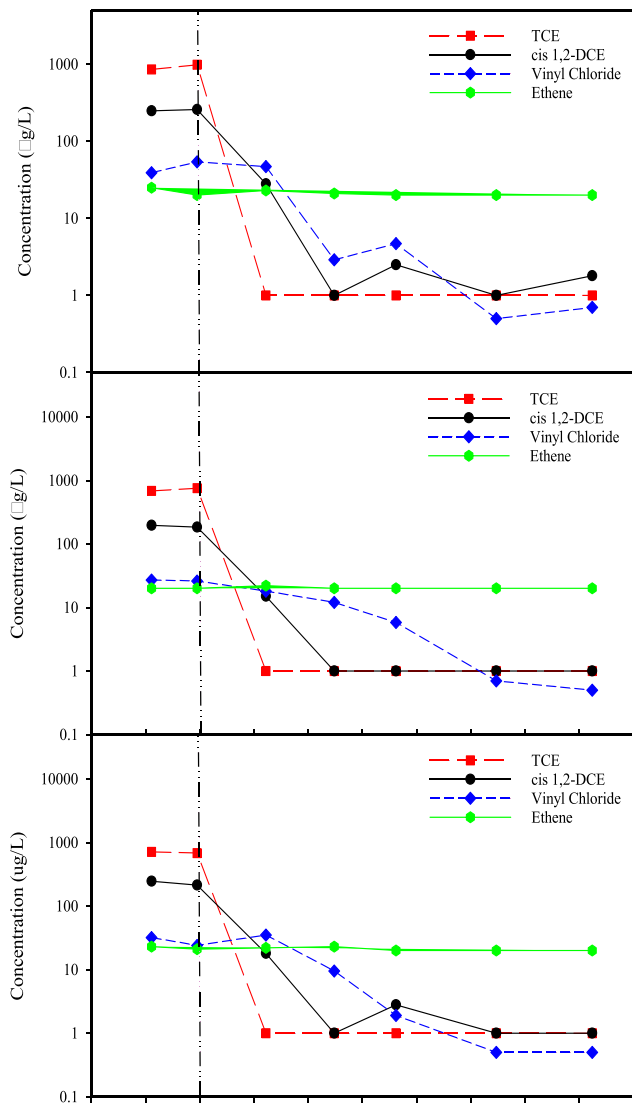


FIGURE 7 TCE, *cis*-1,2-DCE, vinyl chloride, and ethene concentrations within monitoring wells MW1 (top), MW2 (middle), and MW3 (bottom) with time. The vertical dash line represents the injection event. *cis*-1,2-DCE, *cis*-1,2-dichloroethene; TCE, trichloroethene [Color figure can be viewed at wileyonlinelibrary.com]

4.3 | Chlorinate ethene treatment

The groundwater within the injection area was impacted with TCE and its dechlorination byproducts *cis*-1,2-DCE and vinyl chloride. TCE concentrations before the injection of the colloidal activated carbon and micro-SZVI ranged from 687 to 985 µg/L, averaging 781 µg/L ($n = 6$, $SD = 119$ µg/L) (Figure 7). *Cis*-1,2-DCE concentrations ranged from 185 to 258 µg/L, averaging 225 µg/L ($n = 6$, $SD = 30.4$ µg/L), whereas vinyl chloride concentrations averaged 30 µg/L, ranging from 24 to 54 µg/L ($n = 6$, $SD = 11.3$ µg/L) (Figure 7).

Following the injection of the colloidal activated carbon and micro-SZVI, concentrations of TCE decreased to below the method detection (1 µg/L) for groundwater sampled from the three monitoring wells on Days 122, 248, 382, 547, and 724 (Figure 7).

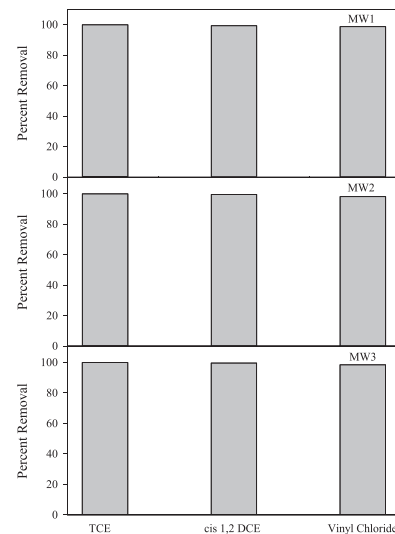


FIGURE 8 Treatment percent for TCE, *cis*-1,2-DCE, and vinyl chloride for groundwater sampled from MW1, MW2, and MW3 after 2 years of treatment. *cis*-1,2-DCE, *cis*-1,2-dichloroethene; TCE, trichloroethene

Treatment removal percentages for TCE after 724 days were greater than 99.9% for TCE sampled from all three monitoring wells (Figure 7).

