# Making Strides in the Management of "Emerging Contaminants"

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# Introduction

The definition and terminology associated with "emerging contaminants" have evolved rapidly in the past few years. The current term of art "contaminant of emerging concern" (CEC) is being applied to compounds where the risk to human health and the environment is not entirely understood, and is thus "emerging." In general, these compounds fall into three categories (Suave and Desrosiers 2014): (1) new compounds that were not previously known and are found to be present in the environment, (2) compounds that were known to exist but whose environmental occurrence was not fully understood, and (3) "old" contaminants, for which there is new information on environmental and human health risks.

Regardless of how they are identified, the realization that CECs represent an ever-growing list of compounds, some with wide-spread presence and limited options for treatment, has driven a significant amount of industry focus and investment to find cost-effective solutions. This has been fueled in part by individual states developing drinking water or health-based standards that vary widely, are very low, and change over time, as opposed to EPA establishing a Federal MCL. The result is a patchwork of standards that are both difficult to understand and a challenge for compliance. Notable historic examples of CECs include perchlorate, methyl tertiary butyl ether, polybrominated diphenyl ether flame retardants, and pesticides. More recent additions include 1.4-dioxane. 1,2,3-trichloropropane,

poly- and perfluoroalkyl substances (PFAS) and dechlorination/disinfection by-products.

For this discussion, we will focus on 1,4-dioxane and PFAS because they represent currently relevant CECs at two different points in the CEC life-cycle and maturation process. 1,4-dioxane has been an issue for nearly a decade in several states, but only recently has it become a more universal driver for private sector and public sector stakeholders. Treatment technologies are evolving and we as an industry are developing more cost-effective and reliable restoration options. In contrast, PFAS is truly emerging in the United States as EPA is works to establish a consensus on toxicology and states begin to prepare to adopt cleanup standards. The better known PFAS compound perfluorooctane sulfonate (PFOS) has been identified internationally as persistent organic pollutants (PoPs) and its production severely restricted by the Stockholm Convention (2009), with PFOA (perfluorooctanoic acid; known as "C8") also currently under consideration to be classed as a PoP by this international treaty. Analytical methods, toxicology, and treatment technologies are evolving in parallel for both, but there is still much uncertainty for stakeholders as they prepare to manage their liabilities.

The lessons learned from restoration and treatment of now "mainstream" contaminants indicate that there will be ways to cost-effectively remediate CECs in groundwater, even if they are difficult-to-treat contaminants. To start, we will look at the historic evolution of attitudes and practices related to chlorinated solvents, as a benchmark for today's CECs. Then we will consider some of the notable strides being made with 1,4-dioxane and PFAS—that offer both parallels to the history of chlorinated solvents and the ability to build on the past and short-circuit what might otherwise be a more lengthy path to meaningful advances.

### A Look Back at Chlorinated Solvents

The evolution of chlorinated solvent remediation was influenced not only by changing regulatory and economic factors, but also by the type and chemical characteristics of the target contaminants. The need to contain contaminated groundwater led to universal application of pump and treat systems for source control and mass removal during the early stages of this evolution. The need for alternative cost-effective solutions with faster cleanup times fostered continuous innovation and led to development of soil vapor extraction, in situ air sparging, and chemical oxidation during the 1990s. Early industry perception was that chlorinated solvents were recalcitrant and not susceptible to natural attenuation, but evidence of anaerobic degradation surfaced during the early and mid-1980s. Still, it was another decade before formal guidance documents were published, and almost two decades before enhanced biodegradation became widely accepted as a leading treatment technology.

Decades of assessing the fate and transport of chlorinated solvents have also enlightened our understanding

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of how stratigraphy, permeability advection/diffusion relationand ships influence plume evolution. The result has been a broad awareness that plumes are commonly spatially thin and flux-focused, which has sharpened our investigation and remediation approaches. For the current suite of CECs, the thought process is still developing around the environmental behavior, transformation mechanisms, and how best to apply remedial strategies to achieve focused, efficient cleanup. However, our previous experience with chlorinated solvents allows some optimism as the scientific body of evidence grows and allows us to identify, develop, and deploy remediation solutions for emerging contaminants such as 1,4-dioxane and PFAS.

