



Natural Attenuation Monitor

March 2006

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.

Table of Contents

	Page
Overview of MNA/EA Project	3
Field Characterization Tools to Support MNA Decision Making	4
EACO Team: Member Survey— Use of MNA and Interest in Enhanced Attenuation	5
Sharing Technical Advances	6
Summary Article on Key Project Concepts	6
Implementing Mass Balance and Enhanced Attenuation	7
Published MNA/EA Project Documents	7

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

The Natural Attenuation Monitor is published under the direction of the U.S. Department of Energy MNA/EA for Chlorinated Solvents Technology Alternative Project. Editor is Karen Vangelas at the Savannah River National Laboratory, 803-725-5223. Please send information, comments, or questions to karen.vangelas@srnl.doe.gov.

On the Cover: Kirk Hatfield, University of Florida, retrieves a passive flux meter from well at Savannah River Site testbed.

Overview of MNA-EA Project

It's an important time for this Alternative Project. We have just completed the first half of the final year of this project. We're coming down to when the research results and final reports are due. The challenge is ours as the Technical Working Group (TWG) deliberates on bringing the mass balance, enhanced attenuation, and monitoring and characterization concepts together with the empirical results from the suite of research projects.

The regulatory piece of the project is advancing nicely. The EACO (Enhanced Attenuation: Chlorinated Organics) Team of the ITRC (Interstate Technology and Regulatory Council) has just met in Austin, TX. The highlight of that meeting was consensus on the design of the Decision Framework Flow Diagram necessary for the transition of a site using the enhanced attenuation strategy. The Flow Diagram includes an iterative process in regards to deciding when to transition a site into a new treatment phase, the basis for selecting EA technologies, and balancing time and sustainability. The framework for the Tech-Reg Guidance Document will ultimately incorporate the Flow Diagram and provide a detailed discussion regarding enhanced attenuation mechanisms. If the options work, MNA-EA could be applicable to additional DOE sites.

We have outdone ourselves in conference participation this spring. We will qualify for overworked elocutionists. In April 2006 we are chairing a session on enhanced attenuation at the National Groundwater Association meeting in San Antonio. There will be 4 papers in that session on the work of this project. In May 2006 we will have a session on new tools and approaches on MNA and enhanced attenuation for chlorinated solvents at the Fifth International Battelle Conference on Remediation of Chlorinated and Recalcitrant Compounds on the west coast. Five of the papers in the session and several poster presentations are from the Alternative Project. Following the tech-

nical session, we are invited to do a panel discussion on advances in MNA for chlorinated solvents with panelists being members of the TWG or principal investigators on the Alternative Project. Hence, if you attend the Battelle Conference, the session and panel are scheduled for Wednesday, May 24.

Simultaneous with the Battelle Conference, the American Geophysical Union Joint Assembly will convene on the east coast. Two invited speakers affiliated with the Alternative Project will present papers on monitoring to demonstrate performance of subsurface remediation techniques. The first paper describes a proposed systems approach to characterization and monitoring of contaminated groundwater; the second paper describes an automated network developed at Idaho National Laboratory that does data collection, analysis, and reporting as applied at the 100-N Area of Hanford.

We're most proud of the three reports on the concepts developed in this Alternative Project: mass balance, enhanced attenuation, and monitoring and characterization. The TWG has deliberated at length and clearly drew the line in the sand to advance cutting edge science. The reports are being finalized following their peer review; they will be available shortly. Their contents will be featured in many of the papers being given at the conferences mentioned previously.

Let us hear your questions and comments. We're glad to hear from our readers and to learn what's on your mind. I am at Claire.sink@em.doe.gov.

Claire H. Sink, Project Manager
Office of Environmental Management

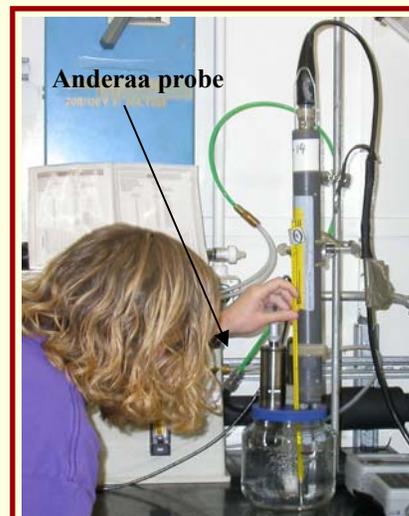


Field Characterization Tools to Support MNA Decision Making

Measurements, either for characterization or monitoring, are the only way to evaluate where MNA is a viable and operating remedial process. Several of the research teams in this MNA/EA project are testing field-based characterization tools to support decision-making to implement MNA. Two research teams are evaluating tools to measure direct parameters. The results of the other two teams, separately, will provide mass flux and reaction rate data.

