Oak Ridge National Laboratory:
Mercury Related Research and Capabilities

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Take Home Message

- ORNL has a rich tradition in conducting mercury-related research
  - Significant capability (institutional knowledge, equipment, and facilities)
  - Translation of new knowledge to support applied research and engineering scale-up (TRL 1-6)
- Value of ORNL's mercury-related research to EM clean-up projects
  - Provide science and engineering leadership in support of project execution
  - Quickly advance or adapt promising technologies for site specific applications
  - Reduces project uncertainty and schedule
  - Increases probability of successful execution within scope and budget
- Demonstrated in previous and existing mercury-related research projects
  - Mercury SFA – DOE SC Funded
  - Mercury AFRI – DOE EM-HQ Funded
  - BMAP – DOE ORO Funded

Present Y-12 End State

Science to Application http://www.esd.ornl.gov/romic_afrc/index.shtml

History of Mercury Related Research at ORNL

- Over 35 years (early 1970s to present) of mercury related research for AEC (successor to ERDA and DOE), NSF, and EPRI
- Projects varied in scope and included aspects of:
  - Atmospheric mercury deposition (power plants), mercury environmental transformation and fate, remediation and technology development, waste disposal, and storage
- Impact of these activities:
  - Resulted in over 200 peer-reviewed publications as well as numerous conference papers, book chapters, and technical reports
  - Provided the technical foundation for a variety of clean-up decisions at Oak Ridge as well as other sites both nationally and internationally
    - Designed and develop techniques for measuring mercury in environmental samples (1972)
    - Clean-up of LEFPC (1995-1997)
    - Evaluated environmental impact of a mercury mine in Almaden, Spain (1974 – 1976)

Science to Application

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History of Mercury Related Research at ORNL

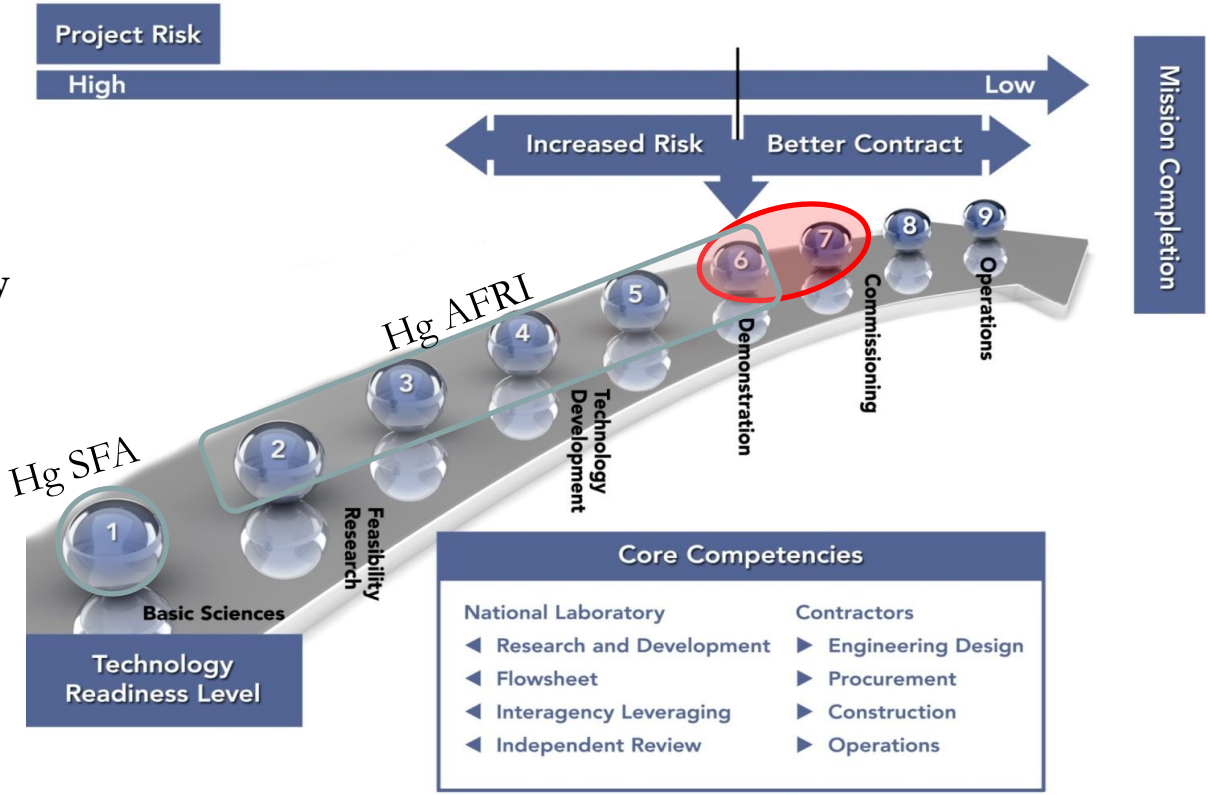
- Examples include:
  - NSF Ecology and Toxic Contaminants Program (1972 – 1975)
  - Biological Monitoring and Abatement Program (1984 – present)
  - Remediation of Mercury in Plant Effluents (1986 – 2002)
  - Lower East Fork Poplar Creek Characterization – Identification of cinnabar/meta-cinnabar species to support remedial decision (1995 – 1997)
  - Mercury Air Surface Exchange in Everglades (MASE) (1999 – 2000)
  - Fugitive Mercury Emissions from Industrial/Commercial Sources (FuME) (2000 – 2003), EPA Region V
  - Mercury Transformations on Land and Water (METALLICUS) (1999 – 2002)
  - Olin Chlor-alkali – mass balance and fugitive emission from chlor-alkali plant (2000 – 2002)
  - Florida Solid Waste – emission from transport and disposal of municipal waste (1997 – 2001)
  - ORNL lead Mercury Working Group – EM-50 Mixed Waste Focus Area (1998 – 2002)
  - Management of Mercury Stockpile – Defense Logistics Agency (2006 – present)