# 1,4–Dioxane and PFAS—An Overview

Most readers will be familiar with 1,4-dioxane as it gained notoriety due to its industrial use as a stabilizer in

1,1,1-trichloroethane. It is now understood that 1,4-dioxane is considerably more widespread due to its use in personal care products and detergents, various chemicals, electronics, fibers, and pharmaceuticals. Data from the EPA's unregulated contaminant monitoring rule (UCMR3) published in June 2015 (US EPA 2015) indicate that 1,4-dioxane has been detected in 6.7% of public water supplies at concentrations above the drinking water health advisory level of 0.35 micrograms per liter (µg/L). Figure 1 illustrates the geographic distribution of 1.4-dioxane in public water supplies above the health advisory level. 1,4-dioxane is a cyclic ether that is not only miscible in water but forms a positive azeotrope. 1,4-dioxane has a very low octanol water partitioning coefficient (Log K<sub>ow</sub> of -0.27) and Henry's constant (5  $\times$  10<sup>-6</sup>), making it prone to migrate in groundwater and unaffected by conventional treatment technologies like air stripping and adsorption to granular activated carbon. Further, the historical perspective has been that 1,4-dioxane is not prone to biodegradation, and that natural attenuation rates are too slow under typical aquifer conditions to provide much benefit when managing these plumes. Fortunately, this perspective is changing, as we will discuss later.

PFAS are a more recent addition to the CEC roster, and represent a very broad class of more than 6000 organofluorine compounds that have been extensively used in personal, commercial, and industrial applications ranging from nonstick and flame/heat resistant fabrics and coatings, water repellant and stain resistant fabrics and coatings, surfactants, lubricant additives, and fire-fighting foams. The most familiar fluoropolymers include polytetrafluorethylene (PTFE), which is used in nonstick coatings and waterproof fabrics. Common PFAS include stain-resistant coatings and aqueous film forming foams (AFFFs) used in fire-fighting at airports and industrial facilities. AFFFs are comprised of



Figure 1. 1,4-dioxane public water supply sampling results from USEPA Unregulated Contaminant Monitoring Rule 3 (UCMR 3) (EPA 2015). Based on results reported through June 2015, nearly 7% of public water supplies tested showed exceedances of the health advisory levels for 1,4-dioxane.

proprietary mixtures of multiple types of fluorinated chemicals including but not limited to: perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, perfluoro betaines, perfluoro sulfonamides, perfluoro sulfonamidoethanol, perfluoro thioamido amino carboxylates, perfluoro sulfonamido amines and fluorotelemer sulfonates.

The PFAS group of compounds comprises perfluorinated compounds, and polyfluorinated compounds. With perfluorinated compounds all the carbons atoms in the alkyl chain are saturated with fluorine atoms whereas polyfluorinated compounds have carbon to hydrogen bonds in the alkyl chain, i.e., the alkyl chain is not fully saturated with fluorine atoms. PFOS and PFOA are the best known perfluorinated compounds. which are octanoates (contain eight carbon atoms); however, multiple analogous compounds exist with varying carbon chains lengths from C2 to C16 that comprise other perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs), collectively referred to as perfluoroalkyl acids (PFAAs). PFAAs have been found to be resistant to biodegradation and are dead end daughter products to the thousands of other PFAS, which biotransform in the environment to yield PFAAs that may remain unaltered in soil and groundwater indefinitely. Biodegradation of PFOS and PFOA has been evaluated under conventional waste water treatment conditions (Dasu et al. 2012) and natural aquifer conditions (Ferrey et al. 2012); however, evidence to support the occurrence of biological degradation of these compounds is lacking, with a similar recalcitrance evident for other PFAAs.

There is a natural "biological funneling" in which a whole host of PFAS compounds (fluortelomers, betaines, sulfonamides, etc.), with various differing perfluorinated alkyl chain lengths and functional groups, bio-transform to form persistent dead end daughter products-the PFAAs. The fundamental current concern here is how to identify, quantitatively measure, and assess the toxicology of this myriad of PFAS compounds and the range of recalcitrant PFAAs which they form. An example of these biotransformation processes is often

seen in biological waste water treatment plants, where significantly more PFOS and PFOA are often measured at the outflow than inflow. The apparent increase is explained by the fact that many PFAS compounds enter the sewage treatment plant uncharacterized and are biotransformed to PFAAs of various chain lengths with PFOS and PFOA often being the only analytes assessed.

