EPA Superfund Program – RPM Technical Bulletin
In Situ Chemical Oxidation (ISCO) Impact on PFAS Fate and Transport
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The EPA's Superfund Program has developed this technical bulletin to guide Remedial Project Managers (RPMs) in evaluating in situ chemical oxidation (ISCO) for sites contaminated with Per- and polyfluoroalkyl substances (PFAS). PFAS, widely used since the 1950s, pose complex challenges due to their persistence and co-occurrence with legacy industrial pollutants. ISCO, traditionally used for contaminants like chlorinated solvents and hydrocarbons, may inadvertently affect PFAS transport and transformation, potentially impacting groundwater contamination and health risks.

The bulletin highlights that ISCO can convert PFAS precursors into more recalcitrant PFAS, complicating remediation efforts. Different oxidants used in ISCO, such as persulfate and hydrogen peroxide, have varying effects on PFAS and their precursors, depending on environmental conditions like pH levels and organic carbon content. While ISCO can degrade some PFAS precursors (such as fluoroalcohols and ethers), degraded PFAS precursors often transform into terminal PFAS (such as PFOA, PFOS) that are more resistant to remediation. It may also enhance PFAS mobility by altering aquifer chemistry.

To address these challenges, the bulletin recommends bench-scale studies and thorough groundwater monitoring to assess ISCO's potential impact on PFAS fate and transport. It suggests using the Total Oxidizable Precursor (TOP) assay, nontargeted analysis (NTA) and organofluorine analysis (AOF/EOF) to identify PFAS precursors that might lead to increased PFAS contamination. The bulletin underscores the importance of site-specific evaluations to determine the feasibility and risks of deploying ISCO and provides examples for how to evaluate a PFAS contaminated site for continued use of ISCO.

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1. Purpose

The purpose of this Bulletin is to assist US EPA Remedial Project Managers (RPMs) in the evaluation of remedies involving in situ chemical oxidation (ISCO) at sites where per- and polyfluoroalkyl substances (PFAS) are present. PFAS are a large, diverse group of fluorinated, synthetic compounds used broadly in commerce and industry since the 1950s. With the development of advanced sampling and analytical methods, greater awareness has been achieved regarding the co-occurrence of PFAS with legacy commercial and industrial wastes released to the environment.

The co-mingling of distinctly different classes of contaminants in groundwater increases complexity and presents new challenges in groundwater remediation and risk mitigation. Consequently, source areas and groundwater contamination plumes may involve the co-mingling of legacy wastes and co-contaminants, such as PFAS. The deployment of ISCO under these conditions is complex and may have unintended consequences regarding the fate and transport of PFAS. Generally, PFAS do not fully degrade through natural chemical, physical, or biological processes. Though some PFAS, known as PFAS precursors, may degrade to terminal PFAS such as perfluoroalkyl acids (PFAAs) under specific biological or environmental conditions. Terminal PFAS are those PFAS that are highly recalcitrant and resistant to natural breakdown pathways. ISCO may increase the transformation of precursor PFAS into terminal (and regulated) PFAS or increase the mobility of PFAS in the subsurface.

ISCO has been widely used for decades, primarily to address legacy contaminants such as chlorinated volatile organic compounds (CVOCs), benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as companion compounds (e.g., 1,4-dioxane, methyl *tert*-butyl ether (MTBE)). Historical use of ISCO in co-mingled plumes containing PFAS precursors could have transformed the PFAS signature in these areas, complicating source attribution and background evaluation.

This Bulletin aims to provide a basic understanding of the role of ISCO oxidants in the fate and transport of legacy wastes, terminal PFAS, and PFAS precursors, as well as present factors to consider when deciding whether to deploy or discontinue ISCO. This Bulletin will be helpful at all phases of the remedial investigation (RI), including scoping, conceptual site model (CSM) development, sampling and data interpretation, remedy selection, and five-year reviews (FYRs). This Bulletin provides recommendations and technical guidelines consistent with existing guidance. It identifies best practices based on a review of how PFAS are being addressed at sites across the United States. This work was supported by ERG[1].

2. Existing EPA guidance

Existing EPA guidance on specific ISCO-PFAS issues addressed in this Bulletin is limited. The EPA ISCO Engineering Issue Paper provides a comprehensive summary of ISCO fundamentals, including commonly used oxidants, process fundamentals, guidelines for bench- and pilot-scale studies, site-

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specific requirements and considerations for deployment, engineering design, performance monitoring, and limitations and interferences (Huling & Pivetz, 2006). The subsurface fate and transport mechanisms of the oxidants used in ISCO, as well as the impact of ISCO on natural attenuation, have also been critically reviewed. These topics are not addressed in this Bulletin for brevity and to avoid redundancy.

3. Summary and lessons learned

ISCO has predominantly been used for site remediation to degrade legacy wastes, including CVOCs, BTEX, MTBE, and 1,4-dioxane. The emergence of PFAS related contamination, often comingled with legacy contamination and potentially unknown at the time of ISCO remedial applications, has triggered the need to 1) understand how prior (ISCO) remedial efforts may have influenced existing PFAS contamination; and 2) evaluate the future use of ISCO on other PFAS sources areas. To evaluate the effects of ISCO on PFAS and build upon the CSM, the following was considered:

Terminal PFAS, PFAS precursors and other contaminants of concern may have been present in the original product spilled or discharged to the environment. Precursor PFAS may transform into terminal PFAS products in the environment over time; the conditions that cause this transformation vary based on the chemical structure of each given precursor. Consequently, groundwater contamination may involve the co-mingling of legacy wastes, PFAS, and PFAS precursor materials. ISCO treatment of these co-mingled wastes may involve unintended consequences, including converting non-regulated PFAS precursors into terminal, regulated PFAS (i.e., PFOA, PFOS) and impacts on subsurface parameters that may result in enhanced PFAS transport in groundwater. These effects can lead to higher concentrations of regulated PFAS and increased mass flux of stable PFAS into downgradient areas, increasing exposure pathways and health risks.

The oxidation of PFAS and PFAS precursor compounds varies depending on the type of oxidant, the activation mechanism, and environmental conditions such as pH conditions (acidic or alkaline), organic carbon content, or cation-exchange-capacity. In general:

- Thermally-activated persulfate (PS) ($S_2O_8^{2-}$) under *acidic* conditions (pH 2-4) can degrade PFAS precursors to PFAAs and other PFAS. PFCAs can potentially further degrade to CO_2 and F^- but PFSAs cannot further degrade. Thermally activated PS under acidic conditions is a specialized application of ISCO that is effective for most contaminants of concern (COCs) and PFCAs but impractical to deploy in the field. For example, thermal temperatures (35-80 ^{0}C) are energy-intensive and costly, and maintaining acidic conditions (pH 2-4) under a pH-neutral buffered aquifer system can be challenging.
- Thermally-activated PS under *alkaline* conditions (pH ≥ 10.5) cannot degrade PFAS but can degrade PFAS precursors to PFCAs and PFSAs, but no further.
- The activation of hydrogen peroxide (H_2O_2) or ozone (O_3) and the formation of hydroxyl radicals ($\cdot OH$) do not effectively treat PFAS but can oxidize PFAS precursor materials to PFCAs and PFSAs without further degradation.

- The impact of potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$) on PFAS is negligible, and the impact on PFAS precursors is currently unknown.

