advances in remediation

A NEW WAY OF THINKING

2016
Our industry-leading scientists and engineers are rethinking the future of site evaluation and restoration and redefining what is possible.
Introduction

The remediation industry is on the cusp of major breakthroughs that will challenge conventional treatment methods and solve some of your most complex environmental issues. Many of these breakthroughs are not only significant to the remediation industry of tomorrow, but are also applicable to your remediation projects today.

At Arcadis, our scientists and engineers are rethinking the future of site evaluation and restoration by improving the application of existing tools, developing the next-generation technologies and overturning outdated scientific models to redefine what is possible. In this book, you will hear from our industry-leading experts on a wide range of environmental topics, such as innovations in the treatment of emerging contaminants, new approaches in the management of NAPL seepage and sheen, and advancements in the remediation of fractured bedrock and large plumes.

Our focus on increasing the certainty of outcomes, attaining sustainability and achieving business objectives is driving innovation in this industry. It requires a new way of thinking to break through the conventional mindset. And these are the discoveries that we’d like to share with you.
Our focus on increasing the certainty of outcomes, attaining sustainability and achieving business objectives is driving innovation in this industry.
# Table of Contents

Introduction ............................................................................................................................................. 3

Leading the Way:  
Transforming Remediation through Arcadis Innovation ................................................................. 7

Targeting the Sources that Matter Most:  
*Smart* Characterization and Return on Investigation ................................................................. 13

Dynamic Groundwater Recirculation:  
Success Where Remediation Was Once Considered Impossible .................................................. 19

Understanding NAPL Seepage:  
A Robust CSM Leads to Cost-Effective Sheen Mitigation ............................................................. 27

An Improving Picture for Site Owners:  
Bringing Large-Plume Sites to Closure ............................................................................................. 33

Focusing on the Mass that Matters:  
Successful Remediation at Fractured Rock Sites ............................................................................. 39

Tackling the In Situ Treatment of Metals:  
The Case for Speciation ......................................................................................................................... 45

Knowledge, Engineering and Partnership:  
Adapting Large-Scale Strategies to Smaller-Scale Sites ..................................................................... 51

Winning with Karst:  
Effectively Managing These Most-Challenging Sites ....................................................................... 57

Innovation as a Mindset:  
Achieving Remediation Endpoints in a Back Diffusion World ....................................................... 65

Poly- and Perfluoroalkyl Substances (PFAS):  
New Tools for Characterization and Treatment .................................................................................. 71

Our Perspective:  
The Future of Site Investigation and Remediation ................................................................................ 79
We are on the cusp of major breakthroughs that are not only significant to the remediation industry of tomorrow, but are also applicable to your remediation projects today.
Innovation is what we do — it’s in our DNA. We believe that great insights are born when innovation is at the core of an organization’s vision and operation. That is why we invest in hundreds of new concepts each year through our global innovation program to bring fresh ideas to the remediation industry. We combine cross-discipline expertise and creativity from more than 27,000 Arcadians worldwide with a network of key clients, national research centers, vendors and partners from the nation’s leading universities to continuously evaluate horizon challenges and develop new and sustainable solutions. We bring Arcadis innovation to each project, producing greater certainty and long-term cost savings.

For more than 25 years, Arcadis has led the way in site remediation, with concepts such as in situ anaerobic reactive zone remediation for metals, chlorinated solvents and nitrates in groundwater. We have pioneered site closure risk management through guaranteed outcome project delivery, leading to the closure of thousands of sites across North America and saving clients over $1 billion in remediation costs. We are now using advances in materials and technology to improve environmental clean-up decision-making through highly accurate subsurface characterization, enhanced in situ remediation alternatives and advanced data analysis platforms. As part of a current pipeline of more than 40 new innovation concepts, Arcadis is demonstrating lower-cost techniques that quickly capture plume and aquifer characteristics for nonaqueous-phase liquid (NAPL) sites, improving the safety of direct-push subsurface investigations, using thermally enhanced in situ remediation to speed site closure, and applying horizontal wells filled with reactive media to passively treat recalcitrant contaminants in situ. These promising innovations are described in further detail in the sections that follow.
NUCLEAR MAGNETIC RESONANCE LOGGING: DISRUPTING CONVENTIONAL SITE CHARACTERIZATION APPROACHES WITH FASTER, CHEAPER AND BETTER TOOLS

Nuclear magnetic resonance (NMR) logging tools are commonly used in the oil and gas industry to estimate reservoir flow and storage parameters and to determine hydrocarbon saturation. Although the size and cost of oil-field tools historically limited their use for near-surface hydrogeologic investigations, smaller and more economical NMR logging tools are now available. These new NMR tools require no radioactive sources, and the small-diameter downhole tools can be either directly pushed or lowered into pre-existing polyvinyl chloride monitoring wells.

Over the past two years, through field testing at several remediation sites, we have demonstrated the viability of NMR to provide high-resolution measurements of important hydrogeologic properties, including porosity, fluid mobility and hydraulic conductivity. This information obtained from NMR can support Smart characterization approaches, resulting in more-reliable conceptual site models and more-effective remediation system designs.

One of the most exciting applications of NMR is for quantifying the porespace saturation of residual hydrocarbons (or light nonaqueous-phase liquid [LNAPL]) in situ. The results of our bench-scale testing (Figure 1) further establish the capabilities of NMR to reliably detect diesel fuel and provide information about the relative degree of saturation of water and of diesel fuel. By integrating NMR for LNAPL management, we can provide more technically based solutions for defining impacts and remediation goals, and measuring progress, while building in cost efficiency.

### ZIPLINERS™: REDUCING SITE INVESTIGATION HAZARDS

Every year, miles of soil cores are collected from site investigation and remediation projects. Soil cores collected by direct-push technology, the most common method, are collected into a rigid plastic tube, which requires a blade to open. Arcadis recognized that serious hand injuries could result from the use of a blade to open these soil liners. We eliminated this hazard by developing the world’s first soil liner that opens without a blade: Zipliners™ (U.S. Patent No. 8,459,374). The concept is simple and removes the potential for hand injury by eliminating use of blades to open soil cores. The liner is available from all major drilling firms and is fully compatible with Geoprobe and PowerProbe direct-push machines, including traditional and track-mounted rigs. And safety

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Target Saturation (% pore vol.)</th>
<th>Presence/Absence</th>
<th>NMR Detected Saturation (% pore vol.)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Diesel</td>
<td>10%</td>
<td>✓</td>
<td>7.3%</td>
<td>0.73</td>
</tr>
<tr>
<td>Fresh Diesel (duplicate)</td>
<td>10%</td>
<td>✓</td>
<td>7.6%</td>
<td>0.76</td>
</tr>
<tr>
<td>Fresh Diesel</td>
<td>5%</td>
<td>✓</td>
<td>2.2%</td>
<td>0.44</td>
</tr>
<tr>
<td>Fresh Diesel</td>
<td>1%</td>
<td>✓</td>
<td>2.4%</td>
<td>2.37 (over-estimate)</td>
</tr>
<tr>
<td>Weathered Gasoline</td>
<td>10%</td>
<td>✓</td>
<td>3.3%</td>
<td>0.33</td>
</tr>
</tbody>
</table>

**Figure 1. Laboratory testing results validating LNAPL quantification with NMR.**
doesn’t add to the price: there is no cost difference from a standard liner. For samples of Zipliners, contact Nick Welty at nicklaus.welty@arcadis.com.

**ScisoR®: IN SITU TREATMENT OF POLY- AND PERFLUORINATED ALKYL SUBSTANCES**

Poly- and perfluorinated alkyl substances (PFAS) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are a class of emerging contaminants that pose a risk to drinking water aquifers, human health or the environment in multiple areas globally. These compounds have had multiple uses in numerous industrial products and can be present in firefighting foams, water- and oil-resistant fabrics, and packaging for many consumer goods. They may be released to the environment at fire training areas; landfills; and chemical manufacturing, blending and storage areas. PFAS compounds are not biodegradable and are very difficult to treat in situ with conventional remediation, such as in situ chemical oxidation, with the exception of Arcadis’ ScisoR® (Smart Combined In Situ Oxidation and Reduction) technology, which has been shown to mineralize PFAS, including PFOS. Other, currently available remedial options to destroy PFAS are limited to incineration above 1,000 °C, which is cost prohibitive and unsustainable. As shown on Figure 2, Arcadis has demonstrated that the ScisoR chemistry can remove PFAS from groundwater, and the approach has been patented (patent status achieved in 2013 for the Netherlands; patent pending in the U.S.).

**Figure 2. ScisoR test data demonstrating effective treatment of PFAS**

The ScisoR technology offers the following advantages and applications:

- It is effective at ambient temperature.
- Reagents can be injected or mixed with impacted soil and groundwater.
- It enables in situ remediation of source areas via injection or mixing with unsaturated soils.
- It effectively treats waste firefighting foam materials.
- It facilitates regeneration of support media (e.g., ion exchange resins and other absorptive media) to destroy PFAS on site.

**THERMAL IN SITU SUSTAINABLE REMEDIATION: LINKING RENEWABLE ENERGY TO ENHANCED SUSTAINABLE SITE RESTORATION**

The goal of Arcadis’ Thermal in Situ Sustainable Remediation (TISR; international patent pending) approach is to increase ambient groundwater...
temperature using renewable energy, thereby enhancing hydrolysis or biodegradation rates three- to fivefold (Figure 3). Hydrogeological thermal modeling and pilot testing are ongoing to support full-scale TISR implementation in the state of New York, where the subject plume spreads across 10 acres. TISR does not entail any groundwater pumping and is focused on capturing solar energy to facilitate subsurface groundwater heating in order to increase degradation rates and enhance physical contaminant mass recovery, thus resulting in increased contaminant attenuation, removal and degradation within the target contaminant zone. Ongoing field testing has confirmed that the target treatment zone can be heated to the desired temperature via a uniform and controlled process (Figure 4).

Salient features of TISR are as follows:

- Bioremediation
- Chemical hydrolysis
- Effective in complex geology
- Enhanced physical recoverability of the contaminants
- Reduced costs/carbon footprint

HORIZONTAL REACTIVE MEDIA TREATMENT WELLS: NEW, SUSTAINABLE, PASSIVE IN SITU REMEDIATION CONCEPT

The Horizontal Reactive Media Treatment (HRX) well concept is a new Arcadis-developed in situ remediation technology (U.S. Patent No. 8,596,351) that provides sustained passive treatment and contaminant flux control for a wide variety of problematic contaminants. Specifically, the technique utilizes large-diameter horizontal wells filled with a solid-phase treatment media (such as granular activated carbon or zero valent iron) installed roughly in the direction of groundwater flow. The concept leverages natural “flow-focusing” behavior caused by the high-permeability contrast between the aquifer and the well to capture and treat large volumes of groundwater (see Figure 5).
Captured groundwater passively flows into the well through the screen at the upgradient portion of the well, is treated in situ as it contacts the treatment media, and then exits the well through the screen along the downgradient sections. The HRX well approach can provide rapid and dramatic reduction in contaminant mass discharge, and it requires no aboveground treatment or footprint, and limited ongoing maintenance.

It is increasingly recognized that contaminant mass flux and discharge may represent the most-appropriate measure of plume strength and potential migration risk. Therefore, remedial objectives and technologies focusing primarily on long-term mass discharge reduction will be increasingly favored, and, consequently, the HRX well concept is particularly well suited for sites where long-term mass discharge control is a primary performance objective.

The concept has been significantly developed and tested through extensive numerical modeling and physical modeling (e.g., tank testing shown on Figure 5), and Arcadis has received funding from the Department of Defense to conduct field testing and validation.

**Figure 5. Left** Conceptual depiction of HRX well installation and performance. **Right** 3-dimensional tank test set-up (the tank is run in upflow mode).
About the authors

Author
CRAIG DIVINE, PhD, PG

Craig Divine, PhD, PG, leads Arcadis North America Site Evaluation and Restoration technical services and is the Environment Business Line representative for Satellite, Arcadis’ global innovation development program. He has 20 years of experience in hydrogeology, geochemistry, subsurface characterization and groundwater remediation.

Co-Author
JASON CARTER, PE

Jason Carter, PE, leads Arcadis North America Delivery and Innovation. He has more than 18 years of experience in water treatment process, strategic planning and compliance services. Currently, he leads the North America Innovation and Intellectual Property Programs that focus on bringing new insight and solutions to emerging challenges across the water, environment, infrastructure and buildings sectors.
Targeting the Sources that Matter Most: *Smart* Characterization and Return on Investigation

The best remediation strategy begins with a fresh look at the way you evaluate your site. Advances in physical, chemical and biological treatment methods enable you to treat contaminants previously considered recalcitrant. But the practical reality is that most remediation efforts take longer, cost more than expected and fall short of performance expectations. While the underlying treatment technology may be sound, successful application depends not only on chemistry or biology, but also on having a clear target. However, that target isn’t clear when you rely on the most common characterization method: monitoring wells.

**THE PROBLEM WITH MONITORING WELLS**

Permanent monitoring wells are the best option for reproducibility of groundwater quality data, but, if the plume is not characterized before the wells are installed, they often give a misleading picture of groundwater concentrations. Because geologic heterogeneity commonly leads to orders-of-magnitude variability in permeability in a few meters, it is also common to see orders-of-magnitude changes in concentrations at this scale in the aquifer. As shown on Figure 1, monitoring wells present an out-of-focus picture of conditions in an aquifer because they average conditions over a relatively large interval. A sharper focus shows us that there is significant variation we were missing.

*Figure 1. Monitoring wells present an out-of-focus picture of conditions in an aquifer.*

For the vast majority of sites, more than 80% of the groundwater plume mass moves in less than 20% of the aquifer volume.
Figure 2. Monitoring wells and Smart characterization lead to dramatically different plume interpretations. The monitoring wells underestimate the groundwater concentrations and overestimate the plume thickness.
THE SMART SOLUTION

Arcadis’ Smart characterization provides a new way to evaluate sites. It enables you to understand where your groundwater plume is moving so it can be cost effectively remediated. Instead of focusing on generalized data from monitoring wells (Figure 2), the Smart approach uses high-resolution sampling to create a flux-based conceptual site model (CSM) to distinguish the contaminant mass that moves, leading to potential off-site liability, from the mass that doesn’t move. Now, you can surgically target the sources that matter most or pursue streamlined management strategies that meet your business objectives.

Using adaptive, real-time methods, we streamline the site evaluation process to cut through the slow, step-wise process of planning, investigating and reporting. New tools and a focus on finding the moving contaminant mass result in a dynamic approach that is not only faster and cheaper, but better because your resources are focused on better decision making and better remedy design.

