Natural Attenuation Monitor

March 2005

Issue 3

This publication is published by the US DOE Monitored Natural Attenuation and Enhanced Attenuation for Chlorinated Solvents Technology Alternative Project to provide to all interested parties the latest information on this project.

SRNL

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Comments and Questions on the MNA/EA Project may be e-mailed to Karen Vangelas at karen.vangelas@srs.gov or she may be reached at (803)-725-5223.

Note to Readers: The Monitor is now available on the Savannah River Site public webpage at www.srs.gov.

Overview of MNA-EA Project

I'll report our major progress from the seven months since we last communicated in the August 2004 issue of the *Natural Attenuation Monitor*. We have made excellent progress in all areas of the project. I will mention our major accomplishments so readers can share our enthusiasm.

The Technical Working Group (TWG) is completing three reports in the technical areas that form the basis for establishing the next generation of monitored natural attenuation. The mass balance report documents our thinking on natural attenuation capacity and was directed by Brian Looney and Frank Chapelle. At the upcoming Conference on In-situ and On-site Bioremediation, Baltimore, we will present a paper that applies the mass balance concept to data from a site in Georgia. Tom Early chaired development of the report on Enhanced Attenuation in which there is a wealth of information. Tom will present a poster session on the work at the Baltimore conference. Tyler Gilmore chaired the team that developed our thinking on characterization and performance monitoring from a systems perspective. Once these reports are peer reviewed, they will be available.

Simultaneously, the 14 research projects/field studies are well under way doing sample collection at Savannah River Site and data analyses. In this issue of the *Natural Attenuation Monitor*, several of the projects are described. We hosted a very successful Visitor Day in early February for regulators and end users to watch a demonstration of the push-pull field tests intended to calculate natural attenuation capacity in situ. As cutting-edge research, several university teams are developing molecular probes to obtain direct measurements for use as future performance monitoring tools. Interest is keen in the results from all research studies; enthusiasm of the researchers is contagious.

Our companion team of regulators, Enhanced Attenuation: Chlorinated Organics (EACO) Team is growing in size and making excellent progress. Regulators from three more states joined the team, meaning there are 11 states and EPA Region 7 represented on the Team. Industrial participants have doubled over 2004 private sector participation. DOE and Savannah River National Laboratory senior management are watching closely the organizational structure of the project. We are unique in that everyone who has a vested interest in the work has a chair at the table. To date, this structure has worked quite well as regulators, stakeholders, end users, state and regional regulators, and technology developers are fully integrated. The Regulator team and the DOE technical team have representation from the other team, meaning broad input and deliberation in our decision-making. As project manager, I monitor multiple interfaces and keep them functioning; but, acceptance of project results is worth the effort. Former stove pipes are dismantled, communication is enhanced, project ownership is broad; decisions usually have consensus, following deliberation and resolving concerns. We are described as a model project.

The project addresses an EM corporate issue. Idaho recently joined the TWG. Hence, we have representation from Savannah River, Richland, Oak Ridge, and Idaho sites. We welcome Mark Ankeny, Idaho National Laboratory, to the DOE Team.