Monitoring of the *cis*-1,2-DCE with time indicated that the concentrations of *cis*-1,2-DCE decreased with time to near or below the method detection limit of 1 µg/L (Figure 7). Treatment removal percentages for *cis*-1,2-DCE after 724 days were greater than 99.3% for groundwater sampled from the three monitoring wells (Figure 7).

Groundwater concentrations of vinyl chloride postinjection showed a similar trend as those observed for TCE and *cis*-1,2-DCE with concentrations decreasing with time (Figure 7). Treatment removal percentages for vinyl chloride after 724 days were 98.1% or greater for groundwater sampled from the three monitoring wells (Figure 8).

Analyses of the molar ratios for the chlorinated ethenes suggest that anaerobic biodegradation reactions are not likely the only attenuation process occurring within the aquifer postinjection of the colloidal activated carbon and micro-SZVI. Comparison of the molar concentrations of TCE, *cis*- and *trans*-1,2-DCE, and vinyl chloride indicates that less than 60% of the TCE and DCE is being degraded by reductive dechlorination processes. This suggests that other processes are occurring including beta elimination and chemical adsorption/absorption.

Ethene is produced during the biotic degradation of TCE as well as during anaerobic biodegradation and beta elimination and thus can be an indicator for biological degradation. Acetylene is a typical byproduct of beta elimination and thus is an indicator of chemical reduction by ZVI. Analysis of ethene and acetylene before the injection of the colloidal activated carbon and micro-SZVI indicated that ethene and acetylene was below the method detection limit (20 µg/L) in groundwater collected from MW1 and MW2.