To obtain a return on investigation (ROI), we use a decision process that aligns your investment in site evaluation with your business objectives. Our experience with Smart characterization shows that, for the vast majority of sites, more than 80% of the groundwater plume mass moves in less than 20% of the aquifer volume. Understanding the mass flux enables you to tailor the remedy to match your business objectives. For example, we recognize that aggressive

![Figure 3](image_url)

**Figure 3.** The Smart characterization mapping used flux instead of concentration and identified a smaller extent of groundwater impacts compared to conventional investigation.
source remediation isn’t always the best approach. Sometimes, it makes more sense to balance capital expenditures with long-term management strategies and focus on optimizing your operational expenditures. We developed the Smart characterization program to help you optimize your existing remedy or develop the best total cost solution to match your business model.

For example, Arcadis has been characterizing a former wood treatment facility located in the southeastern United States. The wood treatment process has left large areas impacted with creosote dense nonaqueous-phase liquid and associated volatile and semivolatile organic compounds. Contaminant concentrations and aquifer permeability were mapped along the property boundary using a Smart characterization program to determine whether impacts are migrating off site and need to be addressed as part of the long-term strategy. The relative permeability and groundwater concentrations were combined to produce a measure of plume strength: mass flux.

Concentration, the conventional measure of contaminant extent, would suggest that the entire perimeter would require a slurry wall (Figure 3). However, the results of the investigation show that 90% of the mass is moving across the property boundary within small areas. The resulting remediation strategy can now be focused in a small area, rather than the entire perimeter, with significant return on investigation.

**SMART CHARACTERIZATION TOOLS**

Instead of using monitoring wells, the Smart characterization approach uses new high-resolution tools in a technical and economic decision-making framework to maximize ROI and:

- Reduce the total cost of remediation
- Better define uncertainty and risk
- Establish achievable endpoints before remediation begins

Every site is different, and no single tool will work at every site. Often, different tools are needed across a single site, especially when moving from a mature source zone to a downgradient groundwater plume. Screening-level tools, such as the membrane interface probe, may be very effective for source prospecting, but generally can’t be used for delineation to meet groundwater quality standards. On the other hand, quantitative sampling can be cost prohibitive and inefficient when little is known about potential sources. Smart characterization tools provide quantitative mapping of the distribution of relative permeability and contaminant concentrations in real time and at high resolution so you can find the flux and focus on the mass that matters.

Now you can surgically target the sources that matter most or pursue streamlined management strategies that meet your business objectives.
THE NEW ROI: RETURN ON INVESTIGATION

Smart characterization methods are transforming the way we investigate and remediate contaminated sites. The new ROI — return on investigation — demonstrates that the biggest impact on remedy performance and total cost is not driven by remedial technology, but by narrowing the focus for remediation based on the Smart characterization approach. Smart characterization:

- Provides quantitative, flux-based CSMs in near real time to increase efficiency and reduce cost.
- Provides the right tools to map geology, permeability and contaminant distribution to separate the mass that moves, and matters most, from the mass that doesn’t.
- Helps us understand plume maturity and trajectory to tailor appropriate remedies.
- Enables us to determine in advance of design and construction whether aggressive source treatment or a management strategy makes better business sense.

The bottom line is this: Smart characterization is one of the most powerful tools available to improve the reliability and cost effectiveness of site remediation.

Smart characterization tools provide quantitative mapping so you can find the flux and focus on the mass that matters.
About the authors

Author

NICKLAUS WELTY, CPG, PG

Nicklaus Welty, CPG, PG, is the Arcadis North America Director of Site Investigations. He specializes in dynamic, adaptive, high-resolution site investigations with real-time 3D hydrostratigraphic and plume modeling and has led the first commercial applications of several advanced site characterization tools and strategies. Welty has presented internal and external workshops to regulators, clients and consultants on innovative site characterization strategies and leads the Arcadis-wide training initiative to improve high-resolution site characterization methods for geologic, permeability and contaminant mapping. He co-authored the upcoming Remediation Engineering: Design Concepts, which explores the history and future of remediation.

Co-Author

PATRICK CURRY, CPG

Patrick Curry, CPG, has 16 years of experience in environmental consulting, primarily focused on site characterization. He is the Practice Lead for the hydrostratigraphy and mass flux disciplines within the Arcadis Technical Knowledge and Innovation Group. He is actively engaged in the development of Smart characterization tools and methodology, including relative mass flux analysis, hydrostratigraphic analysis, 3D data visualization and conceptual site model development.

Co-Author

JOSEPH QUINNAN, PE, PG

Joseph Quinnan, PE, PG, is the Global Director of the Arcadis site investigation community of practice and is co-author of Remediation Hydraulics. He is actively engaged in advancing Smart characterization methods for DNAPL, LNAPL, solvents and emerging contaminants, which enable clients to maximize their return on investigation by determining mass flux and establishing realistic clean-up objectives before beginning restoration.
Dynamic Groundwater Recirculation: Success Where Remediation Was Once Considered Impossible

Groundwater extraction, or pump and treat, is arguably the first groundwater remediation technology and continues to be in widespread use as a strategy to control plume migration and protect critical resources. Conventional pump and treat is a brute-force approach that focuses on controlling rather than remediating a plume. This strategy, while often effective, inherently results in excess groundwater pumping — a shortcoming, stemming from a flawed conceptual model of the process, that has long been recognized but never thought to be critical.

Before the start of the new millennium, the conceptual model of contaminant transport was built upon the notion that a representative elemental volume (REV) can be used to adequately describe groundwater flow dynamics. The idea was that practitioners could simplify the complexity observed in soil borings into a simplified, but equivalent, model and make accurate predictions. This concept would be great if it worked, but it doesn’t because it fails to recognize the importance and presence of heterogeneous flow pathways, which are pervasive in the real world (Figure 1). This has been demonstrated over and over again through tracer studies.

**Figure 1.** Generalized ‘real world’ cross-section illustrating presence and impact of heterogeneous flow paths.
performed in a wide range of geologic settings. The results of these studies have revealed that our plumes were moving three to four times faster than we initially thought, retardation was often solely an emergent property of diffusive storage, and anisotropy always affected contaminant movement and remedy performance. These new perspectives forced us to reconsider (and improve) remedy design and performance assessment of extraction-based remedies.

“AIRING OUT THE HOUSE”

An important element of this new conceptualization is the idea of change. We know that, in the real world, groundwater levels rise and fall, flow patterns shift, and groundwater demands vary over time — but we do not consider, much less try to quantify, how these changes can impact contaminant transport. An appropriate and useful analog for these processes is how a breeze moves through a house with open windows. Interior walls, doors and hallways act as baffles and preferred pathways, with their configuration altering the air flow from room to room. The direction of the prevailing wind further influences how air moves throughout the house. In an aquifer system, high-permeability zones are the rooms and hallways of the house, where groundwater flow will be focused, while the low-permeability zones act as baffles, deflecting/altering flow. The dynamics of variable flow directions across the seasons eventually spread contaminants across all permeable portions of an aquifer downgradient of the source. This is further enhanced by concentration gradients between the high- and low-permeability materials in real soils that, over time, drive diffusion of contaminants into the less-permeable zones (Figure 2).

To successfully restore an aquifer, we believe it is necessary to create dynamic hydraulic conditions by adaptively changing system operation to essentially mimic, even exaggerate, the natural variability to accelerate the removal of contaminants. This process is the basis for the concept we call enhanced groundwater flushing. The technology to implement this concept is known as dynamic groundwater recirculation (DGR).

A DYNAMIC AND ADAPTIVE APPROACH

The concepts described above highlight the fundamental weakness of conventional pump and treat: the temporal changes in aquifer hydraulics are not considered in system design and operation. Typically, extraction wells are located downgradient of source areas with an expectation that steady operation will achieve performance objectives.

Figure 2. Reference CSM at the applied scale showing: 1) the mobile fraction where pure advection dominates (high permeability); 2) the immobile fraction where both mass storage and slow advection occurs (moderate permeability); and 3) the stationary fraction where storage occurs (low permeability).

Figure 3. Conceptual layouts of DGR with groundwater flow vectors. A) 2:1 ratio of injection and extraction wells with injection along plume periphery and extraction in the core. B) 3:1 ratio with injection within and along periphery and extraction within and downgradient.
This strategy tends to create fixed hydraulic conditions, often leading to the development of stagnation zones and limiting flushing to the principal flow pathways while isolating other important zones containing contaminant mass — static (steady-state) groundwater extraction continually drains the same primary flow channels and, thereby, maximizes the distance over which contaminants must diffuse (Figures 1 and 2). These systems frequently demonstrate short-term value, but tend to have an asymptotic performance curve that results in a “pumping forever” mentality.

The primary distinction between DGR and conventional pump and treat is the use of site data (i.e., the conceptual site model [CSM]) to develop an appropriate flushing framework, a dynamic operation plan and an approach for continuous adaption based on remedial performance. After implementation, the goal of DGR system operation is simple: maximize contaminant mass removal by extracting contaminants within the plume core while injecting clean water at strategic locations along the plume periphery to enhance flushing and direct contaminants toward extraction wells. The key to success is dynamic system operation, using performance data to frequently optimize the system by varying pumping/injection rates and locations in response to changes in concentration data to maximize mass removal rates while maintaining hydraulic control of the plume (Figure 3). This can be described as engineered stretching and folding of the plume or chaotic advection. Following this concept, conventional pump and treat systems can be re-engineered and enhanced as a more-effective remedy.

**A MORE-FOCUSED REMEDIAL STRATEGY**

The basis of DGR system design begins with the volume of water contained within the plume and the number of pore volume flushes (PVFs) required to achieve the performance objectives. The primary objective is to accelerate pore volume flushing within the plume to maximize contaminant mass recovery via all advective pathways and diffusive gradients (Figure 4). To that end, an effective DGR design and implementation should:

- Minimize transit times between injection and extraction wells while maintaining hydraulic control. This promotes back diffusion and shortens clean-up times by maximizing the concentration gradient between the more-permeable zones (where clean water flows) and the less-permeable zones (where mass storage occurs).
- Segment the plume through multiple cut-off measures to reduce the overall footprint. This allows for mass removal across the entire plume and better management of transit times and PVFs.
- Make use of quantitative modeling tools to develop and test operational scenarios while weighing site-specific factors.
- Focus efforts in areas that result in the highest rate of return (i.e., contaminant recovery and mass flux reduction) while managing the overall scale of the system.

To successfully restore an aquifer, we believe it is necessary to create dynamic hydraulic conditions to accelerate the removal of contaminants.
Be continuously assessed using performance data – the backbone of DGR system management and optimization.

Following the approach outlined above will lead to a more-focused remedial strategy and, subsequently, a significant reduction in lifecycle remedial costs.

ONGOING SUCCESS

We have successfully implemented DGR systems at numerous sites (both large- and small-scale). Here is a sampling of our recent successes:

- Former Reese Air Force Base, Texas
  - Approximately 700 acres of trichloroethene- (TCE) impacted groundwater extended three miles from former source areas. The original system was a pump and treat with injection system (for disposal only) operating at over 900 gallons per minute (gpm) with little change in aquifer conditions over the first seven years of operation.
  - 2004: We began a program of dynamic system operation (responding to performance data), which led to a system flow reduction to less than 400 gpm, a significant increase in mass recovery rates, and installation of additional wells for extraction and injection.
  - Period of performance was reduced by 20 years, overall remedial costs were lowered by $22 million and a sole-source drinking aquifer was restored (Figure 5).

**Figure 5.** Observed reduction in trichloroethene (TCE) plume over an 8-year remediation period at the Reese Air Force Base (AFB). Shaded plume areas represent plume footprint in excess of the MCL (5 μg/L).
• NAPL Site, Northeastern U.S.
  - Approximately 4-acre hydrocarbon pool of light nonaqueous-phase liquid (LNAPL) and a large diffuse downgradient plume.
  - Initial remedy was extraction only (multi-phase extraction system).
  - Adaptive design implemented during the first two years of operation resulted in the design of a complementary system of 28 injection wells to manage the hydraulics (prevent further migration and recover residual source) and deliver oxygenated treated water into the plume.
  - Hydraulic control and compliance with regulatory requirements maintained through an unbalanced injection-extraction approach (60% reinjected).
  - Dramatic reductions in dissolved-phase concentrations over short period.
• Transportation Warehouse Facility, Northeastern U.S.
  - Approximately 11 acres of chlorinated volatile organic compound-impacted groundwater extended about 1,500 feet from former source area.
  - December 2014: DGR began operation at 65 gpm with 29 extraction wells and 58 injection wells. Contractually driven goal: meet remedial objectives within 18 months.
  - September 2015: More than 90% of the initial plume footprint is below remedial objectives (Figure 6).
• Industrial Site, Southwestern U.S.
  - Approximately 4 acres of TCE-impacted groundwater extended about 1,000 feet from former source area.
  - May 2014: Downgradient DGR (two extraction and three injection wells) installed as an interim measure (IM) to prevent further plume migration and protect downgradient residents.
  - June 2015: More than 60% reduction in TCE plume footprint and more than 40% reduction in estimated plume mass (only three monitoring wells remaining above PCL).
  - Success of DGR IM led to submittal of Revised Remedial Action Plan with DGR as selected remedy for remaining plume.
• Chemical Warehouse Site, Southwestern U.S.
  - Circa 2010: Approximately 67 acres of carbon tetrachloride-impacted groundwater extended about 4,000 feet from source area.
  - 2010–2012: DGR system (six extraction and 11 injection wells) operated intermittently due to mechanical issues; since then, operating between 180 and 200 gpm.
  - 2010–2013: Data showed plume migration halted but limited progress
in plume remediation — minimal footprint reduction (67 acres in 2010 vs. 58 acres in 2013).
- Early 2015: More than 40% reduction in plume footprint (from late 2013).

AN EXCEPTIONALLY PRODUCTIVE STRATEGY

When properly designed and operated, DGR can be a highly effective remedial technology that significantly advances conventional pump and treat applications of the past. It helps maintain water levels; provides an efficient way to manage treated water; reduces time required for remediation through enhanced flushing; and, most importantly, can achieve endpoints that were previously considered impossible to reach. The underlying concept is relatively simple: accelerate the influx of clean groundwater to enhance hydraulic and concentration gradients that, in turn, drive contaminant mass out of the aquifer (both flow and storage zones) by advection and diffusion. Faster cleanup times can be achieved by strategically moving more pore volumes and manipulating gradients to increase mass flux/advective transport through the mobile fraction and mass transfer/diffusive transport across low-permeability zones where contaminant mass is stored, essentially overcoming aquifer heterogeneities and the effects of matrix-controlled back diffusion. When applied to sites with miscible contaminants, complex geology and/or large diffuse plumes, our DGR strategy can be exceptionally productive.