If you have questions or comments, I am at Claire.sink@em.doe.gov

Claire H. Sink, Project Manager
U.S. Department of Energy

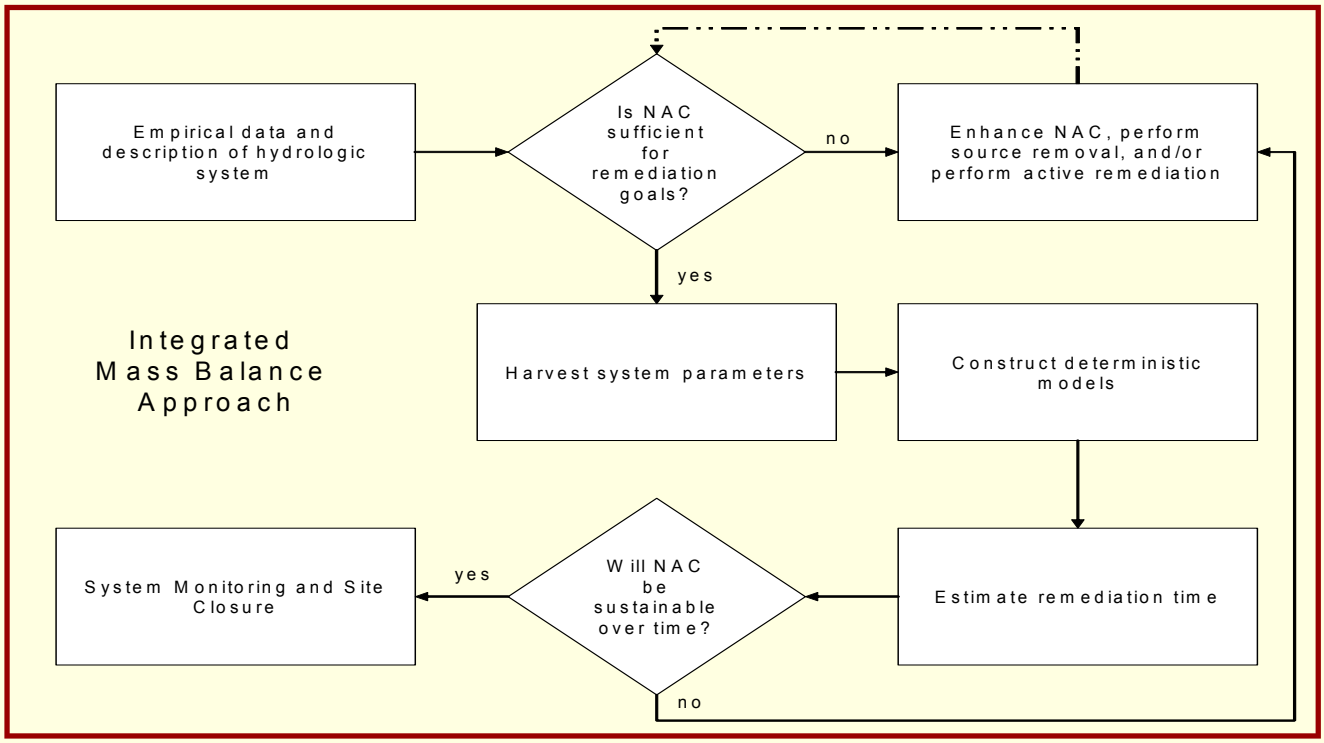
Initial Steps in Developing the Mass Balance concept for MNA/EA

What is the best way to calculate a mass balance? This is a question the Technical Working Group is investigating.

Two distinct philosophies are used for calculating a mass balance – the empirical method and the deterministic method. The 1998 EPA Protocol for MNA of Chlorinated Solvents embodies the empirical method. It relies on historical monitoring data and provides the most accurate description of past and present behavior of the hydrologic system. Because it does rely on historical data, it does not project future behavior nor does it support efficient MNA decision-making at sites with ongoing active treatment, such as pump-&-treat. The deterministic approach is based on physical, chemical, and biological data that can project future behaviors of the hydrologic system and contaminant life cycle. The deterministic approach can assess mass balance and plume stability. The complication in using this approach is it is difficult to cost-effectively measure many of the relevant hydrologic, geochemical , and biological parameters with certainty.

An alternative to either of these approaches is to combine the two. The figure below is a flow diagram of how these two approaches can be combined to take advantage of the strengths of both methods. In this example, the empirical approach is used wherever possible to determine if MNA is viable. The empirical result would be supplemented by a targeted deterministic analysis to evaluate sustainability and to estimate remediation time. The complexity of the required deterministic analysis would vary depending on the complexity of the site and the robustness of natural attenuation processes determined by the empirical analysis.