PFAS may also be subdivided into two broad classes, long and short chain, with long-chain PFCAs comprising those "carboxilic acids" that have seven or more perfluroinated alkyl carbon atoms (e.g., PFOA etc.) and PFSAs comprising those "sulfonic acids" with six or more perfluorinated alkyl carbon atoms (e.g., PFOS). Short-chain PFAAs are not considered by the European Union as a persistent, bio-accumulative and toxic (PBT) substance as a result of diminished bioaccumulation potential; however, there is currently limited data regarding their toxicology and they are thought to be as persistent as long-chain PFAAs, given their structural similarities. The term PFAS "precursor" is applied to those long-chain PFAS compounds that biotransform to yield long-chain PFAAs. However, there will also be many short-chain PFAS compounds that biotransform to evolve short-chain PFAAs, which will also be persistent and are generally very mobile in aquifer systems.

In their anionic forms, PFOS and PFOA are water soluble and have moderate organic carbon partitioning with log K<sub>a</sub> of 2.57 and 2.06, respectively (US EPA 2014a). Recent studies have found that transport potential of PFAS compounds is also based on the charge on the functional group(s) of the PFAS where anionic species are the most mobile, followed by zwitterionic species, and cationic species have the lowest mobility and may create immobile source zones (Backe et al. 2013; Fields et al. 2015). Conventional treatment of groundwater using granular activated carbon (GAC) may be more viable for long-chain PFAS than short, but costs of treatment are high compared to conventional contaminants. GAC has a very limited sorptive capacity for PFAS in general and this decreases as the carbon chain lengths diminish; therefore,

there is a question of whether GAC can treat short-chain PFAS cost effectively. Because the GAC used to sorb PFAS has to be regenerated at specialized facilities at elevated temperatures over 1200 °C, treatment costs are also higher for PFAS.

# Regulatory and Characterization Challenges

The recent pattern of regulation for CECs makes it difficult for stakeholders to develop consistent risk management strategies that provide certainty in outcomes. The trend has been for EPA to develop health-based advisories and for individual states to develop a widely variable patchwork of cleanup standards. Considering 1,4-dioxane as an example, EPA initially developed its health-based drinking water advisory level of 0.35 µg/L in 2006 and reviewed the results in 2012. Since that time, slightly more than half of the states have adopted drinking water criteria, which are often the driver for remediation. Standards currently range from 200 µg/L in Iowa (based on statewide standards for a protected groundwater source; Iowa Department of Natural Resources 2015) to 0.25 µg/L in New Hampshire (as a reporting limit requirement for all public water supplies; New Hampshire Department of Environmental Services 2011) (see Figure 2); but the trend has been to adopt increasingly lower standards in states that have been slow to move. while others have revisited the numbers and are adopting lower standards.

The EPA issued proposed provisional health advisory levels for PFOS  $(0.2 \mu g/L)$  and PFOA  $(0.4 \mu g/L)$  in 2012 (EPA 2012); however, final consensus regarding toxicology and cleanup levels have not yet been attained in the United States. The occurrence of PFOS and PFOA in public drinking water supplies has heightened public awareness and indications are that EPA will finalize its review in the next year. As described above, PFOS and PFOA comprise only two of the thousands of PFAS compounds that are of potential concern. From an international perspective, the trend in Europe has also been to regulate a broader range of PFAS compounds, such as C4-C10 PFAAs. The European Union has set an environmental quality standard



Figure 2. 1,4-dioxane groundwater cleanup standards as of November 2015. Only 33 states have established groundwater cleanup standards for 1,4-dioxane at the present time.

of 0.65 ng/L for PFOS in surface waters. Additional information regarding PFAS regulation in the European Union and current perspective of fate and effects are currently being drafted by Pancras et al. (2015).

Current commercially available analytical methodologies are not capable of quantifying the full suite of PFAS compounds that will exist in soil and groundwater. Because many PFAS compounds in the soil and groundwater will be progressing through a biotransformation funnel that leads to PFAAs as dead end daughter products, this provides a very significant analytical chemistry challenge. Some recent solutions to address this analytical challenge are discussed below.

Characterization of PFAS challenges practitioners on several fronts. Laboratory analytical methods are in some cases being developed at the same time that our working understanding of the chemicals themselves is growing. The fact that PFAS compounds stratify in water as they migrate to the air-water interface means that sampling of groundwater needs to be taken from the surface of the water table and laboratory analytical methods must involve very vigorous shaking of all water samples before a subsample is removed. Specific sampling protocols must be adopted, which also avoid the use of glass or metals, as PFAS bind to these materials. Samples should be collected using polyethylene or polypropylene containers and equipment, avoiding contact with materials that may contain PFAS such as PTFE.