We follow a dynamic and adaptive implementation of DGR, allowing CSM and system performance data to guide design and operation. We continuously evaluate water quality and hydraulic data while continually focusing on improving the rate of cleanup. This approach is currently being applied to numerous contaminated sites with tremendous results. And, while this strategy may not work for every project site (conditions must be conducive), we are able to achieve what was previously unthinkable for many large and/or complex contaminant plumes. This shows that the advancements being made in in situ remediation are supporting the real possibility of large-scale restoration. In fact, the combination of DGR with mass flux-based solutions have made it possible for stakeholders of large plume sites to plan for closure within relatively shorter time frames and under reduced costs where, historically, it was thought that remediation could not be accomplished.
We can achieve endpoints that were previously considered impossible to reach.
About the authors

Author

**SCOTT POTTER, PhD, PG**

Scott Potter, PhD, PG, is the Chief Hydrogeologist for Arcadis North America. He has more than 30 years of experience in groundwater hydrology and remediation. Potter has project experience developing site-wide remedial strategies, groundwater flow and contaminant transport, surface-water flow and transport, and quantitative analysis of hydrogeologic systems.

Co-Author

**MARC KILLINGSTAD, PE**

Marc Killingstad, PE, is a Principal Water Resources Engineer/Groundwater Hydrologist for Arcadis and serves as the Director of Hydrogeology and Remediation Hydraulics within our Technical Knowledge and Innovation Group. He has 20 years of experience developing and applying groundwater models to support site investigation and remedial design in a variety of settings throughout North America, Europe and Australia. Killingstad also provides technical leadership in the areas of remediation well design, installation, development, hydraulic testing/assessment and rehabilitation.
Understanding NAPL Seepage: A Robust CSM Leads to Cost-Effective Sheen Mitigation

When nonaqueous-phase liquid (NAPL) seeps from soil and sediment to the surface of a water body and visible sheens occur, several factors, including the Clean Water Act of 1972 (the “Sheen Rule”), potential ecological risk and public perception, can prompt the requirement that anthropogenic sheens be mitigated.

The ability to predict the potential for NAPL seepage and resulting sheens, as well as their potential magnitude, requires a knowledge of NAPL mobility and natural depletion, hydrogeology, groundwater-surface water hydrology and surface water characteristics. The scale and aggressiveness of mitigation measures should be connected to the existing and future potential for NAPL seepage to generate sheens, rather than—as is too often the case—assuming that all NAPL, both near the groundwater-surface water interface (GSI) and in the upland, will contribute to the generation of sheens.

This article discusses NAPL mobility, the development of NAPL seepage conceptual site models (CSM), the assessment of NAPL assimilative capacity and the state of the art in NAPL seepage mitigation.

Figure 1. Sheens can be generated when NAPL seepage occurs because of NAPL drainage and mobility at low water.
HOW DOES NAPL GET TO THE GSI?

For NAPL released to the subsurface to reach the adjacent water body (to migrate or flow), it must be both mobile and driven by sufficient hydraulic gradient. NAPL is present at many sites at residual saturations that are not mobile. There may also be insufficient gradient to induce flow. NAPL mobility, like the potential productivity of a groundwater aquifer, can be quantified by evaluating transmissivity, which characterizes NAPL properties, soil properties, and site-specific NAPL saturation and spatial distribution all in one parameter. NAPL migration toward the GSI is most generally controlled by the NAPL transmissivity and NAPL gradient, but other mechanisms can change and contribute to NAPL migration.

- Water table variation can control NAPL mobility. When a rising water table submerges NAPL, it can lose larger-scale continuity and therefore mobility. When the water table subsequently drops, water drains from the largest pores. NAPL can then flow through those air-filled pores, because it is easy for NAPL to displace air (Figure 1).
- NAPL wicking is a process where NAPL propagates along the top of the capillary fringe by the same mechanism that causes sheens to spread on a water surface (Figure 2). NAPL flux via wicking is likely low.
- Erosion may contribute to redistribution of NAPL from banks to sediments.

The assimilative capacity of the subsurface naturally mitigates NAPL migration and NAPL seepage. Storage plays a role as an assimilative factor because releases will spread only while the gradient driving NAPL flow can overcome capillary forces resisting NAPL flow. After that, NAPL will no longer migrate. Natural source zone depletion (NSZD) is an assimilative mechanism that continuously acts to naturally reduce the mass of NAPL in the subsurface through dissolution, volatilization and biodegradation.

WHAT ARE THE MECHANISMS FOR NAPL SEEPAGE AT THE GSI?

The generation of sheens is not directly connected to the discharge of groundwater at the GSI. Dissolved chemicals that are discharged with groundwater, even if they came from dissolution of NAPL constituents, cannot recondense into NAPL. When the NAPL migration processes described above act at the GSI, NAPL seeps and becomes a sheen on surface water. There must be flow of NAPL across the GSI for a sheen to be generated. The discharge of groundwater at a GSI, which is due to groundwater mobility and a driving gradient, does not imply that there is NAPL mobility and a driving NAPL gradient to induce NAPL seepage.
Ebullition is a fourth mechanism that can drive NAPL seepage because the NAPL forms an intermediate wetting phase between air and water. The NSZD process of methanogenic degradation can produce methane in excess of its solubility so that it forms gas bubbles. These gas bubbles provide an air-water interface that accumulates a film of NAPL, and that NAPL is carried to the water surface by the bubble’s buoyancy, where a sheen blooms. (Figure 3).

**HOW LONG WILL UPLAND NAPL FLOW RECHARGE NAPL AT THE GSI?**

Understanding the potential contribution of upland NAPL to long-term NAPL seepage and sheen generation potential at the GSI is critical to selection of a long-term mitigation technology. Site-specific characterization of NAPL migration can elucidate whether reduction of NAPL mass in the upland is needed to mitigate NAPL seepage and sheen generation.

High NAPL mobility, and a NAPL gradient in the upland, is necessary for it to continue to feed NAPL seepage at the GSI. Counteracting the NAPL gradient are capillary forces that resist the intrusion of NAPL into pore space not already occupied by NAPL. Counteracting the actual flow of NAPL, and preventing the spread of the NAPL body, is NSZD. Even if there is NAPL flow from the upland toward a NAPL seepage zone at the GSI, the flow may be attenuated by natural depletion before it results in seepage. In this way, the rate of NAPL seepage and resulting rate of sheen generation can be substantially less than what would be inferred from upland NAPL flow.

Performance monitoring of the initial remedy at the Pine Street Canal Superfund Site revealed sheens on the surface water and NAPL on the surface of a 3-foot-thick sand cap in the canal intended to isolate NAPL in the sediment. Arcadis executed a re-design investigation to fill data gaps and develop a CSM that included NAPL mobility within a peat layer. Conducted over three seasons, the investigation included borings, TarGOST™, diver surveys of NAPL seepage and surveying ebullition (Figure 4). NAPL residual saturation testing and bench-scale column testing were conducted to confirm the basis of design. Arcadis concluded that hydraulic gradient and ebullition were causing NAPL seepage into the canal and causing sheens. A reactive cap made of organoclay reactive core mat was placed in areas of NAPL seepage and ebullition to sequester NAPL. The organoclay reactive core mat is effectively controlling NAPL seepage.

Sheen generation processes are complex but can be understood and mitigated when a robust CSM exists.

**Figure 3.** Sheens can be generated by ebullition carrying NAPL to the water surface.
At most NAPL sites, existing NAPL bodies are quite mature, and the majority of the NAPL will not contribute to seepage and sheen generation. Because mechanisms like NSZD and NAPL smearing continually act to reduce overall NAPL mobility, past NAPL seepage and sheen generation rates are not necessarily a good guide to current or future risk. To reduce the generation of sheens, the focus must be on the NAPL at the GSI.

NAPL SEEPAGE AND SHEEN GENERATION MITIGATION MEASURES

The appropriate measures for effective, long-term mitigation of NAPL seeps and resulting sheens should be informed by a CSM. The CSM connects the observed sheen to a NAPL seepage mechanism and to the potential for NAPL recharge from the upland.

Evaluating the rate of NSZD determines the significance of upland NAPL flow to the GSI and helps determine whether measures such as NAPL recovery in the upland, upland barriers that prohibit NAPL migration to the water body or upland excavation of NAPL would be worth the cost.

NAPL recovery can reduce the source but only to a point. Once recovery rates become asymptotic and NAPL transmissivity drops below 0.1 square foot per day (ft²/day) to 0.8 ft²/day, additional recovery effort does little to reduce source longevity. In part, this is due to the fractional reduction of NAPL mass that can be accomplished by hydraulic recovery when NAPL transmissivity is low. More importantly for mitigation of upland fed NAPL seepage at the GSI, low NAPL transmissivity implies low NAPL flow that is likely insufficient to overcome NSZD losses and continue to add NAPL mass to the near GSI environment.

Upland barriers, while they may be a measure that disconnects upland NAPL from the near GSI NAPL, should be used only where there is demonstrated NAPL flow in excess of the rate of NSZD. Similarly, complete removal (excavation) of upland NAPL is a measure that is rarely, if ever, necessary on the sole basis of risk of sheens. Further, the thin
wedge of NAPL-affected soil between the excavation and the body of water can still generate sheens, despite the complete removal of upland NAPL.

The CSM should carefully evaluate NAPL mass near the GSI that is directly connected to NAPL seepage and sheen generation. Through characterization of NAPL seepage mechanisms and rates, and NAPL mass, informed decisions can be made about the use of sorptive, reactive and/or NAPL-wetting flow-through technologies at the GSI and the amount of capacity to design into these measures.

CONCLUSIONS

Sheen generation processes are complex but can be understood and mitigated when a robust CSM exists. Specifically, the CSM clearly explains the significance of NAPL migration to the seepage point and the mechanism(s), rate and longevity of NAPL seepage. Using the CSM, informed decisions can be made on how to effectively and efficiently control the NAPL seepage for mitigation of sheens.

At a petroleum bulk storage facility adjacent to a tidally influenced river, residual NAPL was present in shoreline sediment, and sporadic sheen was observed. Arcadis conducted pilot testing of an oleophilic bio barrier (OBB) that is designed to allow the flow of water and gasses while capturing and storing NAPL on an oleophilic membrane. The OBB is also designed to limit the intrusion of sediment particles, maintaining the flow of water and air. Naturally occurring microbial communities colonize the OBB. Water and/or air exchange freely through the OBB to deliver oxygen and other electron acceptors promoting degradation of the NAPL. Consequently, the NAPL storage capacity of the OBB mat is restored over time.

Since installation of the OBB, no sheens have been observed where the OBB was placed (Figure 5).

Figure 5. Use of OBB to control sheen
About the authors

Author
RICK AHLERS, PE

Rick Ahlers, PE leads the NAPL management community of practice within the Arcadis Global Knowledge Network. He has extensive experience with the evaluation and restoration of NAPL sites, particularly petroleum NAPLs. Ahlers is a contributor to the Interstate Technology & Regulatory Council’s (ITRC) LNAPL guidance and is an instructor for ITRC’s LNAPL classroom and internet training.

Co-Author
SHANNON DUNN, PG

Shannon Dunn, PG leads the sediment management community of practice within the Arcadis Global Knowledge Network. She works on aquatic sites, evaluating the nature of sheen and its transport mechanisms, mass flux and methods of control.
Large plume is a term that covers a wide range of contaminated aquifer scenarios, but they all share four common characteristics:

- Large plumes occur in productive aquifers with high rates of groundwater flow and the potential to transport dissolved contaminants over large distances.
- Large plumes comprise compounds that are not quickly degraded chemically or biologically under natural aquifer conditions.
- Large plumes occur when contaminant compounds don’t interact chemically with the aquifer matrix — either the aquifer matrix has limited sorptive capacity or the contaminant can’t be sorbed due to its molecular structure.
- For most contaminants, there must be a large source mass to generate a large volume of groundwater that exceeds regulatory criteria.

The classic approach to large plumes has been groundwater pumping. In the early years of “pump and treat,” there was an expectation that the process would lead to site closures. Since the mid-1990s, it has been understood that conventional pump and treat approaches can contain large plumes, but cannot be expected to drive them to closure.

Many of the large plumes under treatment today were discovered more than 25 years ago, and more large plumes are being added to the national inventory every year as new risk-bearing compounds are recognized. During the past 15 years, there has been steady progress moving smaller-plume sites to closure through improved technology and increasingly risk-based regulatory standards. However, over that same time period, there has been little progress for large plumes, and the total inventory appears to be increasing due to the recognition of emerging contaminants.
THE CHALLENGE

Smaller sites have benefited significantly from advances in site characterization and remedial technologies during the past 15 years. But site owners, consultants and even regulatory agencies remain pessimistic regarding the prospects for bringing large-plume sites to closure. The challenges that must be overcome are both technical and financial:

• **Technical Challenges** — To move beyond simple containment for large plumes, three major technical problems must be solved:
  1. Development of cost-effective mechanisms to restore groundwater quality over large volumes of contaminated aquifer.
  2. Effective source containment or removal technologies.
  3. Cost-effective characterization tools to develop more detailed mapping of contaminant transport and storage in large-aquifer settings.

• **Business Case** — Many large-plume sites have classic pump and treat systems already in place with significant sunk capital costs. These overhang any discussion of further investment to drive large plumes to closure. In newly discovered large plumes, there is a better case today for closure-oriented strategies, but the business case for containment remains strong.

ARCADIS ANSWERS THE CHALLENGE

Beginning in the 1990s, Arcadis began its performance-based contracting program, through which we committed to achieving closure for several large-plume sites. To meet these commitments, we had to abandon the classic approaches to large plumes. Ultimately, we followed a three-fold path to solving the large-plume challenge:

• Re-examine our understanding of hydrogeology to better understand contaminant storage and transport in aquifers (Figure 1).
• Develop cost-effective characterization strategies and tools to support the improved science of remediation hydrogeology.
• Invent and test technologies to cost effectively treat large aquifers.

Through the reconstituted science of remediation hydrogeology (introduced in our 2008 book, *Remediation Hydraulics*), we learned that, because of the wide range of hydraulic conductivities of the sediments in even the simplest geologic settings, groundwater flow in aquifers occurs in a very small fraction of the total aquifer volume. At typical sites, we saw that more than 90% of the contaminant flows through less than 10% of the aquifer (Figure 2). By improving our mapping of contaminant transport zones, we could reduce the scope of...
Figure 1. Arcadis transport and storage conceptual model for contaminants in large, dilute plumes (redrawn from Remediation Hydraulics).