The ultimate goal of blending empirical and deterministic approaches is to provide a framework to answer the central questions faced by those implementing MNA: Are natural processes sufficient to stabilize and shrink the contaminant plume? When can I turn off a pump-&-treat system and transition to MNA? How much source treatment will be needed to support transition to MNA? If natural processes are not sufficient, can it be enhanced and how much will be needed? The first steps toward this framework appear promising.



An example of integrating the Empirical and Deterministic approaches to determining the Mass Balance for a system where MNA is a potential remedy.

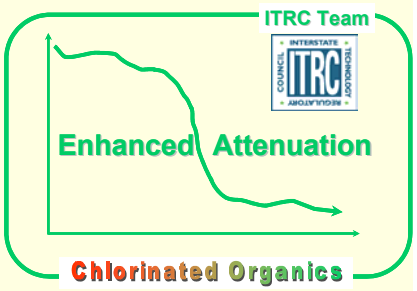
Push-Pull: A Method to Calculate the Natural Attenuation Capacity In Situ?

Is it possible to design a field-based test that will allow scientists and engineers to determine the natural attenuation capacity using in situ methods? That is exactly what a team of researchers led by Jack Istok, professor of Civil Engineering, Oregon State University, and Aaron Peacock, Microbial Insights are attempting. Using Push-Pull tests, this team will attempt to determine the natural attenuation capacity of a groundwater plume contaminated with trichloroethylene (TCE). The main goal of these tests will be to measure contaminant transformation rates at field sites under natural conditions, providing an alternative to doing microcosm studies. On February 9, 2005 a series of 13 push-pull tests were initiated at a testbed on the Savannah River Site. The tests are scheduled to be completed by early June 2005.

Two types of Push-Pull tests are conducted when evaluating the natural attenuation capacity of a system. These are transport tests and transformation tests. A series of these tests are conducted at various wells within the contaminant plume to gather data on the attenuation processes occurring within the entire plume. The transport test is a traditional injection/extraction test in which a solution comprised of an inactive tracer, a surrogate reactive tracer and groundwater from the injection well are injected into the well followed immediately by a period of extraction. The surrogate reactive tracer has breakdown pathways and rates similar to the contaminant of interest. For these tests, trichlorofluoroethene was the surrogate reactive tracer for TCE. The purpose of the transport test is to evaluate the mobility of the solutes in the aquifer that will be used in the transformation tests. In the transformation tests the same inactive tracer, surrogate reactive tracer and groundwater are injected followed by a long (up to 4 months) period of extracting samples. During the transformation test the natural processes acting on the surrogate reactive tracer are monitored. The purpose of the transformation test is to evaluate the rate of destruction of the surrogate tracer. By integrating the results of the two types of tests, the hypothesis is that it is possible to estimate the natural attenuation capacity of the waste unit using in situ methods.

Additional information on Push-Pull tests can be found at the following website: http://web.engr.oregonstate.edu/~istokj/grl-manuscripts.htm. Dr. Istok will be conducting a workshop on the Push-Pull testing at the Eighth International In Situ and On-Site Bioremediation Symposium, June 6 through 9, 2005, Baltimore. A paper on this study will be presented by Eric Raes, Engineering and Land Planning, at this symposium.

EACO Team Moves Full Speed Ahead



The Interstate Technology and Regulatory Council's Enhanced Attenuation: Chlorinated Organics (EACO) Team is nearing its one-year anniversary and is moving forward rapidly. Representatives from three additional states have joined the team. They represent Maine, California and Alabama. A survey developed during the autumn of 2004 was finalized and sent to the 43-member ITRC state Points of Contact in February 2005 for their input. The goal of the survey is to examine regulatory practices and successes, interest in, support of, and hurdles to implementing MNA and EA concepts, as appropriate. A major, ongoing initiative is developing and populating a database of case studies that showcase implementation of MNA and EA technologies. The team has developed criteria for selection of case studies and an outline for the information to be documented in the case studies. In March the team will finalize the criteria and outline.

