

Theoretical evaluation of chemical and physical feasibility of an in situ ultrasonic reactor for remediation of groundwater contaminated with per- and polyfluoroalkyl substances

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Abstract

Per- and polyfluoroalkyl substances (PFAS) have been found in air, water, and soil globally. Groundwater is used as a drinking water supply in many locations and PFAS detections in groundwater occur frequently. Cavitation occurs when ultrasound is applied to liquids and has been shown to be effective for PFAS degradation. Sonolysis is often used to describe the cavity collapse that occurs after cavity expansion. An ideal scenario implements sonolysis in a horizontal well, which allows passive capture of contaminated water while reducing the costs and hazards associated with ex situ remediation. Four PFAS-contaminated site groundwaters were treated in the sonolytic reactor in the laboratory. Data from those experiments were used in a series of hypothetical case studies to evaluate the influence of chemical and physical properties on feasibility of installation of a novel in situ sonolytic reactor. When PFAS precursor species and perfluorobutanoic acid were included in the remediation goals they were found to drive the hydraulic retention times necessary for effective treatment compared to longer-chain PFAS. Improved implementation efficiency occurred when the target treatment area was restricted to a concentrated source zone, rather than less concentrated areas of the down-gradient plume.

1 | INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) exposure can occur through ingestion of contaminated food and water (Hu et al., 2019; Schaidler et al., 2017; Sjogren et al., 2016). PFAS are characterized by the presence of carbon-fluorine bonds, which prevent rapid degradation. In the United States, the U.S. Environmental Protection Agency (U.S. EPA) established a lifetime Health Advisory (HA) for perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) of 70 ppt combined (U.S. EPA, 2016). Individual states have set their own health advisories and the states of New Hampshire and New Jersey have set maximum contaminant levels (MCLs) for specific PFAS compounds (ASDWA, 2019).

An efficient and destructive remediation approach would be valuable to address PFAS contamination in a single, in situ step.

Sonolysis is one of several technologies that can be used to fully degrade PFAS, in addition to other recalcitrant contaminants including *p*-nitrophenol, rhodamine B, and trichloroethylene (TCE; Destailats et al., 2001; Panda & Manickam, 2017). Previous studies have shown that pyrolysis may be the primary destructive mechanism of sonolysis, though radical species are also produced and are likely important for precursor degradation or transformation to perfluoroalkyl acids (PFAAs; Moriwaki et al., 2005; Vecitis et al., 2008). There are mixed reports of aqueous electron formation in ultrasonic systems, which may be an important mechanism in some cases (Bentel et al., 2019; Dharmarathne et al., 2013). When ultrasound is applied to liquids, cavities form and expand before collapsing, which causes increases in temperature and pressure values in the immediate vicinity of the cavity. The sudden temperature increase causes the bond between the PFAS head and tail groups to

break. Additional cycles continue to remove the C–F groups (Vecitis et al., 2008). Sonolysis was examined at different scales *ex situ* for PFAS degradation (Gole et al., 2018; Moriwaki et al., 2005; Rodriguez-Freire et al., 2016; Vecitis et al., 2008) but has not been implemented in the subsurface that we are aware of.

A sonolytic reactor was recently developed for use in a horizontal well. The approach is intended to address the need for *in situ* destructive treatment of PFAS-contaminated groundwater (Laramay & Crimi, 2019). The reactor, called InSRT, was fabricated from stainless steel for durability and was coupled with an ultrasonic transducer. The transducer alternates between operating frequencies of 430 and 1300 kHz, but the frequencies are not used simultaneously to avoid cancellation effects. InSRT was designed to be used in a horizontal well and thus was designed and used at the same scale (12 L volume) that will be applied in the horizontal well. The approach avoids the need to overcome issues of scale in the future because the laboratory experiments were conducted at scale. Previous work has demonstrated that cavitation frequency and intensity decrease moving further from the transducer. Increased power has been used to remedy the loss of cavitation but as volume increases so does total electricity demand. Ultimately, these large-scale systems can become inefficient to operate compared to other options (Gogate et al., 2011). The methods of laboratory tests supporting reaction rate constants reported in the present study are described in the Supporting Information. Details of the reactor are further described in Section 2. The reactor has not been installed *in situ* to date therefore this is a theoretical feasibility assessment.

Horizontal wells have traditionally been used in the oil and gas industry but have also been applied to groundwater remediation at shallower depths (5–50 ft), but application is typically not limited by depth (Divine et al., 2013; Divine Roth et al., 2018). Horizontal wells are advantageous when compared to vertical wells because water capture is passive, rather than active as when using pumps in a vertical

extraction well. In general, passive systems can be characterized as those not requiring regular energy consumption to operate and active sites are those requiring energy to operate. Horizontal wells offer flexible access to contamination when there are obstructions on the surface (i.e., buildings and roads) and can be drilled through many formation types (Lubrecht, 2012; Steward & Jin, 2001). Horizontal wells have also been shown to be a sustainable option in comparison to pump-and-treat systems using vertical wells. Lubrecht (2012) discussed the sustainability benefits of horizontal wells, including reduced life-cycle energy consumption and minimal disturbance of sensitive habitats due to smaller equipment footprint on-site. The horizontal well implementation can save drilling time and may have lower operations costs compared to vertical well systems (Lubrecht, 2012). Operating energy can be avoided because water capture is passive, unlike in *ex situ* systems requiring continuous pumping. Water capture and potential for groundwater remediation applications were further described for the HRX Well[®] concept by Divine, Roth, et al. (2018) and Divine, Wright, et al. (2018).

A recent paper presenting the HRX Well concept used modeling and pilot-scale tests to demonstrate the capture width of horizontal wells. It should be noted that while the term capture width is used, in actuality, the capture is oblong in shape, with a predictable width spanning the depth of the well (Divine, Roth, et al., 2018). When the well hydraulic conductivity is greater than the aquifer hydraulic conductivity the contrast causes flow-focusing into the well. Divine, Roth, et al. (2018) developed a series of equations (below) which were used to model flow in the well, capture width, and residence time. Figure 1 provides a guide to the well structure to better understand the following equations.

The following equations reference Divine, Roth, et al. (2018) but are relevant to horizontal wells operating under similar environmental conditions. Flow rate in the well, Q_{HRX} , is determined by the equation:

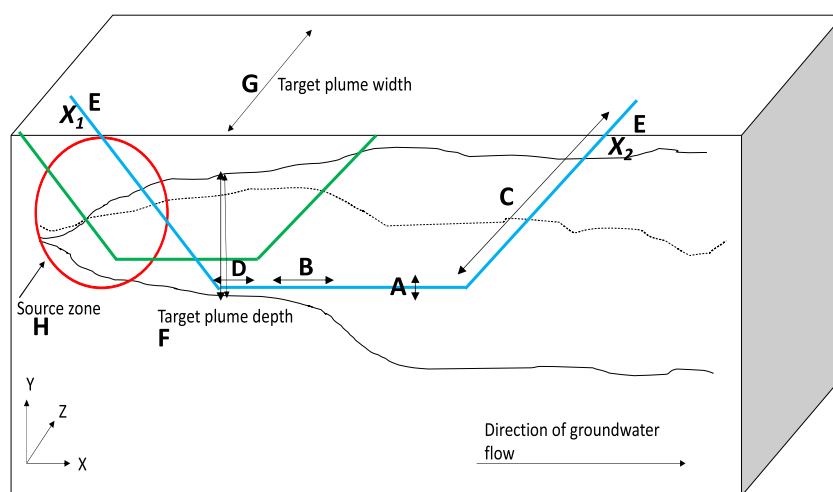


FIGURE 1 Variables related to horizontal well dimensions correspond to the letters in the figure as follows: A, well diameter; B, approximate reactor placement; C, well entry and exit lengths; D, screen length; E, well gradient (indicated from a point X_1 to a point X_2); F, target plume depth; G, target plume width; H, source zone. Note that these representations are not to scale and relative lengths may change. Green and blue lines indicate orientation of multiple wells to each other and to the direction of groundwater flow as may be required for some sites [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

$$Q_{HRX} = K_{HRX} \pi r_{HRX}^2 i. \quad (1)$$

K_{HRX} represents the treatment media hydraulic conductivity, r_{HRX}^2 is the media cartridge radius, and i_{HRX} is the well hydraulic gradient. Q_{HRX} can then be used with aquifer properties in Equation (2) to calculate capture width (W_{AVE}) as

$$W_{AVE} = \frac{Q_{HRX}}{K_A b_A i_A}, \quad (2)$$

where K_A , b_A , and i_A are the aquifer hydraulic conductivity, aquifer thickness, and aquifer hydraulic gradient, respectively. Minimizing the values in the denominator or a higher value for Q_{HRX} will all increase capture width. The minimum average residence time is given in the following equation:

$$t_R = \frac{l_{HRX}}{v_{HRX}}, \quad (3)$$

where t_R is the calculated retention time, which can also be determined from reaction rate constants if retention time is the primary determinant in system design. l_{HRX} is the treatment length and v_{HRX} is the average velocity through the media. In the context of the reactor described in this paper, the treatment length is the active zone of the reactor. Higher values for the treatment length will result in longer residence time and higher values for velocity will make the residence time shorter. The same equations were applied in the study reported here to model capture width and well length for each case study.

Capture widths predicted by models were confirmed in the pilot study conducted by Divine, Roth, et al. (2018). The HRX Well was planned for implementation in California (USA) to treat a TCE plume using zero-valent iron (ZVI; Divine, Roth, et al., 2018). They also described that capture width could be managed by using a pump set to a predetermined flow rate when sufficient hydraulic conductivity contrast is not feasible (Divine, Roth, et al., 2018).

1.1 | Influence of site conditions on horizontal well hydraulics

Cost and effectiveness of horizontal wells for groundwater remediation are also dependent upon the physical (target treatment area) and chemical (retention time and treatment method) remediation goals. The physical target treatment depth and width will determine well riser length and the number of wells installed, respectively (Ellingson-DTD, 2016). The total well length, including the riser, is a cost driver where the screen length depends on treatment length, which is determined from rate constants and the remediation goal. The riser length will depend on the target treatment depth (Divine, Wright, et al., 2018). Increasing treatment length will improve the ability to achieve remediation goals but will also increase well cost because of additional drilling and material costs. That means reducing length would require reaction rate constants to be greater (Divine, Wright, et al., 2018). Targeted plume width will determine the number of wells required. To minimize the number of

wells required, the capture width must be sufficient to cover the targeted plume width. If capture is less than the target treatment width, additional wells would be required. Divine, Wright, et al. (2018) demonstrated this for a site with a targeted width of 150 ft where models showed 50 ft of capture for one well. To address the entire targeted width three wells would be required (Divine, Wright, et al., 2018). Lower target treatment widths are more cost-effective if the well is addressing the source zone. The treatment impact will be higher per unit time when addressing the source zone compared to the dilute plume downgradient.

1.2 | Design and decision-making tools for environmental remediation

Numerous design and decision support tools offer a cost-effective interim option between simple pen-and-paper assessments of remediation alternatives and expensive pilot or full-scale implementations. Design tools have been developed to assist in selection of methods to treat halogenated wastes, remediate groundwater, or quantitatively compare remediation technologies on the basis of sustainability (Battelle & NAVFAC, 2018; Khelifi et al., 2006; Huysegoms & Cappuyns, 2017). The tools typically can be categorized as qualitative or quantitative. For example, a qualitative Decision Support Tool (DST) for groundwater remediation used eight criteria ranging from capital, operations, and management costs to societal factors to assess the effects of remediation outcomes on public health. A weighted decision-making matrix was prepared for the eight criteria and used with a method known as ELECTRE, which evaluates where remediation alternatives outrank each other, based on a matrix (An et al., 2017). Battelle's SiteWise program, currently in version 3.2, is a quantitative sustainability assessment tool that can provide quantitative information to the decision-making process (Battelle & NAVFAC, 2018). SiteWise takes numeric input values for well length, mass of carbon, and number of excavators operating, for example, and quantifies energy used and the resulting emissions. The program also allows multiple remedial alternative inputs to be compared side-by-side (Battelle & NAVFAC, 2018). DSTs may help limit the influence of bias when evaluating technology options, including by weighting the metrics used. Of course, if the metrics are not appropriate for the given scenario, the resulting output may not be valid. If correctly established, a validated decision-making method is also likely to be more acceptable in publications or to stakeholders rather than personal opinion. Ultimately, the value of using DSTs lies in time or dollars saved by selecting the appropriate remediation technology according to the metrics used.

Quantitative design tools that predict physical outcomes based on a set of input characteristics can also be valuable for the design of remediation systems. A high-level example is to follow a guidance document for physical designs, which indicates what the minimum information needed is and the considerations for the specific system (Gavaskar et al., 2000). Such tools are more feasible to use with relatively simple remediation systems with fewer factors to consider.

Similar examples are documents that compile the calculations required to begin assessing a remedial system, for example, the groundwater hydraulics (Kuo, 2014). These guides can be combined with programs such as MODFLOW to further visualize understanding of potential remediation options. Software examples for environmental remediation include system designs for bioremediation, reductive dechlorination, as well as long-term monitoring data evaluation software (EOS Environmental, 2014; Farhat et al., 2011; Viotti et al., 2014). Conceptual design tools provide an opportunity to compare and contrast multiple remediation options. These options could be entirely different systems (e.g., a permeable reactive barrier [PRB], pump-and-treat, and monitored natural attenuation) or variations on a single option (different PRB configurations) without having to prepare laboratory or pilot-scale demonstrations at a much higher cost than many of the available software options. Design tools can also be used for a simple sensitivity analysis by changing input variables one-at-a-time and comparing the tool outputs. Assessing which variables will cause the greatest changes to the design will highlight what additional site investigation is required where values may be uncertain. It is important to note here that the quality of any tool output will only be as high as the quality of the data used. In other words, using unsupported estimations or assumptions may produce a design that is not functional in practice.

The present study used multiple analysis (laboratory data, horizontal well equations, SiteWise) in a process outlined in Figure 2.

Completing an informal sensitivity analysis of parameters relevant to the study demonstrates where the site design is most sensitive to changes. Application of the process does require confidence in values used if the resulting design was to be implemented.