Figure 2. Longitudinal cross-section developed using Arcadis next-generation site characterization tools. More than 90% of the contaminant transport was found to occur in less than 10% of the aquifer matrix.
remedial action to a small fraction of what is needed for a classic remedial method. This has two implications:

- First, closure of large-plume sites is technically feasible and, in many cases, site closure can be the best business case.
- Second, even in cases where containment is the best business-case approach, the costs for long-term containment can be dramatically reduced.

The environmental remediation community has been too pessimistic regarding the prospects for cost-effectively managing large, dilute plumes. Arcadis has developed characterization strategies that yield immediate payback in the form of reduced remedy scope and improved capture efficiency. We have also translated our new understanding of contaminant flow pathways and aquifer matrix storage processes into more-effective remedial technologies, such as Directed Groundwater Recirculation (DGR). Even where long-term containment is still the best business case, new technologies for source mass reduction and DGR can significantly reduce long-term operation and maintenance costs. At Arcadis, we have answered the challenges, and we’re strongly optimistic.

Closure of large-plume sites is technically feasible and, in many cases, can be the best business case. Where it is not, the costs for long-term containment can be drastically reduced.
Even where long-term containment is still the best business case, new technologies can significantly reduce operation and maintenance costs.
About the authors

Author  
FRED PAYNE, PhD

Fred Payne, PhD, is a Senior Vice President and Chief Scientist for Arcadis North America. He has nearly 40 years of environmental industry experience, encompassing a broad range of natural resource, wastewater, stormwater and hazardous waste management. He is a leader in the design and development of in situ reactive zone technologies for aquifer restoration and is the inventor of six patented technologies used in the treatment of contaminated soils and groundwater. Payne is a global leader in the ongoing reformulation of remediation hydrogeology, resulting in more effective site characterization, more cost-effective remediation and more sensible regulation.

Co-Author  
SCOTT POTTER, PhD, PG

Scott Potter, PhD, PG, is the Chief Hydrogeologist for Arcadis North America. He has more than 30 years of experience in groundwater hydrology and remediation. Potter has project experience developing site-wide remedial strategies, groundwater flow and contaminant transport, surface-water flow and transport, and quantitative analysis of hydrogeologic systems.
Remediation of fractured bedrock—sedimentary, igneous or metamorphic—remains one of the most significant challenges facing environmental professionals, responsible parties and stakeholders. While there have been significant advances in the characterization and remediation of alluvial aquifers, much of this progress has not translated to clear strategies for fractured rock sites.

The main challenge for the restoration of fractured rock is to understand the contaminant mass flux from mass storage in low-transmissivity zones to the high-transmissivity fractures that dominate overall groundwater flow and contaminant transport. Additional challenges arise from this dynamic as how best to characterize, set appropriate remedial goals, balance the overall cost in the context of risk, and understand realistic exit strategies and timeframes.

Development and commercialization of characterization technologies such as CORE™ (Figure 1A), FLUTe™ liners (Figure 1B), and downhole geophysical methods have allowed for greater resolution in the investigation of fractured rock, supporting the development of more-robust conceptual site models. However, this improvement in characterization technologies has not materially advanced discussion on the identification of definitive remedial strategies in fractured rock settings. Some of the reasons for this lack of progress are rooted in the misguided assumption that the concept of back diffusion provides...
evidence that we cannot remediate fractured rock plumes to low clean-up standards. Other practitioners fail to adopt new investigation and remediation methodologies or they stand on the sidelines of the innovation process.

However, based on new strategies adapted from alluvial sites and real successes in fractured rock settings, we see reasons for optimism.

A SIGNIFICANT REDUCTION IN COST AND TIME

Our long history of remediation in complex fractured rock settings has provided us with unique insight into remedial strategies that can be effective in meeting remedial goals in the short and long term. We can provide perspective up front in situations and geologic settings where meeting stringent water quality targets is unrealistic and where development of long-term, cost-efficient solutions is the path forward.

Our successes in fractured rock settings are the result of contaminant flux-based approaches and a thorough understanding of potential receptor pathways. Fractured rock sites where the majority of mass resides in fractures and where little or no mass has diffused into the rock matrix (e.g., some igneous and metamorphic rock settings — Figures 2A and 2B) may be associated with large plumes. These sites can be efficiently remediated by applying Arcadis’ large plume philosophy, concepts and strategies: continuously reassessing and retargeting the remedial effort based on performance monitoring data, focusing the effort on the mass flux and overcoming the mass contribution from the low-advection fractures — both in the short and long term. Conversely, fractured rock settings associated with significant matrix porosity provide the potential for matrix diffusion processes and significant mass stored in the low-transmissivity zones (e.g., silt and sandstone settings — Figure 2C) and constitute a different challenge, very analogous to overburden sites with mass storage in silt/clay layers and transport in coarser, more-permeable materials. However, in many cases and counter to much of the current thinking, remediation of these high-matrix-porosity sites does not require unrealistic remediation of the gross contamination residing in the fractured rock matrix to be successful. Rather, by identifying and focusing on the fracture zones that contributes to mass flux and by addressing the rock matrix immediately adjacent to these fractures, we have demonstrated a significant reduction in capital cost, long-term operations and maintenance, and remedial timeframes.

Figure 2. A) Fractured metamorphic rock (biotite gneiss) with matrix porosity less than 1%. B) Road cut in fractured metamorphic rock, providing a sense of the three-dimensional nature of fractures, joints, and cleavage. C) Fractured sandy silt stone with matrix porosity of approximately 12%.

The CSM is a “living” document, becoming more robust and focused as the investigation and remediation progress.
TAILORED INVESTIGATION

We tailor our investigation approach to each site based on our understanding of hydrogeologic conditions, bedrock and fracture characteristics, and the physical and chemical nature of the contaminant(s), and we work closely with our client to define the questions that must be answered by the investigation. All effort is centered on the development of a conceptual site model (CSM) that describes the most important elements of a site and serves as the framework for developing remedial objectives. The CSM (Figure 3) is a “living” document that is continuously tested and updated as more data are collected, becoming more robust and focused as the investigation and remediation progress.

Our characterization generates a flux-based CSM that more clearly distinguishes between the source and the mass that moves. Our objective is to understand and distinguish between the source zone and plume and define the fracture intervals where the majority of mass flux occurs. This enables us to work with our client and stakeholders to formulate clear and well-defined remedial goals, support the selection of remedial alternatives that meet these goals in a timely and cost-efficient manner, and obtain a return on investigation (ROI) by focusing the remedial effort and shortening the remedial timeframes. In many cases, the appropriate remedial goals in the source zone differ from those in the plume. In the source zone, goals may include reducing mass flux by one or more orders of magnitude, whereas achievable goals in the plume often are driven by the risk assessment and regulatory guidance.

A TARGETED APPROACH

Centered on our focused CSM and clearly defined remedial goals, we work with our client to develop the remedial strategy that best fits their needs and objectives — whether they include a fast and dramatic decrease in mass flux and groundwater contaminant concentrations over a short period or longer-term solutions that may be associated with more modest capital investments.

Our remedial approaches are designed to target the mass that matters and reduce the flux in the source area and downgradient plume. In the source area...
(Figure 4), considerations include:

- Mass in the advective zones, including fractures and overburden.
- Slow-advection zones, including micro and blind fractures and overburden sands mixed with silts and clays.
- Storage zones, including primary porosity (unfractured rock matrix), the matrix of highly weathered rock and overburden silts and clays. The storage zone is important in many sedimentary rock settings associated with significant matrix porosity, but less important at many igneous rock sites with matrix porosities of less than 1%.

Figure 5 provides an example of successful fractured rock remediation by applying the large plume strategy. In the source zone, this involved addressing high- and low-advection fractures and reducing concentrations in the rock matrix near fractures by increasing the chemical gradients and driving out mass. In the plume, the main focus was on the high-advection fractures. Even though notable contaminant mass may remain in the matrix, it is far away from the fractures and the effective mass transfer from the matrix to the fractures is very low, resulting in minimal long-term contaminant flux from the source area.

Of course, each fractured rock site is different, and we are not promoting one technology or approach to fit all sites. Our toolbox includes extraction approaches such as multiphase extraction (source zone only) and dynamic groundwater recirculation (source zone and/or plume), as well as injected fluid-based in situ methods such as ERD and in situ chemical oxidation (both may be applicable in the source zone and/or plume). Cutting-edge emerging remedial strategies include moderately low-temperature enhanced hydrolysis with or without pH adjustments. As opposed to conventional thermal treatment, enhanced hydrolysis can focus on the fracture intervals associated with the majority of mass flux and requires significantly less energy input while increasing contaminant breakdown by orders of magnitude in the fractures and in the rock matrix immediately adjacent to these fractures.

Regardless of remedial technology, our successful remediation outcomes in fractured rock settings are directly related to well-developed CSMs and our ability to target the fracture zones associated with flow and mass.

Figure 4. Data from a chlorinated volatile organic compound-contaminated sandstone site in Colorado showed source zone treatment in an fractured rock aquifer resulted in a dramatic and rapid mass discharge reduction. After two years of treatment, which removed 150 kg of source mass, the mass discharge was reduced by approximately 95%. Data are consistent with cleanup of high- and low-advection fractures as well as storage in a “rind” around the high-advection fractures.
SUCCESS
Our implementation of characterization methods focused on identifying the fractures associated with the significant mass flux has greatly improved our understanding of fate and transport and our conceptual site models. The success we have achieved on behalf of our clients at multiple fractured rock sites supports our contention that cost and performance are driven by the selection of the right technologies and remedial alternatives within the framework of appropriate and well-defined remedial goals. Despite widespread industry pessimism, fractured rock sites can be remediated in a timely and cost-efficient manner by focusing on the mass that matters.

Figure 5. Adaptive remedial approach in fractured sandstone, focusing on continuous performance assessment and system optimization. Initial remedial approach involving enhanced aerobic bioremediation (AB) was effective, but, based on new pilot test results, site-wide conversion of the groundwater treatment system from an aerobic to an anaerobic biodegradation remedy would result in a faster clean-up pace. Consequently, the AB system was converted to a full-scale enhanced reductive dechlorination (ERD) system in early 2009. Performance of the full-scale ERD system has matched and, in some cases, significantly exceeded expectations developed from the ERD pilot test. Overall, the remediation actions have been very successful: approximately 90% of the volatile organic compound mass in the off-site plume has been destroyed, and active remediation was discontinued in the off-site area in 2013. Continuous post-remediation monitoring supports the conclusion that no significant rebound has occurred.

We have demonstrated a significant reduction in capital cost, long-term operations and maintenance, and remedial timeframes.
Allan Horneman, PhD, leads the Arcadis community of practice for sedimentary rock and matrix diffusion. He has 15 years of experience in hydrogeology, geochemistry, contaminated site characterization and remediation. He is engaged in multiple North American and European fractured rock projects involving metals, petroleum hydrocarbons, chlorinated volatile organic compounds and emerging contaminants such as poly- and perfluoralkyl substances (PFAS) and 1,4-dioxane.
We have learned a lot over 20 years of in situ groundwater remediation. Solvent and hydrocarbon plumes, large and small, can be successfully addressed when a well-honed conceptual site model that incorporates high-resolution hydrostratigraphic data and the principles of remediation hydraulics underpins your remediation approach and system design.

Applying this framework to your solvent plume results in the predictable and methodical transformation of solvent and hydrocarbon constituents — ultimately, to innocuous end products. However, the treatment of metals and metalloids is a bit different. They cannot be destroyed, and their in situ treatment relies on transforming their solubility, and hence mobility, in soil and groundwater systems. As such, long-term stability and the permanence of the treatment often require long-term alteration of the geochemical environment, controlling solubility and mobility.

Can your toolbox, now fully outfitted to tackle even the most recalcitrant solvent plumes, be used in a similar manner for metals or are you missing something fundamental? Is there something further you must understand before advancing an in situ strategy for metals and radionuclides in groundwater — something so critical that not knowing it will doom you to failure if it is missing? We have found that, when information on speciation is missing, in situ metals remediation projects often fail and sometimes catastrophically.

**ARSENIC – A REASON TO SHARPEN THE AXE**

Speciation in its truest sense is the chemical form of the metal, metalloid or radionuclide in the environmental media of interest. For example, arsenic in groundwater doesn’t exist as a simple pentavalent cation (\(\text{As}^{5+}\)), but rather as the arsenate oxyanion (depending upon pH, either \(\text{H}_2\text{AsO}_4^-\) or \(\text{HAsO}_4^{2-}\)).
or as arsenite ($\text{H}_3\text{AsO}_3$). In the case of arsenic, pH and oxidation state [As(III) or As(V)] matter, and a total of eight different forms of the arsenic oxyanion are possible in aqueous systems. Each behaves differently in terms of sorption to soil surfaces and, therefore, groundwater transport and attenuation. Other, more-exotic forms of arsenic may be present in highly anaerobic, sulfidic environments (e.g., arsenic sulfides in the form of thioarsenic complexes) that may be persistent and resistant to precipitation from groundwater. Arsenic removal from groundwater is highly dependent on which form the arsenic takes; arsenate is much more likely to be removed from solution through precipitation, coprecipitation and sorption than is arsenite or any of the thioarsenic forms. An investigation of the speciation of arsenic is often viewed as an esoteric matter, but if one truly is seeking to understand the mechanisms that control arsenic mobilization (including anthropogenic arsenic from a source material or geogenic arsenic from soil) and arsenic in situ immobilization (via precipitation, coprecipitation or sorption), then understanding speciation is essential.

Arsenic speciation must be unraveled for strategies that rely upon monitored natural attenuation, as well as for passive (permeable reactive barrier) and enhanced attenuation (injection-based in situ) approaches. Speciation often provides the key piece of information necessary for validating or refuting the conceptual site model and efficacy of the treatment approach. In the example noted above, formation of soluble thioarsenic species under reducing conditions represents an impediment to arsenic immobilization in geochemical environments where insoluble arsenic sulfide minerals (orpiment and realgar) may be assumed to dominate. In the research world, this has become a classic example, as epitomized by the work at the Rifle, Colorado, UMTRA site. At this site, microbial reduction strategies for immobilization of uranium under iron- and sulfate-reducing conditions have been shown to generate thioarsenic species upon release of arsenic originally associated with metal oxides. This has resulted in secondary byproducts that do not attenuate as expected outside the immediate treatment zone. Although such secondary geochemical processes present real challenges for in situ treatment, the possibilities are too often ignored in consulting and industry.

