

Comparing PFAS to other groundwater contaminants: Implications for remediation

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Abstract

Established groundwater contaminants such as chlorinated solvents and hydrocarbons have impacted groundwater at hundreds of thousands of sites around the United States and have been responsible for multibillion dollar remediation expenditures. An important question is whether groundwater remediation for the emerging contaminant class comprised of per- and polyfluoroalkyl substances (PFAS) will be a smaller, similar, or a larger-scale problem than the established groundwater contaminants. A two-pronged approach was used to evaluate this question in this paper. First, nine quantitative scale-of-remediation metrics were used to compare PFAS to four established contaminants: chlorinated solvents, benzene, 1,4-dioxane, and methyl tert-butyl ether. These metrics reflected the prevalence of the contaminants in the U.S., attenuation potential, remediation difficulty, and research intensity. Second, several key challenges identified with PFAS remediation were evaluated to see similar situations (qualitative analogs) that have been addressed by the remediation field in the past. The results of the analysis show that four out of nine of the evaluated quantitative metrics (production, number of potential sites, detection frequency, required destruction/removal efficiency) indicate that the scale of PFAS groundwater remediation may be smaller compared to the current scale of remediation for conventional groundwater contaminants. One attenuation metric, median plume length, suggests that overall PFAS remediation could pose a greater challenge compared to hydrocarbon sites, but only slightly larger than chlorinated volatile organic compounds sites. The second attenuation metric, hydrophobic sorption, was not definitive regarding the potential scale of PFAS remediation. The final three metrics (regulatory criteria, in-situ remediation capability, and research intensity) all indicate that PFAS remediation might end up being a larger scale problem than the established contaminants. An assessment of the evolution of groundwater remediation capabilities for established contaminants identified five qualitative analogs for key PFAS groundwater remediation issues: (a) low-level detection analytical capabilities; (b) methods to assess the risk of complex chemical mixtures; (c) nonaqueous phase dissolution as an analog for partitioning, precursors, and back diffusion at PFAS sites; (d) predictions of long plume lengths for emerging contaminants; and (e) monitored natural attenuation protocols for other

non-degrading groundwater contaminants. Overall the evaluation of these five analogs provided some comfort that, while remediating the potential universe of PFAS sites will be extremely challenging, the groundwater community has relevant past experience that may prove useful. The quantitative metrics and the qualitative analogs suggest a different combination of remediation approaches may be needed to deal with PFAS sites and may include source control, natural attenuation, in-situ sequestration, containment, and point-of-use treatment. However, as with many chlorinated solvent sites, while complete restoration of PFAS sites may be uncommon, it should be possible to prevent excessive exposure of PFAS to human and ecological receptors.

1 | BACKGROUND

There has been increasing concern regarding the presence of per- and polyfluoroalkyl substances (PFAS) contamination in soil and groundwater. Based on their current knowledge, a symposium of 60 PFAS experts in mid-2019 developed this consensus (Simon et al., 2019):

The consensus message from the Symposium participants is that PFAS present far more complex challenges to the environmental community than prior contaminants. This is because, in contrast to chlorinated solvents, PFAS are severely complicated by their mobility, persistence, toxicological uncertainties, and technical obstacles to remediation—all under the backdrop of stringent regulatory and policy developments that vary by state and will be further driven by the USEPA.

But even if PFAS ends up being less toxic than currently perceived, their solubility, mobility, and persistence in the subsurface will yield contaminated footprints and plume volumes that dwarf those caused by more common contaminants (e.g., petroleum constituents, chlorinated solvents, etc.).

However, there is still considerable uncertainty as to the nature and ultimate magnitude of PFAS site remediation compared to the remediation of other significant groundwater contaminants such as chlorinated volatile organic compounds (CVOCs), benzene, toluene, ethylbenzene, and xylenes (BTEX), and companion compounds (e.g., 1,4-dioxane for solvents, methyl tert-butyl ether [MTBE] for fuels). These contaminants impact groundwater at hundreds of thousands of sites around the world and have been responsible for multibillion-dollar remediation expenditures.

Having a better conceptual model of the similarities and differences in PFAS remediation as compared to other contaminants would help the groundwater community make better strategic decisions regarding the PFAS problem, such as how to train staff, determining if higher funding in PFAS research is appropriate, the development of new technologies, and deciding whether to invest in

PFAS remediation. The objective of this study was to improve our understanding of the potential magnitude of the PFAS problem by performing a systematic quantitative and qualitative comparison of PFAS site remediation challenges with those for well-established groundwater contaminants.

2 | APPROACH

First, nine different quantitative remediation-related metrics were compiled and compared for chlorinated solvents, 1,4-dioxane, benzene, MTBE, and PFAS (Table 1). Second, several key challenges identified with PFAS site remediation were evaluated to see if similar situations have been addressed by the remediation field in the past.

3 | QUANTITATIVE METRICS

Of the nine quantitative remediation metrics, three were associated with the potential and observed prevalence of each contaminant (or contaminant class) in groundwater:

- Chemical production during a key period when subsurface releases were more common,
- Number of sites with each groundwater contaminant, and
- The frequency of detection of each contaminant in drinking water supplies sourced from groundwater.

Two quantitative metrics attempted to represent the relative fate and transport for the compounds by comparing:

- Plume attenuation based on actual or proxies for median contaminant plumes lengths; and
- The degree of hydrophobic sorption that might be expected by contaminant plumes traveling through the same type of aquifer material.

Three related metrics explored two drivers of remediation difficulty:

TABLE 1 Key quantitative metrics for comparison of common groundwater contaminants

Metric	Proxy	Units/Table No.
1. Potential prevalence of impact	1a. Chemical production during period when subsurface releases were more common	Metric tonnes (Table 2)
	1b. Sites with known groundwater impacts	Number sites (Table 3)
	1c. Impact to public water supplies	Number of public water supplies relying on groundwater with impacts (Table 4)
2. Subsurface attenuation potential	2.1 Plume attenuation: Median plume length for contaminant or contaminant proxy	Feet (Table 5)
	2.2 Hydrophobic sorption	Retardation factor based on assumed typical soil properties (Table 6)
3. Relative remediation difficulty/capability	3.1 Commonly used regulatory criteria	µg/L (Table 7)
	3.2 Required destruction/removal efficiency: Median maximum source concentrations from multiple site databases divided by regulatory criteria	Reduction factor (Table 8) (reported as ratio and as order of magnitude reduction needed)
	3.3 Relative remediation capability: Median reductions in source zone concentrations from in-situ treatment	Reduction factor (Table 9) (reported as ratio and as order of magnitude reduction needed)
4. Relative research intensity	5. Google scholar search terms “DNAPL+ Groundwater” vs. “PFOA and/or PFOS +groundwater”	Number of Google scholar research citations over time (Figure 2)

Abbreviations: DNAPL, dense nonaqueous phase liquid; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid.

- The stringency of key regulatory criteria for each contaminant and the required destruction/removal efficiency of each contaminant (typical maximum source concentration at a site divided by the regulatory criteria); and
- The relative capability of conventional in-situ remediation technologies to reduce groundwater contaminant concentrations.

Finally, a research-related metric was evaluated:

- The relative research intensity for two contaminant classes (chlorinated solvents as represented by dense nonaqueous phase liquid [DNAPL] and perfluorooctanoic acid/perfluorooctanesulfonic acid [PFOA/PFOS] for PFAS) as reported by citations in Google Scholar over time (1980–2019).

Note that while extensive analysis was performed to make “like-for-like” comparisons between the metrics, some comparisons involved similar, but not exact metrics. For example, in comparing detection frequencies in public water supplies, one parameter had data for detections in a large number of groundwater samples, while other parameters only had data on the detections in groundwater supply wells. In addition, proxy values were required in some cases, such as using a database of chloride plume length to represent a nondegrading groundwater contaminant as a proxy for typical PFAS plume lengths due to the paucity of PFAS plume lengths in the scientific literature. Overall, the comparisons do provide useful insights into the differences

between these groundwater contaminants, but some comparisons are less exact than others.

3.1 | Relative prevalence proxies for the five contaminants

3.1.1 | Production estimates

For Metric 1a, U.S. production estimates for key time periods when subsurface releases occur were compiled for PFAS, the major chlorinated solvents, benzene production in gasoline, MTBE, and 1,4-dioxane from available sources (Table 2). The starting dates for the production figures (e.g., 1960 for chlorinated solvents) were primarily fixed by the availability of data in the scientific literature. The ending dates were assumed to be the date of product bans (e.g., 2004 for MTBE) or implementation of key regulations that would tend to greatly reduce releases (e.g., 1988 for when the Resource Conservation and Recovery Act regulations were largely incorporated into the chemical industry).

While these data are based on a number of assumptions that introduce some uncertainty, they can provide a basis for a planning-level comparison. Relative to PFAS, total U.S. production estimates for CVOCs was about 850 times total PFAS production while benzene produced for gasoline was 7,300 times the estimated PFAS production. Interestingly, 1,4-dioxane production was only six times the estimated PFAS production estimate.