Science to Application

http://www.esd.ornl.gov/romic_afrc/index.shtml

Why Science to Application?

- Science to Application in context of technology maturation process
  - Decreases Project Risk
  - Increases Technical Maturity
  - Allows for better contracts
- Example of Success:
  - Salt Waste Processing Facility
    - Caustic Side Solvent Extraction (classic TRL progression)
  - Lower East Fork Poplar Creek Clean-up
    - Mercuric sulfide identification (scientific understanding supported decisions)
    - Characterization technique



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Mercury Applied Field Research Initiative

Principal Investigator: Dr. E. M. Pierce

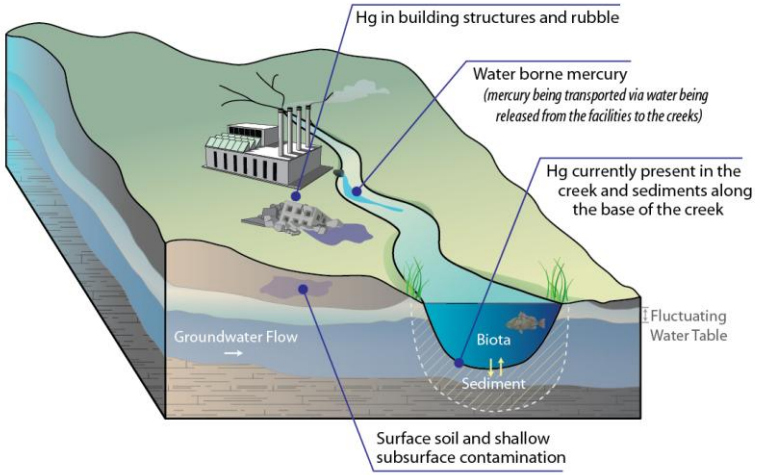
Project Title:
Remediation of Mercury and Industrial Contaminants

Mission:

Develop a systems-based approach to control the flux of contaminants in soil and water to protect surface water, groundwater, and ecological receptors from extensive, recalcitrant, and decades-old contamination at Oak Ridge and other DOE sites.

Strategic Research Needs:

- **Nature and Extent:** Identify, quantify, and determine the release behavior of mercury and other contaminant sources
- **Remedial Design:** Develop a scientifically-defensible approach to treat, stabilize, and dispose of mercury-contaminated waste (soil, sediment, and debris) in a cost-effective manner and
- Develop remediation approaches that control contaminant flux to surface water, groundwater, and ecological receptors
- **Monitoring and Modeling:** Provide the technical underpinning needed to support reaching a scientifically-defensible and regulatory-acceptable end-state



Collaborators:

Oak Ridge National Laboratory
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FIU Florida International University

V.G. Khlopin Radium Institute

SRNL Savannah River National Laboratory

south river Science Team

UCOR

Y12 National Security Complex

Argonne National Laboratory

Queen's University Belfast

Northwestern University

Science to Application

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Oak Ridge National Laboratory

Summary of Mercury AFRI Accomplishments

Research Products	**12 Publications** **29 Presentations or posters (4 invited)** **6 Conferences/workshops attended (2 conference session chairs)** **3 National/international leadership planning activities**
Scientific Highlights	• Evaluation of flow management for mercury flux reduction • Evaluation of novel (magnetic Zn-doped nano-particles) and commercial adsorptive media for waterborne mercury removal • Mercury speciation in sediments from two former Y-12 NSC mercury-use facilities changes with depth • Application of quick screen tools (namely portable XRFs) under estimates the total mercury concentration in sediments
New Developments	• **Plan for Soil and Sediment Remediation Session at the Goldschmidt Conference in Canada June 24 – 30, 2012 (~10 – mercury related research abstracts)** • **Complete and Submit Final Version of the Mercury Remediation Technology Review, June 2012**

