



Chlorinated Solvent Source Zone Remediation

B.H. Kueper
H.F. Stroo
C.M. Vogel
C.H. Ward
Editors



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SERDP and ESTCP Remediation Technology Monograph Series
Series Editor: C. Herb Ward, Rice University

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Edited by

Bernard H. Kueper

Queen's University, Kingston, ON, Canada

Hans F. Stroo

Stroo Consulting LLC, Ashland, OR, USA

Catherine M. Vogel

Noblis Inc., Atlanta, GA, USA

C. Herb Ward

Rice University, Houston, TX, USA

Authors

Michael D. Annable
Robert C. Borden
Michael C. Brooks
Richard A. Brown
Natalie L. Cápiro
Wilson S. Clayton
Michelle Crimi
Kathy L. Davies
Rula A. Deeb
Ronald W. Falta
Jason I. Gerhard
Mark Harkness
Kirk Hatfield
Elisabeth L. Hawley
James W. Jawitz
Paul C. Johnson

Richard L. Johnson
Michael C. Kavanaugh
Jennifer L. Triplett Kingston
Julie Konzuk
Bernard H. Kueper
Herbert Levine
Gregory V. Lowry
David W. Major
Michael C. Marley
James W. Mercer
Kevin G. Mumford
Charles J. Newell
Jennifer L. Nyman
Robert H. O'Laskey
Kurt D. Pennell

P. Suresh C. Rao
Alicia J. Shepard
Robert L. Siegrist
Brent E. Sleep
Hans F. Stroo
Eric J. Suchomel
Neil R. Thomson
Paul G. Tratnyek
Catherine M. Vogel
Douglas I. Walker
Michael R. West
C. Herb Ward
Dean F. Williamson
John T. Wilson
A. Lynn Wood



Springer

Editors

Bernard H. Kueper
Department of Civil Engineering
Queen's University
Kingston, ON, Canada
kueper@civil.queensu.ca

Catherine M. Vogel
Noblis Inc.
Atlanta, GA, USA
catherine.vogel@noblis.org

Hans F. Stroo
Stroo Consulting LLC
Ashland, OR, USA
hans@strooconsulting.com

C. Herb Ward
Civil and Environmental Engineering
Rice University
Houston, TX, USA
wardch@rice.edu

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**SERDP and 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 chlorinated solvent source zone remediation. Previously published volumes in this series include:

- *In Situ* Bioremediation of Perchlorate in Groundwater
- *In Situ* Remediation of Chlorinated Solvent Plumes
- *In Situ* Chemical Oxidation for Groundwater Remediation
- Delivery and Mixing in the Subsurface: Processes and Design Principles for *In Situ* Remediation
- Bioaugmentation for Groundwater Remediation
- Processes, Assessment and Remediation of Contaminated Sediments



U.S. Department of Defense Strategic
Environmental Research &
Development Program (SERDP)
4800 Mark Center Drive, Suite 17D08
Alexandria, VA 22350



U.S. Department of Defense Environmental
Security Technology Certification
Program (ESTCP)
4800 Mark Center Drive, Suite 17D08
Alexandria, VA 22350

Preface

In the late 1970s and early 1980s, North America 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) in the United States, 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 that 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 that the cleanup of its contaminated sites would cost from \$5 billion to \$10 billion, assuming 400–800 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 DoD 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 are 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 18–22 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 has been 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. The second volume, *In Situ Remediation of Chlorinated Solvent Plumes*, addressed 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. The third volume, *In Situ Chemical Oxidation for Remediation of Contaminated Groundwater*, provided comprehensive, up-to-date descriptions of the principles and practices of *in situ* chemical oxidation (ISCO) for groundwater remediation based on a decade of intensive research, development, and demonstration. The fourth volume, *Delivery and Mixing in the Subsurface: Processes and Design Principles for In Situ Remediation*, described the principles of chemical delivery and mixing systems and their design and implementation for effective *in situ* remediation.

The fifth volume, *Bioaugmentation for Groundwater Remediation*, covered the history, current status and future prospects for deliberately adding bacteria and other agents to treat contaminated groundwater. The sixth volume, *Processes, Assessment and Remediation of Contaminated Sediment*, summarized the scientific and practical aspects of managing contaminated sediment sites.

This final volume in the series, *Chlorinated Solvent Source Zone Remediation*, is intended as a companion to the earlier volume that focused on chlorinated solvent plumes. The development of source zone remediation technologies began later in time than the development of plume remediation technologies but has reached the point where practical guidance based on experience and fundamental research can be provided. Remediation of chlorinated solvent source zones is very difficult, at times controversial and must be based on state-of-the-art knowledge of the behavior (migration, distribution and fate) of DNAPLs in the subsurface as well as site-specific geology, chemistry, biology and hydrogeology.

Engineers and scientists with a background in environmental engineering and sciences will find this book helpful in understanding the key issues involved in DNAPL source zone management and remediation. The volume begins with an overview of the current state of the practice that serves as an introduction to the rest of the book. The second chapter summarizes the challenges involved in source zone remediation, which has been and remains contentious, expensive, and difficult, for a variety of reasons. Following are chapters providing more focused discussions of specific aspects of this overall challenge. These chapters cover the following topics:

- Two chapters on source zone characterization, the first summarizing the current issues and techniques and the second focusing on several innovative diagnostic methods.
- Two chapters on modeling, the first focused on modeling source zone remediation itself and the second focused on the responses of downgradient plumes to source remediation.
- A chapter on the use of mass flux and mass discharge information to improve source zone management and remediation.
- A series of chapters on specific source zone remediation methods, including hydraulic displacement and recovery, ISCO, *in situ* chemical reduction (ISCR), enhanced flushing with cosolvents and surfactants, *in situ* bioremediation, and finally source zone monitored natural attenuation. Each of these chapters include a fundamental description of the technology, summaries of their strengths and limitations, specific case studies of their use, and a review of the lessons learned.
- A chapter on combined remedies, discussing the fundamental issues involved in developing effective combined remedies as well as the experience to date in specific combinations of technologies.
- A chapter on the costs of source zone treatment, using several hypothetical but realistic site scenarios, comparing different technologies on a total and net present cost basis.