The relatively low amount of PFAS produced compared to benzene or key chlorinated solvents suggests the overall scale of PFAS

TABLE 2 U.S. production estimates for common groundwater contaminants

Groundwater contaminant	Value (metric tonnes)	Relative to PFAS	Period used (when releases more likely)	Reference
CVOCs (PCE, TCE, TCA, and DCM)	2.2×10^7	850	1960–1988 ^a	Pankow and Cherry (1996); Figure 1.1
1,4 Dioxane	1.7×10^5	6.2	1960–1988	Mohr (2010); Figure 2–4 production figures for 8 years, interpolated/extrapolated for other years.
Benzene (key cleanup driver for BTEX class)	1.9×10^8	7300	1960–1988 (used same period as CVOCs; about 6 years after underground storage tank regulations promulgated)	U.S. Energy Information Agency (EIA) net production of finished motor gasoline $\times 2.5\%$ (fraction of benzene in gasoline; Verma & Tombe, 2002)
MTBE	1.4×10^8	5400	1980–2004 (Period of MTBE use in gasoline)	USEPA, 2008 (Regulatory Determinations Support Document for CCL)
U.S. PFAS Production (POSF+PFCA)	2.6×10^4	1	1958–2002 (POSF production)	Global POSF: Wang, Boucher, Scheringer, Cousins, and Hungerbühler (2017), Table S2
			1951–2011 (PTFE/FEP/PFA/PVDF Usage)	Global PFCA: Wang, Cousins, Scheringer and Buck (2014), Table 1, direct sources.

To account for exports and international production, production was multiplied by 0.36 to represent US share of OECD GDP in 1990.

Abbreviations: BTEX, benzene, toluene, ethylbenzene, and xylenes; CCL, contaminant candidate list; CVOC, chlorinated volatile organic compound; DCM, dichloromethane; MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFAS, per- and polyfluoroalkyl substances; PFCA, perfluorinated carboxylic acids; POSF, perfluorooctanesulfonyl fluoride; PVDF, polyvinylidene fluoride; TCA, trichloroethane; TCE, trichloroethene.

^aMcGuire, Newell, Looney and Vangelas (2003). Survey results indicate 90% of CVOCs releases occurred between 1960 and 1989.

groundwater remediation in the U.S. could be much lower than the scale of cleanup for either hydrocarbon or solvent sites. However, the nature of PFAS releases into the subsurface, and their unique fate and transport properties limit the forecasting power of using production as a metric for the scale of groundwater remediation.

3.1.2 | Number of groundwater remediation sites

For Metric 1b, estimates on the number of sites with releases to groundwater were compiled from the literature for CVOC sites, hydrocarbon sites (which includes MTBE sites), and PFAS sites (Table 3). Note that these values represent the all-time remediation challenge, not just the remaining remediation challenge in 2020.

The nascent state of PFAS site identification means that the ultimate number of PFAS sites has a high degree of uncertainty. The Environmental Business Journal (EBJ, 2019) developed a “working model on the number of sites with PFAS contamination,” which indicated that there could be 42,560 PFAS sites were “significant contamination will likely be identified and treated or remediated at some level.” The number of PFAS sites reported by EBJ was compiled using site count estimates from the U.S. Environmental Protection Agency (USEPA), Interstate Technology & Regulatory Counsel (ITRC), U.S. Census, U.S. Department of Transportation Federal Aviation Administration, water and solid waste industry associations, and a consensus of expert respondents via surveys and interviews.

A second estimate for the number of PFAS groundwater sites was developed from data compiled by the Michigan DEP (2019a), which as of 2020 likely has one of the most developed PFAS identification programs in the U.S. The Michigan PFAS program identified 68 sites with groundwater exceeding the 70 ppt PFOS+PFOA USEPA health advisory level. Extrapolating this

number nationwide based on the relative size of Michigan and the U.S. gross domestic product yields a possible 2,600 sites nationwide, assuming Michigan represents 2.6% of gross domestic product (GDP) as of 2015. A third estimate showed 401 sites at Department of Defense installations (Paley, 2019) as of July 2019 but this number may increase and did not include non defense sites. Therefore, for the relative comparison, the EBJ model was used to compare PFAS to other established groundwater contaminants.

The comparison in Table 3 indicates there will be many fewer PFAS sites (42,560 ultimate PFAS sites) compared to hydrocarbon sites (560,000 sites) but about the same number of chlorinated solvent sites (53,000 sites). Note these estimates have considerable uncertainty and represent a relatively gross comparison of a number of potentially contaminated groundwater sites.

3.1.3 | Frequency of detection in water supply systems

For Metric 1c, available data were compiled to evaluate the frequency of detection in public water supply systems based on studies performed by the U.S. Geological Survey and data from the Unregulated Contaminant Monitoring Rule program (Table 4). Because this latter program focuses on unregulated contaminants, data were available for 1,4-dioxane, and PFOA+PFOS. For this evaluation, two types of data were available: (a) the frequency of detection in public water supply wells (PCE, TCE, benzene, MTBE) from 1993 to 2007; and (b) the frequency of detection from all groundwater samples collected from water supply wells (1,4-dioxane and PFAS). While these two metrics are slightly different, they were considered close enough to allow comparison between the different contaminants.

TABLE 3 Approximate number of groundwater sites

Groundwater contaminant	Representative number sites	Frequency relative to PFAS	Source
CVOCs (Primarily PCE+TCE)	~53,000 Sites (27,000 dry cleaner sites) + (38,000 CERCLA, RCRA, DoD, DOE Fed., State sites × 0.69 = 26,000 sites to remove non-CVOC sites)	1.3	NRC (2013); Table 2–6 (TCE found at 69% of DoD Sites - pg 41)
1.4 Dioxane	~23,000 Sites (38,000 CERCLA, RCRA, DoD, DOE sites × 0.61 (61% of TCE sites with dioxane)	0.5	Adamson et al. (2015) (Dioxane found wt 61% of TCE sites) – Table 1)
Benzene and MTBE	560,000 Sites (represented by Underground Storage Tanks [UST] sites)	13	The National LUST Cleanup Backlog: A Study of Opportunities (2011)
PFAS	42,560 Sites (“EBJ’s Working Model on Number of Sites with PFAS Contamination”; May not all be groundwater sites)	1	Environmental Business Journal, Volume XXXII, Numbers 5/6, 2019
PFAS	2,600 Sites (based on scaling up 68 sites in Michigan to U.S. based on GDP)	Not used	Michigan DEP (2019a)
PFAS (PFOA or PFOS)	401 Sites as of July 2019 (Dept. of Defense Sites)	Not used	Paley (2019)

Abbreviations: CVOC, chlorinated volatile organic compound; MTBE, Methyl tert-butyl ether; PCE, perchloroethane; PFAS, per- and polyfluoroalkyl substances; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; RCRA, Resource Conservation and Recovery Act; TCE, trichloroethene.

TABLE 4 Frequency of detection of three chemicals in public water supply systems

Groundwater contaminant	Frequency of detection	Frequency relative to PFAS	Effective detection limit ($\mu\text{g/L}$)	Source
PCE	18% of public wells 1993–2007	18	0.02	Toccalino and Hopple (2010); Toccalino et al. (2010) in NRC (2013)
TCE	13% of public wells 1993–2007	13	0.02	Toccalino and Hopple (2010); Toccalino et al. (2010) in NRC (2013)
1,4-Dioxane	12% of groundwater samples from public wells	12	0.07	UCMR3; Adamson et al. (2014)
Benzene	1.3% of public wells 1993–2007	1.3	0.02	Toccalino and Hopple (2010); Toccalino, Norman, and Hitt (2010) in NRC, 2013
MTBE	15% of public wells 1993–2007	15	0.02	Toccalino and Hopple (2010); Toccalino et al. (2010) in NRC, 2013
PFOA, PFOS	1.0% of groundwater samples from public wells 2013–2015	1	PFOA > 0.02 $\mu\text{g/L}$ and/or PFOS > 0.04 $\mu\text{g/L}$	UCMR3; Guelfo and Adamson (2018) (pdf page 7)

Abbreviations: MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFAS, per- and polyfluoroalkyl substances; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; TCE, trichloroethene; UCMR, Unregulated Contaminant Monitoring Rule.

PCE had the highest frequency of detection, with 18% of the drinking water samples greater than the detection limit of 0.02 $\mu\text{g/L}$. This rate of detection is about 18 times the 1.0% detection rate for PFOA/PFOS based on reporting limits of 0.02 and 0.04 $\mu\text{g/L}$ respectively. TCE and 1,4 dioxane were also detected at a much higher rate than PFAS, 13%, and 12%, respectively. Benzene was detected above 0.02 $\mu\text{g/L}$ at 1.3% of public water supply wells, similar to the PFOA/PFOS detection rate of 1.0%. As PFAS has been produced since the 1940s and has had time to enter groundwater systems and reach public water supply wells, this detection metric may be a more reliable indicator of the overall impact of PFAS on groundwater supplies than either the production or number of sites metrics. Note that the occurrence data are influenced by laboratory reporting limits (i.e., the actual occurrence frequencies may be higher if the analytical methods were more sensitive), but for this evaluation, all the detection limits ranged between 0.02 and 0.07 $\mu\text{g/L}$ (Table 4).

Taken together, the three different prevalence metrics suggest that ultimately there may be considerably fewer groundwater PFAS sites compared to the established groundwater contaminants. However, the PFAS sites may be more difficult to remediate due to factors such as the limited attenuation and the lower regulatory criteria. These factors were evaluated using the attenuation/remediation metrics discussed below.

3.2 | Relative attenuation proxies for the five contaminants

3.2.1 | Median plume length

The median plume length for a groundwater contaminant, Metric 2.1, is controlled by a variety of factors, such as groundwater velocity, time since the release, the degree of dispersion and diffusion affecting the

plumes, sorption, and degradation processes. In monitored natural attenuation (MNA) projects, biodegradation processes are often the most important mechanism that will limit the migration of contaminant plumes. BTEX and MTBE plumes from hydrocarbon sites are known to attenuate relatively rapidly (Adamson & Newell, 2014), mainly due to biodegradation processes, and therefore are known to have relatively short dissolved plumes. CVOC and 1,4-dioxane plumes can also attenuate via biodegradation but not as strongly and, on average, have longer plumes. For these compounds, multiple-site databases were used to develop median plume lengths to be used as a proxy for their attenuation potential (Table 5). Using these databases, the median chlorinated solvent and 1,4-dioxane plumes were 1,000 feet and 880 feet long, respectively, while BTEX and MTBE median plumes were much shorter, less than 140 feet long.