Additionally, ISCO deployment can have unintended consequences on the fate and transport of PFAS. ISCO can result in the oxidation of natural organic matter (NOM), an important adsorbent for COCs and PFAS compounds, and consequently, the release of sorbed PFAS. In addition to hydrophobic interactions, PFAS compounds may be cationic, anionic, or zwitterionic and, therefore, vulnerable to electrostatic interactions with charged solid surfaces, which ISCO reactions alter (Evich et al., 2025). The injection of strong oxidant and reagent solutions can significantly alter the solution chemistry and surface chemistry of aquifer solids and, therefore, the sorption of PFAS.

Due to the surfactant characteristics of PFAS, the partitioning of some PFAS at air-water interfaces potentially represents a primary reservoir of PFAS in the vadose zone. ISCO activities or naturally occurring conditions that impact the formation or elimination of air-water interfaces (i.e., raising or lowering the water table) may impact PFAS fate and transport. The oxidation of PFAS can result in chain shortening of PFCAs into more soluble, less adsorptive, and more mobile PFAAs. The collective impact of these mechanisms may increase the mobility, concentration, and mass flux of the PFAAs from treatment zones.

Groundwater monitoring, bench- and pilot-scale studies, and a few analytical approaches (such as total oxidizable precursor [TOP], non-targeted analysis [NTA], and organofluorine analysis [AOF/EOF]) are available tools to help assess the impact of ISCO on the fate and transport of PFAS and PFAS precursors. In conjunction with site-specific data, this information can be used to determine whether ISCO should be deployed or discontinued, or whether a more robust and protective remedy should be developed and implemented.

4. ISCO at PFAS Sites - current understanding

4.1. Chemical oxidation of PFAS and PFAS precursor material

Chemical Oxidation. Given the four most common oxidants used in ISCO, the permanganate anion (MnO_4^-) has the lowest electrode (oxidation) potential (E^o = 1.7 V) (reaction 1; Table 1). Under most environmental conditions (pH 3.5-12), chemical oxidation occurs through a direct electron (e^-) transfer reaction between MnO_4^- and the target compound. Two forms of MnO_4^- include $KMnO_4(s)$, which is a solid that is dissolved in water before injection and is soluble up to ~ 60 g/L (6%), and $NaMnO_4$, which is more soluble and supplied as a concentrated liquid (400 g/L; 40%). The Fenton reaction occurs between H_2O_2 and ferrous iron (Fe(II)), yielding the hydroxyl radical (·OH), which exhibits the highest electrode potential (E^o = 2.8 V) of the reactive oxidant species (reactions 2-6; Table 1). ·OH is a highly reactive and self-propagating radical with a wide array of legacy compounds (Buxton et al., 1988) but is less reactive with PFAS compounds (Venkatesan et al., 2022; Alvarez-Cohen et al., 2022). Ozone reacts directly with legacy compounds (E^o = 2.1 V) and undergoes activation reactions to yield ·OH (E^o = 2.8 V) (reactions 7-8; Table 1). The PS anion ($S_2O_8^{2-}$) is a strong oxidant (E^o = 2.1 V). $S_2O_8^{2-}$ can be activated to form a sulfate radical ($\cdot SO_4^-$), a stronger reactive oxidant species ($E^o = 2.6$ V) (reactions 9-10; Table 1). The most common methods for activating $S_2O_8^{2-}$ and forming $\cdot SO_4^-$ can be achieved with elevated temperatures (≥ 35-40 ^oC), ferrous iron (Fe(II)), ultraviolet (UV) radiation, and alkaline conditions (i.e., pH ≥ 10.5) (Zhang et al., 2024).

Table 1. Oxidants used in ISCO, reaction intermediates, reactive species, and electrode (oxidation) potential.

Oxidant Reactions	Electrode Potential (E^o)[1]	Reaction
Permanganate $MnO_4^- + 4\ H^+ + 3\ e^- \rightarrow MnO_2 + 2\ H_2O$	1.7 V (permanganate ion)	1
Fenton's (H_2O_2 Derived Reactants) $H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O$ $2\ \cdot OH + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O$ $\cdot HO_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O$ $\cdot O_2^- + 4\ H^+ + 3\ e^- \rightarrow 2\ H_2O$ $HO_2^- + H_2O + 2\ e^- \rightarrow 3\ OH^-$	1.8 V (hydrogen peroxide) 2.8 V (hydroxyl radical) 1.7 V (perhydroxyl radical) -2.4 V (superoxide radical) -0.88 V (hydroperoxide anion)	2 3 4 5 6
Ozone $O_3 + 2\ H^+ + 2\ e^- \rightarrow O_2 + H_2O$ $2\ O_3 + 3\ H_2O_2 \rightarrow 4\ O_2 + 2\ \cdot OH + 2\ H_2O$	2.1 V (ozone) 2.8 V (hydroxyl radical, see reaction 3)	7 8
Persulfate $S_2O_8^{2-} + 2\ e^- \rightarrow 2\ SO_4^{2-}$ $\cdot SO_4^- + e^- \rightarrow SO_4^{2-}$	2.1 V (persulfate anion) 2.6 V (sulfate radical)	9 10

[1] Reactive species in parentheses; reduction potential is negative.

PFAS and ISCO. Advancements in analytical methods used to measure PFAS compounds in environmental samples have led to the realization that PFAS compounds are widely distributed in the environment, including biota, surface water, and groundwater (Moody & Field, 1999; Moody et al., 2003; Schultz et al., 2004). Due to PFAS bioaccumulation (Blaine et al., 2013), PFAS toxicity (EPA, 2025a), drinking water exposure risks —especially near contaminated sites (Smalling et al., 2023; Tokranov et al., 2024) — and the need to protect human health, the US EPA has currently established health-based drinking water standards and finalized the National Primary Drinking Water Regulation for six PFAS compounds (EPA, 2025b). All six compounds can be analyzed using USEPA Method 537.1, 533, or 1633 (https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research). In addition, EPA has identified risk-based regional screening levels (RSLs) for a larger number of PFAS (https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables), which can be helpful when characterizing the nature and extent of PFAS contamination.

ISCO has been used to treat many legacy wastes (Huling & Pivetz, 2006; Siegrist et al., 2011). Based on the analysis of groundwater and soil at hazardous waste sites involving the relatively new liquid chromatography-tandem mass spectrometry (LC-MS/MS) analytical technology, it is evident that at some ISCO sites, PFAS have been co-mingled with legacy wastes and have been undetected for decades. For example, chlorinated solvents and jet fuels were often used as flammable sources in fire training programs where fires were extinguished with aqueous film-forming foam (AFFF), a significant source of PFAS. This activity has led to the co-mingling of PFAS, CVOCs, fuel components (BTEX), and other companion compounds in soil and groundwater. Other examples of co-disposal and co-mingling of legacy and PFAS wastes in groundwater include landfills (Chen, 2023) and the spreading of PFAS-contaminated biosolids in soil (Holly et al., 2024).

ISCO is moderately effective with legacy contaminants (Huling & Pivetz, 2006; Siegrist et al., 2011; Clu-In, 2025). However, success with PFAS is limited and dependent on the oxidant, PFAS characteristics, aqueous chemistry, and reaction conditions (Table 2). PFAS recalcitrance is primarily attributed to the carbon-fluorine bond's thermal and chemical stability and the fluorine atom's electronegativity, which makes the oxidation of F^- thermodynamically unfavorable. Consequently, the carbon-fluorine bond is difficult to break, which limits the degradation of PFAS and contributes to their long-term persistence in the environment.