The team is planning to develop a resource guide as the basis for the Technical-Regulatory document, the team's final product. The resource

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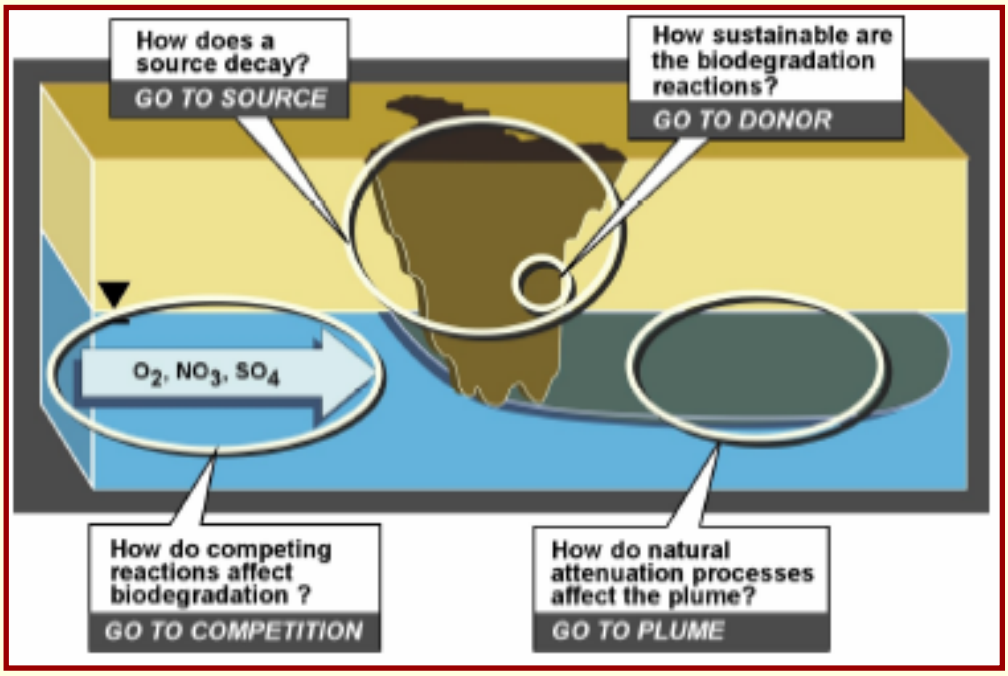
The Mass Balance Kit

For those familiar with BIOCHLOR, we have challenged that development team to design a user-friendly tool that assists in decision-making for evaluating Monitored Natural Attenuation (MNA) and adding enhancements at chlorinated solvent sites. Roopa Kamath and Chuck Newell at Groundwater Services Inc. are developing a spreadsheet-based application that will allow users to: i) evaluate how a source might decay over time; ii) estimate electron donor mass for evaluating sustainability of certain reactions; iii) analyze the impact of competing electron acceptors on attenuation of the contaminants present at that site, and iv) compare the relative effects of different attenuation processes on attenuation of dissolved plumes.

Taking basic hydrologic and geochemical information available at a site, these four issues (see the figure) can be evaluated. The purpose of this tool is to provide those who are responsible for decision-making at a chlorinated solvent waste site a simple method for evaluating natural attenuation by looking at the mass balance of contaminant sources, electron donors, competing electron acceptors, and different attenuation processes in the plume.

The project team believes the Mass Balance Kit will be a useful tool that will help site managers look at natural attenuation and apply mass balance concepts to managing chlorinated solvent sites. Work is progressing well.



The four questions to be answered in the Mass Balance Kit.

Anaerobic Oxidation of Chlorinated Organic Compounds: Does it Contribute to Natural Attenuation?

The official EPA Protocol for evaluating the potential for MNA at chlorinated solvent sites is based on anaerobic reduction, also called reductive dechlorination. To realize the full potential of MNA as a remedial option, the viability of other physical, chemical, and biological processes that may contribute to the natural attenuation capacity of a system must be understood. One research team is investigating the process of oxidative biodegradation under anaerobic conditions and its potential role as a contributor to the natural attenuation capacity of a system. Paul Bradley, a hydrologist with the U.S. Geological Survey, Columbia, South Carolina, has been conducting research in this area since 1993.