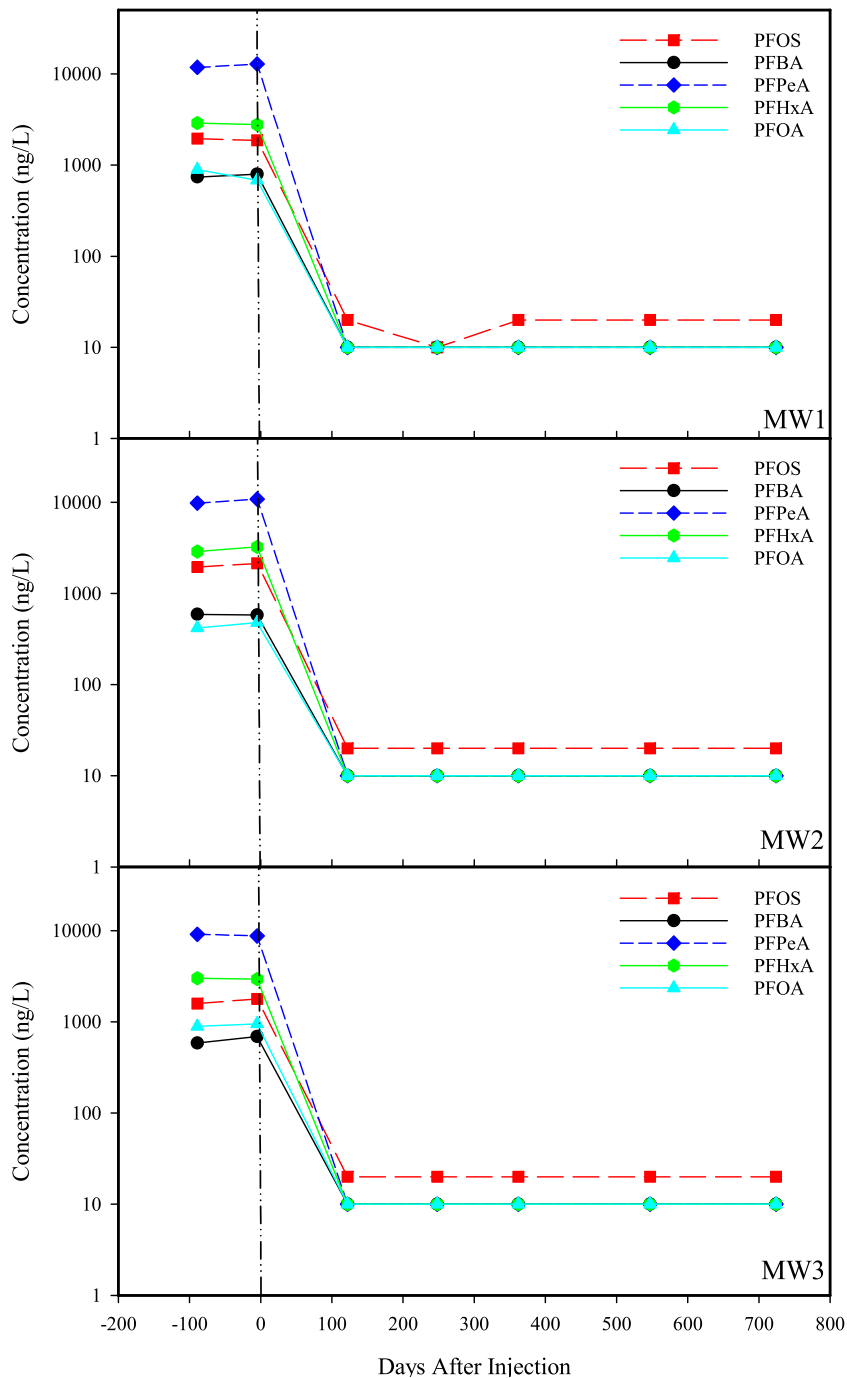


FIGURE 9 Select PFAS concentrations within monitoring wells MW1 (top), MW2 (middle), and MW3 (bottom) with time. The vertical dash line represents the injection event. PFBA, perfluorobutanoic acid; PFHxA, perfluorohexanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonic acid; PFPeA, perfluoropentanoic acid [Color figure can be viewed at wileyonlinelibrary.com]

In monitoring well MW3, the acetylene concentration was below the method detection limit ($20 \mu\text{g/L}$) whereas the mean ethene concentration was $22 \mu\text{g/L}$ (Figure 7). Following the injection of the colloidal activated carbon and micro-SZVI, ethene and acetylene were detected within the groundwater in the three monitoring wells on Day 122 and 248 at higher concentrations than preinjection, suggesting that anaerobic degradation and beta elimination of the chlorinated ethenes were occurring (Figure 7).

Assays for Dhc collected before and postinjection support the hypothesis that anaerobic biodegradation was occurring within the aquifer with Dhc concentrations increasing from an average of

2×10^3 cells per liter preinjection to 8×10^7 enumeration/L postinjection in samples collected on Day 248.

4.4 | PFAS treatment

Before the injection of the colloidal activated carbon and micro-SZVI, five PFAS were detected within the groundwater including PFOS, PFBA, PFPeA, PFHxA, and PFOA. These compounds have carbon chains ranging from five (PFPeA) to eight (PFOS and PFOA) and thus exhibit different fate and transport properties in the subsurface as

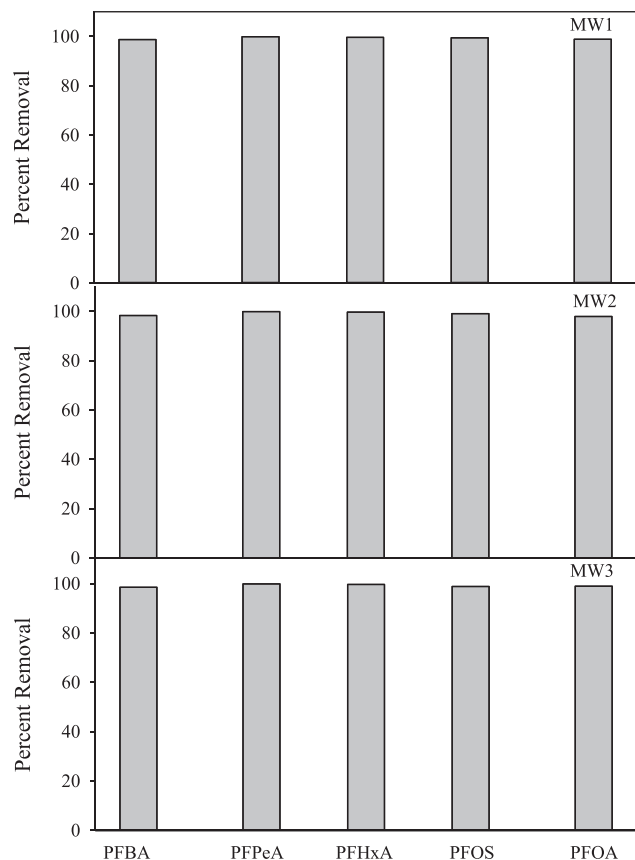


FIGURE 10 Treatment percent for select PFAS for groundwater sampled from MW1, MW2, and MW3 after 2 years of treatment. PFBA, perfluorobutanoic acid; PFHxA, perfluorohexanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonic acid; PFPeA, perfluoropentanoic acid

well as remedial efficiency. In general, the lower the number of carbons the more mobile the compound is within the groundwater (ITRC, 2020). In addition, when treating with adsorption/absorption-based technologies the lower the number of carbons the less affinity the compound will have to the adsorption/absorption-based media (Higgins & Luthy, 2006). Concentrations of the five PFAS ranged from 420 ng/L for PFOA up to 12,800 ng/L for PFPeA before the injection of the colloidal activated carbon and micro-SZVI (Figure 9).