The widespread use of MnO_4^- in the ISCO remediation of legacy contaminants is well-documented (Siegrist et al., 2001; Huling & Pivetz, 2006; Petri et al., 2011; Huling et al., 2017). Nevertheless, scientific literature regarding MnO_4^- and PFAS oxidation is scarce. MnO_4^- was shown to have minimal impact on PFOS removal. However, a significant increase in degradation was measured when electrooxidation was coupled with ferrate generation and oxidation (McBeath & Graham, 2021). Others have reported PFOS decomposition by MnO_4^- yielding F^- and SO_4^{2-} under high temperatures (65 °C) and acidic conditions (pH 4.2) (Liu et al., 2012). It is noted that these two studies employed significantly different reaction conditions compared to conventional MnO_4^- ISCO and would add additional complexity and cost.

H_2O_2, O_3, and PS are oxidants that can be activated through different mechanisms to yield highly reactive intermediate species (Table 1). These reactive species are stronger than MnO_4^-, and are non-specific, playing important roles in a wide range of transformation reactions involving PFAS and PFAS precursor compounds (Alalm & Boffito, 2022). For example, $\cdot OH$ and $\cdot O_2^-$ cleave C-C and C-F bonds; hydrated electrons (e^-aq) directly eliminate the head group, followed by releasing $-CF_2$ units; and $\cdot SO_4^{2-}$ are electrophilic and break the C-S bonds. $\cdot OH$ and $\cdot SO_4^{2-}$ can break C-F bonds in the head groups and scissor the C-C chains.

Table 2. Summary of oxidation reactions involving PFAS and PFAS precursors.
Thermal activation of persulfate, acidic (pH 2-4) $\cdot SO_4^{2-}$ + PFCAs $\rightarrow$ CO_2 + F^- (mineralization) $\cdot SO_4^{2-}$ + PFSAs $\rightarrow$ (no reaction) $\cdot SO_4^{2-}$ + Precursors $\rightarrow$ PFCAs $\rightarrow$ CO_2 + F^- (mineralization) PFSAs $\rightarrow$ (no reaction)
Thermal activation of persulfate, alkaline (pH ≥ 12) (i.e., TOP) $\cdot SO_4^{2-}$ + OH^- $\rightarrow$ $\cdot OH$ + PFAS $\rightarrow$ (no reaction) $\cdot SO_4^{2-}$ + OH^- $\rightarrow$ $\cdot OH$ + Precursors $\rightarrow$ PFCAs + $\cdot OH$ $\rightarrow$ (no reaction) $\rightarrow$ PFSAs + $\cdot OH$ $\rightarrow$ (no reaction)
Alkaline activation of persulfate, alkaline (pH ≥ 10.5) $\cdot SO_4^{2-}$ + OH^- $\rightarrow$ $\cdot OH$ + PFAS $\rightarrow$ (no reaction) $\cdot SO_4^{2-}$ + OH^- $\rightarrow$ $\cdot OH$ + Precursors $\rightarrow$ PFCAs + $\cdot OH$ $\rightarrow$ (no reaction) $\rightarrow$ PFSAs + $\cdot OH$ $\rightarrow$ (no reaction)
Peroxide, Ozone H_2O_2, O_3 (activation) $\rightarrow$ $\cdot OH$ + PFAS $\rightarrow$ (no reaction) H_2O_2, O_3 (activation) $\rightarrow$ $\cdot OH$ + Precursors $\rightarrow$ PFCAs + $\cdot OH$ $\rightarrow$ (no reaction) $\rightarrow$ PFSAs + $\cdot OH$ $\rightarrow$ (no reaction)
Permanganate MnO_4^- + PFAS $\rightarrow$ (no reaction)? MnO_4^- + Precursors $\rightarrow$ (no reaction)?

In a study involving 15 perfluoroalkyl ether acids (PFEAs), all PFEAs resisted $\cdot OH$ transformation, but PFEAs with the -O-CFH-moiety were readily oxidized (Zhang et al., 2019). However, oxidation treatment processes involving $\cdot OH$, such as alkaline ozonation, peroxone, or Fenton's reaction, are relatively ineffective for PFOA and PFOS destruction (Schroder & Meesters, 2005; Moriwaki et al., 2005; Hori et al., 2004). Hydroxyl radical-based advanced oxidative processes (UV/H_2O, UV/Cl_2, UV/TiO_2, O_3/H_2O_2) were ineffective in treating PFAS (Venkatesan et al., 2022). Further, these AOPs are not conducive to in situ deployment, and the same sources of treatment inefficiency (i.e., non-productive reactions and scavenging reactions) known to limit the success of ISCO with legacy wastes are also directly applicable to PFAS contaminants.

PFOA oxidation by $\cdot SO_4^{2-}$ was achieved using thermally-activated (20-40 ^{o}C) PS under acidic conditions ($pH < 3$) (Lee et al., 2012; Wang et al., 2019; Kornuc et al., 2020). Similarly, thermal activation (85 ^{o}C; pH 3.5) of PS mineralized several PFCAs but was ineffective in transforming PFSAs (Bruton & Sedlak, 2017) (Appendix A, Table A.1). In a slurry of groundwater and aquifer solids, thermally-activated (40 ^{o}C; pH 2-3) PS oxidation of PFAS achieved a 90% reduction of PFAA precursors, and over 90% of PFCAs was destroyed (Kornuc et al., 2020). PFOS and similar perfluorosulfonic acids were not degraded, suggesting that this ISCO technology must be combined with pump-and-treat to fully address a mixed

PFAS source zone (Kornuc et al., 2020). These results suggest that PFCA destruction by $\cdot SO_4^{2-}$ can occur under acidic conditions (pH 2-4). The stability of PFSAs may be due to the lack of a stable leaving group when $\cdot SO_4^{2-}$ attacks the sulfonate functional group, whereas with carboxylates, CO_2 can form (Ross et al., 2019). These studies suggest that thermally-activated PS has the greatest potential with PFCAs. At sites where PFSAs are present, thermally activated PS is ineffective; however, it could be used as part of a treatment train to reduce the contaminant mass in source zones. Groundwater extraction and ex-situ treatment by physical processes would still be required (Bruton & Sedlak, 2017).

PFAS Precursor Material. PFAS precursors are diverse in molecular structure and origin. *PFAS precursors in use* vary considerably between manufacturers and often include proprietary mixtures. While some precursor degradation pathways are well understood, transformation pathways for unknown or poorly studied PFAS precursors are still unknown . The diversity of precursor chemistries, coupled with data gaps about transformation products and pathways leads to challenges accurately measuring this group of chemicals. Identification and quantification of many precursors is also hindered by a paucity of analytical standards (Ateia et al., 2023). *B*ecause of this, many precursors cannot be quantified by routine targeted mass spectrometry methods such as EPA 1633A (Alvarez-Cohen et al., 2022). The TOP assay, nontargeted analysis (NTA) or other PFAS proxy measurements such as extractable or adsorbable organofluorine analysis (EOF or AOF) may be useful to identify additional PFAS missed in targeted analyses.

The oxidation of PFAS precursors via ISCO could lead to the unintended formation of terminal PFAS and an increase in regulated PFAS concentration, migration, exposure, and health risk. In some cases, an ISCO-related increase in PFAAs could exceed the EPA MCL drinking water standards (Venkatesan et al., 2022). In preparation for the potential deployment of ISCO, it is important to more comprehensively assess the diversity of PFAS present, including potential contributions from PFAS precursors. This information is also necessary for decision-makers to assess whether ISCO operations should continue.