The prevailing scientific understanding is that while some PFAS precursors will partially biodegrade to terminal perfluoroalkyl acids (PFAAs), no biodegradation pathway has been identified that will completely degrade PFAS to terminal inorganic species such as carbon dioxide, fluoride, sulfate, and so on under typical environmental conditions (Butt, Muir, & Mabury, 2014; Liu & Mejia Avendaño, 2013). Therefore, it has been hypothesized that PFAS plumes may migrate for extremely long distances in groundwater.

However, we are unaware of any existing site databases that can provide a reliable estimate of the median PFAS plume length from multiple sites. Using groundwater fate and transport models was considered but ultimately was rejected due to the current lack of good PFAS modeling studies and modeling protocols for PFAS. Instead, the plume characteristics of another non-degrading groundwater contaminant, chloride, was used as a potential proxy for PFAS plumes.

After examining a 400-site contaminant plume database comprised of many different contaminants (Newell, Hopkins, & Bedient, 1990), plume lengths for ten chloride plumes were compiled and found to have a median plume length of approximately

TABLE 5 Plume length data for contaminant groups

Groundwater contaminant	Median plume length (ft)	Length relative to chloride	Length relative to BTEX	Source
Chlorinated ethenes	1,000	0.80	7.7	Wiedemeier et al. (1999)
1,4-Dioxane	880	0.70	6.7	Adamson et al. (2014)
BTEX	130	0.10	1	Newell and Connor (1998) pg. 3
MTBE	75–140	0.11	~1	Kamath et al. (2012) Figure 3, Table 4
Nonbiodegradable compound (chloride)	1,250	1	10	Newell et al. (1990)

Abbreviations: BTEX, benzene, toluene, ethylbenzene, and xylene; MTBE, Methyl tert-butyl ether.

1,250 feet. While the ability to detect elevated concentrations of contaminant-related chloride is lower than PFAS because of the presence of naturally-occurring chloride and higher laboratory detection limits, the source concentrations can be much higher (e.g., one entry in the database had reported source concentration of 30,000,000 µg/L). Overall, using the chloride plumes proxy for PFAS plumes was considered to be a reasonable starting point for estimating the potential median PFAS plume length at the time of this study, although without a reliable multi-site PFAS database of measured plume lengths, there is considerable uncertainty in this estimate. Nevertheless, the chloride plume data suggest that the median PFAS plume, on average, might be expected to be about 10 times longer than BTEX or MTBE plumes and about the same length as CVOC and 1,4-dioxane plumes. However, this comparison may change in the future as more plume lengths from actual PFAS sites are delineated and compiled.

3.2.2 | Hydrophobic sorption

Metric 2.2 is described by calculated retardation factors (*R*) that indicate the degree to which contaminants in groundwater sorb onto the aquifer solids and describe the partitioning between the aqueous phase and the solid (soil) phase. In addition, the retardation factor describes how an expanding contaminant plume is retarded compared to a non-sorbing dissolved compound. A retardation factor of

1 indicates the plume is expanding at the same average rate as the groundwater seepage velocity while a retardation factor of 2 indicates it travels one half the rate, 3 one-third the rate, and so on.

Table 6 provides a comparison of calculated retardation factors for hypothetical plumes of trichloroethene (TCE), 1,4-dioxane, benzene, MTBE, PFOA, and PFOS assuming an aquifer media with a porosity of 0.25, a bulk density of 1.99 g/cm³, and octanol–water partition coefficients (*K*_{oc}, [L/kg]) obtained from literature sources. As expected, 1,4-dioxane and MTBE have very little hydrophobic sorption and, therefore, retardation factors close to 1.0. TCE, benzene, and PFOA all had retardation factors between 1.3 and 2, but PFOS was much greater with *R* = 6.0.

This comparison assumes that the linear hydrophobic sorption model is useful when applying to PFAS sites. PFAS-specific factors such as surfactant partitioning processes and effects of charges on anionic and cationic PFAS may reduce the accuracy and relevance of the hydrophobic sorption metric, as do factors such as hysteresis during desorption which also affects many non-PFAS contaminants.

3.2.3 | Attenuation metrics

If representative of actual PFAS fate and transport properties, these two attenuation metrics (hydrophobicity and plume length) indicate that PFAS plumes that are decades old will likely be significantly longer than BTEX plumes in a similar hydrogeologic setting. Whether the typical

TABLE 6 Hydrophobic sorption data for contaminant groups

Groundwater contaminant	Representative retardation factor (<i>R</i>) ^a (–)	<i>R</i> relative to PFOA (<i>R</i> = 1.5)	Source of <i>K</i> _{oc} 's
TCE	2.0	1.33	USEPA (2016)
1,4-Dioxane	1.1	0.73	USEPA (2016)
Benzene	1.3	0.87	USEPA (2016)
MTBE	1.1	0.73	USEPA (2016)
PFOA ^b	1.5	1	Concawe (2016)
PFOS	6.0	4	Concawe (2016)

Abbreviations: MTBE, Methyl tert-butyl ether; PFAS, per- and polyfluoroalkyl substances; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; TCE, trichloroethene.

^aUsing literature values for *K*_{oc} (from Concawe, 2016; for min–max ranges, applied median) and assuming aquifer fraction organic carbon (*f*_{oc}) of 0.001, bulk density of 1.99 g/cm³, and porosity of 0.25.

^bUsed for relative comparison to other contaminants.

PFAS plumes will be longer on average than the typical CVOC plumes is a difficult question at this time. As described in later sections, speculations that some emerging contaminants would not degrade in groundwater and, therefore, would generate large numbers of extremely long plumes were later proven to be false (see analog discussion below). In addition, natural attenuation in groundwater occurs even for contaminants that do not biodegrade (e.g., metals and radionuclides; see Truex et al., 2011; see analog discussion below) due to sequestration processes such as precipitation, sorption, and matrix diffusion.

3.3 | Regulatory criteria and relative remediation difficulty

3.3.1 | More stringent regulatory criteria

Metric 3.1 is the commonly used regulatory criteria used to assess if some type of remediation response (e.g., active remediation, containment, MNA, etc.) is required. At sites with TCE, perchloroethene (PCE), carbon tetrachloride, 1,2-dichloroethane, 1,1,2-trichloroethene, and/or benzene plumes, the EPA's drinking water Maximum Contaminant Limit (MCL) of 5 µg/L is often used as regulatory criteria for delineation, assessing the risk of ingesting groundwater, and, in some cases, remedial objectives (Table 7). MTBE has a higher regulatory criterion (15 µg/L) while 1,4 dioxane has a lower criterion (0.35 µg/L). On April 25, 2019, the USEPA published Draft Interim Recommendations to Address Groundwater Contaminated with PFOA and PFOS for public comment with federal preliminary remediation goals (PRGs) for PFOA and PFOS of 70 ppt (0.070 µg/L) combined for groundwater that is a current or a potential source of drinking water (USEPA, 2019). Some jurisdictions have proposed even more stringent standards, such as the New Jersey Department of Environmental Protection/Drinking Water Institute with proposed MCLs of 0.013 and 0.014 µg/L for PFOS and PFOA, which individually are five times more stringent than the's combined 0.070 µg/L criteria.

The PRGs for PFOS+PFOA are about 70 times lower (more stringent) than the MCLs for TCE and benzene, suggesting that the

remediation of PFAS sites can be much more difficult and costly than CVOC or BTEX sites. The PFOS+PFOA criteria are 210 times lower than the MTBE criteria (Table 7). These extremely low regulatory criteria for PFOS+PFOA, combined with the recalcitrance of PFOS and PFOA, may require different and relatively expensive remediation technologies, such as "capture and destroy" processes. Also, the confounding effects of matrix diffusion and nonlinear desorption may be magnified at these low concentrations and make remediation even more difficult and costly.

3.3.2 | Required destruction/removal efficiency

Remediation cost is not solely a function of the absolute remediation goal and, in fact, maybe better represented as Metric 3.2, the reduction factor (RF), or the ratio between the starting concentration in the treatment zone and the remediation goal. McGuire, Newell, Osorio, Walker, and Keat (2020) developed a cost allocation model where costs were linearly related to the log base 10 of the RF (described as an order of magnitude [OoM] reduction between the starting concentration and the regulatory criteria).

The required destruction/removal efficiency (RD/RE) as defined in this paper is the ratio of the median maximum historic site concentration from multiple site databases for each contaminant and their corresponding regulatory criteria are shown in Table 8 and Figure 1. For example, a compilation of pretreatment monitoring data from 99 sites where in-situ treatment had been performed from 1991 to 2011 yielded a median maximum source concentration of 12,200 µg/L (McGuire, Adamson, Newell, & Kulkarni, 2016) compared to the MCL of 5 µg/L for a median RD/RE of 2,400 (or a required reduction of 3.4 OoMs).