In our work, elucidation of speciation has resulted in even more-extreme modifications to the conceptual site model. At a number of sites where we have employed advanced analytical methods for speciation, we discovered a flaw in standard EPA methods for determining arsenic in soil and groundwater: an interference caused by the presence of rare earth elements (lanthanides) resulted in a false-positive detection of arsenic across a site. This error would have never been discovered if we had decided not to dive deeper into understanding arsenic speciation at these sites.

We posit that, because of reliance on these standard analytical methods, there are many other sites where the understanding of arsenic impacts not only may be incomplete, but also may paint a much worse picture than reality. The good
news is that the rationale for speciation when dealing with arsenic is becoming more widely accepted. This is evidenced by the multitude of commercial analytical laboratories and analytical methods for quantifying arsenic speciation. While deduction of aqueous speciation using hydride generation atomic-absorption spectroscopy (via EPA method 1632) has been around for several years, more direct, reliable and elucidative methods that rely on coupling ion chromatography with inductively coupled plasma mass spectrometry are exhibiting increased use.

DON’T IGNORE THE HUMBLE CATIONS — THINGS MAY NOT BE SO SIMPLE

However, even seemingly simple divalent cations, such as lead and nickel, can require a closer look into speciation. Such “simple” systems can present an even greater challenge than “complex” ones when analytical methods are not readily available for determining speciation. Our experience with nickel at plating facilities, and in catalyst manufacturing, shows that its reputation as either being associated with particulates (and detected mainly in the “total” unfiltered groundwater fraction) or dissolved is oversimplified. Nickel can be present in groundwater in colloidal form (e.g., as a pure-phase nanoparticulate or as a sorption complex on organic or inorganic colloids) or as a strong metal-ligand complex (in association with a chelating agent), both of which may pass through a 0.45-micron filter and therefore be considered “dissolved” by conventional analytical methods. Figure 1 provides an example of how nickel speciation can change profoundly in the presence of citrate, an organic chelating agent.

Colloids and complexes were all the rage in PhD theses a decade ago, and they have made the cover of journals such as ES&T on numerous occasions, but such forms are still generally ignored by practitioner community consultants, site environmental managers and regulators. Why? Because identifying these forms of metals in environmental systems is difficult and goes beyond the capabilities of standard EPA methods. In our work, elucidation of speciation has required the development of creative methods. For example, we have used ligand-competition approaches using ion-exchange resins to identify complexed nickel in groundwater systems. We find that conventional in situ treatment strategies that rely upon nickel sulfide formation, or sorption of nickel to iron, do not work when nickel is complexed. A new approach
is needed for complexed or colloidal nickel — focused first on destroying the complex, followed by precipitation.

Lead in groundwater, particularly when present in oxic conditions at neutral pH, serves as another classic example. Although lead can technically be highly soluble at neutral pH, particularly in the absence of sulfide, it nevertheless typically exhibits extremely low mobility in groundwater environments due to its tendency to adsorb strongly to organic matter and mineral surfaces (particularly metal oxyhydroxides). Accordingly, when lead is observed under these conditions, it is very often an early warning that atypical speciation (e.g., nanoparticulate formation or complexation) may be at play.

The chemistry of uranium in soil and groundwater systems absolutely requires that speciation be understood prior to attempting treatment, in both aboveground and in situ systems. It also further highlights the need for understanding speciation of a system as a whole, not just of the target analyte. Uranium is most often present as the uranyl cation (UO$_2^{2+}$) under oxic, acidic to neutral pH conditions in the absence of alkalinity. Most soil and groundwater systems have appreciable alkalinity, and uranyl forms a complex with carbonate such that a myriad of species form: \textit{UO}_2\textit{CO}_3^-, \textit{UO}_2\textit{(CO}_3^2)^2-, \textit{UO}_2\textit{(CO}_3^2)^4-. Uranium can also form ternary complexes such as Ca\textit{UO}_2\textit{(CO}_3^2). The various uranium carbonates that can form have differing thermodynamic stabilities; an understanding of speciation is critical for the success of in situ strategies focused on precipitating uranium through reductive precipitation [with transformation of uranyl to U(IV)] or formation of low-solubility uranium phosphate minerals.

**NOW GO FORTH AND SPECIATE**

Here we make a case for speciation as a proactive component of the conceptual site model (i.e., a key parameter that informs site strategy). In most cases today, speciation is a reactive component of the conceptual site model (i.e., an avenue for exploration only after valuable time and money are spent pursuing ineffective treatment strategies). We argue that the time and expense is worthwhile, lest you “break your pick” on the implementation of a potentially unsuccessful and costly in situ treatment strategy for a metal, metalloid or radionuclide plume. Water chemistry matters when it comes to formulating approaches for these inorganic contaminants, especially approaches that avoid pumping massive amounts of water just to clean up relatively low concentrations of metals. In situ strategies avoid unnecessary contamination of clean water, as well as the generation of aboveground treatment residuals that then must be managed in landfills and waste repositories.

The future of remediation of inorganic contaminants is following closely on the heels of progress made with in situ remediation of solvents. We look forward to the day when all in situ strategies for inorganics are rooted in a well-formulated conceptual site model that incorporates detailed speciation information — and when treatment endpoints are verified using this important tool!
Speciation often provides the key piece of information necessary for validating or refuting the conceptual site model and efficacy of the treatment approach.
About the authors

**Author**

**JEFF GILLOW, PhD**

Jeff Gillow, PhD, has 26 years of experience in environmental science, including 17 years at the U.S. Department of Energy, researching metal and radionuclide mobility in the environment. He provides expertise in the assessment, evaluation and remediation of metals in soil and groundwater systems, with a recent focus on arsenic and other oxyanions for industrial and mining clients.

**Co-Author**

**MICHAEL HAY, PhD**

Michael Hay, PhD, is a Senior Geochemist with 14 years of experience in environmental chemistry. He specializes in the in situ remediation of groundwater impacted with metals and inorganics, with a focus on geochemical and reactive transport modeling. Prior to joining Arcadis, he served as a research hydrologist for the U.S. Geological Survey, studying metals transport at mining- and milling-impacted sites.
Environmental remediation is always changing: it evolves with technological advances, changes in regulatory settings, the current financial climate and political drivers. A company that is aware of these developments and operates in a flexible manner — one that isn’t afraid to work outside the norm and adjust the way environmental remediation projects are managed — is best qualified to deliver solutions relevant to today’s issues and your challenges, regardless of size, scale and complexity.

Arcadis believes that the future of remediation lies in challenging conventional thinking and the status quo. We understand that:

• Expertise in large-plume and complex high-cost sites can be leveraged to develop cost-effective strategies for smaller, less-complicated sites.

• Remedial strategies must match business objectives, and solutions must account for both financial and environmental drivers. In some situations, achieving unrestricted closure or meeting conservative clean-up goals may not make financial sense, while it may be a priority in others.

• Innovation lies not just in developing new technologies, suitable for the most complex or highest-cost sites, but in generating adaptive and original approaches to problems of any size.

There is no one-size-fits-all approach to success in this changing environment. However, adaptive, flexible remedial solutions that match your site’s budget, scale and risk profile can be achieved by:

• Harvesting Knowledge: Distilling the knowledge gained through a broad portfolio of sites into lessons learned and best practices that are
distributed to project teams through national technical networks.

- **Value Engineering**: Focusing strategic decision making while minimizing risk and long-term spending.
- **Partnering for Success**: Building on strengths and bringing in the best teams while accounting for continuity of project management and maintaining existing positive relationships.

HARVESTING KNOWLEDGE

Arcadis’ history of technical excellence, and our emphasis on the development of technical communities and dedicated technical career paths, enables us to keep pace with changing drivers and technological developments. In a climate where many sites require a simplified technical approach, we succeed by leveraging our technical experts and effectively communicating knowledge through established national and international networks — efficiently adapting traditional and cutting-edge approaches to solve any problem.

"If I have seen further, it is by standing on the shoulders of giants."
— Issac Newton

Through this distribution of knowledge and targeted training, we realize project efficiencies and apply lessons learned on projects across the board.

We communicate insights to enhance and expand our understanding of a technology and its application. We also develop procedures and best practices to streamline processes and realize cost and implementation efficiencies without sacrificing quality or reducing credibility with regulators and stakeholders.

Arcadis recently undertook a review of a portfolio of approximately 90 retail gas stations in monitored natural attenuation (MNA). Our objective was to determine if MNA was the most effective remedy, if MNA managed risk adequately or if some form of active remediation was required, or if additional data were required to adequately assess MNA (Figure 1). If continuing MNA was the best approach, it was necessary to optimize the program and reduce overall costs.

To complete the program, Arcadis used technical skills developed through years of experience with natural attenuation assessments and monitoring program optimization to create a streamlined, efficient and consistent screening process. We trained a team of internal staff and two external stakeholders and completed the screening of the 90 sites within a three-month period at a fraction of initial expected costs. This process, training and knowledge have been disseminated through our technical networks and are now an integral part of our toolbox for similar sites.

Figure 1. Strong knowledge management creates efficiency.
VALUE ENGINEERING

Value engineering is a process and set of tools designed to reduce the financial and schedule-related risks associated with long-term projects through the development of efficient, effective and sustainable remedies that capture project lifecycle savings (Figure 2). Value engineering may be applied prior to establishing a remedy or used effectively throughout the lifecycle to review ongoing projects and identify modifications to operating systems where appropriate. Value engineering is relevant for a single project, a portion of a project or consistently throughout a portfolio of projects. The process and level of effort can be tailored to match your objectives.

“Things should be made as simple as possible, but not any simpler.” — Albert Einstein

The primary purpose of any value engineering work is to provide data to inform strategic decision making. Typically, these data relate to reducing project lifecycle costs while minimizing risk. Arcadis applies value engineering to:

- Establish relevant and realistic project endpoints that meet business objectives (which may not always be closure) and identify alternative endpoints as necessary.
- Evaluate and optimize remedial systems. We consider new site characterization tools and remedial technologies as a route to cost effectively modify ongoing response actions.
- Develop metrics and a set of tools to support technical, proactive decision making.
- Further standardize methods and train and empower all stakeholders in their use and applications.

Figure 2. Expedite effective decision making and reduce project life cycle costs.

Typical project remedy-risk profiles are more likely to exceed time and cost estimates than to be completed below estimates. The Value Engineering process is designed to reduce both the Probable Future Cost and the Probable High Future Cost.
PORTFOLIO-WIDE SAVINGS

Arcadis developed a value engineering approach for rail-sector client that addressed 63 sites with a total annual operating cost of $5.9 million. Impacts at these sites ranged in size, complexity and contaminants and employed a range of in situ remedial solutions, including air sparge, soil vapor extraction, bioventing, multiphase extraction, groundwater extraction, enhanced biodegradation, chemical oxidation and natural attenuation.

Each site went through a structured, streamlined and consistent review process, which included the development of performance assessment dashboards and the evaluation of remedial efficiencies against key metrics in the context of individual site objectives. The outcome for each site was a determination of remedial efficiency and suggestions for improving efficiency and reaching goals with a lower risk of overruns. Value engineering resulted in short-term cost savings on the order of $10 million for the 63 sites, with long-term life-cycle costs savings expected to total $20 million. The cost-to-complete assessment averaged 30-35% of the annual spending for each site and was easily outgained by the short-term savings.

AN OPPORTUNITY TO INNOVATE

Arcadis used value engineering to optimize an existing groundwater treatment system at a National Priorities List site where six groundwater plumes containing explosive materials covered more than 5,000 acres and extended up to two miles from the source.

The optimized remedy utilized existing infrastructure and a flexible pumping approach, targeting hotspots and mitigating plume migration. The key to our success was the development of a remedy management framework for the site based on risk and guided by standard statistical procedures well documented in regulatory guidance. Using this framework, Arcadis developed a series of decision trees to trigger and guide remedy optimization, all of which were reproducible, defensible and agreed upon by stakeholders. The remedy management framework identified areas of the plume that required immediate attention and prioritized treatment in those areas over portions of the plume that were lower risk or had favorable concentration trends. Our efforts focused on areas of the plume where remedial spending gave the highest return on investment and on modifying our approach to these areas through time as the remedy.
progressed. This focused, flexible pumping approach with continuous optimization is expected to save up to $35 million over the lifespan of the project, eliminating $15 million in capital expenditure for proposed additional treatment infrastructure and reducing the timeframes over which active pumping is expected by almost 20 years.

PARTNERING FOR SUCCESS

As the remediation market continues to develop, we are noticing an increasing expectation and need to work within partnerships with multiple consultants, with each lending expertise to provide the best value possible. This is a shift from traditional thinking, where consulting firms tended to form partnerships with non-competing entities, such as universities or research organizations. However, our objective remains the same: to efficiently and cost effectively achieve your goals (Figure 3).

COLLABORATION BRINGS STRENGTH AND SUCCESS

When one of our competitors realized they needed additional technical expertise at a high-profile site in Boston, they reached out to Arcadis. The goal was to achieve a remedy in place and site-specific clean-up objectives within a specified amount of time to facilitate a complex $100 million property sale.

Our partnership maximized the strengths of both consultants without disrupting existing, positive working relationships. Our competitor was responsible for investigation, field work and project management, while we used existing data to negotiate and select the remediation strategy to design, install and operate remedial systems for a mixed-contaminant plume. Together, we met remedial targets in less than a year of operation that allowed the sale to move ahead, while maintaining and exceeding health and safety and quality standards for the project.

ADAPTATION IS KEY

Much of the remediation industry is focused on developing solutions for large plumes, complex hydraulic conditions, and new and emerging contaminants. While these are important issues, these types of sites represent a small portion of all environmental challenges. It is critical that we remain focused on ways we can adapt proven and innovative solutions to suit all sites, regardless of size or complexity, to provide flexible remedial solutions that match your site’s budget, scale and risk profile and meet your objectives.

We succeed by efficiently adapting traditional and cutting-edge approaches to solve any problem.
About the authors

Author
FRED PAYNE, PhD
Fred Payne, PhD, is a Senior Vice President and Chief Scientist for Arcadis North America. He has nearly 40 years of environmental industry experience, encompassing a broad range of natural resource, wastewater, stormwater and hazardous waste management. He is a leader in the design and development of in situ reactive zone technologies for aquifer restoration and is the inventor of six patented technologies used in the treatment of contaminated soils and groundwater. Payne is a global leader in the ongoing reformulation of remediation hydrogeology, resulting in more effective site characterization, more cost-effective remediation and more sensible regulation.