The commercially available analytical method for PFAS is by EPA Method 537 (which employs liquid chromatography with tandem mass spectrometry [LCMSMS]) to analyze a suite of only 14 PFAAs (including PFOA and PFOS), following the published methodology with reporting limits ranging from 0.005 to 0.020 µg/L. These reporting limits are capable of achieving the EPA's provisional health advisory of 0.2 µg/L for PFOS and 0.4 ug/L for PFOA. However, this method does not currently report the results for the full range of the more simple PFAAs, or many fluorotelomers, or the many thousands of other PFAS

compounds that biotransform in the environment to produce PFAAs as dead end daughter products. In order to fully understand the potential extent of PFAS contamination in the environment, additional laboratory techniques are being developed including expanding the range of analytes for EPA Method 537 (and similar LC-MS/ MS methods) to include up to 39 PFAS compounds.

Development of other more advanced techniques and alternative approaches are now being used commercially for the first time. For example, there are two methods in development used to quantify total organic fluorine (similar to a total TPH analysis for petroleum hydrocarbons) including particle-induced gamma ray emission (PIGE) and adsorbable organo fluorine (AOF) analysis using combustion ion chromatography (CIC). There are two methods in development to analyze a much more comprehensive range of PFAS compounds. The first is the total oxidizable precursors (TOP) assay, which rapidly converts PFAS compounds into PFAAs using a conventional hydroxyl radical-based chemical oxidation method (replicating what micro-organisms in the environment would achieve after many years) to provide a range of PFAAs which are detectable by LCMSMS (Houtz and Sedlak 2012). The second is LC-OTOF-MS/MS (liquid chromatography quadrupole time of flight mass spectrometry), which is a semiquantitative method revealing the empirical formula of multiple PFAS compounds by assessing the accurate mass of the PFAS's molecular ions, to four decimal places of a Dalton. The TOP assay approach shows promise because it quantifies the sum of PFAS that could be converted to PFAAs in the environment by simulating PFAS biotransformation. This allows assessment of the hidden PFAS mass using the existing LCMSMS methods, with a slightly expanded range of PFSAs and PFCAs quantified. There is value in doing this analysis before and after the PFAS are partially digested by oxidized reaction to assess both the free PFAAs and the PFAAs which were hidden in the form of thousands of PFAS compounds currently not detectable. The TOP methodology has revealed that for AFFF-impacted sites the existing analytical LCMSMS methods are only detecting some 30% of the total PFAAs mass hidden in PFAS, with some analytes such as perfluorohexanoic acid being evolved from PFAS to give an increase in concentration of more than 200 fold. While the TOP assay is now commercially available in the United Kingdom it is not available in the United States. The PIGE method is currently being commercially developed and is available in the United States.

Another challenge is the lack of real-time characterization tools for emerging contaminants. For common contaminants, like chlorinated VOCs, there are a range of real-time methods for cost-effective real-time characterization (mobile lab analysis, membrane interface probe), which occupy a critical portion of the characterization toolbox for these compounds. Real-time analytical methods have been developed for 1,4-dioxane using solid-phase micro-extraction (SPME) and direct sampling ion trap mass spectroscopy (DSITMS) or gas chromatography/ mass spectroscopy (GC/MS). Because real-time analytical methods are in the nascent stages of development for PFAS, the only available option for mapping concentrations is off-site lab analysis, tied with conventional sampling. This creates the risk of relying on sparse data sets with limited horizontal and vertical resolution. Such data sets cannot convey the important geologic and hydrogeologic context necessary to accurately interpret source and plume behavior, limiting the ability to develop reliable conceptual site models and remedial strategies.

# Developing Advancements in CEC Management

While we acknowledge the challenges associated with emerging contaminants, we believe that practitioners and stakeholders can capitalize on the lessons learned from decades of continuous improvement regarding characterization and remediation of chlorinated solvents and other recalcitrant contaminants. We understand the benefits that a flux-based perspective can bring to focus remedies and how combined remedy strategies can be used to optimize performance and improve certainty in outcomes. Successful remediation of CECs such as 1.4-dioxane and PFAS requires that we apply a toolkit of different approaches that are tailored to meet the conditions not only at each different site, but conceivably in different areas of the same plume. The areas where these opportunities are developing most rapidly include:

- *Smart* characterization to map contaminant mass flux and focus remedies
- Source treatment to accelerate mass reduction and reduce contaminant flux
- Dilute plume treatment to optimize management of long-term ground-water clean up

Table 1 provides a summary of the analytical and treatment methods that are currently available for 1,4-dioxane and PFAS. The following discussions explore the opportunities in site characterization and several specific treatment techniques that show promise for more cost-effective management of these (and other) CEC plumes in groundwater.