This remediation database provides an upper level of historic pretreatment maximum source concentrations at TCE sites. A second perspective is based on evaluating the California Geotracker database and compiling estimated historical source zone concentrations at TCE sites (any site with TCE > 5 µg/L) but excluding most dry cleaner sites (by removing any site with PCE source concentrations

TABLE 7 Regulatory criteria for contaminant group

Groundwater contaminant	Regulatory criteria (µg/L)	Concentration relative to USEPA PFAS criteria	Source
Many CVOCs such as TCE, PCE	5	71	Maximum concentration limit (MCL) for many CVOCs
1,4-Dioxane	0.46	6.6	USEPA drinking water screening level
Benzene	5	71	MCL for benzene
MTBE	13	186	California maximum contaminant limit for drinking water (2017)
PFOA+PFOS	0.070	1	USEPA (2016) Health Advisory Drinking Water; USEPA (2019) Preliminary Remediation Goals
PFOS	0.013	0.19	New Jersey DEP/Drinking Water Institute Proposed MCLs
PFOA	0.014	0.20	

Abbreviations: CVOC, chlorinated volatile organic compound; MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; USEPA, U.S. Environmental Protection Agency.

TABLE 8 Example required destruction/removal efficiency RD/RE for PFAS vs. four other groundwater contaminants (Remediation difficulty: Median representative maximum source concentration ÷ regulatory criteria)

Groundwater contaminant	Representative maximum site source concentration ($\mu\text{g/L}$)	Regulatory criteria ($\mu\text{g/L}$)	Median reduction factor required to reach the remedial goal	Median reduction factor as the order of magnitude (OoM)	Relative median reduction factor using PFAS Michigan Data set ^a	Reference
TCE: Median of maximum before treatment source zone concentrations, at actual remediation sites ($n = 99$ sites; median site source data collected in 2002)	12,100	5	2400	3.4	240	McGuire et al. (2016)
TCE: Median of 928 California Geotracker Sites with TCE > MCL excluding primarily PCE sites (no sites max PCE conc. > TCE).	245 ^b	5	49	1.7	4.9	This study
1,4-Dioxane: Recent maximum concentration	252	0.35	720	2.9	72	Adamson et al. (2014) Figure 1.
Benzene: Median of maximum benzene source zone concentration, conventional monitoring wells ($n = 1,128$ sites in California in 2002)	360	5	72	1.9	7.2	This study
MTBE: Median of maximum MTBE source zone concentration, conventional monitoring wells ($n = 109$ sites in California in 2002)	570	15	38	1.6	3.8	McHugh et. al (2014) Figure 2
PFOS+PFOA (sampling method not known) ($n=34$ sites in Michigan)	0.760 ^b	0.07	10	1.0	1 ^a	34 Sites from the Michigan DEP (2019a)
PFOS, PFOA (75th percentile of 7000 groundwater samples from 1600 source zones) ^c	2.8 (PFOS) ^d		48	1.7	4.8	Anderson, H. (2019)
	0.56 (PFOA) ^d	0.07 (PFOS+PFOA)				
	3.4 as an estimate for PFOS+PFOA ^c					

Abbreviations: MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFAS, per- and polyfluoroalkyl substances; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; MCL, maximum concentration limit; RD, required destruction; RE, removal efficiency; TCE, trichloroethene.

^aMichigan dataset used as it represents actual PFOS+PFOA maximum concentrations at PFAS sites.

^bUsed as primary reference in Table 9 and Figure 1.

^cData are shown but were not used for the comparison because (a) these data do not represent site maximum concentrations, and (b) combined PFOA+PFOS concentrations were not available.

^dPFOS+PFOA data for each sample not available, and site maximum data not available. Therefore the 75th percentile for PFOS was added to the 75th percentile for PFOA to provide a proxy for the median site maximum concentration of PFOA+PFOS.

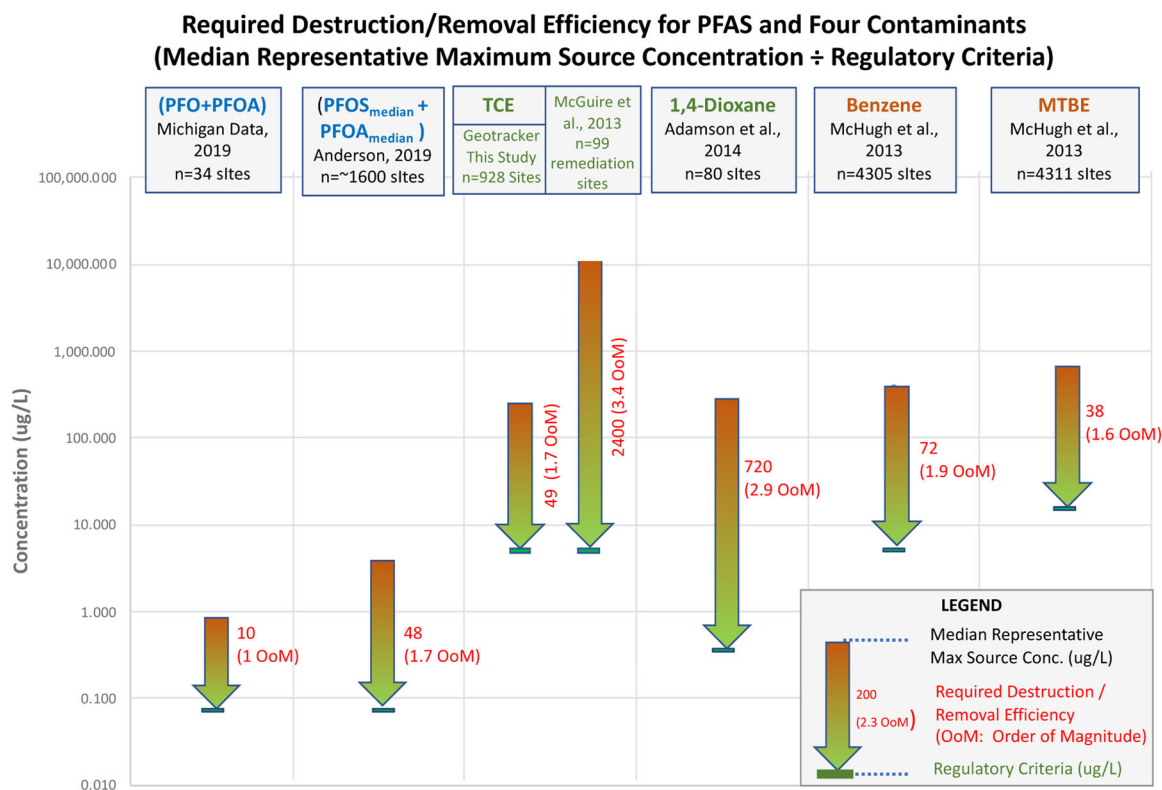


FIGURE 1 Required destruction/removal efficiency expressed by reduction factor and remediation order of magnitude reduction (OoMs). PFAS, per- and polyfluoroalkyl substances; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; TCE, trichloroethene [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.com)]

greater than TCE concentrations). This led to 928 TCE sites with a median maximum historic source concentration of 245 $\mu\text{g/L}$ TCE. This is a lower level estimate of maximum historic TCE source concentrations because it likely includes some low-level TCE at chlorinated ethane sites where TCE is not the remediation driver or where MNA rather than active remediation will be utilized. Using this database for TCE lead to an RD/RE of 49 (1.7 OoMs).

A total of 1,128 benzene sites in California analyzed as part of this paper showed median maximum site concentrations of 360 $\mu\text{g/L}$ in the year 2002 compared to the benzene MCL of 5 $\mu\text{g/L}$ (RD/RE of 72, 1.9 OoMs).

Finally, the median maximum site concentration of PFOS+PFOA from 34 sites in Michigan (Michigan DEP, 2019a) was PFAS sites 0.76 $\mu\text{g/L}$ compared to the regulatory criteria of 0.07 $\mu\text{g/L}$ yielding a much lower RD/RE of only 10 (1 OoM).

Overall, these data indicate that the median PFAS site may have lower RD/RE of 10 (1 OoM) compared to TCE remediation sites (RF = 2400; 3.4 OoMs), 1,4-dioxane (RF = 720; 2.9 OoMs), benzene (RF = 72; 1.9 OoMs), or MTBE (RF = 38; 1.5 OoMs). In other words, this simple but surprising result indicates that PFAS sites may be less challenging on average than TCE, 1,4-dioxane, benzene, or MTBE sites, with maximum PFOA+PFOS site concentrations being, on average, only 1 order of magnitude (OoM) higher than the regulatory criteria of 0.070 $\mu\text{g/L}$.

However, if lower PFAS regulatory criteria are established, the RD/RE will increase accordingly. For example, if the New Jersey PFOA/PFOA criteria are applied the RD/RE metric will increase by a factor of 5.

If the assumed maximum site concentration data are accurate and if remediation cost is roughly proportional to the required remediation OoMs as suggested by McGuire et al. (2020), then on the surface the average remediation activities at a typical PFAS site maybe about one-third the magnitude of active remediation TCE sites and one half the cost of a typical benzene site. However, this RD/RE analysis only considers pretreatment source concentrations and regulatory criteria. Other driving factors, such as the ineffectiveness of in-situ remediation technologies to destroy many PFAS is not considered with the relative remediation difficulty metric. Other potential confounding factors, such as the impact of matrix diffusion on achieving low part-per-trillion regulatory criteria, are also not considered with the relative remediation difficulty concept. Finally, the relative remediation difficulty analysis does not consider the pattern where overall groundwater remediation costs are not driven by the severity of remediating the median site but by remediating the larger sites in a remediation portfolio.

A second PFAS database of approximately 1,600 PFAS Air Force sites with PFOA and PFOS data developed by Anderson (2019) is also reported in Table 8 but was not used because these data do not

directly represent site maximum concentrations and are not combined PFOA+PFOS concentrations. An approximation of the maximum source zone concentration for this database was about 3.4 µg/L for PFOS+PFOA (RD/RE of 48, 1.7 OoMs) compared to 0.76 µg/L for the Michigan database (RD/RE of 10, 1 OoM). If one uses the military database and the Geotracker data set for TCE (a mix of remediation and nonremediation sites), the RD/RE's are identical at 1.7, indicating that remediation at a typical military site might require a similar RD/RE as the wide spectrum of TCE sites.