Reductive dechlorination is usually identified as the preferred attenuation mechanism for the natural attenuation of chlorinated solvents. A key parameter in determining where in the subsurface this mechanism will occur is the level of dissolved oxygen in the system. There are several methods commercially available for measuring dissolved oxygen. Between members of this project team, there were differing opinions on the reliability of the results at the low concentrations (< 1 mg/L) indicating an anaerobic setting.

The Andraea Oxygen Optode, a commercially available oxygen measuring device developed for oceanographic applications, is being tested in this study to evaluate its applicability as a measurement device for such low concentrations of dissolved oxygen. The Andraea Optode uses a sensor that does not consume oxygen, unlike the electrochemical based sensors, potentially increasing the accuracy of reading at low concentrations.



SRNL scientist Maggie Millings calibrating Andraea and YSI probes

The second direct measurement tool is the microsparger, a down-well sampling tool, that when combined with a commercially available field-based gas analyzer can provide screening level data to determine the concentrations of chlorinated solvents and their daughter products. Many gas analyzers are built with internal data logging capabilities which allow the user to remotely collect data for extended periods of time dependent on the frequency of sample collection. Depending on the sophistication of the data logging system, personnel can download data at the site or via remote communication devices. The data when graphed on concentration versus time plots can provide empirical evidence of the biological degradation process occurring in the system.



PNNL and SRNL researchers prepare for installation of microsparger into monitoring well

The passive flux meter (PFM) is a down-well sampling device that provides contaminant data in terms of flux rather than concentration. The developers, professors at the University of Florida, through a Department of Defense funded project have been testing this device at multiple sites across the US. The new twist in this study is to adapt the tool to generate simultaneous field measurements of cumulative water flux and the cumulative fluxes of multiple chlorinated solvents and ancillary solutes (such as chloride).

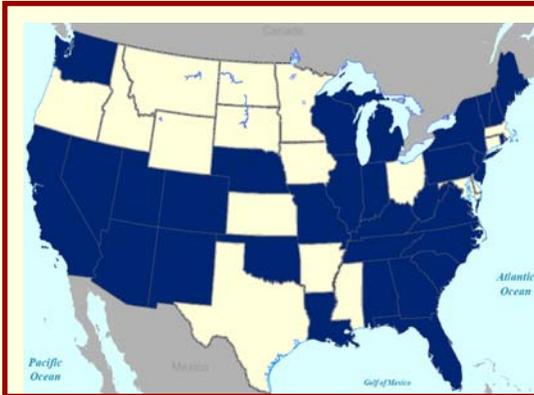
Lastly, one research study is evaluating the use of push-pull tests (see article in March 2005 issue titled "Push-Pull: A method to Calculate the Natural Attenuation Capacity In Situ?") as an in situ test method to calculate degradation rates on a plume-wide basis. A major challenge the researchers face is using the results of a short-term (2-6 month) test to predict long-term degradation rates for processes that can be quite slow.

EACO Team : Member Survey – Use of MNA and Interest in Enhanced Attenuation

By Judie Kean and Kimberly Wilson



In many cases the best way to move forward is to understand the past. As the Interstate Technology and Regulatory Council (ITRC) Enhanced Attenuation Chlorinated Organics (EACO) Team develops



States represented in survey response (darkened states).