# Smart Characterization

Restoration strategies for 1,4dioxane and PFAS are often developed based on the idea that the plumes are diffuse, because source area concentrations are typically measured in the low milligrams per liter (mg/L) (e.g. 1 to 10 mg/L) and distal portions of the plume show dilute concentrations in the single digit to tens of  $\mu$ g/L. The challenge is one of scale and perspective. Because the cleanup standards for 1.4-dioxane, PFOS and PFOA can be less than 1 µg/L, source concentrations of 1,4-dioxane and PFOS/PFOA are often four to five orders of magnitude higher than the cleanup goal. The result is that successful clean-up for 1,4-dioxane and PFOS or PFOA might require more than 99.99% treatment efficiency, which is a similar frame of reference for CVOC dense nonaqueous phase liquids.

In the column on Smart Characterization (Suthersan et al. 2015), we noted that mass flux is typically concentrated in the permeable transport zones, but that diffusion into fine-grained storage zones along the advective transport pathway can lead to instances where the "source" center of mass is often offset from the spill location in mature plumes. The high solubility and limited organic carbon partitioning of 1,4-dioxane and PFAS make it more likely that storage zones along the transport trajectory will serve as "sources" for back diffusion after the advective plume has long since passed. The key is using high-resolution hydrostratigraphy and sampling techniques to target the flux and distinguish contaminant mass transport zones from mass storage zones. Real-time analytical methods are available today for 1,4-dioxane and efforts are underway to develop quantitative screening approaches to evaluate total PFAS. In the interim, it is important that we resist temptation to revert to the use of monitoring wells to characterize these sites.

Figure 3 shows the results of *Smart* characterization applied to a former fire training area. We used a mass-flux transect approach that combined the hydraulic profiling tool and vertical aquifer profile groundwater sampling with fixed laboratory analysis by EPA Method 537. The resulting three-dimensional interpretation of the PFOS

# Table 1

Summary of the Current Understanding of Remediation Options for 1,4-Dioxane and PFAS. Technologies Are Categorized as Follows: Commercial—When Several Examples of Field-Scale Deployment Are Available, or Based on Authors Direct Experience; Emerging—When Literature Reports Results in Lab- or Pilot-Scale; N/A—When Limited Data Were Available to Document Application

	1,4-Dioxane		PFAS	
	(Commonly Used Laboratory Analyses Include USEPA 522, USEPA 8260B [SIM with Isotopic Dilution], and USEPA 8270D [SIM with Isotopic Dilution])		(Commercially Available Laboratory Analysis Using USEPA 537; Other Laboratory Methods in Development Including TOP Assay, LCQTOF MS, PIGE Spectroscopy, and AOF)	
Remedy	Status	Noteworthy Information Provided if Appropriate and References Provided for Emerging Technologies	Status	Noteworthy Information Provided if Appropriate and References Provided for Emerging Technologies
Source treatment				
In situ chemical oxidation	Commercial	Activated/unactivated persulfate, ozone, Fenton's reagent	Emerging	Lab scale (ScisoR <sup>®</sup> for PFOS/ PFOA) (Pancras et al. 2013b)
Enhanced in situ bioremediation	Emerging	Pilot scale (Lippincott et al. 2015; Mora and Chiang 2014)	N/A	—
In situ thermal	Commercial	—	N/A	—
Stabilization	N/A	—	Commercial	Carbon and other commercially available addi- tives such as RemBind <sup>™</sup> and MatCARE <sup>™</sup>
Soil Removal	Commercial	Not typical	Commercial	_
Groundwater trea	tment			
Advanced oxi- dation processes	Commercial	Ozone/hydrogen peroxide, UV light/ hydrogen peroxide	N/A	—
	Emerging	Granulated activated carbon and hydro- gen peroxide used to generate super oxide radicals (Ahmad et al. 2015)	Emerging	_
Sorptive media (GAC)	N/A	—	Commercial	High temperature thermal regeneration required to re-use carbon; PFAS sorption to carbon is very low, ineffective for short chain PFAS
Sorptive media (other)	Commercial	Synthetic media	Commercial	Commercially available additives such as RemBind <sup>™</sup> , MatCARE <sup>™</sup> , and PerfluorAd (Emerging)
	N/A	—	Commercial	Ion exchange media (Bachman et al. 2010; Du et al. 2014)
Co-metabolic bioremediation	Emerging	Pilot scale (Lippincott et al. 2015; Mora and Chiang 2014)	N/A	_
Microbially driven Fenton reaction	Emerging	Lab scale (Sekar and Dichristina 2014)	N/A	_
Ultrafiltration	N/A	_	Commercial	Reverse osmosis and nano filtration
Sonochemical	N/A	_	Emerging	(Cheng et al. 2008, 2009)
Bioreactor	Emerging	(US EPA 2014b)	N/A	_
MNA				
Aerobic bioremediation	Emerging	Lab scale mechanism (Mahendra and Alvarez-Cohen 2005)	N/A	_
Anaerobic bioremediation	Emerging	Lab scale mechanism (Shen et al. 2008)	N/A	—
Co-metabolic bioremediation	Emerging	Lab scale mechanism (Mahendra and Alvarez-Cohen 2006)	N/A	—
Fungi	Emerging	Lab scale (Nakamiya et al. 2005)	N/A	—
Other biological	Emerging	Field scale (Chiang et al. 2008)	N/A	

