

In Situ
**Remediation
of Chlorinated Solvent
Plumes**

SERDP and ESTCP Remediation Technology Monograph Series

Series Editor: C. Herb Ward, Rice University

In Situ Remediation of Chlorinated Solvent Plumes

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Cover design: The image that appears on the cover of this volume is a synthesis of possible scenarios and locations where *in situ* remediation of chlorinated solvents in groundwater has been implemented.

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SERDP/ESTCP Remediation Technology Monograph Series

Series Editor: C. Herb Ward, Rice University

SERDP and ESTCP have joined to facilitate the development of a series of monographs on remediation technology written by leading experts in each subject area. This volume provides a review of the state-of-the-art on *in situ* remediation of chlorinated solvent plumes. Additional volumes planned for publication in the near future include:

- Delivery and Mixing in the Subsurface: Processes and Design Principles for *In Situ* Remediation
- Bioaugmentation for Groundwater Remediation
- *In Situ* Chemical Oxidation for Groundwater Remediation
- Chlorinated Solvent Source Zone Remediation
- Characterization and Remediation of Contaminated Sediments
- Remediation of Munition Constituents in Soil and Groundwater



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Preface

In the late 1970s and early 1980s, our nation began to grapple with the legacy of past disposal practices for toxic chemicals. With the passage in 1980 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund, it became the law of the land to remediate these sites. The U.S. Department of Defense (DoD), the nation's largest industrial organization, also recognized that it too had a legacy of contaminated sites. Historic operations at Army, Navy, Air Force, and Marine Corps facilities, ranges, manufacturing sites, shipyards, and depots had resulted in widespread contamination of soil, groundwater, and sediment. While Superfund began in 1980 to focus on remediation of heavily contaminated sites largely abandoned or neglected by the private sector, the DoD had already initiated its Installation Restoration Program in the mid-1970s. In 1984, the DoD began the Defense Environmental Restoration Program (DERP) for contaminated site assessment and remediation. Two years later, the U.S. Congress codified the DERP and directed the Secretary of Defense to carry out a concurrent program of research, development, and demonstration of innovative remediation technologies.

As chronicled in the 1994 National Research Council report, "Ranking Hazardous-Waste Sites for Remedial Action," our early estimates on the cost and suitability of existing technologies for cleaning up contaminated sites were wildly optimistic. Original estimates, in 1980, projected an average Superfund cleanup cost of a mere \$3.6 million per site and assumed only around 400 sites would require remediation. The DoD's early estimates of the cost to clean up its contaminated sites were also optimistic. In 1985, the DoD estimated the cleanup of its contaminated sites would cost from \$5 billion to \$10 billion, assuming 400 to 800 potential sites. A decade later, after an investment of over \$12 billion on environmental restoration, the cost-to-complete estimates had grown to over \$20 billion and the number of sites had increased to over 20,000. By 2007, after spending over \$20 billion in the previous decade, the estimated cost to address the DoD's known liability for traditional cleanup (not including the munitions response program for unexploded ordnance) was still over \$13 billion. Why did we underestimate the costs of cleaning up contaminated sites? All of these estimates were made with the tacit assumption that existing, off-the-shelf remedial technology was adequate to accomplish the task, that we had the scientific and engineering knowledge and tools to remediate these sites, and that we knew the full scope of chemicals of concern.

However, it was soon and painfully realized that the technology needed to address the more recalcitrant environmental contamination problems, such as fuels and chlorinated solvents in groundwater and dense nonaqueous phase liquids (DNAPLs) in the subsurface, was seriously lacking. In 1994, in the "Alternatives for Ground Water Cleanup" document, the National Research Council clearly showed that as a nation we had been conducting a failed 15-year experiment to clean up our nation's groundwater and that the default technology, pump-and-treat, was often ineffective at remediating contaminated aquifers. The answer for the DoD was clear. The DoD needed better technologies to clean up its contaminated sites and better technologies could only arise through a better scientific and engineering understanding of the subsurface and the associated chemical, physical, and biological processes. Two DoD organizations were given responsibility for initiating new research, development, and demonstrations to obtain the technologies needed for cost-effective remediation of facilities across the DoD: the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP).

SERDP was established by the Defense Authorization Act of 1991, as a partnership of the DoD, the U.S. Department of Energy, and the U.S. Environmental Protection Agency. Its mission is “to address environmental matters of concern to the Department of Defense and the Department of Energy through support of basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.” SERDP was created with a vision of bringing the capabilities and assets of the nation to bear on the environmental challenges faced by the DoD. As such, SERDP is the DoD’s environmental research and development program. To address the highest-priority issues confronting the Army, Navy, Air Force, and Marine Corps, SERDP focuses on cross-service requirements and pursues high-risk and high-payoff solutions to the DoD’s most intractable environmental problems. SERDP’s charter permits investment across the broad spectrum of research and development, from basic research through applied research and exploratory development. SERDP invests with a philosophy that all research, whether basic or applied, when focused on the critical technical issues, can impact environmental operations in the near term.