Co-Author
ELIZABETH COHEN, PhD
Elizabeth Cohen, PhD, has 14 years of experience in geochemistry, site investigation, in situ remedial design and statistical assessment. Her work promotes efficiencies that optimize long-term and performance monitoring programs. In 2014, Cohen was named one of Engineering News-Record’s (ENR) Top 20 Environmental Engineers under 40 for contributions to technical staff development and training.
In terms of groundwater (and contaminant) movement and remediation, karst aquifers are in a league of their own. Groundwater flow in these systems does not follow Darcy’s Law, the fundamental equation that describes the relatively slow movement of fluid through porous media. Furthermore, data from monitoring wells alone cannot definitively characterize groundwater flow directions and rates; nor can they adequately delineate the extent of groundwater contamination. In addition, at the typical site scale, groundwater flow directions and rates cannot be reasonably predicted using computer models. Worse yet, computer models that can simulate contaminant transport in karst aquifers do not even exist.

You may be thinking, “I am glad that none of my sites are karst sites”, but beware: karst is not rare. In fact, the United States Geological Survey estimates that potential karst-forming bedrock is beneath 20% of the United States. This means that, on average, one in five contaminated sites in the U.S. may be underlain by karst-forming rocks!

Despite the significant challenges presented above, contaminant problems in karst aquifers are tractable — that is, contaminated karst sites can be properly understood and managed. That is welcome news. In our experience, this can be done only if the project team possesses bona fide karst expertise, and such expertise in the environmental community is rare. Put simply, your karst site can’t be properly addressed if your team doesn’t understand how karst works.
HOW KARST WORKS

The most important factor for understanding the movement of fluids and contaminants through a karst aquifer is the unique permeability structure of these aquifers. Karst aquifers begin as fractured rock aquifers, where much of the fluid flow occurs through the secondary porosity—the fracture network—of the rock. Inevitably, certain pathways are less resistive to flow than others and are preferentially widened by dissolution over time and distance. Wider pathways can accommodate more flow. The end result of the dissolution process is an integrated network of solution-widened pathways (tertiary porosity) that is organized much like surface streams—where small tributaries join together to form larger and larger drains. These “conduit networks” drain the vast majority of the groundwater moving through the aquifer, with each network ultimately discharging to one, or several, springs.

The unique architecture of karst aquifers presents significant challenges:

- Conduit networks occupy only a tiny fraction of the volume of the bedrock aquifer, and their distribution is not predictable. Furthermore, unless they are large enough to be entered, they cannot be explicitly mapped.
- Lack of a detailed map of the subterranean drainage network means that monitoring wells are installed in a hit-or-miss fashion, and the odds of a well tapping into the drainage network are poor. The implications of this challenge are illustrated on Figure 1.
- A fraction of the solution porosity is often not well integrated into the active drainage network and may be clogged with sediment washed into the bedrock from above. This low-permeability porosity can provide ample, long-term storage capacity for contaminants.
- At many karst sites, the solution porosity facilitates rapid infiltration of stormwater, which can greatly alter groundwater and contaminant transport conditions for periods ranging from hours to weeks. In fact, in some aquifers, large quantities of sediment are flushed through the bedrock in response to storms—a transport phenomenon that is unique to karst.

Figure 1. Challenges of characterizing karst groundwater movement with wells. 
A) In most settings, groundwater is inferred to move toward and discharge to surface streams. B) One or more monitoring wells are typically installed at locations inferred to be upgradient and downgradient of the contaminant source area. C) These inferences aren’t valid in karst, where a conduit network greatly complicates the flow field. In this example, none of the monitoring wells would have actually been monitoring the groundwater intended. Impacted groundwater is shown in purple.
CHARACTERIZING KARST AQUIFERS

The movement of groundwater and contaminants through karst aquifers is complex. In addition, some of our best tools for characterizing contaminated groundwater (for example, monitoring wells and potentiometric maps) are less powerful in karst. Given these realities, a successful characterization approach entails:

1. Forming a project team that includes individuals with karst expertise.
2. Developing a robust, karst-specific conceptual site model to guide data collection. Salient attributes of karst flow systems vary considerably across the globe. One size does not fit all!
3. Focusing efforts on sufficiently identifying risks posed to human health and the environment.
4. Working closely with stakeholders early on to inform them about the unique challenges that karst brings. Karst-savvy stakeholders understand why certain characterization approaches need to be modified for karst.
5. Limiting the number of monitoring wells. Dye-tracing studies should be conducted to identify wells in communication with important karst features, confirm the springs where site groundwater discharges and measure groundwater flow velocities.
6. Focusing attention on those wells and springs traced to the site. It is important to collect samples during base flow and storm flow conditions to obtain a thorough understanding of contaminant transport.

SUCCESSFULLY MANAGING KARST AQUIFERS

Because remediation costs greatly outweigh characterization costs, stakeholders must carefully weigh remedial objectives, strategies and technical approaches before proceeding. Compared to other geologic settings, the science of remediating karst aquifers is immature. It appears that, as an industry, we have understandably saved the most-challenging sites for last.

Of course, this doesn’t mean that you should simply throw in the towel. So how do you deal with a site where the technology to remediate it to prescribed regulatory endpoints is unproven or may not even exist? These are considerable challenges; however, we at Arcadis are not only convinced, but have proven, that contaminated karst aquifers can be properly managed, and remedial objectives that protect human health and the environment can be achieved. The operative term here is managed.
There are situations where, despite the immature nature of karst remediation, active remediation is warranted and becomes an integral element in a site closure strategy. There are also situations where remediation is not practicable, but where risks posed by the site can be properly managed, allowing for no active remediation or even closure.

The four keys to successfully managing a contaminated karst site are:

1. Focusing remedial strategies on reducing the risks to acceptable levels.
2. Building on the relationship developed with stakeholders, explaining why certain remedial approaches are inappropriate and working together to develop and support realistic and achievable remedial objectives.
3. Conducting relevant performance and, if needed, long-term monitoring. When the quality of bedrock groundwater has been impacted, it is critical to understand what effect the remedial action is having on groundwater quality. Even if it is determined that remediation of bedrock groundwater is impracticable, long-term monitoring of groundwater quality is often required.

Here are two examples where Arcadis developed karst-based remedial or closure strategies that resulted in favorable outcomes for our clients.

WOOD-TREATING FACILITY, VALLEY AND RIDGE PROVINCE, VIRGINIA, USA

This site is situated on the floor of a large river valley. Operations conducted over decades resulted in inadvertent releases of creosote, a dense nonaqueous-phase liquid (DNAPL), to the subsurface. The geology generally consists of 15 feet of alluvial sediments overlying a mature karst aquifer. While conducting a RCRA Facility Investigation, the Arcadis team identified creosote in the bedrock to a depth of nearly 100 feet. Groundwater quality at some locations was found to be impacted with compounds dissolved from the creosote. A tracer study found that groundwater flow rates were either very low or that site groundwater was greatly diluted as it moved toward the river that drains the valley. In addition, tracer dye introduced at the site was not detected at a municipal wellfield located several miles down-valley. These findings helped round out the site characterization, but we suspected that tracing could also play a role in the final remedy.

A number of remedial actions were performed, consisting mainly of targeted removal and capping activities. Working closely with stakeholders, we reached agreement that it was impracticable to remediate the creosote in the bedrock. A risk assessment demonstrated that the bedrock groundwater posed no unacceptable exposure risk to humans or the environment. However, a valid concern arose regarding the nature and scope of long-term groundwater monitoring — specifically, we understood that the existing monitoring-well network alone might not reliably detect changes.
in groundwater movement patterns over time. Regulatory stakeholders required more assurance. Arcadis explained that installing additional monitoring wells was not the answer — in this complicated karst aquifer, installing several hundred thousand dollars’ worth of new monitoring wells was not going to appreciably decrease the monitoring uncertainty. Rather, Arcadis proposed a novel, yet more appropriate, approach to monitoring groundwater for changes in established flow patterns: dye tracing. The logic was simple: groundwater flow patterns at the site were characterized using a combination of wells and tracing, so why couldn’t the same be used for long-term monitoring? The benefits of adding periodic tracing to help confirm flow patterns (in this case, once every five years) were multiple: more certainty, a reduction in the size of the monitoring well network and no new (and costly) bedrock wells to maintain (and ultimately decommission). Furthermore, dye tracing is a simple concept that is easily understood and accepted by the public. To Arcadis, integrating periodic tracing into a RCRA Corrective Action Plan for a site situated in karst terrane is commonsense; to the environmental industry, we believe it is a first. And the estimated cost of each trace? Less than the cost of installing one new bedrock monitoring well!

MANUFACTURING FACILITY, PENNYROYAL SINKHOLE PLAIN, KENTUCKY, USA

At this manufacturing facility, a polychlorinated biphenyl- (PCB) based hydraulic fluid (a DNAPL) was inadvertently released to the environment. The nature and extent of contamination in bedrock was characterized using a combination of monitoring wells and dye tracing. The karst aquifer was found to be shallow and relatively thin. The tracing work identified three adjacent springs located a few thousand feet from the site that were discharging to an urban stream that was running on bedrock. Sediments and biota in the stream were impacted by PCBs. In addition, the characterization confirmed that DNAPL was present in the bedrock and had migrated offsite.

When streamflow was bypassed for sediment remediation, DNAPL was discovered seeping from the karst bedrock into the stream channel.
Arcadis worked closely with the Kentucky Department of Environmental Protection (KDEP) to develop and implement a Corrective Action Plan. Groundwater-related elements of that plan consisted of:

1. Collecting impacted groundwater and DNAPL from the downgradient edge of the site, mitigating offsite movement. This was accomplished through a specially designed collection trench.

2. Reducing DNAPL saturations and the potential for mobility offsite. This was accomplished in two ways:
   a. Removing DNAPL accumulating in the three offsite wells where it was encountered, while in turn recognizing that identifying every location in the complicated karstic aquifer where DNAPL might be present was technically impracticable.
   b. Constructing and operating DNAPL/groundwater collection systems beneath two sections of the urban stream where DNAPL was found to be discharging to the stream from the bedrock.
   c. Mitigating PCB loading to the stream. This was accomplished by capturing and treating flow from the three springs shown by tracing to be draining the site.

Arcadis also worked with KDEP to establish a long-term groundwater and surface-water monitoring program to assess the effectiveness of the remedy. During that process, the inherent challenges posed by monitoring wells were mutually recognized. As such, the number of monitoring wells comprising the long-term program was reduced from 54 to 17, and the sampling frequency was reduced from quarterly to annually.

It was agreed that the groundwater dataset would be supplemented with surface-water samples to gauge remedial effectiveness. Perhaps the best gauge of effectiveness, however, was continuing the program of fish monitoring that had been an ongoing element of the site characterization. It was recognized that, in this karst setting, where uncertainties were somewhat greater that at non-karst sites, PCB concentrations in fish that spent their entire lives in the stream that received groundwater from the karst aquifer would be the best measure of remedial effectiveness.

Construction of the groundwater remedy was completed in late 2005, and the results are convincing. Since remedy completion, PCB concentrations in surface water have declined dramatically.

Perhaps more importantly, the concentration of PCBs in fish has followed suit (see Figure 2). Given these results, the frequency of fish monitoring was reduced in 2013 from annual to biennial.
With the groundwater and surface-water programs now in long-term operation, maintenance and monitoring, this project is an excellent example of how an incredibly complex DNAPL-in-karst site, where groundwater clean-up to maximum contaminant levels is truly technically impracticable, can be properly managed through employment of karst-specific knowledge and strategy formulation.

In closing, it is clear that karst aquifers can’t be understood and addressed by following the standard playbook that the environmental industry has honed over the past half century. Worse yet, we have seen well-intentioned practitioners lead sites through the environmental “system” without recognizing that karst is at play. This fatal flaw greatly increases the chances that risks posed by contamination won’t be properly understood. No one wants to make important and costly decisions based on incomplete or faulty information — the potential impacts to human health and the environment are just too high.

Like any other complicated challenge, the best way to hedge against uncertainty and maximize return on investment is to engage the right expertise. A karst expert can help you sift through the chaff, understand what kind of flow system you are dealing with and develop a coherent strategy that supports the sound decision making needed to achieve realistic — and reasonable — outcomes. Contaminated sites in karst terrane have a reputation for leading to protracted studies and less-than-desirable remedial outcomes. We are pleased to say that this does not have to be the case.

Karst-specific knowledge and strategy formulation is the key to success.
About the author

**Author**

**KEITH WHITE, PG**

Keith White, PG, has 28 years of experience as a hydrogeologist. He leads the Arcadis North America karst practice and is responsible for seeing that karst sites are properly identified, characterized and remediated. He has developed and delivered short courses on karst contaminant hydrogeology for the National Ground Water Association and the Alabama Department of Environmental Management. He presented on this topic at Alabama’s 12th Annual Groundwater Conference. White is an active member of the Association of Engineering Geologists’ Groundwater/Karst Technical Working Group and the Geological Society of America’s Karst Division.
Innovation as a Mindset: Achieving Remediation Endpoints in a Back Diffusion World

Decades of site remediation have been highly successful in characterizing, remediating and bringing thousands of contaminated sites to closure. Upon close inspection, however, it is apparent that a large portion of closed or delisted sites were those with limited contaminant mass, naturally degradable contaminants and simple hydrogeologic conditions. As a result, we’re currently left with some of the most complex sites, as well as new challenges that have sprung up along the way.

**BUT THERE’S HOPE.**

Hard-earned technical knowledge acquired through our successes, trials and failures has driven innovation that arms responsible parties, remediation practitioners and regulators with the tools to finally look with clear eyes on the challenges that remain. We understand that more than 90% of contamination moves through less than 10% of our aquifers. We have reliable methods to leverage natural microbial ecology for some of our most-effective treatment regimens. We have tools to directly target and destroy recalcitrant nonaqueous-phase liquids (NAPLs) without excavation. We apply new characterization techniques with traditional hydrogeologic principles to set realistic expectations and guide adaptive designs. We now move through the right remedies with the right benchmarks and cost focus, and with a high degree of success. Above all, we know that detailed questions need both detailed answers and the correct interpretation.

More than 30 years ago, our industry began to seriously address the challenge of chlorinated solvent source zones and their associated plumes. It was an “emerging” contaminant at the time, and it took more than 10 years for us to identify that enhanced solvent bioremediation strategies were feasible, and another decade for these remedies to become “conventional.”
Concurrently, investigation techniques evolved to provide increased resolution to understand solvent source zone architecture, and these have fostered a renaissance in hydrogeology to enable far greater insights into contaminant flux profiles and means to better achieve aggressive clean-up in situ. These insights have allowed us to open the black box and leave us well positioned to address even more recalcitrant contaminants, like 1,4-dioxane and poly-/perfluoroalkyl substances (PFAS), that have sprung up along the way.