Note the RD/RE metric is a function of the regulatory criteria so that regulatory criteria are incorporated into two metrics (Regulatory Criteria and Remediation Difficulty).

3.3.3 | Relative remediation capability

The Relative Remediation Capability, Metric 3.3, is defined as the ability of conventional in-situ remediation technologies (e.g., thermal treatment, bioremediation, chemical oxidation, chemical reduction, surfactant treatment but not MNA or pump and treat) to reduce groundwater contaminant concentrations. Two multiple site remediation performance databases (Farhat, McHugh, & De Blanc, 2019; McGuire et al., 2016) were used to estimate the median RF (reported as a ratio and as OoMs) for in-situ treatment projects at TCE and benzene sites (Table 9). At 99 TCE in-situ treatment sites, the median RF was 10 (1 OoM), while at 40 benzene sites, the median value was 3.1 (0.5 OoMs). At PFAS sites, the expected change in PFOA and PFOS is expected to be zero or close to zero for most in-situ technologies (except potentially for thermal treatment). The general recalcitrance of PFAAs will likely require more expensive treatment technologies. The low PFAS concentrations in soils and groundwater combined with stringent regulatory criteria means that PFAS may need to be concentrated as much as possible to cost-effectively use these expensive treatment technologies.

Note the Relative Remediation Capability metric is a function of median maximum source concentrations from multiple sites, so that source concentration is incorporated into two metrics (remediation difficulty and remediation capability). Overall this metric provides evidence that in-situ groundwater remediation at PFAS sites will be more difficult than TCE or benzene sites.

3.4 | Relative research intensity

Schwartz, Zhang, and Ibaraki (2019) used text mining and machine learning to quantify research trends in subsurface hydrogeology since the 1960s. They identified four phases: embryo, growth, mature, and now an aging phase (Figure 2). During the boom period (1991–2000), subsurface hydrogeology in the journal *Water Resources Research* was dominated by papers with contaminant themes. Subsequently, subsurface hydrogeology has not been competitive with other hydrology fields such as climate change, water cycling modeling, and similar topics. One of the key points that led

TABLE 9 Relative remediation capability

Groundwater contaminant	Pretreatment maximum site source concentration (µg/L)	Post treatment concentration (µg/L)	Median reduction factor achieved by in-situ remediation	Median reduction factor as order of magnitude (OoMs)	Reference
TCE: 99 in-situ remediation projects (thermal, chemox, bioremediation, surfactant, chem. Reduction) from 1991 to 2011 (n = 99 sites: median site source data collected in 2002)	12,100	1210	10	1.0	McGuire et al. (2016)
Benzene: 40 in-situ active remediation projects (excluding solubilizing surfactant and pump and treat)	1000	320	3.1	0.5	Farhat et al. (2019)
PFOS+PFOA	Assume no change from conventional in-situ treatments			0	

Abbreviations: PFAS, Per- and polyfluoroalkyl substances; PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; TCE, trichloroethene.

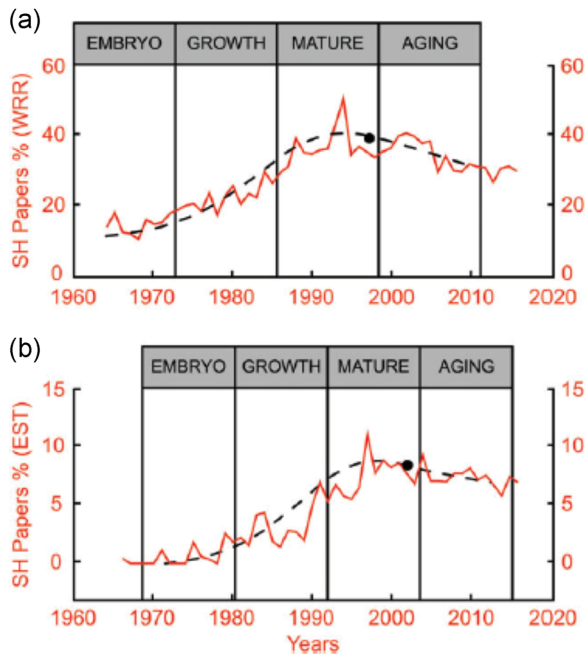


FIGURE 2 A comparison between the hydrogeological research growth curve proposed in 2001 (black lines; Schwartz et al., 2019) and SH article growth trends in WRR and ES&T (red lines). The SH papers are recorded as the percentage of SH papers to the total number of articles in each journal. Panel (a) shows the growth trend of SH articles published in WRR; panel (b) shows the trend of those published in ES&T (Schwartz et al., 2019). SH, subsurface hydrogeology; WRR, water resources research. Reproduced with permission from the publisher [Color figure can be viewed at wileyonlinelibrary.com]

from this analysis is that “Renewed growth is possible for activities with transformational potential,” such as a product line of Apple Inc. Schwartz and his co-authors noted that no transformational renewal is evident in the research trends for subsurface hydrogeology (Figure 1) because “The simple answer is that our research community does not have the power to affect a transformational change of this magnitude. It is out of our hands.”

One of the authors of this paper contacted Dr. Schwartz and agreed with the Schwartz et al. (2019) analysis of the history up to 2017 but noted that an emerging contaminant such as PFAS could present such a technical/economic/societal problem that upon its discovery could lead to a renaissance in subsurface hydrogeology research. To test this hypothesis, a simple search of Google Scholar was performed with two sets of search terms:

- (1) CVOCs Search Term: Groundwater TCE or trichlorethene or trichloroethylene
- (2) PFAS Search Term: Groundwater PFOA or PFOS or “Perfluorooctane sulfonate” or “Perfluorooctane carboxylate.”

Figure 3 shows the results of this search from 1980 to Dec. 2019, which is used as Metric 4. Similar to Figure 2, research trends identified by Schwartz et al. (2019), the first search term (TCE

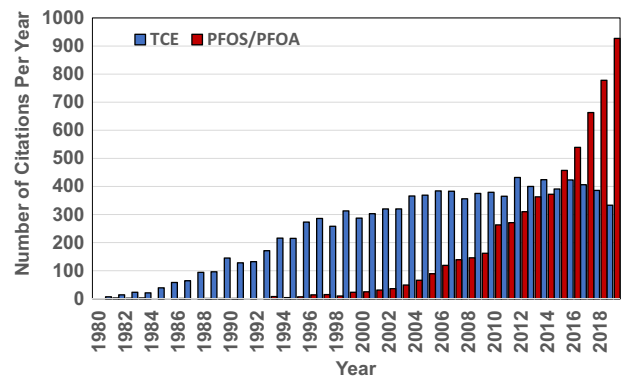


FIGURE 3 Number of Google scholar “hits” on two search terms to represent “Groundwater+TCE” and “Groundwater PFOA or PFOS” from 1985 to 2019 (search conducted December 26, 2019). PFOA, perfluorooctanoic acid; PFOS, perfluorosulfonic acid; TCE, trichloroethene [Color figure can be viewed at wileyonlinelibrary.com]

or trichloroethene or trichloroethylene) shows a definitive embryo, growth, mature, and then aging stage, with the mature stage for groundwater TCE research extending between 2003 and 2015. The second search term shows a very obvious, exponential growth pattern representative of the embryo and early growth stage. Interestingly, the total number of articles for the PFAS-related search term is 927 for and therefore already twice as large as the maximum for the DNAPL search term (432 in 2012) and is still growing. This is either because of the peculiarities of the internet (potentially more “groundwater + TCE” articles were not cataloged on the internet in the early 2000s) or that there is a much higher level of interest to researchers regarding PFAS in groundwater, which itself is driven by recent regulatory, political, and community concerns.

3.5 | Quantitative factors summary

The nine quantitative metrics are presented in Table 10 and Figure 4, along with the key absolute and relative data, and suggest that:

- The three prevalence metrics (amount produced, number of sites, detection frequency) suggest that the overall scale of PFAS remediation may be smaller than the overall scale of groundwater treatment that has been/will be performed for CVOCs, 1,4-dioxane, benzene, and MTBE.
- The first attenuation metric, median plume length, suggests that the scale of PFAS groundwater cleanup could be larger than BTEX/MTBE sites but only slightly larger than CVOC/1,4-dioxane sites. Note the plume length metric uses chloride plumes as a proxy for PFAS plume lengths and therefore has considerable uncertainty.
- The second attenuation metric, hydrophobic sorption, suggests some PFAS compounds could have higher retardation factors than many established contaminants. However, the additional difficulty in removing the increased sorbed mass could be counterbalanced

TABLE 10 Summary of nine quantitative metrics related to potential scale of groundwater remediation from Tables 2 to 7. A: Absolute data for metrics (From Tables 2–7). B: Relative data for metrics

	CVOCs	1,4-Dioxane	Benzene	MTBE	PFAS
A. Absolute data for metrics					
Total Production (tonnes)	2.2×10^7	1.7×10^5	1.9×10^8	1.4×10^8	2.6×10^4
Estimated number of groundwater sites	53,000	23,000	560,000		42,560
Frequency detect public water supply	18% ^a	12%	1.3%	15%	1.0%
Attenuation indicator: Plume length (ft)	1000	880	130	75–140	1,250 ^b
Hydrophobic sorption R (-)	2	1.1	1.3	1.1	1.5–6 ^c
Regulatory criteria (µg/L)	5	0.46	5	13	0.070
Required destruction/removal efficiency	49–2400	720	72	38	10 ^d
Relative remediation capability	10	–	3.1	–	0
Relative research intensity	432	–	–	–	927
B. Relative data for metrics					
Total production (tonnes)	850	6.2	730	5400	1
Estimated number of groundwater sites	1.3	0.5	13		1
Frequency detect public water supply	18	12	1.3	15	1
Attenuation indicator: Plume length (ft)	0.80	0.70	0.10	0.11	1
Hydrophobic sorption R (-)	1.3	0.73	0.87	0.73	1 ^e
Regulatory criteria (µg/L)	71	6.5	71	186	1
Required destruction/removal efficiency	4.9–240	72	7.2	3.8	1
Relative remediation capability	10	–	3.1	–	0 ^f
Relative research intensity	0.46	–	–	–	1

Abbreviations: CVOC, chlorinated volatile organic compound; MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFOA, perfluorooctanoic acid; PFAS, per- and polyfluoroalkyl substances; PFOS, perfluorosulfonic acid; TCE, trichloroethene.