The last two chapters consider the future of source zone remediation, beginning with a discussion of alternate management strategies that may be useful for source zones, followed by a summary of the research and development needed to improve the state of the practice.

In a single volume covering an area this broad there are topics that cannot be discussed fully, but it is hoped that the topics that are emphasized represent the state of the practice of DNAPL source zone characterization, remediation, and management and that the volume will be a resource for those wishing to further explore the primary literature in the field. Also, it is

hoped that the volume will be useful to the technical practitioner as well as the research scientist and engineer in the field.

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 encourage full and effective use of these technologies.

Jeffrey A. Marqusee, PhD, Executive Director, SERDP and ESTCP

Andrea Leeson, PhD, Environmental Restoration Program Manager, SERDP and ESTCP

About the Editors

Bernard H. Kueper

Dr. Kueper is a licensed professional engineer and professor in the Department of Civil Engineering at Queen's University in Kingston, Ontario. He received his BAsC in Civil Engineering and PhD in Earth Sciences from the University of Waterloo.

Dr. Kueper has been a faculty member at Queen's for 23 years where his research is focused on the fate, transport, and remediation of organic contaminants in soil and groundwater. Dr. Kueper has carried out field and laboratory experiments and developed numerical models focused on the behavior and remediation of chlorinated solvents in both porous and fractured media. He has published over 200 papers, abstracts, and book chapters on the topic of contaminant hydrogeology including guidance for the U.S. Environmental Protection Agency and other organizations.

Dr. Kueper is a former Associate Editor for the Journal of Contaminant Hydrology, Groundwater and the Canadian Geotechnical Journal. He has been a member of several expert panels, review committees, and conference organization committees. Dr. Kueper has taught over 8,000 people outside of the university environment in professional short courses and training seminars on the topics of soil and groundwater contamination, groundwater hydraulics, site investigation techniques, and subsurface remediation. This training has been provided to various groups, regulatory agencies, and licensing bodies in Australia, Brazil, Canada, Denmark, England, Hungary, Switzerland, and the United States.

Hans F. Stroo

Dr. Stroo is an environmental scientist and owner of Stroo Consulting, LLC. He provides technical support on remediation projects for private- and public-sector clients and has served as a technical advisor to the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) for 15 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. (later RETEC) and with HydroGeoLogic, Inc. (HGL). He has over 25 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 Dense Nonaqueous Phase Liquid (DNAPL) Source Zones. He is coeditor of the SERDP-facilitated monographs *In Situ Bioremediation of Perchlorate in Groundwater*, *Bioaugmentation for Groundwater Remediation*, and *In Situ Remediation of Chlorinated Solvent Plumes*.

Catherine M. Vogel

Ms. Vogel is an Environmental Engineer with Noblis, Inc. She received her BS (Civil/Environmental Engineering) from the Michigan Technological University, MS (Environmental Engineering) from the University of Arizona, and a JD from the University of Houston. Prior to joining Noblis, she served as the program manager for the Air Force Research Laboratory's Biotechnology Program where she managed a large research and development program to

develop innovative environmental restoration technologies to address Air Force-contaminated groundwater issues. She also has served as the program manager for the SERDP/ESTCP Environmental Restoration program area. She currently provides advisory services to federal agencies on emerging environmental issues and contaminants, regulatory assessments, strategic program planning and evaluation, and technical consultation support.

C. Herb Ward

Dr. Ward holds the A. J. 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 48 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 (USEPA)-sponsored National Center for Ground Water Research and the U.S. Department of Defense (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 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 for Remediation in 2006, the Water Environment Federation Jack Edward McKee Medal for Achievement in Groundwater Restoration in 2007, and the Society for Industrial Microbiology and Biotechnology Charles Thom Award for bioremediation research in 2011 and was recognized as a Distinguished Alumnus by New Mexico State University in 2013.

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About the Authors

Michael D. Annable

Dr. Annable is a Professor in the Department of Environmental Engineering Sciences at the University of Florida. He joined the faculty in 1992 after receiving his PhD in Civil and Environmental Engineering from Michigan State University. Dr. Annable has research interests in physical-chemical processes related to field-scale application of innovative technologies for subsurface characterization and remediation. His research includes use of the passive flux meter approach for groundwater monitoring, which has been used at more than 60 field sites. Interests also include impacts of groundwater management on water quantity and quality of lakes, wetlands, and springs.

Robert C. Borden

Dr. Borden serves as Principal Engineer with Solutions-IES, a women-owned, small business, environmental engineering firm located in Raleigh, North Carolina. Much of his work is focused on the natural and enhanced remediation of petroleum hydrocarbons, fuel oxygenates, ethers, chlorinated solvents, explosives, and propellants, including laboratory studies, fieldwork, and mathematical model development.

Dr. Borden received his BS and ME in Civil and Environmental Engineering from the University of Virginia and a PhD in Environmental Engineering from Rice University. He is the author of over 100 publications, principal investigator on over 40 different projects, and Professor of Civil, Construction, and Environmental Engineering at North Carolina State University.

Michael C. Brooks

Dr. Brooks is an Environmental Engineer in the Ground Water and Ecosystems Restoration Research's Subsurface Remediation Branch at the U.S. Environmental Protection Agency (USEPA), Ada, Oklahoma. He received his PhD from the University of Florida in 2000. He has been engaged in groundwater contaminant characterization and remediation work for two decades in the private, academic, and government sectors. His research has included experimental and theoretical studies of air sparging flow patterns, innovative dense nonaqueous phase liquid (DNAPL) characterization and remediation techniques, and energetic contaminant remediation. While a significant portion of this research has been field based, it has also included the use of both deterministic and stochastic modeling approaches to help evaluate field results.