Notes: GAC = granular activated carbon; SIM = selective ion monitoring; TOP = total oxidisable precursors; QTOF MS = quadrupole time of flight mass spectroscopy; PIGE = particle induced gamma emmission; AOF = adsorbable organo fluorine; other biological = evidence for degradation via iron-reducing bacteria.



Figure 3. Smart characterization results for PFOS at a former fire training area. Based on application of mass flux transects using HPT and VAP groundwater sampling, the core of the plume is concentrated in the vertical and horizontal dimensions. As a result, the majority of PFOS mass discharge is concentrated in less than 20% of the aquifer volume.

plume clearly shows that the majority of the mass discharge is concentrated within a fraction of the plume footprint. The geometry of the plume and mass distribution suggests that focused treatment along the core could significantly reduce the mass flux. While additional source characterization is necessary to evaluate the residual mass at the fire training area and potential benefits of source treatment, the results indicate that a flux-based remedy strategy could enable focused treatment of the PFOS plume.

#### In Situ Chemical Oxidation

Treatment of high concentrations of 1,4-dioxane in groundwater is typically accomplished using varieties of advanced oxidation processes, combined with conditioning tailored to the site geochemistry for best results. Recent applications of regenerable media show promise under the right geochemical conditions, particularly with higher influent concentrations. As shown in Table 1, source treatment methods using in-situ chemical oxidation (ISCO) via persulfate, ozone and Fenton's chemistry have also been successfully applied and proven in the field. In one example, we applied persulfate chemistry in a pilot to evaluate options for full-scale treatment. As ISCO applications are less effective when contaminant mass has diffused into the less permeable portions of the aquifer stratigraphy, oxidants with greater longevity are preferable as they are better suited to target such stored contaminant mass. This makes persulfate a good choice. The free radical cascade developed during persulfate applications also yields hydroxyl, perhydroxyl, and superoxide radicals, among others, and can be engineered with a variety of activation chemistries.

Data collected following one-field persulfate injection for 1,4-dioxane treatment is shown in Figure 4. Initial persulfate bench-scale treatability testing was completed using site soil and groundwater to assess 1,4-dioxane and chlorinated VOC treatment using chelated iron, alkaline, and ambient (persulfate alone) activation techniques. Both alkaline and ambient activation chemistries demonstrated near complete removal of 1,4-dioxane within 7 days of reaction (with chelated iron showing no change, and ambient persulfate activation [approximately 5% by weight]) was selected for field trial. As shown in Figure 4, significant destruction of both 1,1-dichloroethene and 1,4-dioxane were observed following injection. Some rebound was observed approximately 6 months postinjection (and following complete persulfate exhaustion), which was attributed to the presence of 1.4-dioxane within the interbedded sand and clay injection area hydrostratigraphy. This example demonstrates the viability of various persulfate oxidation approaches to achieve complete oxidation, but also demonstrates that successful oxidation performance will require design and deployment to account for mass in lower-permeability storage zone and appropriate injection hydraulic principles-as with any other mainstream contaminants.