A DoD partner organization, ESTCP, was established in 1995 as the DoD’s environmental technology demonstration and validation program. ESTCP’s goal is to identify, demonstrate, and transfer technologies that address the DoD’s highest priority environmental requirements. The program promotes innovative, cost-effective environmental technologies through demonstrations at DoD facilities and sites. These technologies provide a large return on investment through improved efficiency, reduced liability, and direct cost savings. The current cost and impact on DoD operations of environmental compliance is significant. Innovative technologies are reducing both the cost of environmental remediation and compliance and the impact of DoD operations on the environment, while enhancing military readiness. ESTCP’s strategy is to select laboratory-proven technologies with potential broad DoD application and use DoD facilities as test beds. By supporting rigorous test and evaluation of innovative environmental technologies, ESTCP provides validated cost and performance information. Through these tests, new technologies gain end-user and regulatory acceptance.

In the 14 to 18 years since SERDP and ESTCP were formed, much progress has been made in the development of innovative and more cost-effective environmental remediation technology. Since then, recalcitrant environmental contamination problems for which little or no effective technology had been available are now tractable. However, we understand that newly developed technologies will not be broadly used in government or industry unless the consulting engineering community has the knowledge and experience needed to design, cost, market and apply them.

To help accomplish the needed technology transfer, SERDP and ESTCP have facilitated the development of a series of monographs on remediation technology written by leading experts in each subject area. Each volume will be designed to provide the background in process design and engineering needed by professionals who have advanced training and five or more years of experience. The first volume in this series, *In Situ Bioremediation of Perchlorate in Groundwater*, met a critical need for state-of-the-technology guidance on perchlorate remediation. This second volume, *In Situ Remediation of Chlorinated Solvent Plumes*, addresses the diverse physical, chemical, and biological technologies currently in use to treat what has become one of the most recalcitrant contamination problems in the developed world. Other volumes will follow on such topics as the remediation of DNAPL chlorinated solvents source zones, bioaugmentation to enhance bioremediation processes, delivery and mixing strategies and technologies to enhance subsurface remediation, chemical oxidation technologies to treat groundwater contamination, and remediation of contaminated sediments. Additional volumes will be written as new remediation technologies are developed and proven to be effective.

This volume provides a review of the past 10 to 15 years of intensive research, development and demonstrations on the *in situ* remediation of chlorinated solvent plumes. The intended audience includes the decision makers and practicing engineers and hydrogeologists who will select, design and operate these remedial systems, as well as researchers seeking to improve the current state of the art. Our hope is that this volume will serve as a useful resource to assist remediation professionals in applying and developing the technology as effectively as possible. Topics addressed in this volume include:

- A brief history and technology overview of groundwater contamination by chlorinated solvents (Chapter 1).
- A detailed review of the chemistry of chlorinated solvents that underlies remediation technology development (Chapter 2).
- The state of the science for key microbial processes involved in the biodegradation of chlorinated solvents (Chapter 3).
- A summary of the abiotic processes responsible for chlorinated solvent degradation (Chapter 4).
- An analysis of the challenges associated with remediating chlorinated solvent sites and recommendations for overcoming some of these challenges (Chapter 5).
- The evolution and current state of the art of groundwater modeling applicable to chlorinated solvent remediation, with emphasis on the modeling tools available to practitioners (Chapter 6).
- An assessment of how source zone architecture impacts the characterization and remediation of chlorinated solvent plumes and the effects of source treatment on source strength, mass flux and plume longevity (Chapters 7 and 8).
- An introduction to the technology-specific chapters, including a summary of the advantages and limitations of the major *in situ* groundwater remediation technologies to help the reader through the technology selection process (Chapter 9).
- A thorough review of the diverse physical, chemical and biological technologies currently in use for remediating chlorinated solvent plumes, including: biological processes such as monitored natural attenuation, biostimulation and bioaugmentation (Chapters 10-13); physical-chemical technologies such as air sparging; chemical oxidation and reduction; and barrier walls, including the use of zero-valent iron, and the less well known use of electrolytic reactive barriers (Chapters 14-17); in-well treatment technologies (Chapter 18); and phytoremediation (Chapter 19).