Richard A. Brown

Dr. Brown joined ERM in 1999 as the Director of Technology Development. His responsibilities at ERM include development and implementation of remediation technologies such as bioremediation, chemical oxidation, ozonation, *in situ* metal fixation, *in situ* chemical reduction (ISCR), and evaluation of new technologies for soil and groundwater treatment. He has extensive experience with organic and inorganic contaminants. In 2010, Dr. Brown was made a Technical Fellow at ERM.

Dr. Brown received his BA (Chemistry) from Harvard and an MS (Inorganic and Analytical Chemistry) and PhD (Organometallic Chemistry) from Cornell University. Before joining ERM, Dr. Brown held positions as Senior Technical Consultant for IT Corporation, Vice President for Remediation Technology for Fluor Daniel GTI, Director of Business

Development for Cambridge Analytical Associate's Bioremediation Systems, and Technology Manager for FMC Corporation's Aquifer Remediation Systems. He has worked on new technologies for the investigation and treatment of complex contaminated sites and currently holds 20 U.S. patents.

Natalie L. Cápiro

Dr. Cápiro is a Research Assistant Professor in Civil and Environmental Engineering at Tufts University. She earned her BS in Biological and Environmental Engineering from Cornell University and her MS and PhD in Civil and Environmental Engineering from Rice University. She also completed 3 years of postdoctoral research in Environmental Engineering at the Georgia Institute of Technology. Dr. Cápiro's research interests include environmental biotechnology and bioremediation, fate and transport of persistent organic contaminants, and development and testing of innovative *in situ* remediation technologies.

Wilson S. Clayton

Dr. Clayton is Technical Services Business Unit Manager at Trihydro Corporation. He earned his PhD at Colorado School of Mines (CSM) (Geological Engineering) and BS and MS degrees in Geology from Clemson University and the University of Connecticut, respectively. Dr. Clayton has over 28 years of *in situ* remediation experience spanning the full spectrum of technologies, including biological and chemical technologies as well as more traditional technologies such as air sparging, soil venting, and pump and treat. While being broadly involved in all aspects of remediation implementation, Dr. Clayton's special area of technical expertise is in the application of subsurface reactive transport for *in situ* remediation.

Dr. Clayton previously founded Aquifer Solutions, Inc., and in prior years, served as a corporate-level technology director at Groundwater Technology, Fluor Daniel GTI, and IT Corporation, where he managed research, development, and commercialization of *in situ* oxidation technology.

Michelle Crimi

Dr. Crimi is an Associate Professor in the Institute for a Sustainable Environment at Clarkson University. She received her BS degree in Industrial Hygiene and Environmental Toxicology from Clarkson University, an MS in Environmental Health from Colorado State University, and a PhD in Environmental Science and Engineering from the CSM.

Dr. Crimi's research is focused on *in situ* remediation of contaminated soil and groundwater, chemical oxidation and degradation of organic compounds, impacts of *in situ* remediation on aquifer quality, and human health risk assessment. Dr. Crimi has published extensively in these areas and has delivered invited presentations at numerous workshops and conferences in the United States and abroad. Dr. Crimi is coauthor of the first reference text on ISCO: *Principles and Practices of In Situ Chemical Oxidation Using Permanganate* (2001) and co-edited a more recent book in the SERDP/ESTCP Remediation Technology Monograph Series: *In Situ Chemical Oxidation for Groundwater Remediation*.

Kathy L. Davies

Ms. Davies is a Senior Hydrogeologist with the USEPA Region III office in Philadelphia, Pennsylvania. She received her BS (Geology/Geochemistry) from the University of Michigan and her MS (Geology/Geochemistry) from Arizona State University. She has more than 25 years of experience in the characterization and remediation of contaminated groundwater at hazardous waste sites, with particular interests in contaminant plumes associated with DNAPLs and present in fractured rock environments.

Rula A. Deeb

Dr. Deeb is a Principal at Geosyntec in Oakland, CA. Dr. Deeb's technical expertise includes the cross-media fate and transport of contaminants and the remediation of complex soil and groundwater sites impacted by nonaqueous phase liquids. She received her PhD from the University of California at Berkeley in Civil and Environmental Engineering. Following the completion of her graduate work, she taught environmental engineering principles at Stanford University. As a postdoctoral fellow at UC Berkeley, she developed and implemented research programs in collaboration with scientists and engineers at other universities, consulting firms, and the U.S. Air Force on the remediation of sites impacted with contaminant mixtures. She joined Malcolm Pirnie, Inc. in 2000 where she managed commercial, federal, and municipal projects and clients and served as a technical specialist on key projects company-wide. Following the acquisition of Malcolm Pirnie by ARCADIS in July 2009, Rula served as Vice President and Technical Director for External Outreach in ARCADIS' Environment Division.

Dr. Deeb is heavily engaged in the National Academy of Engineering Frontiers of Engineering program which brings together emerging engineering leaders from industry, academia, and government to discuss pioneering technical work and leading-edge research in various engineering fields and industry sectors. She is the recipient of the 2008 Berkeley Engineering Innovation Young Outstanding Leader Award and is a Board-Certified Environmental Engineering Member of the American Association of Environmental Engineers.

Ronald W. Falta

Dr. Falta is a Professor of Environmental Engineering and Earth Sciences at Clemson University in South Carolina. He received his BS and MS degrees in Civil Engineering from Auburn University and his PhD degree in Mineral Engineering from the University of California, Berkeley.

Dr. Falta's research is primarily in the areas of contaminant transport and remediation, including laboratory- and field-scale studies, as well as mathematical model development. Much of his work has focused on source remediation at sites contaminated by DNAPLs and on assessing the impact of source remediation on plume evolution.