Source treatment options for PFAS have generally been limited to excavation and treatment of vadose zone soils. Because treatment is generally limited to high-temperature thermal methods (>1200 °C), many facilities in North America and Europe have stockpiled and contained these materials pending development of more cost-effective methods. Considerable efforts are being expended to evaluate ISCO as a source treatment option, but PFAS is not an easy target. The strength of the carbon-fluorine bond makes achieving complete in situ PFAS destruction infeasible with most standard oxidation chemistries. While the hydroxyl radical discussed for 1,4-dioxane is sufficient to oxidize PFAS precursors to various perfluorinated carboxylate or sulfonate intermediates (Houtz and Sedlak 2012)-as utilized to perform the TOP assay digest-it is insufficient for complete destruction of PFAS compounds. In fact it mobilizes many PFAS. A variety of chemical oxidation methodologies have been attempted



Figure 4. Field data collected from monitoring well within radius of persulfate injection influence. 1,4-dioxane treatment reduced by 90% postinjection. Observed 1,4-dioxane rebound following persulfate consumption attributed to retained diffuse mass in fine-grained soils.

including Fenton's and modified Fenton's, activated persulfate, sonolysis, ozonolysis, sonochemical, photocatalysis, zero-valent iron, in addition to others and various combinations of these techniques. While some of these have been demonstrated effective for specific PFAS compounds, such as PFOA they are either not applicable for in situ treatment or have not been effective for the full suite of regulated PFAS constituents—notably PFOS.

Focused research over many years has evaluated oxidant and activator combinations to cause degradation of PFOS (Kingshott 2008; Hawley et al. 2012; Ross 2012; Pancras et al. 2013a). Recent laboratory work has demonstrated that a specific method of activated persulfate oxidation is capable of mineralizing PFOS via a hypothesized series of mechanisms that include both oxidation and reduction. As defluorination is observed, creation of a redox couple involving both chemical oxidation and reduction, likely forming reductive radicals or solvated electrons is theorized. The decreases in PFOS concentrations and fluoride evolution are only observed when a specific activation method is employed, as with the smart combined in situ oxidation and reduction (ScisoR®) technology (Pancras et al. 2013b, 2013c; Ross et al. 2015). Demonstrated to be effective for treatment of a variety of C4-C8 perfluorinated carboxylates and sulfonates, ongoing work has been focused on confirming that complete oxidation

is achieved—opposed to the generation of incomplete PFAS oxidation byproducts. Fluoride analysis can be used to assess the total fluoride released during oxidation for comparison to the equivalent stoichiometry based on PFOS loss. Comparative PFOS and F results are currently being finalized, but the results are currently looking very positive. With additional work ongoing, results and field-derived data are expected for publication during 2016.

#### Dynamic Groundwater Recirculation

In a recent column (Suthersan et al. 2014), we described the benefits of dynamic groundwater recirculation (DGR) to remediate large plumes in groundwater, not simply capturing and controlling the plumes. The basic premise behind the approach is that adaptively changing the reinjection and withdrawal patterns on a frequent basis accelerates flushing in the advective transport zones, while maintaining a state of disequilibrium between the transport and storage zones to enhance the back diffusion of stored contaminant mass. Because 1,4-dioxane and PFAS plumes often exhibit displacement between the center of mass and the release location, DGR is wellsuited to remediate large plumes where conventional source treatment technologies would be impracticable and cost prohibitive.

Treatment technologies currently exist to enable successful application of DGR for restoration efforts involving 1,4-dioxane. While further advancement is required for costeffective treatment of PFAS using DGR, additional technologies are emerging, with significant emphasis being placed on regenerable sorptive media, ultrafiltration, and advanced oxidation processes.

### **Biological Degradation**

As indicated above, there is significant evidence in the literature of aerobic biotransformation of the PFAS compounds to PFAAs as recalcitrant dead end daughter products. There is no data indicating that PFAAs will attenuate via any biodegradative processes. Our understanding of biological degradation of 1,4-dioxane is maturing thanks to the application of molecular biology tools including biomarkers, genetic enzyme analysis, and compound-specific isotope analysis. Before the advent of molecular biology tools, it was possible to use plume retraction as a line of evidence for natural attenuation, but the mechanism for mass reduction was not clearly understood.

Recent research indicates increaspotential for biodegradation ing 1.4-dioxane through aerobic of (Mahendra and Alvarez-Cohen 2005). co-metabolic (Mahendra and Alvarez-Cohen 2006), and anaerobic pathways (Shen et al. 2008). While field data are emerging, and processes are not understood at all sites and conditions, Adamson et al. (2014) completed meta-data analysis that showed significant evidence for ongoing natural degradation at some California and Air Force sites. Molecular biology tools now enable one to use genetic testing to evaluate potential pathways and confirm that bacteria are actively transforming 1,4-dioxane (Gedalanga et al. 2014). These recent developments provide practitioners a necessary line of evidence to evaluate natural attenuation at sites or to enhance in situ bioremediation through the addition of substrates that facilitate co-metabolic processes.