There is gathering scientific evidence that anaerobic oxidation plays a role in the attenuation of chlorinated solvent plumes. A key difficulty in measuring the process is the end products, carbon dioxide and water, are already present. Paul is using radio-labeled cis-dichloroethylene (cis-DCE) and vinyl chloride (VC) to

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MNA/EA Project Introduced to Florida Department of Environmental Protection Dry Cleaner Program

For years, dry cleaners across the United States have used chlorinated solvents. This has led to these facilities representing numerous point sources of contamination. Florida, as a charter member of the states having a fund to remediate historical dry cleaner contamination, is aggressively working towards assessment and remediating these contaminant sources. A key to the success of the program is incorporating new technology and remediation strategies and sharing the information among regulators and contractors. From February 16th through 18th, 2005 the Florida Department of Environmental Projection Hazardous Waste Cleanup Section (HWC) hosted their annual Hazardous Waste Cleanup Contractor Workshop for Dry Cleaner Fund Regulators section staff and HWC State Cleanup Contractors, in Tallahassee, Florida. The attendees shared their successes and lessons learned, as well as discussed and brainstormed on new technology options for characterizing and

Florida regulators and contractors discuss progress in remediating dry cleaner sites at their annual workshop.

remediating dry cleaners facilities. The workshop was well attended with about 50 participants representing regulators and state cleanup contractors. Judie Kean, co-chair of the ITRC Enhanced Attenuation Chlorinated Organics Team, coordinated this annual workshop and invited representatives from the MNA/EA Team to present their

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Molecular Probes – Direct Assessment Tools for Bioremediation Monitoring

Implementation of MNA at chlorinated solvent sites may eventually be based solely on molecular assessment. Nucleic acid (i.e., DNA and RNA) probes target genes of microorganisms that are responsible for the microbial detoxification of chlorinated solvents. Some molecular methods can quantify concentrations of DNA in a sample, can directly identify the presence of a target organism, and can provide quantitative information (i.e., abundance) of an organism of interest. Such DNA-based tools, however, cannot measure if those organisms are actively degrading the contaminants. Molecular methods that quantify concentrations of RNA in a sample focus on the "expression" of a target pathway and may correlate better with actual degradation rates. As in medicine, the development of an appropriate suite of nucleic acid-based probes may provide rapid and inexpensive techniques that more accurately describe the microbial community and its activity compared to the indirect measures that are available today.

Preparation of a DNA microarray. This photo was supplied courtesy of Elizabeth Edwards.

Several research teams supported by this project are working on the design of such tools. Frank Löffler, a professor at Georgia Tech, and Elizabeth Edwards, a professor at the University of Toronto, are collaborating to develop DNA- and RNA-based molecular probes for the detection of specific *Dehalococcoides* bacteria that reductively dechlorinate the pervasive groundwater pollutants tetrachloroethene (PCE) and trichloroethene (TCE) to harmless ethene. Jim Gossett, a professor and department chair of Civil and Environmental Engineering, Cornell University, is developing DNA-based molecular probes for de-

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Communication: A Key to Success

For this project, communication is part of the key to success. Throughout this project, we have and continue to work to communicate our progress. We gather feedback to enable our technical team to direct their efforts towards those issues and activities that will make the greatest impact to future decision-making on and implementations of MNA and EA. During the past six months, we have met with representatives of EPA Region IV, regulators from the states of South Carolina and Tennessee, and stakeholders and end users associated with Oak Ridge, Hanford and Savannah River Sites. The general consensus of the participants is that the project is moving in a good direction and there is much interest in the results of the research studies.

On February 11, 2005, we hosted a visitor day for the Push-Pull Field Study. Approximately 50 people attended, representing the South Carolina Department of Health and Environmental Control, the U.S. Department of Energy, and the WSRC Soil and Groundwater Closure Project who are the end users at Savannah River. "The presentations made today were interesting and informative. The Push-Pull tests have a wide range of application and should be considered as a potential characterization tool for making decisions on appropriate enhanced attenuation applications" stated Mark Amidon, a senior geologist for the Soil and Groundwater Closure Project (SGCP), Savannah River Site. As an end-user, Mark is leading several investigations at some of the largest and more complex SRS waste units.