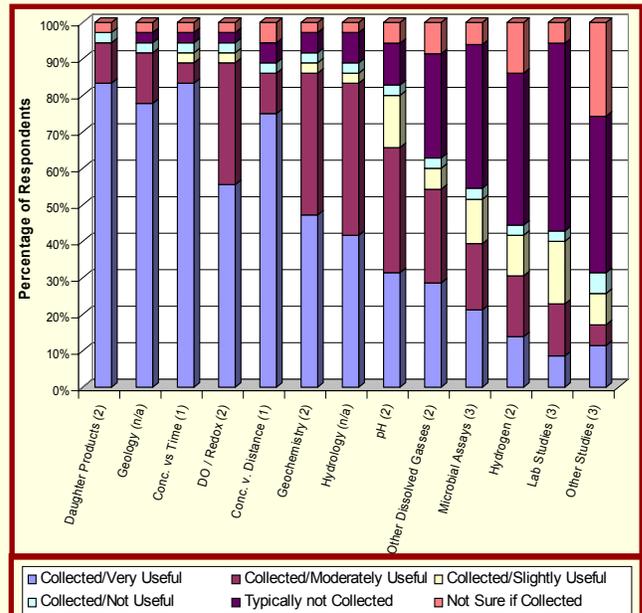
the concept of Enhanced Attenuation for chlorinated organics, they chose to survey the ITRC member states to determine the use of MNA, factors contributing to its acceptance or rejection, and interest in technical processes that can be implemented using an Enhanced Attenuation concept. The web-based survey was conducted in the summer of 2005 with 39 responses representing 31 states and a diversity of programs (e.g., RCRA, Dry Cleaner, Brownfield).

The results indicate MNA is being employed as all or part of remedial actions for chlorinated organic sites, with the majority of sites in progress. The majority of respondents use either the EPA guidance or guidance based on the EPA guidance as the basis for their evaluation of MNA. Measurement of daughter

products evaluated over time was identified as the most collected data. In making decisions on MNA, most respondents identified results based on hand calculations and risk concentrations and exposure as most used and most important.

The final section of the survey asked each respondent to identify their level of interest in several areas where changes from the status quo are being considered. In general the respondents were supportive of all the areas. These topic areas are: use of mass balance in deciding when and how to transition from the various stages of remediation; including flux measurements in making these determinations, having two phases to both characterization and monitoring, and uses of various processes to enhance attenuation.

Highlights of this survey will be presented by Judie Kean, co-chair of the EACO team, at the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, sponsored by Battelle, May 22-25 in Monterey, California. A document presenting the complete survey results is in draft form and when complete will be available on the ITRC website. Watch the *Natural Attenuation Monitor* for updates on availability of this document.



NOTE: (1) primary line of evidence, (2) secondary line of evidence, and (3) tertiary line of evidence

Use and importance of data collected for MNA decision-making

Sharing Technical Advances

A key component of research and development is disseminating the results and products to facilitate their use by the scientific technical community, regulators, stakeholders, and the general public. Development activities, as well as the concepts of mass balance, enhanced attenuation, and characterization and monitoring, will be presented at three national conferences this spring. Groundwater Summit 2006, sponsored by the National Groundwater Association, will be held April 23 -26 in San Antonio, Texas, and will include a technical session on Enhanced Attenuation, chaired by Karen Vangelas, the Operations Lead for the MNA/EA Project. The emphasis of this session will be to define and describe enhanced attenuation and present case studies of technologies that can be used as EA technologies. Presentations will represent work associated with the Air Force Center for Environmental Excellence, University of Waterloo, Interstate Technology and Regulatory Council (ITRC), Groundwater Services Inc., and the U.S. Department of Energy. Information on this conference can be obtained at www.ngwa.org.



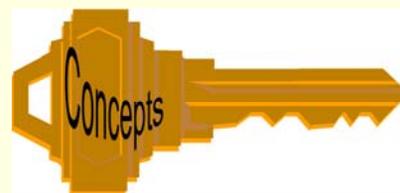
A technical session and a panel discussion will provide the project team the opportunity to present results of this project and other projects associated with MNA at the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, sponsored by Battelle, May 22-25 in Monterey, California. The technical session is titled “MNA and Enhanced Attenuation for Chlorinated Solvents: New Tools and Approaches” and the panel discussion is titled “Advances in Monitored Natural Attenuation for Chlorinated Solvents”. Both the session and discussion provide an avenue to present and describe the three concepts identified in the previous paragraph, as well as present tools and methods to facilitate use of natural attenuation processes for

treatment of chlorinated solvents. Claire Sink, Project Manager of the MNA/EA Project, and Kimberly Wilson, South Carolina Department of Health and Environmental Control and co-leader of the ITRC Enhanced Attenuation: Chlorinated Organics (EACO) team, will co-chair the technical session. Presentations will represent work associated with private industry, international organizations, universities, and the Departments of Defense and Energy. Claire Sink and Tyler Gilmore, a member of the MNA/EA Project Technical Working Group (TWG), will be co-moderators of the panel discussion. Panelists will be representatives from the TWG, ITRC EACO team, and researchers funded through the MNA/EA Project. Information on this conference can be obtained at www.battelle.org/chlorcon.