All of the above have yielded two key concepts that serve as the backbone of next-generation remedies:

1. Partial reductions in contaminant source mass can drive significant reductions in groundwater concentrations (Figure 1).
2. Large portions of our aquifers are relatively clean, and these zones provide significant natural assimilation capacity to deal with the challenges of back diffusion (Figure 2).

The above concepts have fed a dichotomy in site remediation, with levels of treatment aggressiveness determined by the value of the contaminated resource. Contamination in non-potable aquifers and without exposure risk can be effectively pointed toward alternative clean-up standards and acceptable natural attenuation programs. In these cases, flux-based remediation and orders-of-magnitude reduction are reasonable strategies and enable effective long-term liability management. Comparatively, where required, these principles also enable us to achieve low drinking water standards in order to return potable supply aquifers and surface-water bodies to beneficial re-use. The awareness that only minor portions of an aquifer contribute to contaminant transport allows us to:

- Develop better monitoring strategies focused on the mass that moves.
- Deploy highly focused remediation strategies at increased certainty and lower cost.
- Implement dynamic remedies tailored to maximize mass recovery or destruction at all phases of the remedy life-cycle.
- Effectively leverage the assimilative capacity of the aquifer to support treatment and manage long-term risk.

We now move through the right remedies with the right benchmarks and cost focus, and a high degree of success.

**Figure 1.** Sample relationships between source mass reduction (i.e., NAPL) and observed groundwater concentration or mass flux reduction. **A)** Demonstrates that minor reduction in source mass can achieve significant groundwater concentration declines. **B)** Demonstrates proportional source mass removal and concentration decline. **C)** Demonstrates cases where source removal should be completed to reduce groundwater concentrations. (Adapted from Falta et al. 2005 and Brusseau 2008)
Where drinking water clean-up goals are required, we cannot be discouraged by overly simplistic back diffusion calculations that suggests restoration is impossible. True, the challenge is great — particularly in fractured rock settings — but we have successfully restored contaminated plumes that are miles in length for drinking water use (Figure 3). As witnessed recently in California, where drought conditions and demand from residential, commercial and agricultural users have placed a premium on clean water supplies, the demand for our natural resources will always maintain a high bar for site remediation — and this trend will only increase as our ever-growing population continues to need accessible, inexpensive water. We must be committed to overcoming the remaining challenges.

**INNOVATION AS A MINDSET**

In an industry where risk and cost serve as yin and yang, we strike a constant balance between restoration and the protection of receptors with minimizing costs. This has never been more important than today, where market forces and financial pressures require innovative solutions that will be successful within defined fiscal limits. Arcadis has always led the industry in this regard, having invented the guaranteed remediation concept and performance-based remediation. Now widely adopted by many federal and private remediation programs, these contracting vehicles place our own “skin in the game,” allow us to double down on our technical knowledge and ability to deliver and carry restoration programs through the clean-up process to closure. This concept is not just applicable to fixed-price remediation, but is a philosophy that permeates Arcadis and drives us to make remedy decisions with our clients’ best interests in mind. It fosters creative remedy development and drives innovative solutions for each individual site.

A retrospective review of past clean-up performance often indicates that remedies fail due to inadequate characterization and poor conceptual site models (CSM), which result in treatment approaches and designs that are inadequate, fall behind the expected pace of performance, or require long-term operation and maintenance. It is the ongoing operation of these remedies that has resulted in the pervasive industry pessimism that more-stringent maximum contaminant levels (MCLs) cannot be achieved.

As part of any cleanup, we need to learn from both our successes and failures and be willing to constantly modify and
update our CSMs — we simply must be unburdened by allegiance to historical precedent or previous interpretation and overturn incorrect understandings when new data demand it. This is a real challenge, as sites that have trudged through decades of characterization and remediation likely need to be reassessed and re-evaluated through the view of new characterization tools and with new vision. While not every site is “complex,” most sites require unique attention. In order to achieve earlier clean-up off-ramps or stringent clean-up goals, predictive foresight is required to plan and implement remedy-train solutions that can respond to the site data and allow best use of remedial capital. We need to expect that our remedies will change over the course of operation, driven by actual site data to continuously sharpen the approach.

Smart characterization yields smarter remediation. We identify source mass, its distribution and the primary transport pathways that contribute to the majority of mass flux. This information feeds remedies that address contaminants in high- and low-permeability lithologies using combinations of innovative and conventional technologies. Where clean closure is required, this information allows adoption of remedy-train remediation programs with specific technologies to address both advective and diffuse contamination. But solid remedy selection and design are not enough. Achieving clean closure endpoints requires a steadfast focus throughout the course of remediation to continually refine and focus operations (Figure 4). This process, dynamic remedial implementation, is ideally suited to: 1) addressing contaminants migrating via advective transport; 2) maximizing diffusion gradients between advective and diffusive lithologic strata; and 3) eliminating remedial stagnation.

We strike a constant balance between restoration and the protection of receptors with minimizing costs.

Figure 3. The closure of the 3-mile Reese AFB TCE plume, with groundwater returned to potable use following eight years of in situ bioremediation and dynamic groundwater recirculation.
Predictive foresight is required.

**IT’S A TIME FOR OPTIMISM**

Our technical tools will continue to improve, and the regulatory landscape will continue to evolve. These developments will have a bearing on how we approach NAPLs, large plumes and emerging contaminants. The widespread pessimism surrounding back diffusion isn’t a reason to give up, because diffusion mechanisms provided by an aquifer’s assimilation capacity can actually *aid* the process of achieving stringent MCLs. The most fundamental skill is just knowing the difference: deploy the right remedy, pay attention and transition the remedy to the next phase at the right time.

Advancements in characterization and remediation are supporting the real possibility of large-scale restoration at a time when clean groundwater is becoming our most important natural resource. Achieving this is not accomplished by a new characterization tool or new remediation technology; it’s shepherded by the right people applying the right information for the best outcome.
Matthew Schnobrich is the Director of Remediation for Arcadis North America. He has more than 15 years of experience in the design, implementation and completion of a variety of remediation technologies in addition to the characterization, pilot testing and strategy behind their development. He continues to develop innovative approaches and remedial solutions to enhance existing technologies for future implementation.
The group of chemicals known as PFAS (poly- and perfluoroalkyl substances) has come under increasing scientific and regulatory scrutiny in recent years as more is understood about their toxicity, their environmental persistence and their potential to bioaccumulate. PFAS are used in a wide range of industrial applications and commercial products due to their unique surface tension and levelling properties. They include stain repellents for textiles and carpeting, grease-proof paper, water- and oil-resistant coatings, and mist suppressants. PFAS are also major components of the class B (flammable liquid) firefighting foams known as aqueous film forming foam (AFFF) (Figure 1).

PFAS comprise both perfluorinated compounds, where all carbons are saturated with F atoms, and polyfluorinated compounds, where both fluorine-saturated carbons and carbons with hydrogen bonds are present. The critical importance of this to understanding the analytical challenge and environmental fate of PFAS is that polyfluorinated compounds are typically not detected by conventional commercial analytical methods, but slowly biotransform in the environment to produce extremely persistent perfluorinated compounds as dead-end daughter products. Tools to assess both polyfluorinated and perfluorinated compounds are needed to protect human health and the environment.

Two specific PFAS species have previously focused concern: perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). PFOS was added to Annex B of the Stockholm Convention in 2009 as a persistent organic pollutant because it
is persistent, bioaccumulative and toxic. PFOS and PFOA are, to date, the most commonly found and highest occurring PFAS in the environment and in tissues of wildlife species, but there are thousands of PFAS in total. PFOS and PFOA have reported human elimination half-lives of 5.4 and 3.8 years, respectively.

PFOS was a common ingredient of many 3M AFFF formulations, but there are also a number of polyfluorinated compounds found in AFFF formulations (Figure 1). These polyfluorinated AFFF-related species have been measured only semi-quantitatively in academic labs and cannot be commercially measured.

Polyfluorinated compounds are often referred to as precursors to the perfluorinated sulfonic acids and perfluorinated carboxylic acids, collectively referred to as perfluoroalkyl acids (PFAAs). PFAA precursors are so named because they transform slowly over time through abiotic and biological processes to the PFAAs. There is a natural “biological funneling” in which PFAA precursor compounds containing a range of perfluorinated alkyl chain lengths and functional groups aerobically biotransform to persistent PFAA products (Figure 2). PFAAs are known for their extreme non-reactivity. They have never been observed to biotransform, and they do not react with traditional oxidants like hydroxyl radical. The most common form of PFAA destruction is incineration at temperatures >900 °C.

**Figure 1.** Sample structures of polyfluorinated compounds found in AFFF formulations. Structures courtesy of “Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS” by Backe et al., 2013.

**SOLUTIONS FOR PFAS-IMPACTED SITES**

Assessing and remediating PFAS- and AFFF-impacted sites present many challenges. First, there are the typical challenges associated with remediating any site, such as correctly identifying the
source zone and the hydrostratigraphy that drives plume distribution. Second, measuring PFAS is more challenging than measuring other contaminants, such as 1,4-dioxane and trichlorethene, because commercial methods measure only a small portion of the relevant PFAS species that may be present. A significant portion of PFAS mass will be overlooked if only the PFAAs are measured, but constructing a comprehensive analytical method to measure each individual PFAS species is impractical to impossible. Finally, the options for remediation are extremely limited. Pump and treat with granular activated carbon (GAC) is the current best practice for treating groundwater, but significant amounts of GAC are needed to treat PFOS or PFOA, and GAC cannot effectively retain many short-chain PFAS species. Excavation of source soils and subsequent landfilling and incineration are extremely costly.

To address the uncommon challenges of remediating AFFF-impacted sites for PFAS, Arcadis is bringing unique solutions to site characterization and treatment. Arcadis has commercialized methods for measuring precursor mass (the total oxidizable precursor [TOP] assay) and total organic fluorine as surrogate metrics for quantifying the total PFAS mass in soil and groundwater. Arcadis is also the first to develop an in situ chemical method, Smart Combined In Situ Oxidation Reduction (ScisoR®), which is capable of mineralizing PFOS, PFOA and other PFAS. This technology has been demonstrated to degrade PFOS and PFOA in multiple treatability studies using AFFF-impacted site soil and groundwater.
CONCEPTUAL SITE MODEL DEVELOPMENT USING ADVANCED PFAS CHARACTERIZATION TOOLS

AFFF formulations are composed of many PFAS that are PFAA precursors (Figure 1). Unlike the PFAAs, these species are not strictly anionic because some contain multiple charges (zwitterionic) and some are positively charged (cationic). These zwitterionic, anionic and cationic PFAA precursors are currently undetected by conventional analytical tools and are thus termed “dark matter.” A significant mass of PFAA precursors in addition to the PFAAs have been detected in both AFFF-impacted soil and groundwater. A conceptual site model describing PFAS fate and transport at a firefighter training area is hypothesized and presented on Figure 3, and a description follows.

Cationic PFAA precursors (and some zwitterions) will be retained in the soils at the source zone via strongly binding ion exchange processes. The source zones will be anaerobic as a result of the presence of residual hydrocarbons used in firefighter training, so these strongly sorbing cationic precursors will biotransform very slowly to simpler, anionic PFAA precursors and PFAAs under these redox conditions. Anionic PFAAs and PFAA precursors will migrate away from the source as they enter the redox recharge zone where conditions become increasingly aerobic, thus promoting in situ generation of detectable PFAAs from the hidden anionic PFAA precursors. PFAAs will not break down further, and they will continue to migrate as a plume, with shorter-chain PFAAs generally migrating farther.

ADVANCED PFAS CHARACTERIZATION TOOLS

To characterize PFAS-impacted soils, sediments and groundwater, a fundamental concern is how to identify, quantitatively measure and assess the toxicology of this wide range of PFAS compounds and the range of recalcitrant PFAAs that they form.

Figure 3. Diagrammatic conceptual site model for an AFFF-impacted firefighter training area.

Figure 4. Range of PFAAs detected before and after application of TOP assay in A) groundwater and B) soil. Increases occurred from the oxidation of PFAA precursors.
The commercially available analytical method for measuring PFAS is EPA Method 537, which measures 14 PFAS, including PFOS and PFOA, with reporting limits ranging from 0.005 to 0.020 microgram per liter (µg/L). However, this method does not currently report the results for the full range of the more simple PFAAs, or many common fluorotelomer intermediates found at AFFF sites, or the many thousands of other PFAS that biotransform in the environment to produce PFAAs. 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 more PFAS compounds. Other, more advanced techniques and alternative approaches are now being developed and used commercially for the first time.

Arcadis is assessing a number of more comprehensive analytical techniques to assess PFAS concentrations on several sites impacted with AFFF:

- **Total Oxidizable Precursor (TOP) Assay**
  To measure the total mass of precursors to the PFAAs, the TOP assay was commercialized for analysis of soil and groundwater. Samples are oxidized with hydroxyl radical using thermal activation of persulfate under highly basic conditions. Precursors are converted to a mixture of PFAAs after treatment with TOP assay. Prepared samples are measured by LC-MS/MS before and after oxidation. The amount of PFAAs produced is roughly equivalent to the total

---

**Figure 5.** Correlations of organofluorine equivalent concentrations measured in AFFF-impacted groundwater between LC-MS/MS-Post TOP and AOF, PIGE and LC-MS/MSPost-TOP, and PIGE and AOF.
concentration of PFAA precursors in the sample. Detection limits are in the low nanogram-per-liter range. In composite groundwater and soil samples from an AFFF-impacted source zone, 75% and 240% more PFAS were revealed upon application of TOP assay (Figure 4A-B).

- **Particle Induced Gamma Emission Spectroscopy (PIGE)**
  This method is performed to measure total organic fluorine in groundwater samples. Groundwater samples are extracted using a weak anionic exchange solid-phase extraction cartridge prior to analysis. Detection limits of total fluorine are in the low µg/L range.

- **Adsorbable Organic Fluorine (AOF)**
  This method is also performed to measure the total organic fluorine in groundwater. PFAS and other organic constituents are sorbed to an activated carbon matrix, the matrix is combusted, and resultant fluoride is measured via ion chromatography. Detection limits are around 1 µg/L.

These new analytical techniques allow assessment of the hidden PFAS mass (“dark matter”). Best agreement in AFFF-impacted groundwater occurs between LC-MS/MS post-TOP assay and AOF (Figure 5A), while rough agreement also occurs between PIGE and LC-MS/MS post-TOP assay (Figure 5B) and PIGE and AOF (Figure 5C). LC-MS/MS post-TOP appears to detect more PFAS than AOF, possibly because it can better capture short-chain PFAS. All three methods detect more PFAS as organofluorine than EPA Method 537.