Jack Istok describes Push-Pull Test details to attendees at the Field Visitor Day at the Savannah River Site.

In communicating beyond the Department of Energy, we published two articles in the winter 2004 issue of Remediation, The Journal of Environmental Cleanup Costs, Technologies & Techniques. These articles are in the Published Documents listing at the end of this newsletter. In addition, the project team will be presenting 4 papers at the following two conferences: ASCE's World Water & Environmental Resources Congress 2005, May 15 - 19, in Anchorage and the Eighth International In Situ and On-Site Bioremediation Symposium, June 6 – 9, in Baltimore.

(Continued from page 7) Florida Dry Cleaner Program

project. Brian Looney attended the workshop and presented an overview of the DOE Alternative Project – Monitored Natural Attenuation and Enhanced Attenuation of Chlorinated Organics.

There was significant support for the direction of the DOE Alternative Project and significant interest in the results and products from the project to date. There was also interest in the project's partnership with the ITRC. The HWC Contractor workshop in Florida provided the project with a unique opportunity to access an interested and cutting-edge group. The interaction resulted in a positive information exchange and the possibility of future cooperation.

(Continued from page 5) EACO Team

guide will provide a comprehensive look at MNA and EA, what they are, and what regulations and technical guidance documents are available. Information from the case study database will be in the resource guide.

If anyone has a case study they think may be appropriate for the case study database please contact Judy Kean at judie.kean@dep.state.fl.us, or Kimberly Wilson at [wilsonka@dhec.sc.gov] for information related to submitting case studies.

(Continued from page 7) Molecular Probes

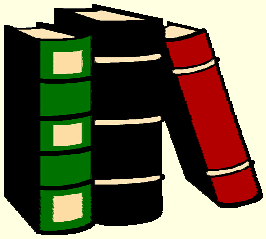
tection of *Polaromonas* strain JS666, a microorganism that is responsible for aerobic degradation of *cis*-dichloroethene (cDCE). Ruth Richardson, a professor at Cornell University, is conducting research to establish correlations between concentrations of RNA from *Dehalococcoides* and dechlorination rate constants for PCE and TCE degradation obtained by standard analytical and field methods.

This cutting edge innovative research and development promises to simplify site characterization efforts and to promote implementation of MNA at chlorinated solvent sites.

(Continued from page 6) Anaerobic Oxidation

conduct microcosm studies with soils at two SRS waste units where there is evidence of plume shrinkage via biological processes. By using ^{14}C-radio-labeled compounds, Paul is able to assess biodegradation to CO_2 with certainty. Early results indicate that anaerobic oxidation is occurring to some extent for both cis-DCE and VC in the sediments from these two units. Work will progress to determine the relative importance of anaerobic oxidation in the natural attenuation capacity of these two systems. Work will begin on isolating the microorganisms responsible for anaerobic oxidation of the cis-DCE and VC. If successful, these efforts may allow development of molecular tools for identifying oxidative microorganisms in situ.

Published MNA/EA Project Documents



A running list of all documents that are a product of this project is presented here. Documents will be added to the list once they are approved for public release. Most documents will be available from the Office of Scientific and Technical Information's website (www.OSTI.gov). Each listing will include the document title, hot link, and short description. Those documents that were presented in previous issues will not include a description.

Two articles were published in the journal *Remediation, The Journal of Environmental Cleanup Costs, Technologies, & Techniques*, Winter 2004, Volume 15, Number 1. Published by Wiley Publishers. The two articles and authors are listed below.

"Accelerating Environmental Cleanup at DOE Sites: Monitored Natural Attenuation/Enhanced Attenuation – A Basis for a New Paradigm", Claire H. Sink, Karen M. Adams (US DOE), Brian B. Looney, Karen M. Vangelas (SRNL), and Norman H. Cutshall. This article describes the organizational structure of the project and its relevance to conducting high quality research.