Following the injection of the colloidal activated carbon and micro-SZVI, the concentrations of the five PFAS within the groundwater sampled from the three monitoring wells decreased to below their respective method detection limits of 10 ng/L for PFBA, PFPeA, PFHxA, and PFOA and 20 ng/L for PFOS for all five postinjection sampling events (Figure 9). The only exceptions were detections of PFPeA within the groundwater sampled from monitoring wells MW1 and MW2 on Day 248 and from monitoring well MW3 on Day 362. These groundwater samples each had PFPeA measured at the detection limit of 10 ng/L (Figure 9).

Analysis of the removal rates after 2 years for the five PFAS detected within the groundwater before the injection of the colloidal activated carbon and micro-SZVI, indicates that removal rates were

98.3% or greater. The mean removal rates for PFPeA were the greatest at 99.9%, whereas PFBA and PFOA were the lowest at 98.5% (Figure 10). It should be noted that after 2 years none of the five PFAS detected before the injection of the colloidal activated carbon and micro-SZVI were detected at concentrations greater than their respective, method detection limits (Figure 9). Additional monitoring of other PFAS not detected within the influent during the study failed to detect any other PFAS with the exception of the five PFAS detected in the original influent samples suggesting the source of PFAS was consistent with time and that the remedial reagents added to the aquifer were not promoting degradation of the five PFAS to other PFAS analyzed.

5 | CONCLUSIONS

Chlorinated ethenes such as TCE, *cis*-1,2 DCE and vinyl chloride along with PFAS have been identified by many regulatory agencies as chemicals of concern in groundwater with many of the chemicals being confirmed as being carcinogens or suspected carcinogens. This field study evaluated the fate, transport, and ultimate remediation of a mixed plume consisting of PFAS and chlorinated ethenes at a site near Shanghai, China. The groundwater within the silty sand unconfined aquifer was impacted with the chlorinated ethenes; TCE, *cis*-1,2-DCE, and vinyl chloride at concentrations up to 985, 258, and 54 µg/L, respectively. Concentrations of PFAS ranged up to 12,800 ng/L for PFPeA, 3240 ng/L for PFHxA, 795 ng/L for PFBA, 950 ng/L for PFOA, and 2140 ng/L for PFOS.

To mitigate the chlorinated ethenes and PFAS within the groundwater a combination of colloidal activated carbon and micro-SZVI was injected into a series of injection wells over a 3 m vertical target injection zone. Sampling of the groundwater over a 24-month period indicated that the five PFAS detected within the groundwater before treatment were treated to their analytical detection limit over the monitoring period. Postinjection results for TCE, *cis*-1,2-DCE, and vinyl chloride determined that the concentrations of the three compounds decreased by an order of magnitude within 4 months of injection, with TCE decreasing to below the analytical detection limit over the 24-month monitoring period. *Cis*-1,2-DCE and vinyl chloride concentrations decreased by over 99% within 8 months of injections and remained at or below these concentrations during the 24-month monitoring period. The attenuation of the chlorinated ethenes appears to be the result of a combination of adsorption/absorption, abiotic and biotic degradation reactions, whereas the PFAS removal is attributed to adsorption/absorption processes associated with the colloidal activated carbon. The results of the study to date suggest that the both the short carbon and long carbon chain PFAS as well as the chlorinated ethenes detected within the groundwater are effectively attenuated. However, it is expected that over time as mass loading increases and adsorption/absorption sites decrease, the longer carbon chain compounds will be preferentially attenuated compared to the shorter carbon chain compounds. Numerical modelling by Carey and McGregor (2019) indicated that competitive

attenuation is expected to occur when comingled plumes are present. Long-term release of adsorbed compounds is not likely to occur at concentrations of concern due to the kinetics and bonding associated with activated carbon adsorption/absorption, however, if in the unlikely event compounds that have a higher affinity for the activated carbon are exposed to the activated carbon, then it is possible for the release of the shorter carbon chain PFAS and chlorinated ethenes to be released to the groundwater. Further study of these processes is required to determine the magnitude of release and conditions required for the release of these compounds.

Analysis of soil cores collected pre- and post-injection indicated that the distribution of the colloidal activated carbon was influenced by small scale heterogeneities within the aquifer. However, all aquifer samples collected within the targeted injection zone showed an average increase in TOC concentration of greater than 1000% compared to the preinjection TOC concentrations. Sampling of the aquifer also indicated that most of the colloidal activated carbon was delivered into the target zone with only 13% of the samples collected outside of the target zone having detectable TOC. Mass balance calculations using the TOC analysis following injection indicated that approximately 71% of the injected TOC mass could be accounted for within the target injection zone.

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