Jason I. Gerhard

Dr. Gerhard is an Associate Professor at the University of Western Ontario. He has BA, BSc, MSc, and PhD degrees from Queen's University (Canada) and was an Assistant Professor at the University of Edinburgh until 2007 when he joined Western as the Canada Research Chair in Geoenvironmental Remediation.

Dr. Gerhard has over 15 years of experience leading a research program that illuminates contaminant behavior with experiments from the pore to the field scales. He has also led the development of several numerical models to assist the design and optimization of remediation systems. As co-director of Research for Subsurface Transport and Remediation (RESTORE), he has generated new understanding of DNAPLs in soil and fractured rock and developed a new remediation technique for coal tars and petroleum hydrocarbons. In addition, he has acted as an expert consultant and an Associate Editor for *Water Resources Research*.

Mark Harkness

Mr. Harkness is a Remediation Engineer at GE Global Research in Niskayuna, New York, where he is part of a multidisciplinary team providing consulting support to GE project managers who wish to apply innovative remedial solutions to soil and groundwater issues. Mr. Harkness received his BS and MS degrees in Chemical Engineering from Rensselaer Polytechnic Institute.

In 23 years at GE, his work has focused on the development of novel remedial solutions for polychlorinated biphenyls (PCBs), petroleum hydrocarbons, and chlorinated solvents. His current specialty is the design of passive bioremediation systems for chlorinated solvents in groundwater. He has served as the GE representative on the steering committee of the Remediation Technologies Development Forum Bioremediation Consortium, and more recently Project SABRE, and is a frequent contributor to journal articles and book chapters in the field of bioremediation.

Kirk Hatfield

Dr. Hatfield is Director of the Engineering School for Sustainable Infrastructure and Environment (ESSIE) at the University of Florida and has been a Professor in the Department of Civil and Coastal Engineering since 1987. He received his MS in Environmental and Civil Engineering from the University of Iowa and a PhD in Civil Engineering from the University of Massachusetts. Dr. Hatfield specializes in groundwater flow and contaminant transport modeling, water resource allocation modeling, surface water and groundwater monitoring, and groundwater remediation. A recent focus has been on application of passive techniques for characterizing mass flux in complex flow systems such as fractured media.

Elisabeth L. Hawley

Ms. Hawley is a Senior Environmental Engineer at ARCADIS, U.S. in Emeryville, California. She earned a BS in Environmental Engineering Science from the University of California at Berkeley in 2000 and an MS in Civil and Environmental Engineering from the University of California at Berkeley in 2001. As a consultant, she has worked on a variety of environmental restoration projects involving site characterization, remediation, fate and transport, sustainability analyses, and emerging contaminants. Ms. Hawley has conducted research and prepared guidance materials on technical impracticability assessments and alternative groundwater remedial strategies for the Air Force, Army, and ESTCP. She is a registered professional engineer in California.

James W. Jawitz

Dr. Jawitz is a Professor in the Soil and Water Science Department at the University of Florida. He received his PhD from the University of Florida in 1999. Dr. Jawitz has research interests that include conflicts between expanding demand for freshwater resources to provide drinking water for the growing population and irrigation water for agriculture and simultaneous pressures to prevent pollution and leave enough water for natural ecosystem functions. Research includes quantifying the benefits of partial removal of aquifer contaminant source zones and evaluating the effects of land use change on water resources.

Paul C. Johnson

Dr. Johnson is the Dean of the Ira A. Fulton Schools of Engineering at Arizona State University and a Professor in the School of Sustainable Engineering and the Built Environment. Prior to that he was a Senior Research Engineer at the Shell Oil/Shell Chemical Westhollow Technology Center in Houston, Texas. He received BS and PhD degrees in chemical engineering from the University of California at Davis and Princeton University, respectively.

Dr. Johnson's research, teaching, and other professional activities include modeling and monitoring to support risk assessment at contaminated soil and groundwater sites as well as the selection, design, monitoring, and optimization of remediation technologies for managing those sites. Dr. Johnson was the Editor in Chief for the National Ground Water Association's journal *Ground Water Monitoring and Remediation* from 2003 to 2012 and serves as a peer reviewer and consultant to the USEPA, state regulatory agencies, DoD, and industry.

Richard L. Johnson

Dr. Richard L. Johnson is Professor in the Division of Environmental and Biomolecular Systems (EBS), Institute of Environmental Health (IEH) at the Oregon Health & Science University (OHSU). His research concerns the transport processes that control the fate and effects of environmental substances, including metals (for remediation), organics (as contaminants), and nanoparticles (for remediation and as contaminants).

He received his PhD in Environmental Science and Engineering from the Oregon Graduate Institute in 1985. He was a Postdoctoral Fellow at the University of Waterloo (Waterloo, Ontario, Canada) from 1985 to 1986 before joining the faculty at OGI and then OHSU.

Michael C. Kavanaugh

Dr. Kavanaugh is a Senior Principal with Geosyntec Consultants, Inc. He is a registered professional engineer and a Board-Certified Environmental Engineer (BCEE) and has over 39 years of consulting experience on water quality, water and wastewater treatment, and groundwater restoration issues. In addition to his consulting practice, Dr. Kavanaugh has completed several assignments with the National Research Council (NRC) including chairing the Water Science and Technology Board and the Board on Radioactive Waste Management. He also chaired the NRC committee on alternatives for groundwater cleanup (1994) and recently chaired an NRC study on the future of subsurface remediation efforts in the United States.

Dr. Kavanaugh was elected into the National Academy of Engineering (NAE) in 1998. He has a BS and MS degrees in Chemical Engineering from Stanford and the University of California, Berkeley, respectively, and a PhD in Civil/Environmental Engineering from the University of California, Berkeley.