The goal of the present study was to examine the feasibility of implementing sonolysis in a horizontal well and understand which factors support success. The data from the sonolysis treatment experiments were used to determine hydraulic residence times and associated in-well velocities. Four hypothetical sets of site conditions were established and the Vandenburg Air Force Base (VAFB) site information was used as a baseline case of the horizontal well implementation (Divine, Roth, et al., 2018).

Well capture width and length were calculated using the equations presented in Section 1. Each site was assessed for different treatment goals, which demonstrated specific challenges and areas for future work.

2 | MATERIALS AND METHODS

2.1 | Treatability testing

The goal of the study presented here was to use results of laboratory experiments treating PFAS-contaminated site groundwaters in the reactor and site aquifer characteristics to assess what chemical and physical conditions are appropriate for reactor implementation. Four contaminated site groundwater samples were obtained, one sample per site for four sites total and labeled S1, S2, S3, and S4 for confidentiality. Each sample was treated in a 12-L sonolytic reactor alternating between 430 and 1300 kHz for 30 min, followed by 30 min off for temperature maintenance. S1 and S2 were treated for 24 h and S3 and S4 were treated for 36 h. The reactor is a 12-L rectangular tank constructed from 304-gauge stainless steel coupled with a 600 W transducer purchased from Blackstone-NEY Ultrasonics. Application of the reactor for treatment of PFAS-contaminated groundwater and further description of the operating conditions are described in Laramay and Crimi (2019).

A Thermo Scientific High-Performance Liquid Chromatograph coupled to a Triple Quadrupole Mass Spectrometer (HPLC-MSMS) was used to quantify PFAS in each sample in electrospray ionisation (ESI) negative mode according to parameters detailed in the Supporting Information and in a doctoral dissertation (Laramay, 2020). A calibration curve for PFAAs and precursors was prepared from native mixtures and used to quantify PFAS concentrations. The Total Oxidizable Precursor Assay (TOP Assay) was used to estimate the total burden of oxidizable precursors (Houtz & Sedlak, 2012). The initial measured concentrations and TOP data for each site sample are given in Table 1.

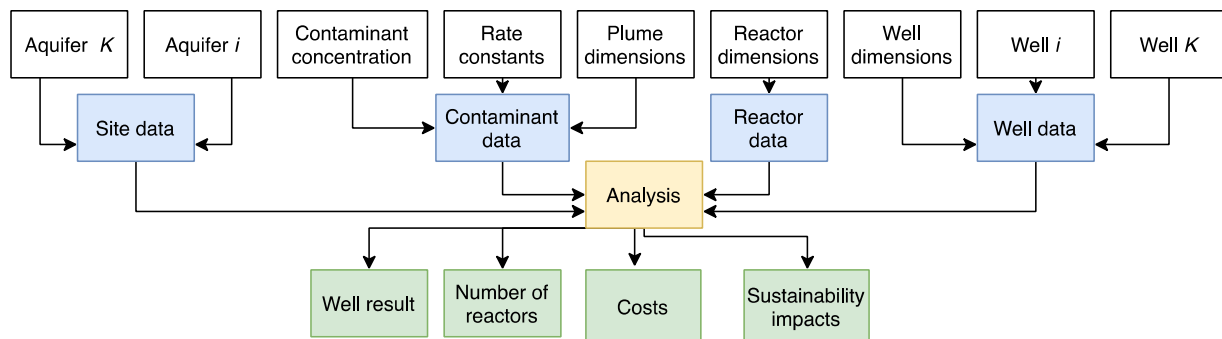


FIGURE 2 Description of design process for InSRT. White boxes represent data used, blue boxes represent organizational categories, yellow represents all calculations (laboratory data, hydraulic retention time and capture width calculations, SiteWise analysis), and green represents the results [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

PFAS	S1 concentration, nM (ppt)	S2 concentration, nM (ppt)	S3 concentration, nM (ppt)	S4 concentration, nM (ppt)
4:2 FTS	2761 (967)	Not present	0.09 (0.03)	0.1 (.04)
6:2 FTS	766 (327)	Not present	6 (2)	4 (1)
8:2 FTS	61 (32)	Not present	0.3 (0.15)	0.27 (0.1)
FOSA-1	Not present	21 (11)	8 (4)	1 (.3)
PFBA	1382 (296)	225 (48)	8 (1)	3 (0.6)
PFBS	768 (230)	89 (27)	16 (4)	15 (5)
PFPeA	1413 (373)	155 (41)	12 (3)	5 (1)
PFPeS	Not present	Not present	12 (4)	7 (3)
PFHxA	1312 (412)	318 (100)	61 (19)	11 (4)
PFHxS	1663 (665)	317 (126)	58 (23)	32 (13)
PFHpA	Not present	Not present	3 (1)	2 (0.7)
PFHpS	157 (71)	Not present	5 (2)	4 (2)
PFOA	544 (225)	151 (62)	6 (2)	5 (2)
PFOS	803 (402)	482 (241)	200 (99)	88 (44)
PFCA	2150	NA	4930	190
increase from TOP				

Note: Concentrations in ppt in parenthesis.

Abbreviations: FOSA, perfluorooctane sulfonamide; FTS, fluorotelomer sulfonate; nM, nanomoles; PFAS, polyfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanesulfonate; PFCA, perfluorocarboxylic acid; PFHpA, perfluoroheptanoic acid; PFHpS, perfluoroheptanesulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate; PFPeA, perfluoropentanoic acid; PFPeS, perfluoropentanesulfonate; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonate; TOP, Total Oxidizable Precursor Assay.

2.2 | Case study structure and analysis

The HRX Well described in the introduction was investigated for potential implementation at the VAFB. The site characteristics and well design described in their work were used as a benchmark for the hypothetical case studies described below because of their extensive analysis completed. The VAFB installation was planned for remediation of TCE, not PFAS, but the site conditions that drive well design are useful for comparison. Unlike the sonolysis application for PFAS remediation described in this paper, reactive ZVI was planned at the HRX installation but this may not be viable for PFAS (Hori et al., 2008). The well was described as 10 in in diameter and the length was 550 ft. Granular ZVI has an associated hydraulic conductivity estimated around 180 ft/d. They noted that a complete site installation could require three wells to cover the entire treatment width (if the target were 150 ft; Divine, Roth, et al., 2018).

Four cases were created around the S1-S4 site groundwater samples. To prevent site identification, site conditions for each case are hypothetical but reasonable, environmentally relevant values. A guidance document for establishing case studies to evaluate methods and tools was used to guide the case study structure by answering questions posed in their paper (Kitchenham et al., 1995). For example, they

TABLE 1 Initial PFAS concentrations (nanomoles) and increase in their concentration from oxidation of PFAS precursors present for site samples S1, S2, S3, and S4; concentrations in ppt in parenthesis

posed the question: "How do you define, in measurable terms, what you want to evaluate?" (Kitchenham et al., 1995). The answer given to prepare for these case studies was, "Retention time and corresponding velocity will be calculated from the concentration data and rate constants for each site. The effect of velocity on capture width will be the second point of evaluation." The questions were simple and straightforward but valuable nonetheless for clearly defining the case study objectives, metrics, and how to produce useful data. The resulting site characteristics needed for site design are provided in Table 2.