Science to Application

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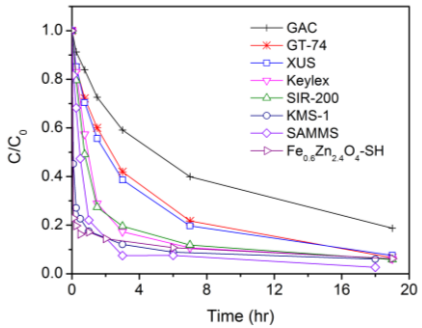
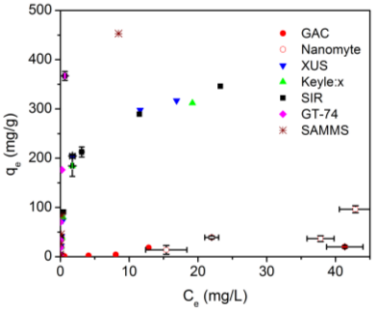
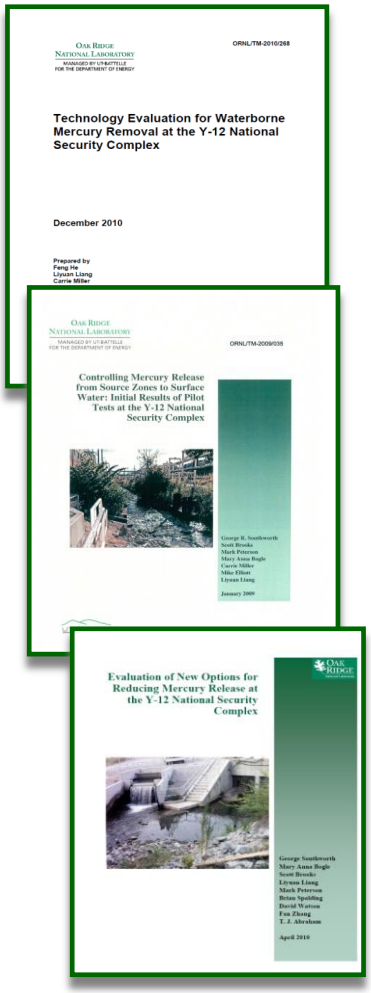
AFRI Task I: Remedial Design

Task Leads: Dr. Feng He and Dr. Liyuan Liang

- **FY09 – FY11 focus waterborne Hg flux**
  - Flow augmentation
  - Stannous chloride treatment
  - Adsorbent technologies
- **FY12 – FY13 focus soil treatment**
  - Literature review of soil treatment technologies
  - Debris disposal paper study
  - Lab-scale evaluation of select technologies for Hg(0) treatment
  - Chemical treatments (calcium polysulfide or hydrogen sulfide gas)
  - Soil washing and thermal treatment – joint with Russia's V.G. Khlopin Radium Institute (EM international program funded proposal)







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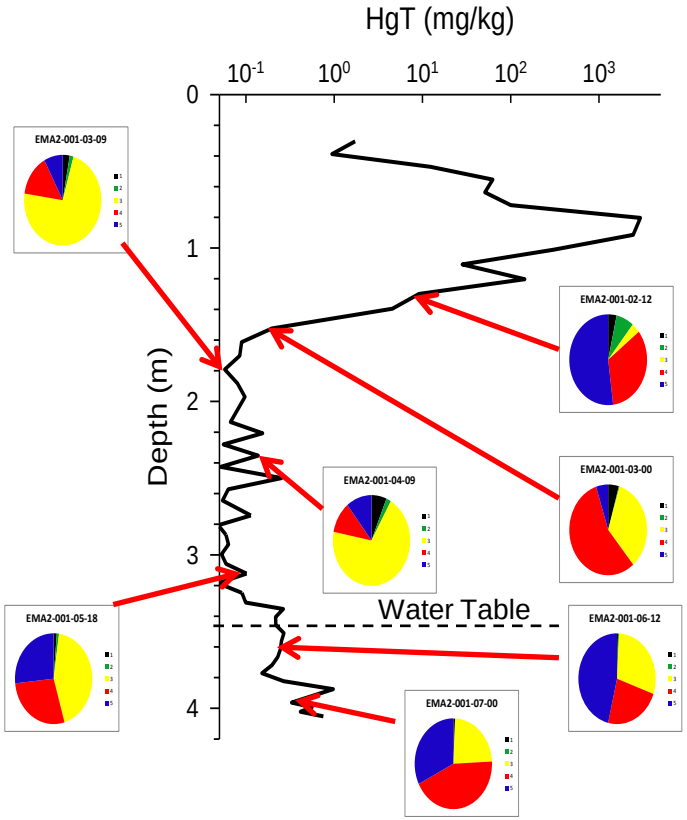
AFRI Task II: Nature and Extent