Jennifer L. Triplett Kingston

Dr. Kingston is a Technical Specialist with Haley & Aldrich, Inc. in Overland Park, Kansas, where she directs remediation projects and provides technical evaluations for remediation technologies. She has also served as an adjunct professor in the Geological Engineering Department at the Missouri University of Science and Technology.

Dr. Kingston received BS and MS degrees in Geological Engineering and a PhD degree in Civil and Environmental Engineering from the University of Missouri – Rolla and Arizona State University, respectively. Her experience and research include evaluation, selection, and optimization of remediation technologies along with project implementation. She has also assisted in the development of an innovative technology and its eventual design and construction.

Julie Konzuk

Dr. Konzuk is an Associate Engineer with Geosyntec Consultants and has over a decade of environmental consulting experience in the United States, Canada, and Australia. She has BS and PhD degrees in Civil Engineering from Queen's University in Ontario, Canada.

At Geosyntec, Dr. Konzuk has implemented remediation programs in subsurface environments ranging from fractured bedrock to sand and silt/clay environments as well as cleanup of soil and groundwater contaminated with chlorinated solvents, DNAPLs, unexploded ordnance and munitions constituents, heavy metals, nitrated and chlorinated benzenes, and chlorofluorinated compounds. Prior to joining Geosyntec Consultants, she spent several years researching DNAPL and groundwater transport behavior in fractured bedrock and has continued with the applied research during her consulting career. Most recently, Dr. Konzuk was part of a project team that completed an evaluation of DNAPL remediation technology performance and the factors that impact performance, and her team at Geosyntec Consultants developed a software tool (DNAPL TEST) that provides a screening-level analysis of potential DNAPL remediation technology performance given user-inputted site conditions.

Herbert Levine

Mr. Levine is a Regional Hydrogeologist for Superfund, with the USEPA, Region IX in San Francisco, California. He serves as a technical expert for USEPA project managers on hydrogeology issues related to characterization and cleanup of Superfund sites.

Mr. Levine received his BS and MS degrees in Geology from the University of Illinois, Chicago. Over the past 23 years he has provided technical support to Superfund sites throughout the multiple phases of site characterization through remedy selection, implementation, and optimization. He is a coauthor of the USEPA guidance document *Performance Monitoring of MNA Remedies for VOCs in Ground Water*.

Gregory V. Lowry

Dr. Lowry is a Professor in the Department of Civil and Environmental Engineering at Carnegie Mellon University. He teaches Environmental Engineering, Water Quality Engineering, Environmental Fate and Transport of Organic Compounds in Aquatic Systems, Environmental Nanotechnology, and Environmental Sampling and Sample Characterization. Dr. Lowry received his BS (Engineering) from UC Davis and MS and PhD in Civil–Environmental engineering from the University of Wisconsin and Stanford University, respectively.

Dr. Lowry's research interests include mineral-organic macromolecule–water interfacial processes, and transport and reaction in porous media, with a focus on the fundamental physical/geochemical processes affecting the fate of engineered nanomaterials and organic contaminants in the environment. He is also investigating the processes affecting the permanence of CO₂ injected underground for carbon sequestration. He is an experimentalist working on a variety of fundamental and application-oriented research projects developing novel environmental technologies for restoring contaminated sediments and groundwater. His current projects include *in situ* sediment management using innovative sediment caps, DNAPL source zone remediation through delivery of reactive nanoparticles to the NAPL–water interface, and CO₂ capture, sequestration, and monitoring.

David W. Major

Dr. Major is a Principal of Geosyntec Consultants Inc., Associate Editor of Ground Water Monitoring and Remediation, and an Adjunct Professor in the Department of Chemical Engineering and Applied Chemistry, University of Toronto. He received his BSc (1981), MSc (1984), and PhD (1987) in Biology from the University of Waterloo (UW). Dr. Major has over 23 years of experience working with clients, researchers, and regulators to develop practical biological, chemical, and thermal based solutions to remediate contaminated sites. He was inducted into the Space Hall of Fame®, received a UW Science's Alumni of Honor Award, and is a Board-Certified Environmental Scientist of the American Academy of Environmental Engineers and Scientists. Dr. Major has served on several national scientific and regulatory advisory boards.

Michael C. Marley

Mr. Marley is president and co-founder of XDD, LLC in Stratham, New Hampshire, and has over 29 years of experience in environmental and civil engineering. He earned a BS in Civil Engineering from Queen's University in Belfast, Northern Ireland, performed doctoral research and received his MS in Civil and Environmental Engineering from the University of Connecticut, and is a Licensed Environmental Professional (LEP) in the state of Connecticut.

Mr. Marley's expertise focuses on strategies for site closure, including the development and application of innovative remediation technologies for contaminated soils and groundwater.

He has been at the forefront of developing design and application protocols for soil vapor extraction, air sparging, and most recently *in situ* chemical oxidation and reduction technologies. As XDD's primary technical expert Mr. Marley directs all applied research and development efforts and serves as the firm's quality assurance officer. Mr. Marley lectures widely on the design and application of vapor extraction, bioventing, sparging/biosparging, chemical oxidation, and innovative remediation technologies for volatile and semivolatile organic compounds and inorganic compounds. He has been responsible for the modeling support, review, or design of several hundred pilot- and full-scale remediation systems. More recently, Mr. Marley was the principal author of the Electric Power Research Institute-funded study on field applicability of persulfate for chemical oxidation of manufactured gas plant residuals. In addition, Mr. Marley has served as a peer reviewer for Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) research on *in situ* technologies.

James W. Mercer

Dr. Mercer is a hydrogeologist with Tetra Tech GEO, Inc. He received a BS (Geology) from Florida State University and MS and PhD degrees in Geology from the University of Illinois. Dr. Mercer spent 8 years with the U.S. Geological Survey in the Northeastern Research Group working on contaminant and heat transport issues, including multiphase flow. He cofounded GeoTrans (now Tetra Tech GEO) in 1979 and in 1980 began working on DNAPL issues at Love Canal.