In one example, historical manufacturing practices at a former automotive manufacturing facility, now RACER, resulted in release of CVOCs and 1,4-dioxane to groundwater in both a perched groundwater zone and deeper underlying weathered rock aquifer. Groundwater concentration trends and geochemical data suggested intrinsic reductive dechlorination of CVOCs in the perched zone and correlated to a shrinking 1,4-dioxane plume footprint; while, trends within the deeper aquifer were less straightforward. As part of the remedy selection process, additional lines of evidence were needed to support a natural attenuation approach in the perched zone and determine if bioremediation was an appropriate strategy in the deeper aquifer. Here we focus on the natural attenuation assessment of the perched zone.

Molecular biology tools were used to evaluate biodegradation perched zone (Figure 5). The first step included collection and analysis of dissolved gas samples to quantify the concentrations of cometabolic substrates (i.e., methane and propane) and electron acceptor (i.e., oxygen). The second step included deployment of Bio-Trap<sup>®</sup> samplers for 30 days at similar locations to collect microbial samples for DNA and RNA molecular analyses. The DNA-based molecular analyses quantified soluble methane monooxygenase (SMMO) and propane monooxygenase (PMO) functional gene targets, an indication of the potential for the subsurface microbial population to cometabolically degrade 1,4-dioxane. The RNA-based molecular analyses quantified similar targets in an effort to identify active generation of these enzymes under current conditions by the intrinsic microbial population.

The dissolved gas analyses yielded elevated concentrations of methane (>1000  $\mu$ g/L) in the perched zone. Dissolved oxygen was lower in the perched plume (200  $\mu$ g/L) and propane was not detected at any of the sample locations. DNA-based analyses indicate potential for both SMMO and PMO production by indigenous microorganisms. RNA-based analyses identified SMMO activity at most locations, but not PMO activity (as expected based on the dissolved gas analyses). These results provide an additional line of evidence in support of a natural attenuation approach. When combined with stable and decreasing concentration trends, the results suggest feasibility in implementing a natural attenuation approach in the perched zone.

## Summary

The challenges associated with emerging contaminants such as 1,4-dioxane and PFAS might seem insurmountable, given the low standards being promulgated coupled with their persistence in the environment and perceived resistance to treatment. However, there are opportunities to leverage our lessons learned over the



Figure 5. 1,4-dioxane natural attenuation case study results. Upper panel shows perched 1,4-dioxane plume in pink and highlights locations where dissolved gases were sampled and biotraps were deployed. Lower panel shows summary of dissolved gas and molecular analyses in the perched zone. Solid bars represent DNA results for SMMO (left graphs) and PMO (right graphs). Open bars represent RNA results for SMMO (left graphs) and PMO (right graphs). Solid circles represent methane (left graphs) and propane (right graphs). Solid triangles represent dissolved oxygen. Open symbols and ND markers represent values less than reporting limit (250 cells/bead for DNA or 250 transcript copies for RNA).

past two decades with chlorinated solvents and other "mainstream" contaminants that were once classified as emerging.

Notably, we understand how to use smart characterization methods to develop an understanding of contaminant flux as part of the conceptual site model, so that we can focus restoration efforts and tailor remedies to match the conditions and risks at the source and in downgradient/distal portions of a plume. Similarly, advances in analytical methods and the science behind remediation technologies support faster development of more costeffective options for characterization and treatment. This includes methods for evaluating natural attenuation and optimizing biological degradation for 1.4-dioxane and advanced methods to characterize and apply in situ reductive/ oxidative approached to destroy PFAS in situ, all of which should accelerate the pace of developing ways of managing 1,4-dioxane and PFAS more cost-effectively.

While the patch work of regulatory standards and developing understanding of toxicology is still a source of uncertainty for stakeholders in the United States and globally, collaboration among the regulatory and stakeholder communities is occurring more effectively now than in the past, which fosters innovation. We are optimistic that the challenges of emerging contaminants will be shorter-lived than our past experience with chlorinated solvents. Continued focus on improving key elements in our remediation tool kit is essential to be sure we capitalize on our lessons learned and translate them into more certainty in outcomes for all stakeholders.

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