Figure 6. PFOS loss (left) and corresponding fluoride generation (right) after ScisoR treatment of PFOS in triplicate aqueous reactors.
ScisoR REMEDIATION

The Arcadis-developed ScisoR technology has been demonstrated to degrade PFOS and PFOA in multiple treatability studies using AFFF-impacted site soil and groundwater. Recent characterization of impacted matrices using advanced analytical tools such as the TOP assay and PIGE has revealed significant decreases in sum PFAS, including PFAA precursors.

Continued research has focused on proving that the ScisoR technology is mineralizing PFOS by quantitatively measuring fluoride evolved during destruction of 10-milligram-per-liter PFOS in aqueous solutions while demonstrating that PFOS was simultaneously removed from solution. The fluoride mass balance results from triplicate analyses (Figure 6) show that PFOS was mineralized during the trials as fluoride concentrations corresponding to those present in mineralized PFOS were evolved into solution. These trials demonstrate that perfluorinated sulfonates such as PFOS can be effectively mineralized using the ScisoR technology.

Arcadis is now preparing for a field demonstration of ScisoR at an AFFF-impacted site. Comprehensive characterization of PFAS content and groundwater and soil conditions will be conducted throughout the trial to demonstrate ScisoR’s efficacy in situ along a plume.

These new analytical techniques allow assessment of the hidden PFAS mass.
About the authors

Author
IAN ROSS, PhD

Ian Ross, PhD, is a biochemist and remediation technical expert with 23 years of experience. In 2011, he won a Brownfield Briefing award in the UK for designing and implementing the world’s first in situ remediation of carbon disulfide using activated persulfate. In 2012, he won another Brownfield Briefing award for designing a combined soil washing and chemical oxidation project for a contaminated landfill. Ross’ recent focus has been on developing in situ remedial solutions for poly- and perfluorinated alkyl substances (PFAS). He was involved in the development of the CONCAWE PFAS guidance document published in 2015.

Co-Author
JEFF BURDICK

Jeff Burdick has 24 years of experience as a hydrogeologist for Arcadis and currently serves as the lead for the Arcadis North America Chemical/Pharmaceutical and PFAS teams. He spent six years as a technical director for Arcadis in Europe and 10 years as a technical lead for PFAS-related investigations, risk assessments and restoration. This included research and development on PFAS chemistry and destruction technologies that are being used for both federal and industrial clients.

Co-Author
ERIKA HOUTZ, PhD

Erika Houtz, PhD, has seven years of experience analyzing poly- and perfluoroalkyl substances (PFAS) and characterizing their fate in the environment. Houtz developed the total oxidizable precursor (TOP) assay to measure PFAS compounds.
The remediation industry, now more than three decades old, continues to evolve. This is driven by many factors: technological developments, a need to address emerging contaminants, regulatory changes and sustainability considerations. These factors have created both challenges and opportunities at different stages of the industry’s evolution.

Today’s problems are getting larger and more complicated, and addressing these challenges will require significant advances in investigation and remediation technologies. Furthermore, economic pressures will push practitioners to do more with less and to prioritize the generation of value from impaired assets. In this article, we highlight what we see as some of the most significant trends and innovations that will drive the evolution of remediation.

Figure 1. Pilot testing of an oleophillic biobarrier, a technical innovation for sheen management that Arcadis is developing in partnership with others.
RISK WILL DRIVE LNAPL MANAGEMENT AND REMEDIATION GOALS

Driven by the growing recognition that most light nonaqueous-phase liquid (LNAPL) plumes are stable and pose little or no risk, it is increasingly recognized that the rate of contaminant treatment by natural processes often greatly exceeds the performance of active LNAPL removal approaches. Arcadis has been very active in the Interstate Technology Regulatory Council, which has led the development of the technical basis, evaluation methods and training of LNAPL mobility to the remediation community. We are developing several technical innovations that support this trend in LNAPL management, including:

- LNAPL tracer testing to directly measure LNAPL flux.
- Use of down-hole nuclear magnetic resonance (NMR) geophysical tools to measure LNAPL saturation in situ.
- Thermal in situ sustainable remediation to enhance natural attenuation of NAPL.
- Oleophillic biobarriers to more effectively control LNAPL sheens on surface-water bodies (Figure 1).

In the near future, the characterization of mobility and recoverability will be widely used to establish LNAPL remediation objectives that are site specific and risk based. Furthermore, remediation strategies will rely heavily on natural source zone depletion (Figure 2).

**Figure 2.** Conceptual model of LNAPL depletion mechanisms that depict natural source zone depletion (NSZD). The NSZD depletion rates in both the saturated and vadose zones are quantified as part of a comprehensive NSZD assessment. At sites where the authors have completed NSZD evaluations, the contribution of vadose zone depletion was greater than 90% of the total NSZD rate.

EMERGING CONTAMINANTS WILL DRAMATICALLY CHANGE OUR FOCUS AND ENERGIES

The definition and terminology associated with “emerging contaminants” has evolved rapidly in the past few years. The current term 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.” As such, this term may represent new compounds that were not previously known and are found to be present in the environment, compounds that were known to exist but whose environmental occurrence was not fully understood, and “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 widespread presence and limited options for treatment, has driven a significant amount of industry focus and investment.

Addressing today’s challenges will require significant advances in investigation and remediation technologies.
to find cost-effective solutions. This has also been fueled in part by individual states developing drinking water and other health-based standards that vary widely, are very low and change over time, as opposed to the EPA establishing a federal maximum contaminant level. This results in a patchwork of standards that are both difficult to understand and a challenge for compliance. Notable historical 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, per-/polyfluoroalkylated substances (PFAS) and dechlorination/disinfection by-products — all of which persist in the environment.

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, we have developed methods for real-time Smart characterization to understand 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 technology support faster development of more cost-effective options for characterization and treatment. This includes methods for evaluating natural attenuation and optimizing biological degradation, both of which should accelerate the pace of developing ways of managing 1,4-dioxane and PFAS more cost effectively. Because of the large unknown risk, organizations will increasingly rely on structured risk management programs that consider the dynamic uncertainties associated with regulatory standards, toxicology and treatment technologies as the basis for their strategies to address CECs.

**PUMP-AND-TREAT SYSTEM DESIGNS WILL EVOLVE TO DYNAMIC GROUNDWATER RECIRCULATION APPROACHES**

Groundwater extraction (e.g., pump and treat) is arguably the first groundwater remediation technology and continues to be in widespread use as a strategy to control plume migration and protect critical resources. Conventional pump and treat is a brute-force approach that focuses on controlling rather than remediating a plume. This strategy,
while often effective, inherently results in excess groundwater pumping — a shortcoming, stemming from a flawed conceptual model of the process, that has long been recognized but never thought to be critical. An appropriate and useful analog for these processes is how a breeze moves through a house with open windows. Interior walls, doors and hallways act as baffles and preferred pathways, with their configuration altering the air flow from room to room. The direction of the prevailing wind further influences how air moves throughout the house. In an aquifer system, high-permeability zones are the rooms and hallways of the house, where groundwater flow will be focused, while the low-permeability zones act as baffles deflecting/altering flow. The dynamics of variable flow directions across the seasons eventually spread contaminants across all permeable portions of an aquifer downgradient of the source. This is further enhanced by concentration gradients between the high- and low-permeability materials in real soils that, over time, drive diffusion of contaminants into the less-permeable zones.

To successfully restore an aquifer, we believe it is necessary to create dynamic hydraulic conditions by adaptively changing system operation, essentially mimicking, even exaggerating, the natural variability to accelerate the removal of contaminants. The process is the basis for the concept we call enhanced groundwater flushing, and the technology to implement this concept is known as dynamic groundwater recirculation (DGR). The primary distinction between DGR and conventional pump and treat is the use of site data to develop an appropriate flushing framework, a dynamic operation plan and an approach for continuous adaption based on remedial performance. After implementation, the goal of DGR system operation is simple: maximize contaminant mass removal by extracting contaminants within the plume core while injecting clean water at strategic locations along the plume periphery to enhance flushing and direct contaminants toward extraction wells (Figure 3). The key to success is dynamic system operation: use performance data to frequently optimize the system by varying pumping/injection rates and locations in response to changes in concentration data to maximize mass removal rates while maintaining hydraulic control of the plume. For many old plumes, evolving to a DGR framework will result in much more efficient and accelerated cleanup.

**BIG DATA WILL RESULT IN FASTER UNDERSTANDING AND OPTIMIZED CONTAMINATED SITE PORTFOLIO MANAGEMENT**

Since the invention of the world wide web 25 years ago, a lot of data sources collected in the past, and currently being collected, have been digitized and become easily accessible. Today, it is easy to locate, collect and analyze digitized data and information that would have taken weeks or months in the past. The expanding access to huge data sets and emergence of powerful and real-time technologies represent opportunities for analysis that were never possible in the past — thus leading to the term *big data*. In a digitized world, big data refers...
to the things one can do at a large scale that cannot be done at a smaller one, to extract new insights or create new forms of value in ways that can change markets, organizations, the relationships between various stakeholders and more. It has been transformative within many industrial sectors and has been heralded as the next frontier for innovation and competitiveness. Large volumes of data have accumulated within the remediation industry, primarily driven by the requirements of regulatory compliance and risk management, and all stakeholders stand to benefit from their application (Figure 4). For example, in the past, we learned slowly and gradually about natural attenuation of petroleum hydrocarbons and chlorinated solvents from data collected from thousands of sites. In the future, insights gained from data points across many sites will be realized much faster and more reliably. Big data also offers the opportunity to incorporate data from technical performance, regulatory frameworks and real estate markets to assist with the optimized management of contaminated site portfolio management. For example, Arcadis is currently engaged in a partnership to develop an IBM Watson-powered cognitive application to leverage big data to improve prioritization of monies and focus to reduce liability uncertainty and maximize the value of asset restoration efforts.

“Big data” has been heralded as the next frontier for innovation and competitiveness.
MANY VERY LARGE PLUMES CAN BE CLEANED UP

Large plume is a term that covers a wide range of contaminated aquifer scenarios, but they all share four common characteristics:

1. Large plumes occur in productive aquifers with high rates of groundwater flow and the potential to transport dissolved contaminants over large distances.
2. Large plumes comprise compounds that are not quickly degraded chemically or biologically under natural aquifer conditions.
3. Large plumes occur when contaminant compounds don’t interact chemically with the aquifer matrix — either the aquifer matrix has limited sorptive capacity or the contaminant can’t be sorbed due to its molecular structure.
4. For most contaminants, there must be a large source mass to generate a large volume of groundwater that exceeds regulatory criteria.

Figure 5. Complete cleanup of a 3-mile-long large plume in less than 10 years.
The conventional approach to large plumes has been groundwater pumping. In the early years of pump and treat, there was an expectation that the process would lead to site closures. Since the mid-1990s, it has been understood that conventional pump and treat approaches can contain large plumes, but cannot be expected to drive them to closure.

Through the reconstituted science of remediation hydrogeology (introduced in Arcadis’ 2008 book, Remediation Hydraulics), we learned that, because of the wide range of hydraulic conductivities of the sediments in even the simplest geologic settings, groundwater flow in aquifers occurs in a very small fraction of the total aquifer volume. At typical sites, we saw that more than 90% of the contaminant flows through less than 10% of the aquifer. By improving our mapping of contaminant transport zones, we could reduce the scope of remedial action to a small fraction of what is needed for a classic remedial method. In many cases, closure of large-plume sites is technically feasible and may be the best business case. In other cases, a refreshed review of the conceptual site model (CSM) and remediation operation can result in performance improvements that greatly reduce the near- and long-term project risks and costs. The environmental remediation community has been too pessimistic regarding the prospects for cost-effectively managing large, dilute plumes. Insights related to plume structure and solute transport processes at the remediation system scale now provide the opportunity to move from merely plume management to successful remediation with shorter time frames for closure of many large plumes (Figure 5).

**INNOVATION WILL CONTINUE TO HAVE A PROFOUND EFFECT ON THE REMEDIATION INDUSTRY FOR THE FORESEEABLE FUTURE**

Recall that, within the past decade, innovations in site characterization techniques have greatly transformed our ability to map and target high contaminant flux zones, resulting in CSMs that are more accurate and robust, and remediation system designs that are more efficient and effective. There have been significant advances in all general classes of in situ remediation categories. In some cases, approaches based on completely new chemistry or targeted for a new contaminant have been developed (e.g., the use of soluble phosphate to immobilize uranium and other metals); in others, dramatic improvement in the application and performance of long-established techniques has been achieved (e.g., incorporating a variety of electron donor types and utilizing key performance data to optimize enhanced reductive dechlorination approaches).

Great insights are born when innovation is at the core of an organization’s vision and operation. That is why Arcadis invests in hundreds of new concepts each year through our global innovation program to bring new ideas to the remediation industry. For more than 25 years, Arcadis has led the way in site remediation, with concepts such as in

---

**Figure 6.** Laboratory testing setup for in situ LNAPL detection using down-hole nuclear magnetic resonance techniques.
Great insights are born when innovation is at the core of an organization’s vision and operation.
About the authors

Author

CRAIG DIVINE, PhD, PG

Craig Divine, PhD, PG, leads Arcadis North America Site Evaluation and Restoration technical services and is the Environment Business Line representative for Satellite, Arcadis’ global innovation development program. He has 20 years of experience in hydrogeology, geochemistry, subsurface characterization and groundwater remediation.

Co-Author

JOHN HORST, PE

John Horst, PE, is the Executive Director of Technical Knowledge and Innovation for Arcadis North America. He is an expert in the development, application and optimization of new and innovative environmental restoration technologies. Horst has published on remediation topics ranging from restoration geochemistry to specific treatment technologies and has presented courses on in situ bioremediation.

Co-Author

SUTHAN SUTHERSAN, PhD, PE

Suthan Suthersan, PhD, is Chief Technical Officer and Executive Vice President at Arcadis. He has more than 35 years of experience in environmental remediation and has worked on projects in the U.S., Canada, Europe, Latin America and Asia. Suthersan is the author of Remediation Engineering, Natural and Enhanced Remediation Systems and In Situ Remediation Engineering. He has been awarded 20 patents (and more pending) for remediation technology applications. His column, “Advances in Remediation Solutions,” is regularly featured in Ground Water Monitoring and Remediation.
For more information on how Arcadis has driven advances in remediation, email us at askus@arcadis.com.