In 1985, Dr. Mercer received the Wesley W. Horner Award of the American Society of Civil Engineers for the work performed at Love Canal. Dr. Mercer continued to work on DNAPL issues and coauthored a book on *DNAPL Site Evaluation* in 1993. In 1994, he received the American Institutes of Hydrology's Thesis Award for contributions to groundwater hydrology. Dr. Mercer has served on the National Research Council's Water Science and Technology Board and was a member of the USEPA Science Advisory Board. He is currently on the Scientific Advisory Board of SERDP.

Kevin G. Mumford

Dr. Mumford is an Assistant Professor in the Department of Civil Engineering at Queen's University, whose research focuses on groundwater contamination and *in situ* remediation. He received his BS and MS degrees from the University of Waterloo and his PhD from McMaster University and held a postdoctoral fellowship at the University of Western Ontario before joining Queen's University in 2010. Dr. Mumford's expertise is in the study of multiphase flow in porous media and mass transfer related to both NAPLs and gases. His research interests include mass transfer and gas dynamics in NAPL source zones, under natural conditions, during remediation applications, and at elevated temperatures during *in situ* thermal treatment.

Charles J. Newell

Dr. Newell is a Vice President of GSI Environmental Inc. and an Adjunct Professor of Civil and Environmental Engineering at Rice University. He received a BS degree in Chemical Engineering and MS and PhD degrees in Environmental Engineering from Rice University.

Dr. Newell has served as a Principal Investigator or Co-PI for five SERDP projects and ten ESTCP projects in the environmental restoration/technologies field. He has been awarded the Hanson Excellence of Presentation Award by the American Association of Petroleum Geologists, the Outstanding Presentation Award by the American Institute of Chemical Engineers, and the 2001 Wesley W. Horner Award by the American Society of Civil Engineers. In 2008 he was cited as Rice University's Outstanding Engineering Alumni.

Jennifer L. Nyman

Dr. Nyman is a Senior Environmental Engineer in the Oakland, California, office of Geosyntec, where she manages large groundwater investigation and remediation projects. She has previously served as technical lead or expert for remediation projects for industrial and government clients. She received her BS degree in Chemical Engineering from Montana State University and her MS and PhD degrees in Environmental Engineering and Science from Stanford University.

Dr. Nyman has specialized expertise in the areas of geochemistry, remedial design, microbiology, bioremediation, and advanced diagnostic tools. She serves on and is a trainer for the Interstate Technology & Regulatory Council team on Attenuation Processes for Metals and Radionuclides.

Robert H. O'Laskey

Mr. O'Laskey is a Senior Geologist at the Emeryville, California, office of ARCADIS U.S., Inc. where he serves as the technical lead for environmental and water resource investigations. He received his BS degree in Geology from State University College of New York at Brockport and his MS degree in Geology from the University of Massachusetts at Amherst. Specific experience includes the design or the rehabilitation of groundwater extraction and water supply wells, planning and implementation of remedial programs for chlorinated solvent contamination sites, development of groundwater monitoring programs at solid waste landfills, and hydrogeologic analysis in support of numerical groundwater fate and transport modeling.

Kurt D. Pennell

Dr. Kurt Pennell is Professor and Chair of the Department of Civil and Environmental Engineering at Tufts University. Dr. Pennell received his BS from the University of Maine, MS from North Carolina State University, and PhD from the University of Florida and completed a postdoctoral fellowship at the University of Michigan.

Prior to moving to Tufts in June 2009, Dr. Pennell was a Professor in the School of Civil and Environmental Engineering at the Georgia Institute of Technology and holds an adjunct appointment in the Department of Neurology at the Emory University School of Medicine. His current research focuses on the environmental fate and neurotoxicity of engineered nanomaterials, groundwater remediation technologies, and role of persistent organic pollutants in Parkinson's disease. Dr. Pennell serves as an Associate Editor for the Journal of Contaminant Hydrology and is a registered professional engineer (PE) and a BCEE.

P. Suresh C. Rao

Dr. Rao is the Lee A. Rieth Distinguished Professor of Civil Engineering and Agronomy at Purdue University. He received his PhD from the University of Hawaii and spent 25 years at the University of Florida before joining Purdue University. Dr. Rao has research interests in multi-scale modeling and analysis of landscape hydrologic and biogeochemical process linkages across human-impact gradients, including intensively managed croplands, urban catchments, and wetlandscapes, with pristine catchments serving as the reference. This work includes resilience-based analysis of coupled natural and engineered complex systems, including food-bioenergy-water sustainability issues and use of models for research and for decision making. Applications include catchment-scale water-quality analyses and aquifer-scale studies on industrial land uses, assessments of groundwater vulnerability, contaminated site remediation, and watershed management.

Alicia J. Shepard

Ms. Shepard is an environmental scientist with HydroGeoLogic, Inc., located in Reston, Virginia. She received her BA (Biology) degree from Macalester College. Ms. Shepard has more than 11 years of experience in project management, communication and outreach activities, and conference/workshop planning relevant to the Department of Defense (DoD).

Ms. Shepard has managed numerous technical workshops that convene groups of experts from multiple disciplines and organizations to review the state of the science, identify gaps, and prioritize research, development, technology demonstration, and technology transfer needs. She has directed the development of strategic plans based on the results of these workshops, including SERDP/ESTCP workshops on coastal and estuarine ecosystems, contaminated sediments, bioavailability, and range sustainability.