The final chapters provide insight into the factors that most influence technology costing and a view of the research needed to more cost-effectively address what remains of a multi-billion dollar legacy environmental contamination problem. Chapter 20 provides cost information needed to evaluate the applicability of the most frequently used technologies for the treatment of dissolved chlorinated aliphatic compounds in groundwater. Cost information for each technology has been derived for several template sites in order to objectively compare the relative economics of applying select technologies at other sites. Chapter 21 considers important unknowns and uncertainties that impact the state-of-the-science that underpins remediation technology development, including the potential role of rapidly developing molecular biological tools. This chapter, written in consultation with a broad range of experts in the remediation field, should help guide the research agenda on remediation of chlorinated solvents.

Each chapter in this volume has been thoroughly reviewed for technical content by one or more experts in each subject area covered. The editors and chapter authors have produced

a well-written and up-to-date treatise that we hope will prove to be a useful reference for those making decisions on remediation of chlorinated solvents, for remediation practitioners, and for those involved in development of advanced technology for the *in situ* remediation of dissolved chlorinated solvents in groundwater.

SERDP and ESTCP are committed to the development of new and innovative technologies to reduce the cost of remediation of soil, groundwater and sediment contamination as a result of past operational and industrial practices. We are also firmly committed to the widest dissemination of these technologies to ensure that our investments continue to yield savings for not only the DoD, but also the nation. In facilitating this monograph series, we hope to provide the broader remediation community with the most current knowledge and tools available in order to bring these technologies to bear on the remediation of chlorinated solvents.

Jeffrey A. Marqusee, Ph.D., Executive Director, SERDP and ESTCP

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About the Editors

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Dr. Stroo is a Principal Technical Advisor with HydroGeoLogic, Inc. He provides technical support on large remediation projects for private- and public-sector clients and has served as a technical advisor to the SERDP and ESTCP programs for over 10 years.

Dr. Stroo received BS degrees in Biology and Soil Science from Oregon State University, an MS in Soil Science from West Virginia University, and a PhD in Soil Science (soil microbiology) from Cornell University.

He was formerly a Principal with Remediation Technologies, Inc. (RETEC). He has over 20 years of experience in the assessment and remediation of contaminated soil and groundwater, particularly in the development and use of *in situ* bioremediation.

Dr. Stroo has served on several Expert Review Panels for SERDP, other government agencies and private companies. Recently, he served as Co-Chair of the SERDP workshops on Remediation of Chlorinated Solvents in Groundwater and Remediation of DNAPL Source Zones. He is coeditor of the SERDP-facilitated monograph on *In Situ* Bioremediation of Perchlorate in Groundwater.

C. Herb Ward

Dr. Ward holds the Foyt Family Chair of Engineering in the George R. Brown School of Engineering at Rice University. He is also Professor of Civil and Environmental Engineering and Ecology and Evolutionary Biology.

Dr. Ward has undergraduate (BS) and graduate (MS, PhD, MPH) degrees from New Mexico State University, Cornell University, and the University of Texas School of Public Health, respectively. He is a registered professional engineer in Texas and a Board Certified Environmental Engineer by the American Academy of Environmental Engineers.

He has been a faculty member at Rice University for 43 years where he has served as Chair of the Department of Environmental Science and Engineering and the Department of Civil and Environmental Engineering, and as the founding Director of the University's Energy and Environmental Systems Institute. He has also served as Director of the U.S. Environmental Protection Agency (ESEPA)-sponsored National Center for Ground Water Research and the DoD-sponsored Advanced Applied (Environmental) Technology Development Facility (AATDF).

Dr. Ward has been a member of the USEPA Science Advisory Board and served as Chair of the SERDP Scientific Advisory Board. He is the founding and current Editor-in-Chief of the international scientific journal *Environmental Toxicology and Chemistry*.

Dr. Ward received the Frederick George Pohland Medal for Outstanding Contributions to Bridging Environmental Research, Education, and Practice and the Brown and Caldwell Lifetime Achievement Award in 2006 and the Water Environment Federation Jack Edward McKee Medal for Achievement in Groundwater Restoration in 2007.

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His research includes studies on surface and groundwater hydrology, subsurface contaminant transport, *in situ* remediation and mathematical model development. Recently, he has focused on remediation of chlorinated solvents, perchlorate, chromium and acid mine drainage using emulsified oils. At Solutions-IES, Dr. Borden supports many of the firm's projects including traditional remediation approaches, *in situ* bioremediation, *in situ* chemical oxidation (ISCO), monitored natural attenuation (MNA) and expert witness testimony.