Overall reaction rate constants previously determined from treatment of the contaminated groundwaters are provided in Table 3 (Laramay, 2020; Supporting Information).

For each PFAS present at each site the time to reach the U.S. EPA lifetime HA level of 70 ppt was calculated using the following equation:

$$\ln\left(\frac{C_t}{C_i}\right) = -kt. \quad (4)$$

The initial concentrations (C_i) were laboratory-measured values for each site groundwater and C_t was the target treatment concentration based on different remediation goals. The reaction

TABLE 2 Hypothetical site characteristics for four site groundwaters

Initial input values	Baseline: VAFB (Divine, Roth, et al., 2018)	S1	S2	S3	S4
Known contaminant	Trichloroethylene	PFOS	PFOS	PFOS	PFOS
Plume width (ft)	150	200	60	350	77
Plume depth (ft)	8	20	50	15	80
Initial contaminant concentration ($\mu\text{g/L}$)	50,000	400	241	100	44
Target concentration ($\mu\text{g/L}$)	50	0.07	0.07	0.07	0.07
Rate constant (min^{-1})	0.002 ³	0.002	0.01	0.001	0.001
Site hydraulic conductivity (cm/s)	0.0001	0.00006	0.00001	0.00005	0.000008
Site hydraulic gradient	Used ratio equal to 1 based on Divine, Roth, et al. (2018)	0.02	0.003	0.02	0.08
Target thickness, b_A (ft)	6	20	40	15	33
Well hydraulic gradient	N/A	0.025	0.0035	0.03	0.14

Note: PFOS, perfluorosulfonic acid; VAFB, Vandenburg Air Force Base.

³Estimated from concentrations and half-life in Divine, Roth, et al. (2018).

rate constant (k) was determined from the laboratory tests and Equation (4) was used to calculate the time required (t) to reach C_t . It is important to note here that (1) the U.S. EPA level is well above levels set by several states and (2) the 70 ppt HA has only been established for PFOA and PFOS combined, not the other compounds considered in this study. While 70 ppt does provide a baseline to compare treatment outcomes, its use in this study should not be

TABLE 3 Overall reaction rate constants for the PFAS detected in the groundwater samples

PFAS	S1 (h^{-1})	S2 (h^{-1})	S3 (h^{-1})	S4 (h^{-1})
4:2 FTS	0.001	Not present	0.06	0.02
6:2 FTS	0.13	Not present	0.14	-0.01
8:2 FTS	0.002	Not present	0.07	0.06
FOSA-1	Not present	0.09	0.18	0.01
PFBA	0.01	-0.01	0.03	-0.02
PFBS	0.06	-0.06	0.08	0.03
PFPeA	0.05	0.04	0.21	0.10
PFPeS	Not present	Not present	0.12	0.04
PFHxA	0.22	0.11	0.29	0.15
PFHxS	0.17	0.08	0.15	0.06
PFHpA	Not present	Not present	0.18	0.06
PFHpS	0.07	Not present	0.12	0.05
PFOA	0.22	0.09	0.21	0.11
PFOS	0.15	0.13	0.13	0.07

Abbreviations: FOSA, perfluorooctane sulfonamide; FTS, fluorotelomer sulfonate; PFAS, polyfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanesulfonate; PFHpA, perfluoroheptanoic acid; PFHpS, perfluoroheptanesulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate; PFPeA, perfluoropentanoic acid; PFPeS, perfluoropentanesulfonate; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonate.

used to support other guidelines or regulations. Recent MCLs established in New Hampshire for PFOA (12 ppt), PFOS (15 ppt), and PFHxS (18 ppt; New Hampshire Department of Environmental Services (NHDES), 2019) were also used as target treatment concentrations in this study.

In the horizontal well, two sonolytic reactors were assumed, each with an active length of 1.5 ft. The active length corresponds to the length of the reactor where the water is affected by ultrasonic irradiation. Therefore, in the sonolytic reactor-horizontal well combination the treatment area was always 3 ft for this study although more reactors may be feasible. The water velocity through the well was specified based on 3 ft of treatment length, a 12-in well radius, and the calculated rate constants in Table 3. The flow rate was then used to calculate the capture width according to Equation (2). The costs of PVC and stainless steel were estimated using data from material suppliers and manufacturers (ESP Drilling Supply, 2018; FlexPVC, 2020; Metals Depot, 2010) and general well installation costs reported by Divine, Roth, et al. (2018). Where supplier and material data were used, costs from multiple references were compared to ensure listed costs were similar. SiteWise was used to complete the sustainability analysis (Battelle & NAVFAC, 2018). The total mass or length and diameter of PVC, steel, bentonite, and sand were entered into the appropriate cells in SiteWise. The results were reviewed and analyzed in a separate spreadsheet. When a multi-year analysis was completed the annual impacts were multiplied by the respective number of years.

2.3 | Sensitivity analysis

A one-at-a-time sensitivity analysis, as described by Hamby (1994), was completed using Microsoft Excel. The analysis compared the effects of well diameter, media hydraulic conductivity, aquifer depth, and aquifer hydraulic conductivity on well capture and hydraulic retention time (HRT) Equation (4). A table of values for the variables

TABLE 4 Range of values used in the sensitivity analysis

K_w (ft/s)	K_A (ft/d)	r (ft)	b_A (ft)	i_w, i_A	Reaction rate constant (h^{-1})
0.28	0.00028	0.33	5	1	0.00006
3	0.0028	0.42	15		0.0006
14	0.028	0.5	25		0.006
28	1	0.58	50		0.06
57	3	0.67	75		0.6
283	14	0.75	100		6
1417	28				
2835	283				
5669	1417				
14,173	2835				

in each equation was prepared based on the order of magnitude ranges and specific values in Divine, Wright, et al. (2018) and Horst et al. (2019) (Table 4).

One variable at a time was changed by approximately one order of magnitude within the environmentally relevant range, except where additional detail was needed and a half-way point was used. The constants used to calculate each variable were assigned median values from those in Table 4. In all cases well hydraulic conductivity was assumed greater than aquifer hydraulic conductivity but the magnitude of difference between the values was increased. If K_A was greater than $K_{w,well}$, capture would not be possible. The well radius and aquifer thickness were also varied individually. As described for the case study above, the ratio of the hydraulic gradient in the well and in the aquifer set equal to 1 for the sensitivity analysis. The results were compared and analyzed to determine which variables contributed most significantly to increasing capture width or reducing HRT.

3 | RESULTS

3.1 | Treatment feasibility

Overall reaction rate constants were determined for the PFAS detected in each site groundwater, including precursors (Table 3). The minimum HRT in the horizontal well required to reach the current U.S. EPA lifetime HA for combined PFOA and PFOS concentrations of 70 ppt was then calculated using the reaction rate constant and the initial PFAS concentration (Table 5).