^aPCE value was used to represent CVOCs.

^bChloride plumes used as a nondegrading proxy.

^cFor PFOA and PFOS, respectively.

^dMichigan PFAS dataset.

^eBased on PFOA $R = 1.5$.

^fReporting absolute value because PFAS assumed to be zero.

by the smaller PFAS plume footprint caused by retardation. However, higher retardation factors could be a favorable process for implementing MNA at PFAS sites where retention of PFAS in the subsurface reduces long-term risk to receptors.

- The RD/RE metric indicates PFAS groundwater remediation will be at a smaller scale than the other contaminants using the Michigan database. However, a similar scale of remediation is indicated if a second database from Anderson (2019) is used for this metric.
- The regulatory criteria metric and in-situ Relative Remediation Capability metric indicate PFAS will be a larger problem than the existing remediation target compounds, while the research intensity metric indicates PFAS in groundwater is now perceived as being a larger, more significant problem than TCE in groundwater in the early 2010.

Overall, four quantitative metrics (production, number of sites, detection frequency, required destruction/removal efficiency) indicate the scale of PFAS groundwater remediation will be smaller than the current scale of groundwater remediation for conventional groundwater contaminants. One metric, plume length as an attenuation proxy, suggests overall PFAS could be a larger potential remediation challenge compared to hydrocarbon sites, but only slightly larger than CVOC sites. The hydrophobic sorption metric

suggests that higher retardation factors may counterbalance the increased remediation difficulty based on higher sorbed mass with the smaller PFAS plume footprint. The final three metrics (regulatory criteria, in-situ remediation capability, and research intensity) all indicate that PFAS remediation might end up being at a larger scale than the four established contaminants.

4 | QUALITATIVE PFAS ANALOGS FROM CVOC AND BTEX REMEDIATION EXPERIENCE

There are several qualitative analogs to the PFAS remediation challenge from past experience remediating CVOC and BTEX sites. A few of the more noteworthy ones are briefly described below and highlighted in Figure 5.

4.1 | Development of analytical capabilities

Analytical developments are a key driver of the groundwater remediation field. Pankow and Cherry (1996) developed a DNAPL

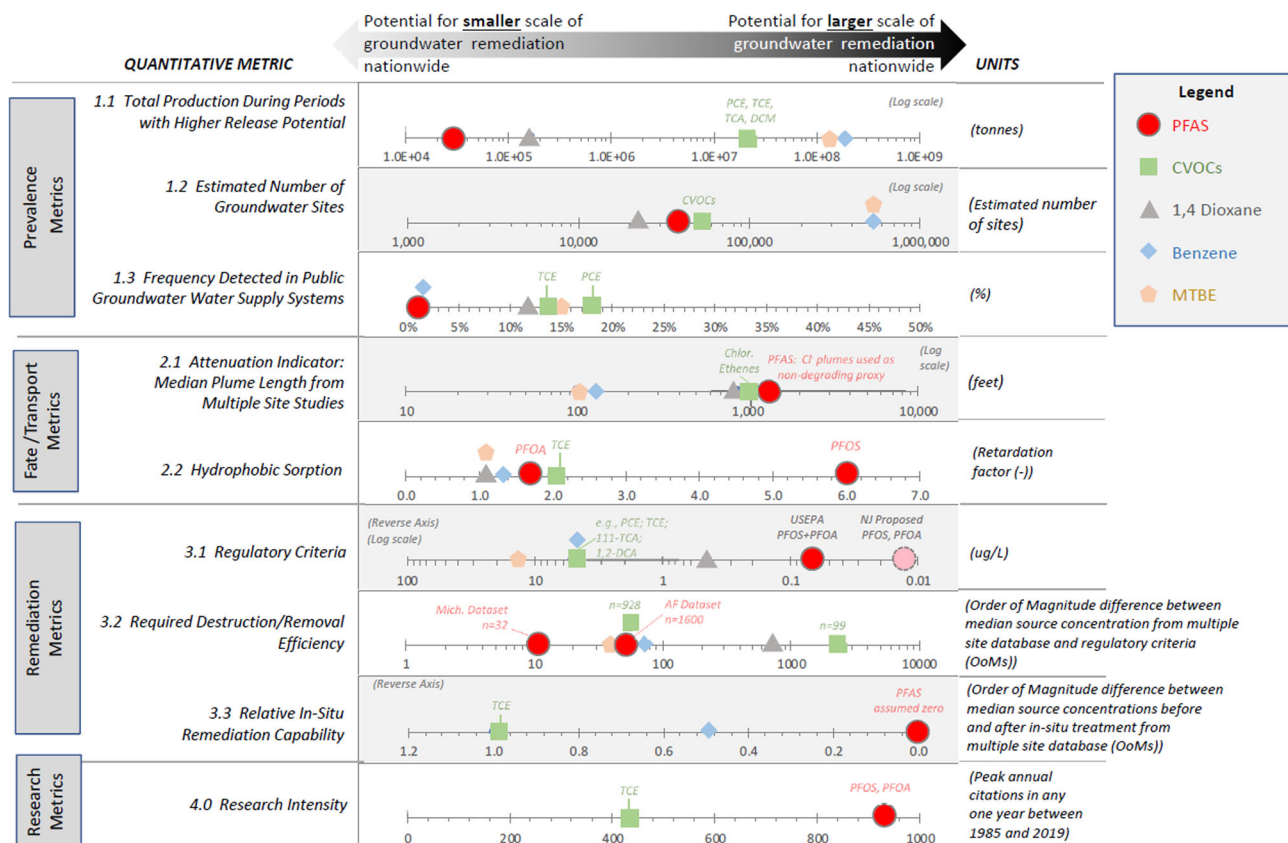


FIGURE 4 Comparison of nine quantitative metrics of potential ultimate nationwide scale of groundwater remediation at PFAS sites compared to sites with established groundwater contaminants. PFAS, per- and polyfluoroalkyl substances [Color figure can be viewed at wileyonlinelibrary.com]

timeline describing the evolution of knowledge regarding chlorinated solvents and highlighted four areas: Societal and Anecdotal Events, Literature Reports, Federal (U.S.) Government Actions, and Analytical Developments. They wrote:

Analytical Developments is a crucially important category for the history in Table 1.14 since it may have been unreasonable to have expected industrial or consulting parties to analyze groundwater for chlorinated solvents before routine analytical methods were available. For example, since analytical methods were not readily available in the early 1960s to detect chlorinated solvents at a level like 5 µg/L, then that situation makes it difficult to argue that a site owner should have been analyzing groundwater samples at that time to ensure that contamination at that type of level had not occurred.

The emergence of analytical technologies that can reliably delineate concentrations of PFAS in water to the ppt level is an important advancement that has permitted the evaluation of PFAS in groundwater and soil. Although PFAS was produced in relatively large quantities since the early 1950s, it was only in the 1990s that it was realized that PFAS was present in the environment on a global

scale, which prompted the development of improved analytical methods (Trojanowicz and Koc, 2013). Currently, PFAS analysis is still hampered by the lack of regulatory-approved methods for most PFAS in water and all PFAS in soils and by interferences due to the presence of PFAS in consumer products and sampling and lab equipment (Simon et al., 2019). However, the current methods can detect PFAS at ppt levels in groundwater, providing an important driver for identifying a large number of sites.

4.2 | Analyzing the risk associated with complex mixtures

Simon et al. (2019) concluded that “Uncertainties remain related to human health and ecological effects for most PFAS; however, regulatory standards and guidance are being established incorporating safety factors that result in part per trillion (ppt) cleanup objectives. Given the thousands of PFAS that may be present in the environment, a more appropriate paradigm may be to develop toxicity criteria for groups of PFAS rather than individual PFAS.”