Total Oxidizable Precursor Assay. The total oxidizable precursor assay (TOP) was developed to convert unknown and/or difficult-to-quantify PFAS precursors into terminal PFAAs (Houtz & Sedlak, 2012). TOP is a proxy measurement technique measuring changes in concentrations of stable PFAS before and after oxidation and does not directly measure individual precursors. Many legacy PFAAs can be reliably measured by LC-MS/MS methods, such as EPA Method 537.1 or EPA Method 1633A, and have commercially available mass-labeled standards ensuring accurate quantification (Ateia et al., 2023). However, no published, standardized reference method or consensus guidelines exist for the use of TOP, although it has been widely used (Ateia et al., 2023). This bench top assay has been demonstrated in various media: groundwater, surface water, sediment, and biological tissues via peer-reviewed literature.

The TOP method exposes samples to $\cdot OH$ radicals from thermally activated PS under alkaline conditions ($pH > 12$) (Table 2). While $\cdot SO_4^{2-}$ can react directly with PFOA, its conversion to $\cdot OH$ is much faster than its reaction with PFOA at elevated pH values (Houtz & Sedlak, 2012). This method converted 23 precursor compounds to PFCAs and PFSAs (Martin et al., 2019). Using ·OH via TOP, many precursors can be transformed into PFCAs and PFSAs, but ·OH cannot transform the PFAAs further (Houtz & Sedlak, 2012). By measuring the PFAAs and/or other terminal PFAS before and after the TOP reaction using a targeted analysis method, one can evaluate the presence of precursor PFAS available for oxidation in the sample (Alvarez-Cohen, 2022).

One study measured twenty-two PFAS precursors in environmental samples collected at a firefighter training area (Houtz et al., 2013). PFAA precursor residuals, found in environmental samples greater than 20 years after AFFF applications ceased, indicate a slow transformation rate to terminal PFAAs. TOP results indicated significant production of PFSAs and PFCAs from AFFF-derived PFAA precursors. These PFAS precursor residuals generated significant amounts of additional PFCAs and PFSAs upon ISCO treatment (Houtz et al., 2013). At another site where TOP was used to characterize AFFF-impacted groundwater, the summed pre-oxidation PFAS concentrations were measured as high as 5 mg/L, and the post-oxidation increase in PFCAs was measured up to +2300% (Martin et al., 2019). Overall, when $[\text{PFAS}]_{\text{Post-TOP}} > [\text{PFAS}]_{\text{Pre-TOP}}$, these results indicate the presence of PFAS precursors. Some research has suggested TOP may be used to estimate the mass or identity of precursors present by incorporating advanced statistical techniques.

TOP limitations and challenges. TOP has several potential limitations that may lead to underestimation of PFAS precursors. The incomplete oxidation of PFAS precursors may occur during the TOP assay (Martin et al., 2019). This may be due to recalcitrant functional groups on the precursor or competition from other oxidizable reactants in the sample, including ·OH scavengers, NOM, and soil. Sample heterogeneity is also a concern. Heterogeneous samples from the same location may result in highly variable TOP results based on impacts to oxidation efficiency related to sample makeup. Furthermore, the power of the assay is limited by the number of terminal PFAS measured before and after the assay. The final products of transformation are not yet determined for all precursors, meaning some precursors may transform to short-chain PFAAs or other stable PFAS not included in the selected analytical method (for instance, EPA 1633A). As a result, the assay is unable to document changes to those compounds not included in the targeted analyte list. For example, the oxidation of PFAS precursors and formation of short carbon chain PFAS (Amin et al., 2021) may not be detected by EPA Method 537.1 or other targeted methods. It is noted that PS activation by non-alkaline methods (i.e., Fe^{+2}, thermal) produces $\cdot SO_4^{2-}$ that could react directly with PFCAs, potentially breaking them down to short-chain compounds not measured in EPA methods. Additionally, the TOP assay currently only evaluates those water-soluble or semi-soluble compounds readily measured via liquid chromatography mass spectrometry (LC-MS/MS). Some precursors or stable products may be volatile or neutral in nature, and therefore unlikely to be captured in LC-MS/MS analysis. These concerns mean the TOP assay may underestimate or mischaracterize the presence or magnitude of PFAS precursors. Recent developments in the TOP method are helping to address some of these limitations (Amin et al., 2021; 2023).

For the purposes of ISCO deployment, it may be more beneficial to complete a site-specific bench scale study with the planned reagents and field conditions than perform a TOP assay to determine precursor transformation potential. However, if no particular ISCO amendment has been selected, TOP is a relatively affordable (<$1000/sample) and more standardized option for basic results.

Non-targeted analysis. Targeted analysis involves the measurement of pre-determined analyte lists composed of chemicals that have analytical standards. This limits the number of PFAS that can be measured using this technique, as relatively few standards are commercially available. Non-targeted analysis (NTA) uses high resolution mass spectrometry (HRMS) to measure chemicals without analytical standards; this highly sensitive technique has been used to characterize the molecular formula and structure of unknown or understudied terminal PFAS and PFAS precursors at contaminated sites and in the wider environment. NTA can be a key analytical tool to detect precursors present at a given site that may be impacted by ISCO activities. However, this approach can be time-consuming and expensive, as advanced chemical knowledge and statistical background is required to *identify unknown compounds*. NTA data is often considered qualitative or semi-quantitative, as analytical standards are required to produce *confident* concentration measurements of any given chemical, though recent work has developed robust statistical tools to provide more accurate estimates of sample concentration for chemicals that lack standards. NTA is also only offered by a subset of laboratories across government, academia, and industry (EPA ORD Labs Narragansett, Cinncincinnati, RTP, and Athens currently offer NTA; ~$1200/sample via contract labs); there are currently no standardized or validated EPA methods to perform NTA.

Total organofluorine analysis. Organofluorine analysis relies on combustion ion chromatography to measure total organofluorine (OF) in a given sample. Organofluorine includes any compound that contains at least one carbon-fluorine bond. This approach does not provide concentrations of individual PFAS or precursors. However, the presence of precursors can be estimated using this technique by conducting a mass-balance using targeted measurements of PFAAs or other PFAS, by determining the molar ratio of OF accounted for by known, measured PFAS. This technique also compliments the TOP assay. EPA Method 1621 provides standardized guidance to measure adsorbable organofluorine (AOF) in aqueous matrices. Methods in peer-reviewed literature have measured extractable organofluorine (EOF) from sediments, solids, or biota. Importantly, this measurement captures any inorganic fluorine and any organic compound containing a carbon-fluorine bond and can thus be biased by those fluorine-containing compounds not considered PFAS, such as naturally occurring trifluoroacetic acid (TFA) or pharmaceuticals or pesticides that contain single –CF3 groups. Sample preparation and extraction procedures should account for potential non-PFAS OF using blanks, inorganic fluorine removal techniques, and appropriate QA/QC; continued work seeks to address these limitations. Utility of AOF/EOF may also be limited by high laboratory detection limits that preclude detection of OF at ambient or background locations.