The total HRT calculated varied from site to site, and the individual PFAS compounds detected at each site varied. The U.S. EPA health advisory currently covers PFOA and PFOS, which may be the only target contaminants for some sites; however, 70 ppt was deemed an appropriate target concentration level for this study. The HRTs for PFOS and PFOA ranged from 1 day (S4 PFOA) to 5 days (S3 PFOS) with most sites requiring 1–3 days. In addition to PFOA and

TABLE 5 Hydraulic retention times to 70 ppt calculated for each detected PFAS at four sites based on reaction rate constants from laboratory experiments

PFAS	Time to 70 ppt (days)			
	S1	S2	S3	S4
4:2 FTS	491	Not present	0.8	1
6:2 FTS	3	Not present	2.2	0.3
8:2 FTS	149	Not present	0.5	1
FOSA-1	Not present	2	1.9	11
PFBA	29	46	8.9	4
PFBS	6	4	4.5	7
PFPeA	7	6	1.6	1
PFPeS	Not present	Not present	3	4
PFHxA	2	3	1.7	1
PFHxS	2	4	3.4	4
PFHpA	Not present	Not present	1.5	2
PFHpS	4	Not present	2.4	3
PFOA	2	3	1.5	1
PFOS	2	3	4.7	4

Abbreviations: FOSA, perfluorooctane sulfonamide; FTS, fluorotelomer sulfonate; PFAS, polyfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanesulfonate; PFHpA, perfluoroheptanoic acid; PFHpS, perfluoroheptanesulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate; PFPeA, perfluoropentanoic acid; PFPeS, perfluoropentanesulfonate; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonate.

PFOS, four known precursor species were quantified with variable frequency. The known precursors were 4:2 FTS, 6:2 FTS, 8:2 FTS, and FOSA-1. The precursors had variable estimated HRTs. For example, 4:2 FTS (at site S1) was estimated to require 491 days for removal to 70 ppt but did not exceed 1 day at the other sites.

The HRT data in Table 5 highlights two important points. First, no site is the same and treatability testing is absolutely necessary. The variability between each site would require different in-well velocities from site to site and compound to compound. Other contaminants present may contribute to extended retention time via reduction of reaction rate constants for PFAS. Cheng et al. (2008) demonstrated that when volatile organic compounds (VOCs) were present, reaction rate constants for PFAS were reduced. The VOCs were presented in the cavity interior and interfered with collapse energy. Second, the complete suite of PFAS present at any given site will determine treatment outcomes. An abundance of precursors that can be transformed to PFAAs will ultimately slow PFAA degradation as some PFAA concentrations initially increased before fully decreasing. For example, the PFBA data from S2 show that measured precursors may not be the only factor. Unknown precursor species were present, as affirmed by the TOP Assay data, and their transformation may have contributed to lower PFBA rate constants (Houtz et al., 2013).

TABLE 6 Minimum in-well velocity (ft/d) values needed to achieve the calculated retention times in Table 3

PFAS	Time to 70 ppt (days)			
	S1	S2	S3	S4
4:2 FTS	0.006	ND	4	2
6:2 FTS	1	ND	1	11
8:2 FTS	0.02	ND	6	6
FOSA-1	ND	1	2	0.3
PFBA	0.1	0.1	0.3	0.8
PFBS	0.5	0.7	0.7	0.5
PFPeA	0.4	0.5	2	3
PFPeS	ND	ND	1	0.8
PFHxA	2	1	2	3
PFHxS	1	0.8	0.9	0.8
PFHpA	ND	ND	2	2
PFHpS	0.7	ND	1	1
PFOA	2	0.9	2	2
PFOS	1	1	0.6	0.8

Abbreviations: FOSA, perfluorooctane sulfonamide; FTS, fluorotelomer sulfonate; ND, not detected; PFAS, polyfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanesulfonate; PFHpA, perfluoroheptanoic acid; PFHpS, perfluoroheptanesulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate; PFPeA, perfluoropentanoic acid; PFPeS, perfluoropentanesulfonate; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonate.

Two reactors were assumed to be installed in-line when calculating in-well velocity for each data point in Table 6. Additional reactors could be used which would result in longer HRTs but would increase capital and operating costs.

At S1 the in-well water velocity needed to achieve the minimum HRTs in Table 6 ranged from 0.006 ft/d (4:2 FTS) to 2 ft/d (PFOA) for all compounds. At S2 the velocity range was 0.1 ft/d (PFBA) to 1 ft/d (FOSA-1, PFHxA, PFOS). At S3 the velocity values ranged from 0.3 ft/d (PFBA) to 6 ft/d (8:2 FTS) and at S4 from 0.3 ft/d (FOSA-1) to 11 ft/d (6:2 FTS). Of all sites, S4 exhibited the most variability in terms of orders of magnitude between velocity values where the minimum was 0.3 ft/d and the maximum 11 ft/d.

In all cases the slowest velocity value would be used to ensure removal to 70 ppt (Table 6). Comparing each site by calculated velocity, the most significant points are 4:2 FTS in S1, PFBA in S2 and S3, and FOSA-1 in S4. Comparing velocity values based on PFOA and PFOS alone, PFOS would be the basis for establishing in-well velocity which has previously been shown in the literature to be the limiting rate compared to PFOA (Campbell et al., 2009; Moriwaki et al., 2005). It is also important to note that pretreatment of precursors could also be implemented in situ to limit the HRT and number of reactors needed. The need for pretreatment will be discussed later in this paper. A summary of the HRT and velocity values is provided in Table 7, below.

TABLE 7 Summary of maximum HRT and minimum velocity

Time and velocity summary	S1	S2	S3	S4
Maximum time PFAAs (days) [†]	29	46	9	7
Lowest velocity for PFAAs (ft/d) [†]	0.1	0.1	0.3	0.5
Maximum time for PFOA, PFOS (days) [‡]	2	3	5	4
Lowest velocity for PFOA, PFOS (ft/d) [‡]	1.2	0.9	0.6	0.8
Maximum time for precursors (days) [§]	491	2	2	11
Lowest velocity for precursors (ft/d) [§]	0.006	1	1	0.3
Maximum time for NH MCL (days) [¶]	3	5	3	5
Lowest velocity for NH MCL (ft/d) [¶]	1	0.7	1	0.6

Note: The applicable PFAS represented in the table by a symbol and corresponding site identifier are as follows: [†]S1–S3 PFBA, S4 PFBS; [‡]S1 PFOS, S2 PFOA, S3–S4 PFOS; [§]S1–S4: 2 FTS, S2 FOSA, S3 6:2 FTS, S4 FOSA-1; [¶]S1 PFOS and PFHxS, S2–S4 PFHxS.

Abbreviations: FOSA, perfluorooctane sulfonamide; FTS, fluorotelomer sulfonate; HRT, hydraulic retention time; NH MCL, New Hampshire set Maximum Contaminant Level; PFAA, perfluoroalkyl acid; PFAS, polyfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanesulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate; PFHxS, perfluorohexanesulfonate.

3.2 | Horizontal well designs based on treatability testing and aquifer parameters

The capture width was calculated using Equation (2) where n was within an environmentally relevant range and i was estimated from known site information. The velocity value used depended on the site and specific PFAS being considered and was calculated from Equations (3) and (4). The results are provided in Table 8 where compounds listed represent the maximum capture width value achieved for the given conditions where PFOA and PFOS, C4–C7 PFAAs, and precursor compounds were assessed using the U.S. EPA health advisory level and PFOS, PFOA, and PFHxS were also assessed against the corresponding NH MCL values.