Two presentations representing this project will be presented at 2006 Joint Assembly, sponsored by the American Geophysical Union, to be held May 23—26 in Baltimore, Maryland. The two talks present characterization and monitoring approaches and tools that can be employed with remedies relying on natural attenuation processes. These talks are included in the technical session titled, Monitoring to Demonstrate Performance of Subsurface Remediation Techniques. Information this conference can be obtained at www.agu.org.

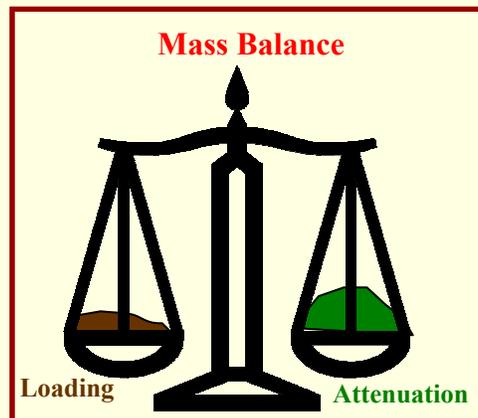
Summary Article on Key Project Concepts

An article summarizing the development efforts to date in the areas of mass balance, enhanced attenuation, and characterization and monitoring associated with this project has been submitted to *Remediation, The Journal of Environmental Cleanup Costs, Technologies, & Techniques* for publication in the Summer 2006 issue.



Implementing Mass Balance and Enhanced Attenuation

Case studies providing examples of various approaches to performing a mass balance of a waste site and of the implementation of different technologies per the Enhanced Attenuation concept are currently under development by the project's Technical Working Group. Five case studies will describe how a simple method such as taking contaminant data from wells that are located in parallel transects perpendicular to the flow of groundwater can be employed for mass balance determinations to complex methods such as the use of deterministic models that can predict the growth and eventual shrinkage of a plume through the use of various attenuation mechanisms and various active treatments. These five case studies will look at sites at Hill Air Force Base, Utah; Plattsburg, New York; the Hanford Site, Washington; Kings Bay, Georgia; and Savannah River Site, South Carolina. The four Enhanced Attenuation case studies look at the use of biomulch walls, alternative caps, phytoremediation, and bioaugmentation. Once complete, these case studies will be compiled into a document that will be available through the Office of Scientific and Technical Information as www.osti.gov.

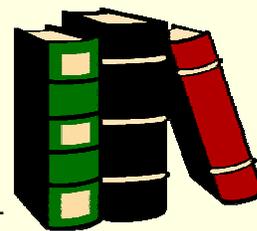


Published MNA/EA Project Documents

A running list of all documents that are products of this project will be presented here. Documents will be added to the list once they have been approved for public release. Most documents will be available from the US DOE Office of Scientific and Technical Information's (OSTI) website (www.OSTI.gov). Each listing includes the document title, hot link, and short description. Previously presented documents will not include a description.

Characterization and Monitoring of Natural Attenuation of Chlorinated Solvents: A System Approach, WSRC-TR-2005-00199, Rev. 0. February 2006. Tyler Gilmore (Pacific Northwest National Laboratory (PNNL)), Brian B. Looney (Savannah River National Laboratory (SRNL)), David Major (GeoSyntec, Inc.), Todd Wiedemeier (T.H. Wiedemeier & Assoc., LLC), Michael Heitkamp (SRNL), Jody Waugh, David Peterson (S.M. Stoller), Gary Wein (Bechtel Savannah River, Inc. (BSRI)), Christopher Bagwell (SRNL), Mark Ankeny (Idaho National Laboratory (INL)), Karen M. Vangelas (SRNL), Karen M. Adams (US Department of Energy (DOE)), Claire H. Sink (US DOE). As of this printing, this document has not

been posted on the OSTI website. Contact K. Vangelas to obtain a copy of this document.