Robert L. Siegrist

Dr. Robert L. Siegrist is a University Professor Emeritus of Environmental Science and Engineering at the CSM. From 2001 to 2010, he served as Director of the Environmental Science and Engineering Division at CSM, and during a transitional retirement period, he is sustaining his affiliation with CSM as a Professor in the Civil and Environmental Engineering Department. Dr. Siegrist earned his BS (High Honors) and MS in Civil Engineering and his PhD in Environmental Engineering at the University of Wisconsin. He is a registered Professional Engineer and an AAEEES BCEE.

Before joining CSM in 1995, Dr. Siegrist held academic and research positions with the University of Wisconsin, Norwegian Institute for Georesources and Pollution Research, and Oak Ridge National Laboratory. He also served as Founding Partner of RSE, Inc. and a Senior Project Manager with Ayres Associates, Inc. Dr. Siegrist is an internationally recognized expert in *in situ* remediation of contaminated soil and groundwater. He has published 300 technical papers and two reference books and holds two U.S. patents. He was lead author of the first reference text concerned with *in situ* chemical oxidation (ISCO): *Principles and Practices of In Situ Chemical Oxidation Using Permanganate* (2001). He was also lead editor on another text, *In Situ Chemical Oxidation for Groundwater Remediation* (2011). Dr. Siegrist has given invited lectures at more than 100 workshops and conferences in more than 30 countries worldwide. He also has served as a science and engineering advisor to agencies and organizations in the United States and abroad, including the USEPA, Department of Energy, DoD, National Research Council, and the U.S. Government Accountability Office. He also served as a Fellow with the NATO Committee for Challenges to Modern Society.

Brent E. Sleep

Dr. Sleep is currently Chair of the Department of Civil Engineering at the University of Toronto. His research group conducts laboratory and computer modeling studies of bioremediation, thermal remediation, and applications of chemical oxidants and nanoscale zerovalent iron for subsurface remediation. His group is also investigating the transport of pathogens in fractured rock aquifers. Dr. Sleep is an Editor in Chief of the *Journal of Contaminant Hydrology* and an Associate Editor of *Advances in Water Resources*.

Eric J. Suchomel

Dr. Suchomel is a Project Engineer with Geosyntec Consultants, Inc. in San Francisco, California. He received his BSE degree in Chemical Engineering from the University of Iowa and his MSEnvE and PhD degrees in Civil and Environmental Engineering from the Georgia

Institute of Technology. His doctoral research focused on evaluating reductions in mass flux and discharge downgradient of DNAPL source zones following partial source zone mass removal and assessing *in situ* biological reductive dechlorination of residual DNAPL source zones.

Since accepting a position with Geosyntec, Dr. Suchomel has managed remediation projects for government and private clients throughout California. His current work is focused on the development and demonstration of innovative technologies for the remediation of emerging contaminants such as 1,2,3-trichloropropane. He is a registered professional engineer in the State of California.

Neil R. Thomson

Dr. Thomson is a Professor of Civil and Environmental Engineering and a member of the Environmental Modeling and Analysis Group and the Water Institute at the University of Waterloo, Ontario, Canada. At the University of Waterloo he teaches undergraduate and graduate courses in areas such as environmental chemistry, organic contaminants, contaminant transport, and remediation technology design. He received his PhD in Environmental Engineering from the University of Waterloo.

Dr. Thomson provides expert technical assistance on topics that include conceptual groundwater model development, groundwater flow and fate analysis, and remedial alternative selection and system design. He also is a featured lecturer in short courses in North America, the United Kingdom, Brazil, and Mexico. He has over 25 years of research experience in the use of field investigations, laboratory experiments, and numerical models to explore subsurface contaminant fate and remediation issues. His research interests are focused on the environmental fate of contaminants in subsurface systems including immiscible liquids, vapors and pathogens, development and application of simulation tools, and development and assessment of soil and groundwater remediation technologies. He is currently the Editor in Chief of *Groundwater Monitoring & Remediation*.

Paul G. Tratnyek

Dr. Tratnyek is Professor and Associate Head of the Division of EBS, Institute of Environmental Health (IEH) at the Oregon Health & Science University (OHSU). He received his PhD in Applied Chemistry from the CSM in 1987. He served as a National Research Council Postdoctoral Fellow at the USEPA Laboratory in Athens, GA (ERD-Athens), during 1988 and as a Research Associate at the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG) from 1989 to 1991. He then served as a National Research Council Postdoctoral Fellow at the USEPA Laboratory in Athens, GA, during 1988 and as a Research Associate at the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG) from 1989 to 1991.

Dr. Tratnyek's research concerns the physicochemical processes that control the fate and effects of environmental substances, including minerals, metals (for remediation), organics (as contaminants), and nanoparticles (for remediation, as contaminants, and in biomedical applications). Since 1992, Dr. Tratnyek has led research on the chemistry of permeable reactive barriers containing zerovalent iron and other chemical reductants.

Douglas I. Walker

Mr. Walker is a PhD candidate in the Department of Civil and Environmental Engineering at Tufts University. He received his BS in Civil Engineering from the University of Massachusetts at Dartmouth. Mr. Walker's research involves the fate and transport organic contaminants and engineered nanomaterials in the environment and the role of environmental

contaminants in neurodegenerative diseases. His PhD research focuses on the sequestration and metabolism of organic contaminants in cellular components, providing insight into the role of environmental exposures on the onset and progression of Parkinson's disease.

Michael R. West

Dr. West is a licensed professional engineer and holds BSc and PhD degrees from the Department of Civil Engineering at Queen's University in Kingston, Ontario. His PhD dissertation focused on the development and application of three-dimensional numerical models to simulate enhanced *in situ* biodegradation, ISCO, and surfactant flushing. Dr. West has published several articles on the topics of chlorinated solvent source zone remediation, matrix diffusion in fractured rock, and solute transport in fractured media. He is employed at B. Kueper & Associates Ltd. where his work focuses on the analysis and design of groundwater remediation systems, development of geologic models, litigation support, and delineation of NAPL source zones.