4.2. Environmental implications of PFAS oxidation: chain-shortening and transformation products

Transformation of terminal PFAS. During chemical oxidative treatment, transformation of the parent PFAS may involve various pathways and mechanisms (Alalm & Boffito, 2022). Under specific ISCO conditions, PFAA compounds *may* be degraded (Table 2), potentially forming short-chain PFAS products. *Hypothetically*, the longer and/or more aggressive the ISCO activities, the greater the extent of possible PFAS degradation and alkyl chain unzipping. For example, bench-scale experiments evaluating the thermally-activated PS (pH 2-4) oxidation of PFOA resulted in the sequential removal of CF_2 groups (unzipping), yielding shorter chain PFCAs. It was assumed to follow a simple pathway (PFOA / PFHpA / PFHxA / PFPeA / PFBA / PFPrA / TFA /….) (Park et al., 2016). Under similar conditions, thermally activated PS (pH ~ 3), PFOA was transformed into shorter-chain PFCAs, some of which were eventually mineralized to CO_2 and F^- (Bruton & Sedlak, 2018). Importantly, *complete* degradation of PFCAs *or* other stable PFAS via ISCO has not been verified in field-scale studies, therefore ISCO should not be considered a viable mechanism to breakdown PFCAs in situ at this time.

Limitations in chemical oxidation efficiency occur under most environmental conditions relative to ideal, homogeneous systems in the lab. Lower efficiency can be caused by various mechanisms, including non-productive reactions, reactions that do not form radicals, and scavenging reactions which are reactions between radicals and non-target reactant species. Solid mineral surfaces in aquifer materials can be a significant source of $\cdot OH$ and $\cdot SO_4^{2-}$ scavengers (Rusevova & Huling, 2022; Rusevova et al., 2022). The presence of aquifer solids and chloride (Cl^-), a well-known radical scavenger, reduced the oxidation efficiency of PFOA compounds in acidic (pH 2-4) thermally activated PS systems (Bruton & Sedlak, 2017; 2018). Additionally, insufficient oxidant delivery and/or volume can limit the rate and efficiency of oxidation, resulting in incomplete oxidation conditions that include the formation and accumulation of short-chain PFCA daughter products. As PFCAs are degraded into shorter-chain compounds, they become less reactive, more soluble, and more resistant to oxidation. Similarly, field observations at ISCO-treated sites frequently report increases in the concentrations of short-chain PFAS downstream from the treatment zone, indicating incomplete rather than complete degradation (Ateia et al., 2019). In some cases, oxidation may result in ultra-short PFCAs which are excluded from targeted analyte lists. This further complicates the detection of PFAS oxidation products.

The formation of PFAS into shorter-chain PFCAs and PFSAs is undesirable for several reasons. Short-chain PFAS exhibit lower organic carbon partition coefficients (K_{OC}), are not highly sorbed (Park et al., 2016) and are more mobile in groundwater systems (Higgins & Luthy, 2006). Consequently, this may lead to wider environmental distribution and greater exposure pathways and risks. Assuming a downgradient in situ colloidal activated carbon barrier or ex-situ pump-and-treat system with granular activated carbon is used to capture and control the PFAS plume, the short-chain PFAS will exhibit a lower sorption affinity and will be more difficult to remove using these treatment methods. Short-chain PFAS have lower bioaccumulation potential and are less toxic than long-chain PFAS. However, they still exhibit toxicity (https://www.epa.gov/iris; Hogue, 2019).

To mitigate these risks, monitoring downgradient wells will help track PFAS composition and concentration changes during ISCO application. Conducting site-specific bench- and pilot-scale studies can help to evaluate the extent of PFAS degradation, formation, and mobility under simulated and/or actual ISCO conditions. The development of a contingency plan with remedial measures, such as hydraulic barriers or pump-and-treat systems, can help mitigate the potential migration of PFAS compounds, especially short-chain PFAS.

4.3. ISCO Deployment Impact on PFAS Fate and Transport

Most, if not all ISCO remedial systems were originally deployed to address legacy wastes. As a result, these oxidative treatment systems impact the fate and transport of PFAS co-mingled with the legacy wastes. ISCO involves the injection of strong oxidant solutions into the subsurface, resulting in significant changes in the physical and chemical conditions. Although the desired outcome is to chemically oxidize the COCs into non-toxic byproducts, it is recognized that ISCO impacts on solution chemistry, geochemistry, and aquifer parameters can alter the fate and transport of PFAS. The magnitude and direction of the effect on transport (increased or decreased) depend on the characteristics of PFAS, oxidant characteristics, and site-specific factors (McKenzie et al., 2015). Site-specific factors that should be considered in evaluating the impact on transport of PFAS are discussed below.

Natural Organic Matter (NOM). Organic carbon in aquifer solids plays a major role in PFAS sorption (Higgins & Luthy, 2006; Li et al., 2018). The organic carbon content in aquifer materials was found to be the dominant solid-phase parameter affecting the sorption of PFAS including PFCAs, PFSAs, and perfluorooctanesulfonamide (PFOSA), indicating the importance of hydrophobic interactions (Higgins & Luthy, 2006). The perfluorocarbon chain length was the dominant PFAS structural feature influencing sorption, with each -CF2 segment contributing to the organic carbon partition coefficient (K_{OC}); the sulfonate functional group contributed more to K_{OC} than the carboxylate functional group. Further, the adsorption of 8:2 fluorotelomer alcohol (8:2 FTOH) in soil, a PFAS precursor to PFOA, was strongly correlated with the fraction of organic carbon (f_{OC}) in the soil (Liu & Lee, 2005). Similarly, PFAS precursors partitioned to soil organic matter, especially those containing perfluorinated groups with more than seven carbon atoms (Higgins & Luthy, 2007).

The sorption behavior of several PFAS could not be explained by a single soil or sediment property such as organic carbon, indicating that other parameters, including pH, silt and clay, and divalent metals-solution chemistry, can also play a role in PFAS sorption (Li et al., 2018). PFAS fate and transport models developed to predict sorption of PFAS in soil are based on various mechanisms and soil properties, including electrostatic and hydrophobic interactions (Higgins & Luthy, 2007; Evich et al., 2025). For example, PFOA sorption was correlated with organic carbon (0.1–3.5%), silt, and clay content (Knight et al., 2019); and with organic carbon, PFAS chain length (3–11 fluorinated carbons), and silt and clay content (Fabregat-Palau, et al., 2021). In summary, the observed trends with chain length, organic carbon content, pH, and cation composition suggest that a combination of hydrophobic, electrostatic, and ion exchange mechanisms collectively contribute to PFAS sorption to aquifer and soil solids (Guelfo et al., 2021).

Chemical oxidation preferentially degrades NOM in soil and aquifer material, an important sorbent material for legacy wastes and PFAS compounds. For example, adsorbed polycyclic aromatic hydrocarbons (PAHs) were released into solution upon PS oxidation of NOM in soil (Cuypers et al., 2000); a lag in the PS oxidation of trichloroethene (TCE) and trichloroethane (TCA) was attributed to the oxidation of NOM followed by contaminant desorption and oxidation (Liang et al., 2003); the desorption release of sorbed RDX occurred as a result of $KMnO_4$ oxidation of soil (Struse et al., 2002); the PS and MnO_4^- oxidation of NOM in soil was followed by increased chlorinated compound bioavailability and the increased rate of biological reductive dechlorination (Droste et al., 2002); and $O_3(g)$ treatment of a soil column resulted in a 30% reduction in the soil NOM (Shin et al., 2004). In summary, these bench-scale study results indicate that ISCO treatment of soil and aquifer solids, intended for the degradation of target contaminants, also results in the degradation of NOM. The loss of NOM diminishes sorption capacity and increases the potential for desorption and PFAS mobilization, including contaminants of concern.