One analog to the paradigm of assessing the risk for groups of chemicals is the experience of the total petroleum hydrocarbons (TPH) Criteria Working Group (TPHCWG, 1998). TPH represents the concentration of all or a subset of the hundreds of

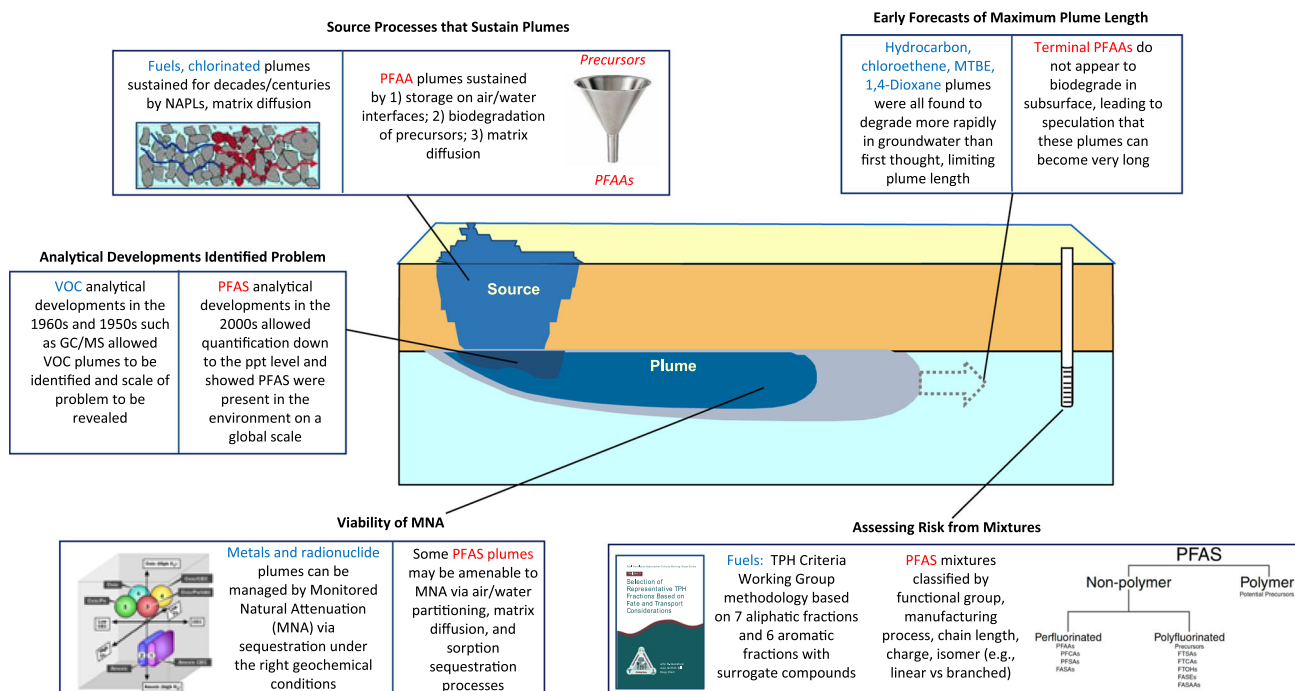


FIGURE 5 PFAS issues with analogs from remediation of other groundwater contaminants [Color figure can be viewed at wileyonlinelibrary.com]

hydrocarbons that comprise petroleum and refined petroleum products. Originally TPH was used to measure the amount of petroleum in the soil for protection of plants and water resources (American Petroleum Institute, 2001), with a value of 10,000 mg/kg in soil being a limit not having an adverse effect on plants or leaching to groundwater. However, much more stringent criteria started to be applied to underground storage tank releases. With the advent of risk-based corrective action (ASTM, 1995; Wiedemeier, Rifai, Newell, & Wilson, 1999; the Michigan DEP, 2019b), a more suitable risk-based management approach was needed to reflect that different component of the TPH have vastly different risk profiles.

To better assess the risk with hydrocarbon releases, the TPHCWG (1998) developed a methodology where analytical testing is performed to determine the TPH concentration in soils for 13 fractions. The results can be used in risk assessments using representative toxicity values and for each different fraction derived from a surrogate compound (e.g., MADEP, 2002; TPHCWG, 1998). While typically used to demonstrate that soils containing petroleum hydrocarbons have heavier, low-risk fractions, the method can also be applied to groundwater samples. This same concept may be useful for dealing with the thousands of different PFAS with widely different fate, transport, and risk properties. The development of a streamlined risk approach for PFAS sites might serve as a catalyst for more remediation projects as the risks are better quantified or, alternatively, if the risks are lower than first thought, then the number of sites warranting some type of active treatment may decrease.

4.3 | Source processes that sustain plumes

One of the key paradigm shifts in the understanding of CVOC sites was the realization that the dissolved groundwater contaminant plumes were not alone in the subsurface but were being sustained by significant subsurface sources comprised of DNAPL (e.g., Mackay & Cherry, 1989; Pankow & Cherry, 1996). Some of the key changes to the chlorinated solvent conceptual model included:

- DNAPL was present at most of these sites and often contained more mass than the dissolved phase plumes;
- DNAPL dissolution was a slow process because the released mass was much higher than the mass transfer rate of DNAPL chemicals to the aqueous phase;
- The effective (mole fraction corrected) solubility of the DNAPL chemicals was often orders of magnitude higher than the remedial goals;
- Pump and treat remediation systems could not efficiently remove the DNAPL mass;
- DNAPL sources could persist for decades or years.

Many PFAS sites may have two different types of reservoirs of mass near the original release points that can sustain downgradient dissolved PFAS plumes for extended time frames. First, as visualized by Suthersan et al. (2016) as a funnel, the PFAS sources include hundreds or thousands of PFAA polyfluorinated precursors that can slowly biodegrade aerobically to form approximately 25 PFAAs such as PFOA and PFOS (two key PFAAs). These precursors tend to sorb more strongly to the soil media and, therefore, are typically found

near the original release point of a PFAS site, such as the area underlying a fire fighting training area.

Second, because the chemical structure of PFAS has surfactant-like properties, the PFAS released to surface water and the subsurface will partition and collect on air/water interfaces. Most sources resulted from releases of PFAS at the ground surface, and some of the PFAS has leached through the unsaturated zone to the capillary fringe, and then slowly partitioned to groundwater in the saturated zone. This is why, at some PFAS sites, the concentrations of PFAS in the capillary fringe are much higher than PFAS concentrations in deeper groundwater (Costanza, Arshadi, Abriola, & Pennell, 2019).

The implications of this surfactant behavior are seen in a compartment model developed by Brusseau et al. (2019), where the retardation factor for PFOS through unsaturated sand was 7, compared to a retardation factor of 1.8 for completely saturated conditions. Other work has shown that a significant fraction of the PFAS (well over half the total mass in coarse soils) can be retained in the unsaturated zone due to this accumulation at air-water interfaces (Costanza et al., 2019). Overall the presence of long-term sustained PFAS source processes increases the need for some type of active remediation (e.g., removal or containment of source materials) but with the realization that not all the source mass can likely be removed at larger PFAS sites.

4.4 | Early predictions of long plume lengths

In 1999 Chapelle wrote "Bioremediation of petroleum hydrocarbon-contaminated groundwater: The perspectives of history and hydrology." In this landmark review article, Chapelle described that up to the 1970s and 1980s, it was generally assumed that shallow aquifers were largely sterile and that molecular oxygen was necessary to biodegrade petroleum hydrocarbons for surface oil spills (e.g., Borden, Bedient, Lee, Ward, & Wilson, 1986; Chapelle 1999). Then intense research began to change this view; by 1983, Wilson, McNabb, Balkwill, and Ghiorse (1983) proved that microorganisms that could degrade toluene were widespread in shallow aquifers. By 1990, the presence of anaerobic biodegradation was demonstrated to biodegrade petroleum hydrocarbons (Cozzarelli, Eganhouse, & Baedecker, 1990). Then in the mid- to late 1990s, multiple plume studies showed that, on average, the typical BTEX plumes were relatively short (less than 200 feet long) and either stable or shrinking in size (e.g., Newell & Connor, 1998).

A similar shift occurred for chlorinated ethenes. Before 1980, the consensus was that chloroethenes were compounds that were not found in nature and were recalcitrant to biodegradation (Bradley, 2003) and, therefore, would create long plumes. However, the accumulation of daughter products was widely reported in the scientific literature in the 1980s, and by the end of this decade, the consensus had switched entirely the view that biological reductive dechlorination was basically ubiquitous in anaerobic chloroethene plumes (Bradley, 2003).

MTBE and 1,4-dioxane had similar changing paradigms. Initial work in the 1990s indicated that MTBE was generally recalcitrant to naturally occurring biodegradation and MTBE releases would

generate long persistent plumes, but then several key studies and review documents indicated that MTBE could degrade in both aerobic and anaerobic environments (Adamson & Newell, 2014; Wilson, Adair, Kaiser, & Kolhatkar, 2005). A follow-up study by McDade, Connor, Paquette, and Small (2015) showed that nine exceptionally long MTBE plumes of the past were greatly diminished by the mid-2010s. Similarly, 1,4-dioxane was perceived to be recalcitrant in groundwater to the extent 1,4-dioxane plumes could leap ahead of the co-mingled chlorinated solvent plume, but there is now strong evidence that natural attenuation via aerobic biodegradation limits the overall length of 1,4-dioxane plumes to about the same length as the co-mingled chlorinated solvent plumes (Adamson, Anderson, Mahendra, & Newell, 2015).

For PFAS, there is strong evidence to suggest that biodegradation of PFAAs does not occur in the natural environment. The ITRC (2018) states that some of the PFAAs such as PFOA and PFOS are "mobile, persistent, and bioaccumulative, and are not known to degrade in the environment." However, a recent study by Huang and Jaffé (2019) documented the biological defluorination of PFOA by an ammonia-oxidizing and iron-reducing strain under acidic conditions. This finding shows that the biological transformation of a compound that was previously thought to be recalcitrant can occur under specific conditions. While we are not predicting that complete biodegradation of PFAS under more typical environmental conditions will be discovered in the same type of paradigm shift that occurred historically for chlorinated ethenes, MTBE, and 1,4-dioxane, the authors note that the history of the contaminant transport field is more heavily weighted to underestimating the attenuation of emerging contaminants rather than overestimating it. The ultimate length of PFAS plumes is an important remediation driver; long plumes require more remediation in the form of removal/destruction (such as via pump and treat technology) or some form of containment.