Dean F. Williamson

Mr. Williamson is a Principal Technologist with CH2M HILL, Inc., where he has worked for 25 years. As a project manager and senior consultant, he works on some of the most challenging remediation projects across the United States and internationally. He earned a BS at the University of Florida in 1978 and MS at Stanford University in 1986, both degrees in Environmental Engineering. He has over 33 years of experience in the field of soil and groundwater remediation and is a registered Professional Engineer in several states. Mr. Williamson has been involved in the design and implementation of remediation systems with a combined value of over \$200 million and covering a wide range of technologies including *in situ* bioremediation, ISCO, *in situ* thermal treatment, *ex situ* thermal desorption, *in situ* air sparging, biosparging, ISCR, SVE, soil mixing, groundwater and leachate extraction and treatment, permeable reactive barriers, and MNA.

John T. Wilson

Dr. Wilson is a research microbiologist for USEPA. He has a BS in Biology from Baylor University, an MA in Microbiology from the University of California at Berkeley, and a PhD in Microbiology from Cornell University.

Dr. Wilson has worked at the Robert S. Kerr Environmental Research Center in Ada, Oklahoma, since 1978. Currently, he conducts research on *in situ* bioremediation of chlorinated solvents and on natural attenuation of BTEX compounds, fuel additives, and chlorinated solvents. In addition to his research activities, he provides training and technical assistance to the USEPA regions and to state agencies on natural attenuation of chlorinated solvents, fuel additives, and BTEX compounds in groundwater.

A. Lynn Wood

Dr. Wood is a Soil Scientist in Ground Water and Ecosystems Restoration Research's Subsurface Remediation Branch, USEPA, Ada, Oklahoma. He holds BS and MS degrees in Agronomy from Oklahoma State University and a PhD in Environmental Science from the University of Oklahoma. He has worked for EPA's Office of Research and Development since 1975. Dr. Wood has conducted extensive research into the transport of organic contaminants in both aqueous solutions and complex mixtures. He led a multidisciplinary work group consisting of scientists from EPA and academia in developing conceptual and mathematical models to describe the influence of organic solvents on the sorption and mobility of nonpolar organic chemicals in porous media. Numerous publications were produced from this work, including EPA reports, journal articles, and dissertations.

External Reviewers

Robert C. Borden

Civil, Construction and Environmental
Engineering
North Carolina State University
Raleigh, NC 27695 USA

Richard A. Brown

Environmental Resources
Management (ERM)
Ewing, NJ 08618 USA

Mark L. Brusseau

Soil, Water and Environmental Science
The University of Arizona
Tucson, AZ 85721 USA

Elizabeth C. Butler

School of Civil Engineering
and Environmental Science
University of Oklahoma
Norman, OK 73019 USA

John Christ

U.S. Air Force Academy
Colorado Springs, CO 80840 USA

Jim Cummings

OSWER Technology Assessment
Branch, USEPA
Washington, DC 20460 USA

Thomas Early

Oak Ridge National Laboratory (retired)
Oak Ridge, TN 37831 USA

Murray Einarson

Haley & Aldrich
Walnut Creek, CA 94596 USA

Linda Fiedler

Office of Superfund Remediation
and Technology Innovation USEPA
Washington, DC 20460 USA

John Fountain

Marine Earth and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695 USA

Michael Gefell

ARCADIS U.S., Inc.
Lakewood, CO 80401 USA

Gorm Heron

TerraTherm, Inc.
Keene, CA 93531 USA

George J. Hirasaki

Department of Chemical & Biomolecular
Engineering, Rice University
Houston, TX 77005 USA

David Huntley

Geological Sciences
San Diego State University
San Diego, CA 92182 USA

Richard Jackson

Geofirma Engineering Ltd.
Heidelberg, ON Canada N0B 2M1

James W. Jawitz

Environmental Hydrology
University of Florida
Gainesville, FL 32611 USA

Stephen S. Koenigsberg

Brown and Caldwell
Irvine, CA 92612 USA

Fritz Krembs

Trihydro, Inc.
Laramie, WY 82070 USA

Paul D. Lundegard

Lundegard USA
Fullerton, CA 92835 USA

Kira Lynch

Superfund Technology Liaison (STL)
Region 10 ORD, USEPA,
Seattle, WA 98101 USA

Tamzen W. Macbeth

CDM
Helena, MT 59601 USA

Pat McLoughlin

Microseeps, Inc.
Pittsburgh, PA 15238 USA

James W. Mercer

GeoTrans, Inc. (a Tetra Tech Company)
Sterling, VA 20164 USA

John Molson

Département de géologie et de
génie géologique
Université Laval
Québec, QC, Canada G1V 0A6

Robert D. Norris

Brown and Caldwell (retired)
Longmont, CO 80501 USA

Matthew A. Petersen

GE Global Research Center
Niskayuna, NY 12309 USA

Albert Ricciardelli

GZA GeoEnvironmental, Inc.
Norwood, MA 02062 USA

Hanadi S. Rifai

Department of Civil and Environmental
Engineering
University of Houston
Houston, TX 77204 USA

Thomas J. Simpkin

CH2M HILL
Englewood, CO 80112 USA

Brent Sleep

Department of Civil Engineering
University of Toronto
Toronto, ON Canada M5S 1A4

Amy L. Teel

Department of Civil and Environmental
Engineering
Washington State University
Pullman, WA 99164 USA

René Therrien

Department of Geology
and Geological Engineering
Université Laval
Québec, QC, Canada G1V 0A6

Richard J. Watts

Department of Civil and Environmental
Engineering
Washington State University
Pullman, WA 99164 USA

Todd H. Wiedemeier

Wiedemeier & Associates
Evergreen, CO 80439 USA

A. Lynn Wood

Robert S. Kerr Environmental
Research Center, USEPA
Ada, OK 74820 USA

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