pH, oxidation of mineral surfaces, and multivalent cations. A multiple regression model highlighted that organic carbon (OC), pH, and clay content significantly affected PFAS sorption. However, only weak correlations were established between OC or pH and the PFAS soil partition coefficient (K_d) across a range of environmentally relevant pH values (Li et al., 2018). Electrostatic interactions between anionic PFAS compounds, such as PFOS, and mineral surfaces were found to be responsible for the partitioning of PFAS between aqueous and solid phases (Higgins & Luthy, 2006). Additionally, PFAS precursors exhibited strong affinities for soil and aquifer solids due to the presence of anionic, cationic, or zwitterionic alkyl moieties and are likely to undergo ion exchange processes (Houtz et al., 2013). Authigenic minerals (e.g., calcite, halite, gypsum, and various clay minerals), often abundant in soil and aquifer material, exhibit surface charges available for electrostatic sorption. Aluminosilicate clays bear permanent negative surface charges, presenting potential sorption sites for cationic and zwitterionic PFAS. Ferric and aluminum (oxy)hydroxides exhibit pH-dependent, positive surface charges below their zero point of charge ($pH_{PZC} \sim 8$), allowing these minerals to electrostatically sorb anionic PFAS (Evich et al., 2022).

Electrostatic interactions are functionally dependent on PFAS charge (i.e., anionic, zwitterionic, cationic), pH, and the ionic strength of the aqueous solution. Therefore, ISCO activities that impact the organic carbon content, pH, ionic strength of groundwater in subsurface systems, geochemistry, or the PFAS compound (i.e., chain length, sulfonate, or carboxylate functional groups) can ultimately affect the fate and transport of PFAS compounds. During ISCO, significant shifts in the solution chemistry and geochemistry potentially impact PFAS fate and transport. The injection of an alkaline solution (i.e., pH 10.5-12) used to activate PS can neutralize positively charged mineral surfaces, releasing anionic PFAS compounds, and increase the affinity of cationic PFAS compounds for the anionic mineral surfaces. Similarly, injection of an acidic (pH 2-4) PS or H_2O_2/ferrous iron solution can neutralize negatively charged surfaces (like aluminosilicate clays), releasing cationic PFAS compounds, and increase the affinity of anionic PFAS compounds for positively charged mineral surfaces (a "salting out" effect). Many PFAS shift between anion, acid, and salt forms depending on pH, therefore the effect of ISCO on PFAS under these extreme pH conditions is still not well understood and is an active area of research. Further, the oxidation of reduced mineral surfaces changes the overall redox and surface charge of mineral species and, in return, shifts electrostatic interactions affecting the fate and transport of PFAS. For example, the injection of oxidants will chemically oxidize inorganic mineral surfaces (e.g., Fe(II)/Fe(III), Mn(II)/Mn(IV), H_2S/SO_4^{2-}). As described above, alterations in the charge of mineral surfaces can change the electrostatic interaction and the affinity of ionically charged PFAS compounds.

PFAS surfactant properties pose unique challenges to their environmental and experimental detection and monitoring. For example, high concentrations of chloride salts of Na^+, K^+, Mg^{2+}, and Ca^{2+} decrease apparent PFOS concentrations by a "salting out" effect (Steffens et al., 2021). Elevated concentrations of these cations can occur during ISCO from injecting oxidants and activators. This could lead to potential under-reporting of PFOS concentrations in aqueous solutions under conditions relevant to ISCO and is especially applicable to PFOS fate and transport assessments in saltwater-impacted zones (Steffens et al., 2021).

Accumulation at the air-water interface. In the vadose zone, the surfactant nature of PFAS fosters preferential accumulation at the air-water interface, and retards PFAS migration (Brusseau, 2020; Brusseau & Guo, 2022; Gnesda et al., 2022). For example, breakthrough curves for unsaturated conditions exhibited greater retardation than those obtained for saturated conditions, demonstrating the significant impact of air-water interfacial adsorption on PFOA retention (Lyu et al., 2018). In another study involving batch desorption isotherms, the PFAS porewater concentrations were overestimated (Schaefer et al., 2022). When a second analysis included PFAS adsorption at the air-water interface, an improvement in the PFAS porewater concentrations resulted, emphasizing the importance of this transport mechanism. The complex and spatially variable PFAS retardation profiles found in the unsaturated zone are attributed to the dominance of air-water and organic carbon solid-phase adsorption processes, and the strong sorption heterogeneity driven by depth-dependent adsorption mechanisms (Gnesda et al., 2022).

Given the changes in groundwater elevation resulting from wetting events and seasonal variation throughout the year, changes in moisture content and air-water interfacial area are expected. Consequently, due to PFAS sorption at the air-water interface, it has been proposed that this could result in the dynamic status of PFAS storage in the groundwater table fluctuation zone (Divine et al., 2024). For example, during low water table conditions, PFAS may be sequestered in the vadose zone; during high water table conditions, PFAS will migrate in groundwater subject to conventional transport processes (Divine et al., 2020). These conditions may drive complex temporal changes in groundwater PFAS concentrations measured in monitoring wells and may influence long-term PFAS mass flux or discharge within the plume. Overall, the meta-analyses of field investigations have determined that the vadose zone is a primary reservoir of PFAS compounds at many PFAS-impacted sites (Anderson et al., 2019; Brusseau et al., 2020).

The extent to which ISCO activities impact the vadose zone is unclear. Gas generation and/or gas injection into the subsurface may occur as a result of various ISCO remedial actions. Historically, large volumes and high concentrations of H_2O_2 have been injected into the subsurface. H_2O_2 is 94.1% oxygen, and when reacted in the subsurface, it forms large volumes of O_2(g) in the saturated zone. H_2O_2-based proprietary reagents (i.e., stabilized H_2O_2, Oxygen BioChem, Cool Ox®) are also injected, imparting significant volumes of O_2(g) to the saturated zone. Ozone sparging involves the injection of a gaseous mixture of O_3(g) at 1-10% and air into the saturated zone. Ideally, the entrapment of gas in the saturated zone, either as gas bubbles or collapsed gas channels, could form new air-water interfaces that serve as sorption sites for the preferential aggregation of long-chain PFAAs. Studies involving ISCO, gas entrapment, formation of new air-water interfaces, and PFAS retardation are lacking in the scientific literature.

The potential fate and transport mechanisms are primarily based on bench-scale studies conducted under ideal controlled conditions. Few field-scale studies provide definitive evidence that differentiates between ISCO-related enhanced transport and unrelated transport mechanisms. For example, injecting oxidant solutions into a source area containing both legacy wastes and/or PFAS will result in the hydraulic displacement of the co-mingled contaminant groundwater plume, and partial elimination of air-water interface sorption sites by groundwater mounding. It is plausible that other ISCO-related PFAS transport mechanisms discussed above will also play a role. Given the various fate and transport mechanisms associated with ISCO, it is difficult to distinguish between mechanisms responsible for post-injection changes in groundwater contaminant concentrations.

4.4. Available tools and approaches to address PFAS mobilization issues

Groundwater monitoring. At sites where ISCO has been deployed or is under consideration, groundwater sampling and analysis are crucial to assess whether PFAS are present in the targeted zone. Groundwater sampling plans can focus on specific PFAS or a broader suite of PFAS using appropriate analytical methods (https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research). However, all existing EPA methods are restricted by limited analyte lists that do not include the diversity of precursors potentially impacted by ISCO. Assuming the presence of PFAS is confirmed, more extensive groundwater sampling is likely needed to assess the areal and vertical extent of the PFAS plume. These data and information are used to assess potential exposure pathways and risk and to plan future remedial action as needed.