The results show that capture width was highly variable because of the difference in the calculated velocities shown in Table 6. The treatment length is restricted to the number of reactors used in-line in the horizontal well. Cost of the reactors limits the feasibility of implementing unlimited numbers of reactors, as does energy consumption versus remediation benefit. Velocity and treatment time are known for each PFAS at each site, because they were determined from reaction rate constants and specific remediation goals. When velocity is known and the well diameter is known, flow rate in the well can be determined, which also means flow rate is dependent upon specified velocities. Equation (2) shows that in-well flow rate is one variable in determining capture width in the well. Velocity determines capture width because of the constraints on treatment length from using reactors. In addition to the capture width varying with changes in calculated velocity, it is also limited by velocity as determined by reaction rate constants. To have a larger capture width, the slowest rate constant must be improved. At S1 PFOA treated to 70 ppt, or PFHxS and PFOS treated to the NH MCL (18

TABLE 8 Calculated capture width at each site

W_{AVE} (ft)	S1	S2	S3	S4
PFOA and PFOS	4	61	0.3	18
PFAA	0.3 (PFBA)	4 (PFBA)	0.1 (PFBA)	10 (PFBS)
Precursors	0.02 (4:2 FTS)	84 (FOSA-1)	1 (6:2 FTS)	6 (FOSA-1)
NH MCL	4 (PFOS, PFHxS)	42 (PFHxS)	0.7 (PFHxS)	13 (PFHxS)

Abbreviations: FOSA, perfluorooctane sulfonamide; FTS, fluorotelomer sulfonate; NH MCL, New Hampshire maximum contaminant level; PFAA, perfluoroalkyl acid; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanesulfonate; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate; PFHxS, perfluorohexanesulfonate.

and 15 ppt, respectively) had the largest calculated capture width when velocity was used as the starting point. The calculated velocity for 4:2 FTS was 0.006 ft/d and the resulting capture width was 0.02 ft. The capture width for 4:2 FTS at S1 was lower than typically predicted for the HRX Well, where W_{AVE} must be at least equivalent to the well diameter (Divine, Wright, et al., 2018). The results for S1 4:2 FTS suggest that the flow rate is too low such that no gradient was established. Therefore, at the velocity required to achieve the HRT in Table 7, no flow occurred. The number of reactors was increased to 4 so that velocity, and the flow rate, would increase. However, that additional treatment length was not sufficient to increase in-well velocity and capture width. Due to the slow 4:2 FTS rate constant, additional calculations found that the treatment length of the well would need to be 255 ft long, requiring 170 reactors at a cost of \$2.5 million, a scenario that is not feasible or practical. The capture widths in Table 8 for PFBA were each too small to be useful in practice. Installing multiple wells is a reasonable option for some sites but including PFBA in the treatment goal would require more than four wells to be feasible or more than five reactors in a single well and either option may be cost-prohibitive.

PFOA and PFOS have been the focus of many remediation technology studies because of the prevalence of these compounds in the environment and that these two PFAS are the most commonly regulated in the United States both by the U.S. EPA and state regulatory agencies. When the U.S. EPA HA for PFOA and PFOS were the focus of the treatment goals (Table 8) viable capture widths were only determined for S2 and S4. Both S1 and S3 would require additional engineering interventions to improve capture width.

The target treatment widths for each site were 200 ft for S1, 60 ft for S2, 350 ft for S3, and 77 ft for S4, which represent areas of concentrated PFAS rather than the entire plume width. The well and reactor act as a barrier to contaminant migration rather than a complete site cleanup method. A site schematic was given in Figure 1 to describe the implementation of one or more wells.

Several of the calculated capture widths (Table 8) did not fully cover the target treatment areas. Therefore, each site would require multiple wells, or the target width would need to be decreased. Figure 1 shows the well placement in those cases. The system

TABLE 9 Well length, cost, and sustainability assessment results

Impact category	S1	S2	S3	S4
Total well length (ft)	239	439	189	879
Total capital cost (\$)	\$400,000	\$660,000	\$330,000	\$1,220,000
Energy consumed (MMBTU)	309	569	245	1139
Electricity consumed (MWh)	91	167	72	334
Kg CO ₂ e	35,453	65,120	28,036	130,389
Kg NO _x	70	130	56	260
Kg SO ₂	94	173	74	347
Kg PM ₁₀	11	21	9	43

Abbreviations: CO₂ e, carbon dioxide equivalents (are the summation of greenhouse gases as their equivalent mass of CO₂), MBTU, million British thermal units; NO_x, nitrogen oxide; PM₁₀, particulate matter smaller than 10 μm in diameter; SO₂, sulfur dioxide.

footprint, relative to the treatment achieved, should be considered with budget and well cost (Table 9).

Costs ranged from \$336,000 to \$1.2 million as a result of the target depth which drove riser costs and, subsequently, cost of materials and drilling. Divine, Wright, et al. (2018) showed that capital costs for a single 12-in diameter well with 50 ft of capture were approximately \$200,000–\$300,000. Only S2 consistently had reasonable calculated capture widths. The associated costs were high due to the target drilling depth and resulting riser length. Costs were identified for S1 and S3 but installing wells with limited capture width may not be economical compared to other options. Costs were considered favorable when the budget remained comparable to cost estimates by Divine, Wright, et al. (2018). While capital costs have been higher for other options the appeal of a lower cost but effective system is likely greater than an infinitely higher priced system (U.S. EPA, 2001). Four wells would need to be installed at S4, at a cost of \$4 million, when the capture width was 18 ft per well to address the total treatment width (77 ft). Each scenario offers opportunity for optimization, beginning with treatment in the reactor.

In addition to capital costs for each site, the sustainability impacts of the materials used were also included in Table 9. The materials expected to be used at S1–S4 were stainless steel reactor housings, stainless steel well screens, and steel and PVC well casing sections. Impacts in each category increased with increasing well length, which determined the mass of stainless steel used at each site. If the maximum kilowatt rating for one reactor is 2.4 kW and 60% of that is drawn on average at any given time, then two reactors draw approximately 2.8 kW. Assuming the reactors cycle off and on such that for every 24-hour period the reactors operate a total of 12 hours then 12,614 kWh (12.6 MWh) of electricity would be consumed by the two reactors in 1 year. Compared to the MWh

TABLE 10 Comparison of CO₂ equivalents to HRT resulting from electricity consumption by the reactor for the given retention times in Table 4

Site	HRT (days)		kWh to reach 70 ppt		Kg CO ₂ e
	PFOA	PFOS	PFOA	PFOS	
S1	2	2	69.12	69.12	48.9
S2	3	3	103.68	103.68	73.3
S3	1.5	4.7	51.84	164.16	36.7
S4	1	4	34.56	138.24	24.4

Abbreviations: HRT, hydraulic retention time; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonate.

consumption associated with stainless steel production, the impacts per year of reactor operation were less than stainless steel production. Depending on lifecycle duration, the impacts of the operations may approach or surpass those from materials manufacture. To provide some context for the values given in Table 9, the U.S. EPA Equivalencies Calculator was used to find impacts equivalent to the CO₂ emissions equivalents for S1 (U.S. EPA, 2015). The well designed for S1 would cause 35,453 kg CO₂ equivalents to be released from well materials manufacture alone. The calculator determined that the emissions were equivalent to the carbon sequestered by 46.6 acres of forest in the United States in 1 year. While the reactor is not expected to sequester carbon, the benefits from remediation using the reactor system should exceed the environmental and human health impacts.