"Historical Analysis of Monitored Natural Attenuation: A Survey of 191 Chlorinated Solvent Sites and 45 Solvent Plumes", Travis M. McGuire, Charles J. Newell (GSI), Brian B. Looney, Karen M. Vangelas (SRNL), and Claire H. Sink (US DOE). This article is a synopsis of the *Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents* document published early in the project.

The following are the documents described in previous issues of the *Monitor*.

Scientific Basis for Monitored Natural Attenuation and Enhanced Passive Remedation for Chlorinated Solvents – DOE Alternative Project for Technology Acceleration Implementation Plan. (www.osti.gov/bridge/product.biblio.jsp?osti_id=810006&queryId=1&start=0), WSRC-RP-2003-00286, Department of Energy, Office of Scientific and Technical Information, Oak Ridge TN, February 20, 2003.

Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting

(Continued from page 9) Published Documents

Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents. (www.osti.gov/bridge/product.biblio.jsp?osti_id=820972&queryId=1&start=0), WSRC-TR-2003-00333, Department of Energy, Office of Scientific and Technical Information, Oak Ridge TN, October 20, 2003.

Summary Document of Workshops for Hanford, Oak Ridge and Savannah River Site as part of the Monitored Natural Attenuation and Enhanced Passive Remediation for Chlorinated Solvents - DOE Alternative Project for Technology Acceleration. (www.osti.gov/bridge/product.biblio.jsp?osti_id=820971&queryId=1&start=0), WSRC-RP-2003-1044, Department of Energy, Office of Scientific and Technical Information, Oak Ridge TN, October 20, 2003.

Natural and Passive Remediation of Chlorinated Solvents: Critical Evaluation of Science and Technology Targets. (www.osti.gov/bridge/product.biblio.jsp?osti_id=822824&queryId=2&start=0), WSRC-TR-2003-00328, Department of Energy, Office of Scientific and Technical Information, Oak Ridge TN, February 2004.

Baseline Natural Attenuation Processes: Lines of Inquiry Supporting Monitored Natural Attenuation of Chlorinated Solvents. (www.osti.gov/bridge/product.biblio.jsp?osti_id=828468&queryId=1&start=0), WSRC-TR-2003-00329, Department of Energy, Office of Scientific and Technical Information, Oak Ridge TN, May 18, 2004.

Five papers were presented at the Battelle sponsored Remediation of Chlorinated and Recalcitrant Compounds, The Fourth International Conference, May 24—27, 2004, Monterey California. Battelle press publishes the proceedings in which all five papers are published. The titles of the papers and authors are:

"A Mass Balance Approach to Monitored Natural Attenuation", Frank Chapelle, C. Journey (USGS) B. B. Looney, M. Heitkamp, Robin Brigmon (SRTC), D. Major (GeoSyntec Consultants), T. Early (ORNL), T.H. Wiedemeier (T.H. Wiedemeier & Assoc.), T. Gilmore (PNNL), G. Wein (BSRI), C. Sink (US DOE).

"Facilitating MNA and Enhanced Passive Remediation (EPR) of Chlorinated Solvents", Brian B. Looney, K. M. Vangelas (SRTC), C. Sink (US DOE).

"Trends in Monitored Natural Attenuation Application at Chlorinated Solvent Sites", Charles J. Newell, T.M. McGuire (Groundwater Services, Inc.), B.B. Looney, K.M. Vangelas (SRTC), C. Sink (US DOE).

"Putting the Third Line of Evidence First—Advances in Molecular Technologies", David W. Major (GeoSyntec), M. Heitkamp (SRTC), C. Sink (US DOE).

"Characterization and Monitoring Strategy for Monitored Natural Attenuation", Tyler Gilmore (PNNL), B. B. Looney, B. Riha (SRTC), J. Waugh (S.M. Stoller), C. Sink (US DOE).