4.5 | Monitored natural attenuation of PFAS

Is it possible for non-degrading contaminants to be managed by natural attenuation processes in groundwater? One potential analog for PFAS MNA is the's guidance documents regarding Monitored Natural Attenuation of Inorganic Contaminants in Ground Water (USEPA, 2007). This guidance covers how to evaluate MNA of eight inorganic compounds and 11 radionuclides. The observes that for MNA of organic contaminants in groundwater, determining the mechanism of degradation is a key consideration. For inorganics and radionuclides, however, understanding the degree of immobilization on aquifer solids is the primary means of attenuation. Using the's approach, a system for evaluating the mobility and therefore the MNA potential for a number of metals and radionuclides in groundwater was developed based on key geochemical data such as oxidation-reduction potential, cation exchange capacity, sediment iron oxide, and pH (Truex et al., 2011).

Some PFAS compound classes such as perfluorinated carboxylic acids (PFCAs) have transport and partitioning behavior that has

elements of both organic compounds (partitioning to organic carbon on soil) and inorganics/radionuclides (partitioning cations on the soil as expressed by cation exchange capacity) (ITRC, 2018). Therefore, the experience of MNA for inorganics/radionuclides may be a useful analog for understanding potential PFAS MNA. MNA of PFAS plumes will likely focus on (Simon et al., 2019):

- In-situ sequestering processes such as hydrophobic and ionic sorption, air/water partitioning, and, particularly, matrix diffusion; and
- dilution processes such as dispersion and mixing with surface water.

A key element of an MNA evaluation for PFAS sites will be understanding the time-scale of the sequestering processes and the general mass discharge versus time pattern near potential receptors. A site where the sequestering only delays the arrival but not the strength of a migrating plume may be less amenable to MNA. However, a site where the PFAS is sequestered for years or decades (such as in low permeability zones due to matrix diffusion, Sale et al., 2013) could be a good candidate for MNA, as these long-term sequestering processes can act as an effective “peak-shaving” process that converts a strong signal (mass discharge of PFAs toward receptors) to a much lower but longer-lasting signal. This peak shaving may be particularly important at sites where PFAS plumes discharge to surface water. If this low strength, long time frame signal is below acceptable discharge limits such as a Total Maximum Daily Loads, then MNA could be viable at certain PFAS sites.

Adding sequestration capacity to the subsurface is commonly practiced now by the addition of sorbents and other more novel methods (e.g., adding gases or oils to the subsurface) may also be possible. Because of the lack of any proven, cost-effective in-situ destructive remediation process today, understanding the nature and benefits of PFAS sequestering may become a key element in

managing PFAS sites and reducing the need for expensive active remediation at some sites.

5 | IMPLICATIONS

The remediation industry has gone through at least two jarring changes to the approach to remediation since in-situ remediation started in the early 1980s (Hadley & Newell, 2012). Initially, source zones were thought to be confined to the unsaturated zone, and after this source mass was removed, the dissolved phase contaminant plume could be pumped out. However, by the late 1980s, it was recognized that remediation using pump and treat systems was “slower than expected,” and the presence of DNAPL in the saturated zone signaled a dramatic change in the remediation conceptual site model. An era of incredible ingenuity ensued, partly as a function of the subsurface hydrogeology boom identified by Schwartz et al. (2019) and in-situ treatment to remove the NAPLs became the standard approach. Even with a multitude of new technologies, complete restoration of groundwater was still an elusive goal (McGuire et al., 2016) and the importance of matrix diffusion was identified as a further constraint to achieving remedial goals (e.g., Chapman & Parker, 2005; Sale et al., 2008).

The Strategic Research and Development Program (SERDP), the environmental research arm of the U.S. Department of Defense, commissioned a state of the science review of matrix diffusion issues (Sale et al., 2013) that evaluated the physio-chemical processes, characterization, modeling, and remediation of chlorinated solvent sites affected by matrix diffusion. Also, they identified ten key implications for this difficult-to-remediate subsurface contaminant compartment (Table 11). Several of these matrix diffusion/chlorinated solvent implications (Sale et al., 2013) are potential analogs to remediation of PFAS sites because both are affected by matrix

TABLE 11 Matrix diffusion sources vs. PFAS cleanup

SERDP State of Science Review of Matrix Diffusion Issues (Sale et al., 2013)	Potential analog to PFAS remediation?
<i>Matrix diffusion sources are more like nonpoint sources in surface water systems (diffuse contaminants spread over a large area) rather than a concentrated source.</i>	<i>Some PFAS plumes manifest themselves as very low concentration plumes that extend over a large area and sometimes appear to be feed by multiple sources.</i>
<i>In the 1980s and 1990s, physical and hydraulic containment were more common for contaminant remediation compared to the 2000s and 2010s. However, because of the difficulty in removing contaminants from low permeability media, “containment may make a comeback.”</i>	<i>Due to the difficulties in removing PFAS from the subsurface, long term containment of sources and/or plumes may end up being the most common method for managing PFAS groundwater sites.</i>
<i>Due to the difficulties in remediating matrix diffusion sources, the “laws of science” may conflict with the “laws of society.” As such makes matrix diffusion a management and regulatory problem</i>	<i>As discussed in Simon et al. (2019), due to the technical challenges in PFAS remediation, the same tension may spill over to the cleanup of PFAS sites where PFAS remediation challenges implies that complete restoration in the near term is unlikely at most PFAS sites.</i>
<i>Recasting remedial goals from strict concentration-based goals to more risk-based mass discharge/mass flux goals is one way to deal with the tension between what regulations expect and what is achievable/attainable.</i>	<i>By using a mass flux approach, key concepts such as sequestration can be utilized to keep unacceptable amounts of PFAS out of surface water and away from receptors. The mass flux paradigm is described in more detail in Hadley and Newell (2012), and ITRC (2010) and may be helpful for managing PFAS sites.</i>

Abbreviation: PFAS, per- and polyfluoroalkyl substances.

diffusion, both are difficult to remediate, both have an inherent tension between cleanup expectations and remediation technology limitations, both could see renewed use of alternative remediation strategies such as contaminant containment, and both may see increased use of alternative performance metrics such as mass flux. Overall, these matrix diffusion analogs suggest PFAS remediation will be a large scale endeavor that could match the current effort focused on CVOC and hydrocarbon remediation.

The remediation of PFAS sites represents a new set of challenges to the groundwater remediation community. However, similar challenges have been presented and managed in the past for other, more mature groundwater contaminants, such as:

- Adjusting to improved analytical methods that can detect even extremely low concentration plumes;
- Understanding the risk from complex mixtures of contaminants;
- Dealing with source processes that sustain plumes for decades or more;
- Initially focusing on a few extremely large plumes that may not have been representative of the true nature of a plume fate and transport;
- Realizing that MNA may play an important role, even for groundwater contaminants that do not degrade;
- Adapting to the different nature of matrix diffusion sources and how they may provide a roadmap for PFAS remediation.

While acknowledging that some information is incomplete, the nine quantitative metrics provide conflicting signals about the overall scale of the PFAS problem in groundwater relative to the overall scale of chlorinated solvent and fuel releases. Importantly, the quantitative metrics do not provide overwhelming evidence that the scale of PFAS remediation in groundwater will be larger than the scale of remediation for established contaminants. In addition, the qualitative analogs described above provide some insights on aspects of the PFAS challenges that have been previously encountered and managed in one way or another.

The qualitative analogs do provide some comfort that while remediation of the potential universe of PFAS sites will be extremely challenging, the groundwater community has dealt with related challenges before. While complete restoration of most PFAS sites may not be possible, it should be possible to prevent excessive exposure of PFAS to human and ecological receptors via a combination of remediation measures discussed below.

5.1 | Potential triage approach for remediation

The quantitative metrics and the qualitative analogs suggest a different combination of remediation approaches may be needed to deal with PFAS sites. For example, Simon et al. (2019) suggested a potential triage approach consisting of: (a) complete source treatment (e.g., excavation) combined with natural attenuation at minor PFAS sites; (b) partial source treatment with natural attenuation

and/or active controls (e.g., containment) at intermediate sites; and (c) partial treatment of concentrated sources and providing alternative water supplies or point-of-use treatments at major sites.

As with many CVOC sites, complete restoration of PFAS sites may be uncommon. Sequestration-based natural attenuation, containment, and, where needed, point of use treatment for drinking water may become front line technologies for dealing with PFAS sites.

Finally, the remediation industry has demonstrated remarkable ingenuity in the past and can be expected to develop solutions to the unique problems posed by PFAS. As Sale et al. (2013) concluded regarding the problems resulting from matrix diffusion for CVOC cleanups:

The authors have been constantly delighted and surprised by the ingenuity of projects coming from SERDP, ESTCP, other technology development groups, and the marketplace. If matrix diffusion becomes the new target (or a companion target along with DNAPL), someone will invent the better mousetrap. We emphasize the better mousetrap may be a new technology, a clever enhancement or twist to existing technologies, or a new concept in the management/regulatory arena.

Although the problem of PFAS in groundwater appears to be a daunting one, we feel confident that a similar level of ingenuity will lead to surprising technical developments in remediating PFAS sites in the future as well.

ACKNOWLEDGMENTS

Work on this paper was funded by GSI Environmental Inc. The authors would like to thank GSI summer interns Grayson Uhlir, Crystal Ngo, and Anika Singh for their contributions to the paper.

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How to cite this article: Newell CJ, Adamson DT, Kulkarni PR, Nzeribe BN, Stroo H. Comparing PFAS to other groundwater contaminants: Implications for remediation. *Remediation*. 2020;30:7–26. <https://doi.org/10.1002/rem.21645>