In addition to the data in Table 9, CO₂ was produced as a result of electricity generation to operate the reactor for the given HRTs for PFOA and PFOS treated to 70 ppt. The analysis in Table 10 shows the CO₂ equivalents per 24 L batch according to the calculated HRTs for PFOA and PFOS.

Impacts from electricity consumed by the reactors to treat 24 L of water varied between 24 and 116 kg CO₂ equivalents with variation in HRT from 1 day to 5 days. At the HRTs for sites S1 and S2, the CO₂ emissions equivalents were equal for PFOA and PFOS. The retention time was greater for PFOS than PFOA at S3 and S4. In comparison, the emissions in Table 10 were orders of magnitude less than those resulting from well materials production per 24 L treatment batch. Based on the CO₂ emissions data in Table 10, a minimum of 573 and a maximum of 2666 24 L batches would be treated for 24 h each (assuming the electricity consumption rate was 2.8 kW per batch) before the CO₂ equivalents from manufacturing well components were exceeded.

3.3 | Sensitivity analysis of site conditions

The results of the sensitivity analysis are provided in Figure 3 which shows the resulting capture width when well hydraulic conductivity, aquifer hydraulic conductivity, well radius, and aquifer thickness were varied one at a time. Note that well hydraulic gradient relates to well flow rate and can be converted using Equation (1).

Median values were selected for constants for each portion of the analysis to represent the central point in the available range, rather than a mean value which could be influenced by the large range of values. Increasing well hydraulic conductivity from 0.28 to 1417 ft/d results in an increase in W_{AVE} from 0.004 to 70 ft when K_A was 1.42 ft/d. Increasing aquifer hydraulic conductivity had a greater and opposite effect where increasing conductivity toward the well conductivity values caused capture width to decrease as shown in the upper right panel of Figure 3. Aquifer hydraulic conductivity is not an adjustable parameter at a site; however, the analysis does indicate the importance of having contrast between the two conductivity values. Increasing well radius had minimal effect on capture width in the given scenarios with increases in capture width less than one order of magnitude with increasing well radius. A lower permeability site or higher well hydraulic conductivity may demonstrate the difference more clearly. Finally, the influence of aquifer thickness was found to be minimal relative to changing aquifer hydraulic conductivity but was an important parameter to consider in the well design. When aquifer thickness increased from 5 to 100 ft, well capture width decreased from 70 to 3 ft. The sensitivity analysis results indicated that improved capture could be realized by changing the well hydraulic conductivity. In either case, as was previously noted, increasing capture and velocity in the well decreased retention time. While the sensitivity analysis was valuable to understand opportunities for design optimization, the benefits from optimizing the four variables were secondary to the need to reduce retention time in the reactors.

4 | DISCUSSION

4.1 | Physical feasibility implications from treatability testing

Laboratory experiments highlighted the important differences between site groundwaters and between the compounds detected at each site. The variability was particularly apparent in the retention times required to treat PFOS, PFBA, and the four known precursors (Table 5). The results emphasized that, for retention times greater than 2 days, the feasibility of implementing the reactor system with limited energy consumption is greatly diminished. Longer-chain compound removal appeared to be more rapid than short chain, which has been previously demonstrated (Campbell et al., 2009; Cheng et al., 2008). PFBA HRTs were 29, 46, 9, and 4 days (in order of sites S1, S2, S3, and S4).

Minimum HRTs for PFBA were noticeably longer at S1, S2, and S3 than HRTs for other PFAAs. In addition to the known precursor species discussed above, unknown precursor PFAS may have been present at any of the four sites and further influenced the calculated treatment times for PFBA, as well as other PFAS (Houtz & Sedlak, 2012; Schaefer et al., 2017). A pretreatment step is being investigated to determine if it increases reactor operation efficiency by transforming PFAS precursors ahead of the reactor.

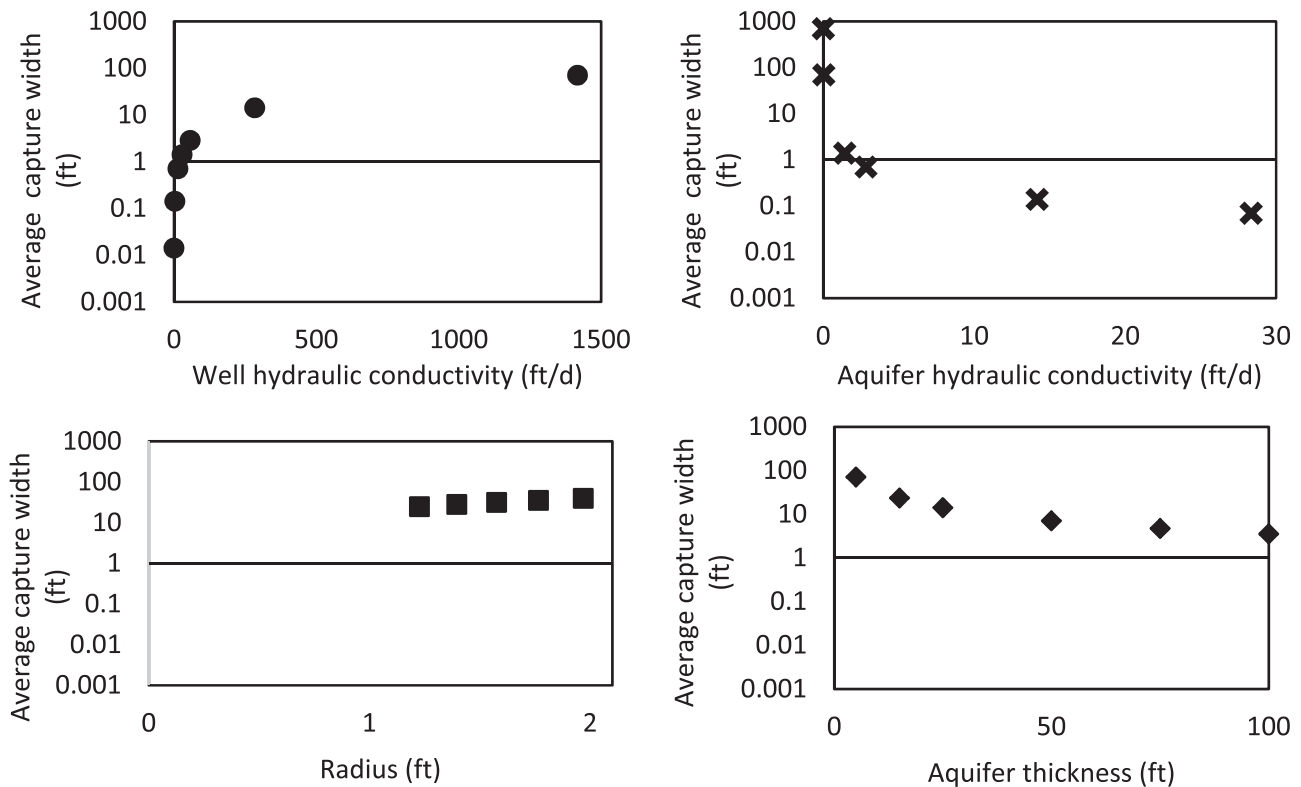


FIGURE 3 Top left (black circles): Increasing capture width with increasing well hydraulic conductivity. Top right (black x symbol): Decreasing capture width when aquifer hydraulic conductivity increased and well conductivity was held constant (0.5 cm/s). Bottom left (black squares): Capture width increased marginally when well radius was increased. Bottom right (black diamonds): Slight decrease in capture width when aquifer thickness was increased.