Enhanced Attenuation: Approaches to Increase the Natural Treatment Capacity of a System, WSRC-TR-2005-00198, Rev. 0. January 2006. Tom Early (GEO Consultants), Bob Borden (North Carolina State University), Michael Heitkamp, Brian B. Looney (SRNL), Dave Major (GeoSyntec, Inc.), Jody Waugh (S.M. Stoller), Gary Wein (BSRI), Todd Wiedemeier (T.H. Wiedemeier & Assoc., LLC), Karen M. Vangelas (SRNL), Karen M. Adams (US DOE), and Claire H. Sink (US DOE). As of this printing, this document has not been posted on the OSTI website. Contact K. Vangelas to obtain a copy of this document.

Remediation Forum Question to the Panel on the Acceptability of the term Integrated Mass Flux. Karen M. Vangelas (SRNL). *Remediation, The Journal of Environmental Cleanup Costs, Technologies, and Techniques*. Winter, 2005. Wiley Publishers. A question related to the comfort level

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with and application of using flux in the determination of whether natural attenuation is a viable remedy was posed to a panel of respected technical personnel from industry, federal agencies, and universities.

Previously described articles, documents, and presentations. Only the lead author is identified for previously presented items.

Papers presented at the Battelle sponsored 8th International *In Situ* and On-Site Bioremediation Symposium, June 6 - 9, 2005. Battelle Press.

Next Generation – Monitored Natural Attenuation and Enhanced Attenuation – Chlorinated Solvents. Karen M. Vangelas (SRNL).

Empirical and Deterministic Methods for Assessing Monitored Natural Attenuation. Francis H. Chapelle (USGS).

Enhancements to Natural Attenuation Processes: New Approaches to Plume Management. Thomas O. Early (GEO Consultants).

Push-Pull Tests to Determine In Situ Site Wide Natural Attenuation Capacity and Microbial Activity at Savannah River CMP Pits and C-Area. Eric J. Raes (Engineering & Land Planning).

Paper presented at the American Society of Civil Engineers (ASCE), World Water & Environmental Resources Congress 2005, May 15 – 19, 2005. ASCE.

Monitored Natural Attenuation and Enhanced Attenuation for Chlorinated Solvent Plumes – It's all about balance. Karen A. Adams (US DOE).

Articles published in Remediation, The Journal of Environmental Cleanup Costs, Technologies, & Techniques, Winter 2004, Volume 15, Number 1. Wiley Publishers.

Accelerating Environmental Cleanup at DOE Sites: Monitored Natural Attenuation/Enhanced Attenuation – A Basis for a New Paradigm, C. H. Sink (US DOE).

Historical Analysis of Monitored Natural Attenuation: A Survey of 191 Chlorinated Solvent Sites and 45 Solvent Plumes, T. M. McGuire (GSI).

Project Documents (all are available at the US Dept. of Energy, Office of Scientific and Technical Information, Oak Ridge, TN www.osti.gov)

Multiple Lines of Evidence Supporting Natural Attenuation: Lines of Inquiry Supporting Monitored Natural Attenuation and Enhanced Attenuation of Chlorinated Solvents. WSRC-TR-2003-00331, December 2004. As of this printing, this document has not been posted on the OSTI website. Contact K. Vangelas to obtain a copy of this document.

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

Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00333, October 20, 2003. (www.osti.gov/bridge/product.biblio.jsp?osti_id=820972&queryId=1&start=0).

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, WSRC-RP-2003-1044, October 20, 2003. (www.osti.gov/bridge/product.biblio.jsp?osti_id=820971&queryId=1&start=0).

Natural and Passive Remediation of Chlorinated Solvents: Critical Evaluation of Science and Tech-

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(Continued from page 8) Published MNA/EA Project Documents

nology Targets, WSRC-TR-2003-00328, February 2004. (www.osti.gov/bridge/product.biblio.jsp?osti_id=822824&queryId=2&start=0).

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

Papers presented at the Battelle sponsored 4th International Conference for Remediation of Chlorinated and Recalcitrant Compounds, May 24—27, 2004. Battelle Press.

A Mass Balance Approach to Monitored Natural Attenuation, F. Chapelle (USGS).

Facilitating MNA and Enhanced Passive Remediation (EPR) of Chlorinated Solvents, B. B. Looney (SRTC).

Trends in Monitored Natural Attenuation Application at Chlorinated Solvent Sites, C. J. Newell (Groundwater Services, Inc.).

Putting the Third Line of Evidence First—Advances in Molecular Technologies, D. W. Major (GeoSyntec).

Characterization and Monitoring Strategy for Monitored Natural Attenuation, T. Gilmore (PNNL).