TOP. The TOP assay can be used to indirectly measure the presence of PFAS precursor materials in groundwater. The presence of PFAS precursors suggests the potential for formation of additional terminal PFAS to be released from ISCO deployment. This information is useful for decision-makers to assess whether ISCO could increase the concentration and mass flux of terminal (and regulated) PFAS from the targeted treatment zone, identify potential PFAS exposure pathways and risks, evaluate the impact on downgradient PFAS treatment technologies, and determine the need for downgradient PFAS treatment technologies. NTA and EOF/EOF are also appropriate analytical tools to ascertain the presence of precursors at a given site.

Bench- and pilot-tests. Bench- and pilot-scale ISCO studies can provide insight into the potential PFAS responses that could occur, assuming full-scale ISCO deployment. These studies could provide empirical data and information used to assess site-specific PFAS questions, including the effectiveness of the remedial treatment, oxidation of PFAS precursor material, changes in PFAS concentrations, enhanced PFAS fate and transport, and whether screening (https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables) or regulatory levels (https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas) are exceeded. Decision-makers can then assess the technical and economic feasibility of the technology before it is implemented at field scale, weigh potential risks associated with PFAS fate and transport, and decide whether full-scale deployment is appropriate.

A pilot test was conducted to assess the impact of thermally activated (40-70 ^{o}C) PS oxidation of chlorinated aliphatic hydrocarbons (CAHs) and PFAS (Ding et al., 2024). Significant reductions in PFCAs were measured (43.7-66.0 %), and the degradation of CAHs (cis-1,2-DCE, dichloromethane, trichloromethane) met remediation target values in most monitoring wells; however, no effective degradation for PFSAs was observed. An increase in PFAS concentration was attributed to the oxidation of PFAS precursors, which was verified using TOP. Information from the pilot test provided insight regarding field-scale deployment, the degradation of CAH and PFCA compounds, precursor oxidation, terminal PFAS formation, and PFSA recalcitrance. Collectively, this would help to screen remedial technologies, treatment train needs, and PFAS fate and transport issues. Another bench-scale study evaluated the advanced oxidative process (AOP) impact on transforming unknown PFAS precursors using site-specific groundwater. It was demonstrated that the ·OH-based AOPs were ineffective in treating PFAS, but they helped to reveal the presence of precursor materials and, therefore, the true extent of PFAS contamination (Venkatesan et al., 2022). ISCO bench-scale studies often involve ideal reaction conditions leading to definitive results, e.g., homogeneous, complete-mix. Pilot-scale studies reflect non-ideal fate and transport conditions, and results are less definitive, e.g., heterogeneities, back diffusion, and rebound (Huling et al., 2017).

Decisions regarding ongoing ISCO operations. The question may arise as to whether ISCO should be discontinued, given the potential impact of PFAS precursors and enhanced PFAS concentrations. Several site-specific factors may influence this decision. They include but are not limited to the following: relative risk of other COCs versus PFAS – e.g., indoor air or drinking water risk from COCs, like TCE, versus PFAS; presence/absence of PFAS precursor material (TOP and/or bench-scale study results); bench- or pilot-study results indicating enhanced PFAS transport attributed to site physical and chemical parameters (i.e., NOM, pH, oxidation of mineral surfaces, multivalent cations, sorption at air-water interface); groundwater PFAS concentrations – presence/absence of a PFAS plume relative to compliance plane; groundwater PFAS trending upward/downward; PFAS concentrations relative to the US EPA established health-based drinking water standards; downgradient remedial technology successfully intercepting PFAS and/or COCs, e.g., hydraulic capture by downgradient pump-and-treat system and/or immobilization using activated carbon. The following three illustrative examples assume a generalized condition where ISCO has been deployed in a source area where COCs and PFAS compounds are co-mingled, and site-specific factors are used to assess risk.

Example 1. Assuming the COCs exposure pathways in groundwater represent a low risk to human health and environment; bench- and/or pilot-scale study results indicate enhanced PFAS transport from the impact of ISCO on site physical and chemical parameters; TOP results indicate the presence of PFAS precursor material in the ISCO source area; groundwater PFAS concentrations are trending upward with time and distance from the ISCO deployment area; the PFAS groundwater plume has migrated beyond the compliance plane; the US EPA established health-based drinking water standards have been exceeded; and there is no downgradient PFAS containment or immobilization system. In this case, the weight of the data and information suggests that ceasing ISCO activities would reduce PFAS concentrations, mass flux, and exposure pathways in the groundwater until a more protective and robust remedy can be expediently designed and deployed.

Example 2. Assuming the COCs exposure pathways represent an immediate risk to human health and environment; bench- and/or pilot-scale study results indicate limited or negligible PFAS transport from ISCO impact on site physical and chemical parameters; TOP results indicate negligible concentrations of PFAS precursor material in the ISCO source area; groundwater PFAS concentrations are steady or declining with time and distance from the ISCO deployment area; the PFAS groundwater plume has not migrated beyond the compliance plane; PFAS concentrations are at or below US EPA established health-based drinking water standards; and there is an existing and effective downgradient PFAS containment and/or immobilization system. In this case, the weight of the data and information suggests that continuing ISCO activities in conjunction with the downgradient remedy is protective of human health and the environment.

Example 3. In 2018, ISCO injections involving sodium permanganate were initiated to target CVOCs in groundwater. Currently, the site has mostly reached remedial action objectives but several hot spots remain with persistently high concentrations of TCE. Based on recent groundwater monitoring results, PFOS and PFOA concentrations have also been measured and are significantly (100×) above the maximum concentration limits (MCL) near one of the CVOC hot spots. Groundwater geology and site characterization results indicate that the groundwater contaminants are highly mobile and the groundwater flow path travels towards a nearby residential community representing an exposure pathway and unacceptable health risk. It is unlikely that PFOS or PFOA will be affected by permanganate ISCO, and it is currently unknown whether permanganate ISCO will breakdown PFAS precursor compounds and forming new PFAS compounds. Overall, at this site, it is important to address the TCE hotspots to prevent the CVOC contamination from reaching the residential community where vapor intrusion is an exposure pathway. Given these factors, it was determined that (1) ISCO injections should continue to address the TCE hot spots, and (2) continue monitoring CVOCs and PFAS concentrations in groundwater to assess the treatment performance of ISCO and the fate and transport of PFAS compounds. If a PFAS groundwater plume develops and represents unacceptable health risks downgradient, a more robust treatment system may eventually be needed to intercept the plume and protect downgradient receptors.

5. Key Takeaways:

- In general, thermally activated persulfate (PS) under both acidic conditions (pH 2-4) and alkaline conditions (pH ≥ 10.5) can degrade PFAS precursors to PFCAs and PFSAs. Thermally activated PS may further degrade PFCAs to CO_2 and F^- under acidic conditions, but otherwise, PFCAs and PFSAs are not further degraded
- The activation of hydrogen peroxide (H_2O_2) or ozone (O_3) and the formation of hydroxy radicals (·OH) do not effectively degrade terminal PFAS but can oxidize PFAS precursor materials to PFCAs and PFSAs without further degradation.
- The impact of potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$) on PFAS is negligible, and the impact on PFAS precursors is currently unknown.
- ISCO deployment can have unintended consequences on the fate and transport of PFAS: The loss of NOM diminishes sorption capacity and increases the potential for desorption and PFAS mobilization, especially for long-chain PFCAs and PFSAs.
- Elevated concentrations of Na^+, K^+, Mg^{2+}, and Ca^{2+} can occur during ISCO from injecting oxidants and activators. This could lead to potential under-reporting of PFOS concentrations in aqueous solutions due to temporary salting out and altered partitioning dynamics.
- During low water table conditions, PFAS may be sequestered in the vadose zone; during high water table conditions (for instance, during injection), PFAS will migrate in groundwater subject to conventional transport processes.
- At sites where ISCO has been deployed or is under consideration, groundwater sampling and analysis are crucial to assess whether PFAS are present in the targeted zone.
- Chain shortening as a result of partial degradation can make the resulting PFAS less amenable to MNA or sorption technologies.