4.2 | Influence of remediation goals on system design

Possible well designs were modeled using Equations (2) and are reported in Table 8. At each site, different well configurations were proposed based on the calculated velocities in Table 6. In cases where capture width was less than the target treatment width, multiple wells would be required to address the total area. It is important to separate target treatment width from plume width because addressing the entire plume width is unlikely to be efficient. For example, a plume 600 ft wide with individual well capture widths of 40 ft would (1) require 15 wells and (2) may be treating dilute portions of the plume which increases total remediation time for the site. As a general rule, if more than four wells (based on target per-well costs from Divine, Wright, et al. (2018)) are required, either capture width is insufficient, or the target area is too wide. The horizontal well-reactor system is most effective and efficient as a plume cutoff technology. Treating dilute (relative to the source zone) portions of the plume increases the total site lifetime and energy consumption. In contrast, treating the source zone prevents future migration downgradient while treating a smaller total volume, thereby decreasing site lifetime. The target dimensions represent fractions of the plume depth and width because targeting the downgradient plume sections would require a large number of wells (e.g., four or more) where manufacturing costs of the reactors alone would exceed \$280,000 (based on cost to manufacture

a complete assembly of \$35,000 and assuming two reactors per well). The estimated cost of \$280,000 for four wells and eight reactors is the estimated cost of a single HRX Well, which was used as a benchmark (Divine, Roth, et al., 2018). Focusing on the source zone area would allow the number of wells to be minimized which was particularly beneficial given the low capture widths presented in Table 8. The source zone application is also favorable because the total energy demand, based on total lifecycle operating time, versus the concentration reduction is smaller than that expended to remediate larger volumes. If the whole plume were addressed, it would require treating a comparably larger volume of water and would require a longer lifecycle to do so. Targeting a high concentration source zone requires treating a smaller water volume.

When PFOA and PFOS were the only target contaminants and the U.S. EPA HA of 70 ppt was the treatment goal, well capture widths varied from 0.3 to 61 ft. At S3, 0.3 ft was calculated demonstrating that without additional process improvements (i.e., decreased HRT) the design was not feasible. Moreover, it was anticipated that the U.S. EPA could issue an MCL in 2020. If a future federal MCL were set below 70 ppt, the feasibility of the S1 and S3 designs in Table 8 will be further reduced, and, possibly, for S4, depending on the final HRT required. The NH MCL results for capture width were similar to those calculated when the PFOA and PFOS treatment goal was 70 ppt. Capture widths calculated from HRTs to meet the NH MCL were too small to be feasible at S1 and

S3, based on the resulting total number of wells. The capture width was 13 ft at S4 and was 42 ft at S2. The S2 and S4 results showed that there are feasible scenarios for the reactor even when meeting MCL-based treatment goals. PFBA, PFBS, and precursor PFAS do not currently have MCLs in any state. If these PFAS were included in future state or federal MCLs and the in situ reactor was considered an option for remediation, treatment rates must be improved to achieve sufficient capture width to use four or fewer wells.

Comparing the impacts based on well materials used and the number of reactors operating demonstrated that decreasing the number of wells did decrease the materials used and, subsequently, the cost and emissions. The conclusion is obvious but important because any intention of reducing materials and cost cannot compromise meeting remediation goals. Increasing capture width is necessary to reduce the number of wells, thereby reducing cost and sustainability impacts. For example, if the S4 treatment goal was to reduce PFHxS at least to the NH PFHxS MCL, the capture width would need to increase from 13 ft (Table 8) to between 40 and 77 ft. Doing so would reduce the capital cost from approximately \$6 to \$2 million. The cost would still be substantial, but the treatment goal would be achieved.

4.3 | Pretreatment of PFAS precursors to improve physical feasibility

An oxidative pretreatment step using activated persulfate may improve efficiency of reactor operation by converting PFAS precursors ahead of the reactor and possibly reducing retention time. For example, S3 had 4:2 FTS, 6:2 FTS, 8:2 FTS, and FOSA-1 present in the groundwater. 8:2 FTS is a precursor to C4–C9 perfluorocarboxylic acids (PFCAs), FOSA-1 is a PFOA precursor, and 4:2 FTS and 6:2 FTS are C4–C7 precursors. By oxidizing these compounds in a pretreatment process, the time and energy expended on precursor transformation are instead spent on degrading the PFAAs. It is important to note that no precursor PFAS are currently regulated and pretreatment is considered solely to improve reactor efficiency, not to meet certain remediation goals.

If PFCA retention times can be reduced the in-well velocity can be faster. When the velocity value is higher, the capture width will also be greater, according to Equations (2) and (3). Pretreatment would occur ahead of the reactor, increasing efficiency of the reactor (lower HRTs) because energy would not be expended transforming precursors to PFCAs. Capture widths calculated for different remediation goals at sites S1 and S3 were not sufficient to make InSRT feasible at those sites. Of the perfluorinated compounds PFBA contributed the most to longer retention times, and it was noted that PFBA precursors were prevalent in the site groundwaters. Therefore, if PFBA were included in remediation goals, then pretreatment may be effective in reducing the HRT. Only a single preliminary study has been completed for pretreatment, using only the S3 sample and therefore additional work is needed. The sonolysis retention time

for other site groundwaters could increase significantly due to increases in reactor inlet concentration due to pretreatment.

There are likely sustainability and cost implications to using activated persulfate. For example, Siegrist et al. (2011) reported that producing 40 metric tons of sodium persulfate would cause 50 metric tons CO₂ emissions, equivalent to the emissions from driving 16 passenger cars for 1 year. The actual emissions produced will be site-dependent because the amount of persulfate required will depend on the specific site groundwater.

5 | CONCLUSIONS

The application of an ultrasonic reactor and horizontal well for PFAS remediation (InSRT) has been demonstrated to be theoretically feasible, depending on the specific site conditions and treatment goals. High variability in the number and concentration of PFAA precursors present complicated system designs. Precursor transformation may cause PFAA degradation rates to slow considerably as PFAA concentrations initially increase. The slower rate constants can theoretically be mitigated by an oxidative pretreatment step, currently under investigation.

If the retention time needed for sonolysis can be minimized the in-well velocity can be increased along with capture width, subsequently decreasing the number of wells needed. These system improvements minimize costs, materials used, and environmental impacts, working toward a positive net impact from remediation activities.

CONFLICT OF INTERESTS

The authors (Fiona Laramay and Michelle Crimi) declare the following financial interests: We have co-founded RemWell, LLC, a company that intends to market the device described in this article pending complete field validation. However, we recognize the need for transparency regarding all methods and results. We also do not promote the reactor as a solution for all sites.

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