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He received his BA (Chemistry) from Harvard and MS (Inorganic and Analytical Chemistry) and PhD (Organometallic Chemistry) degrees from Cornell University. Dr. Brown has worked on new technologies for the investigation and treatment of complex, contaminated sites including wood treating, coal gasification, mining and Superfund sites. He currently holds 20 U.S. patents and has two additional patent applications on the *in situ* ozonation of recalcitrant organics and two on the use of sodium persulfate for ISCO. Dr. Brown has authored over 100 technical papers.

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Mr. Duchene is co-author of several PRB-related publications, including the Interstate Technology & Regulatory Council (ITRC) guidance document, *Permeable Reactive Barriers: Lessons Learned/New Directions* in 2005, and served as an instructor on the related ITRC training sessions.

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David Gilbert

Dr. Gilbert was a Research Scientist in the Department of Civil and Environmental Engineering at Colorado State University from 2002 through 2008. Areas of expertise included electrically induced redox barriers for *in situ* treatment of contaminated groundwater and chemical thermodynamics of contaminant release from anoxic reservoir sediments. His educational background included a BS degree in Geology, an MS degree in Environmental Engineering and a PhD in Hydrology. In addition, Dr. Gilbert had ten years of industry experience in groundwater and surface water. Unexpectedly, Dr. Gilbert passed away in 2008.

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Dr. Gossett received all of his university degrees from Stanford University—a BS in Chemical Engineering and an MS and PhD in Civil and Environmental Engineering. He joined the Cornell faculty in 1976. He was a North Atlantic Treaty Organization (NATO) fellow (1987–92), participating in a pilot study on remedial-action technologies for contaminated land and groundwater, and a Pacific Northwest National Laboratory (PNNL) Affiliate Staff Scientist (1996–1999).

Dr. Gossett's research has been featured frequently in the media including in *The Washington Post*, *The New York Times*, *News Day*, *Le Figaro*, *Scientific American Explorations*, *Chemical and Engineering News*, and *Civil Engineering*. He has also appeared in numerous broadcast-media reports, including interviews with BBCWorldService, RTL (a German TV network) and CNN, as well as a segment on CNN's weekly magazine show, *Science & Technology Week*.

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Mr. Henry provides project management and technical direction for the *in situ* remediation of fuel hydrocarbons and chlorinated solvents in groundwater. He has worked with the U.S. Air Force to develop technical protocols for enhanced *in situ* bioremediation of chlorinated solvents and is the primary author of the Air Force *Principles and Practices of Enhanced Bioremediation of Chlorinated Solvents* and the *Technical Protocol for Enhanced Anaerobic Bioremediation using Permeable Mulch Biowalls and Bioreactors*. Mr. Henry provides technical support on remediation projects for private- and public-sector clients.

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For over 20 years he has been active in the development and evaluation of technologies and strategies for the management and cleanup of contaminated soil and groundwater sites. He has also developed approaches for assessing the risks of chemicals posed in the subsurface. His work in the areas of soil vapor extraction, *in situ* air sparging, aerobic biobarriers, thermal treatment, vapor intrusion to buildings, and risk-based corrective action is reflected today in practice and in many guidance documents related to these topics.

Dr. Johnson is the editor of the Nation Ground Water Association journal *Ground Water Monitoring and Remediation* and serves as a consultant to regulatory agencies, government agencies and industry.

Richard L. Johnson

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He teaches in the areas of groundwater flow and transport and more broadly in all aspects of chemical mass transport in the environment. His research includes laboratory and field studies of chemical transport and fate, *in situ* remediation using chemical oxidation and reduction, and heat to facilitate remediation, and the application of molecular tools to demonstrate microbiological activity.

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Dr. David Major is a Principal of Geosyntec Consultants, Inc. since 1998, Associate Editor of *Ground Water Monitoring and Remediation*, and an Adjunct Professor at the Department of Chemical Engineering and Applied Chemistry, University of Toronto and Department of Earth Sciences, University of Waterloo. Dr. Major has over 20 years of consulting experience, and has helped to develop and commercialize environmental technologies such as zero-valent iron (ZVI) PRBs, molecular biomarkers, and bioaugmentation cultures. He was recently inducted into the

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He also served as a member for the U.S. Environmental Protection Agency (USEPA) RTDF, the USEPA Expert Panel to address the benefits of partial source treatment of dense nonaqueous phase liquids (DNAPLs), and the U.S. National Research Council Committee on Geological and Geotechnical Engineering in the New Millennium. Dr. Major has been an active member of the ITRC since 1996 and co-developed and taught ITRC courses on MNA, accelerated anaerobic bioremediation of chlorinated solvents, and bioremediation of DNAPLs. Dr. Major is also on the Steering Committee of the Sustainable Remediation Forum (SuRF).

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