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Appendix A. Table A.1. A partial list of PFAS and PFAS precursor compounds; oxidants used in ISCO and a general description of oxidation effectiveness reported in the literature; and US EPA Methods used to analyze PFAS and PFAS precursors in environmental media. US EPA Method 537.1 (version 2) is a solid phase extraction (SPE) LC/MS-MS method for the determination of 22 selected PFAS in drinking water matrices (14 of 22 PFAS listed); US EPA SW-846 Method 3512/8327 addresses 24 PFAS analytes in groundwater, surface water, and wastewater effluent matrices (22 of 24 PFAS listed); US EPA Method 533 addresses short chain PFAS (C4-C12) and can be used to test for 11 additional PFAS in drinking water matrices (19 of 25 PFAS listed); CWA Method 1633, a method developed via collaboration between EPA and the Department of Defense, is an LC-MS/MS method to test for 45 PFAS compounds in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue (38 of 44 PFAS listed).

PFAS Compounds	Acronym[A]	Oxidant Effectiveness		USEPA[B,C] Method 537.1	USEPA SW-846[D] Method 3512/8327	USEPA Method 533	CWA Method 1633
		$S_2O_8^{2-}$	$\cdot OH$, H_2O_2, O_3				
Perfluoroalkyl Carboxylic Acids	*PFCAs*						
Perfluorobutanoic acid	PFBA	$C(T)^{2}$, $P(T)^{6,7}$	$P(UV)^{10}$ $N(BAP)^{16}$		X	X	X
Perfluoropentanoic acid	PFPeA	$C(T)^{2}$, $P(T)^{6,7}$	$N(BAP)^{16}$		X	X	X
Perfluorohexanoic acid	PFHxA	$P(T)^{6,7}$	$N(BAP)^{16}$ $N(UV)^{17}$	X	X	X	X
Perfluoroheptanoic acid	PFHpA	$C(T)^{2}$ $P(T)^{6,7}$	$N(BAP)^{16}$ $N(UV)^{17}$	X	X	X	X
Perfluorooctanoic acid	PFOA **	$C(T,M)^{2,4}P(T)^{1,2,6,7}$	$N(UV)^{11}$ $P(UV,A)^{10,12}$	X	X	X	X
Perfluorononanoic acid	PFNA *, **	$P(EP)^{19}$	$N(BAP)^{16}$ $N(UV)^{17}$	X	X	X	X
Perfluorodecanoic acid	PFDA	$P(EP)^{19}$		X	X	X	X
Perfluoroundecanoic acid	PFUnA			X	X	X	X
Perfluorododecanoic acid	PFDoA			X	X	X	X
Perfluorotridecanoic acid	PFTrDA			X	X		X
Perfluorotetradecanoic acid	PFTA			X	X		X
Perfluoroalkyl Sulfonic Acids	*PFSAs*	$N(T)^{15}$					
Perfluorobutane sulfonate	PFBS *	$N(T)^{15}$	$N(UV)^{17}$	X	X	X	X
Perfluoropentane sulfonate	PFPeS				X	X	X
Perfluorohexane sulfonate	PFHxS *, **	$N(T)^{15}$	$N(UV)^{17}$	X	X	X	X
Perfluoroheptane sulfonate	PFHpS				X	X	X
Perfluorooctane sulfonate	PFOS **	$N(T)^{1,15}$	$N(UV)^{3,17}$ $P(A)^{12}$	X	X	X	X
Perfluorononanesulfonic acid	PFNS				X		X
Perfluorodecanesulfonic acid	PFDS				X		X
Fluorotelomer sulfonates	*FtSs*						
1H, 1H, 2H, 2H- perfluorohexane sulfonic acid	4:2 FtS	$P(T)^{13}$			X	X	X
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid	6:2 FtS	$N(T)^{15}$ $P(T)^{1,2,13}$	$P(UV)^{10,3}$		X	X	X
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid	8:2 FtS	$P(T)^{13}$			X	X	X
Perfluorooctane sulfonamides	*FOSAs*						
Perfluorooctane sulfonamide	FOSA		$P(BAP)^{13,16}$ $N(UV)^{18}$		X		X
Per- and polyfluoroether carboxylates	*PFECAs*						
Tetrafluoro-2-eptafluoropropoxy-propanoic acid	HFPO-DA *, **	$P(T)^{2,7,15}$	$P(UV)^{10}$	X		X	X
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	$P(UV)^{10}$		X		X	X

Appendix A. Table A.1 continued … Description of oxidants and extent of oxidation achieved.

C- complete degradation (mineralization, complete Fl- recovery)
P - partial degradation (chain shortening; shorter chain PFCAs and/or PFSAs, Fl- release)
N - no transformation
U - unclear or conflicting results
T - thermally activated
B - base activated (strongly alkaline conditions)
UV - ultraviolet activation
M - metal activation (alumina)
A - alkaline conditions
BAP - base activated persulfate yields hydroxyl radical at pH ≥ 10.5
EP - electrochemical activation of peroxymonosulfate.

* EPA has set a hazard index level for two or more of four PFAS as a mixture: PFHxS, PFNA, HFPO-DA, and PFBS (EPA, 2025b).
** EPA enforceable levels for five PFAS (ppt): PFOA (4), PFOS (4), PFHxS (10), PFNA (10), and HFPO-DA (10) (known as GenX Chemical) (EPA, 2025b).

A PFAS compounds in blue are included in the EPA drinking water standards (above); PFAS in red are PFAS precursor compounds.
B Shoemaker, J. & Tettenhorst, D. 2020. US EPA Method 537.1, version 1.1. Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). U.S. EPA, Washington, DC.
C US EPA Method 537.1 version 1.1 includes PFOA and PFOS - linear isomers and branched isomers; US EPA Method 537.1, version 2.0 includes the 18 compounds in US EPA Method 537.1 version 1.1 plus the two ether compounds, 11Cl-PF3OUdS and 9Cl-PF3ONS, and two Per- and polyfluoroether carboxylate compounds, ADONA and HFPO-DA.
D US EPA SW-846 Methods 3512 and 8327 do not differentiate linear and branched isomers of PFOA or PFOS.

1 Park et al., 2016
2 Lee et l., 2012
3 Yang et al. 2014
4 Wang et al. 2019
5 Yang et al. 2013
6. Alvarez-Cohen et al., 2022
7 Bruton & Sedlak, 2017
8 Liu, et al., 2012
9 McBeath & Graham, 2021
10 Zhang et al., 2023b
11 Javed et al., 2020.
12 Lin et al., 2012.
13 Martin et al. 2019.
14 Bruton & Sedlak, 2018.
15 Ding et al., 2024.
16 Houtz and Sedlak, 2012
17 Venkatesan et al., 2022.
18 Plumlee et al., 2009.
19 Wang et al., 2012