Task Leads: Mr. David Watson and Dr. Carrie Miller

- **FY10 – FY11**
  - **Characterization of mercury contaminated sediment**
    - **Key knowledge for soil treatment technology**
- **FY12 – FY13**
  - **Complete sediment characterization data collection**
  - **Refine conceptual model uncertainty**
    - **WEMA Fluxes, storm events, and specific outfalls**

	Extracting solution	Operationally defined fraction	Potential Hg species
F1	DI water	Water soluble	$HgCl_2$, $HgSO_4$
F2	HCl/Acetic acid (pH 2)	acid soluble	HgO, Hg sorbed to oxides (Fe, Mn)
F3	1 N KOH	Organo-chelated	Hg-organic, Hg_2Cl_2
F4	12 N nitric acid	Elemental Hg, mineral lattice	Hg(0), Hg_2Cl_2 m-HgS w/ impurities
F5	Aqua regia	HgS	HgS, m-HgS



Science to Application

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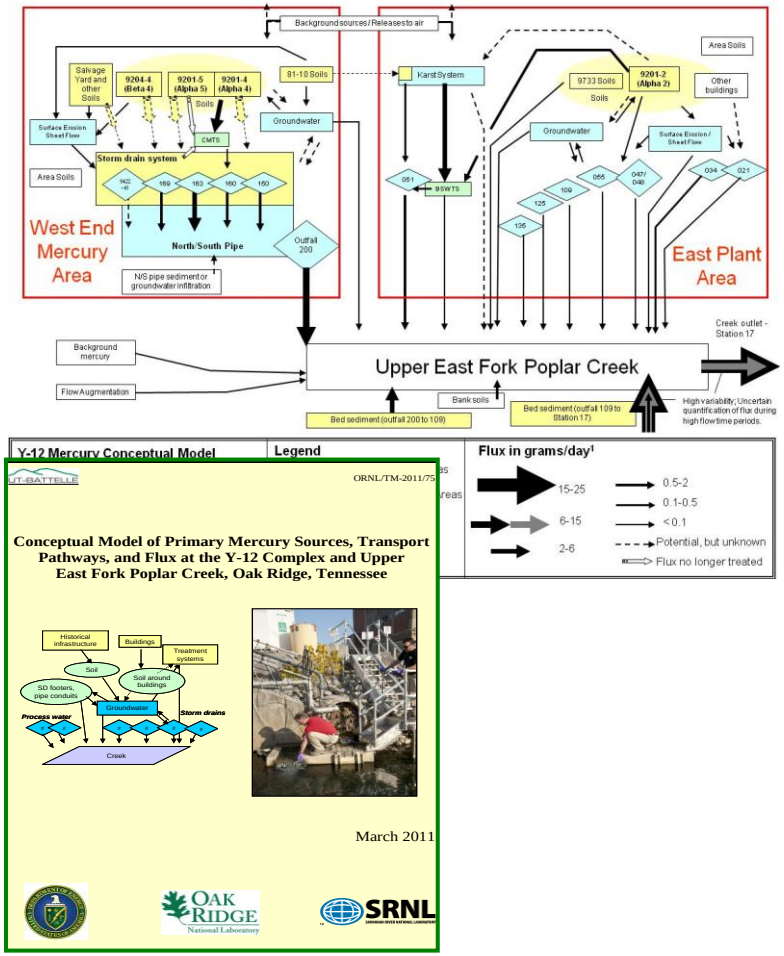
AFRI Task III: Monitoring and Modeling

Task Leads: Mr. Mark Peterson and Dr. Teresa Mathews

- **FY09 – FY11**
  - **Conceptual Model Development**
    - **Focuses on understanding mercury sources, transport, and flux at the Y-12 Complex**
    - **Used best available and most recent data**
    - **Storm drain sources upstream of Outfall 200 remain greatest contributor of current mercury inputs to EFPC**
    - **Recent measured flux numbers from storm drain conduits are higher than used for past remedial decision-making**
  - **Scientific Opportunities for Monitoring Environmental Remediation Sites (SOMERS) – surface water monitoring**
- **FY12**
  - **Complete fate of tin in the environment study**
  - **Begin evaluating mercury sources and process that control in-stream flux and bioavailability**



Science to Application

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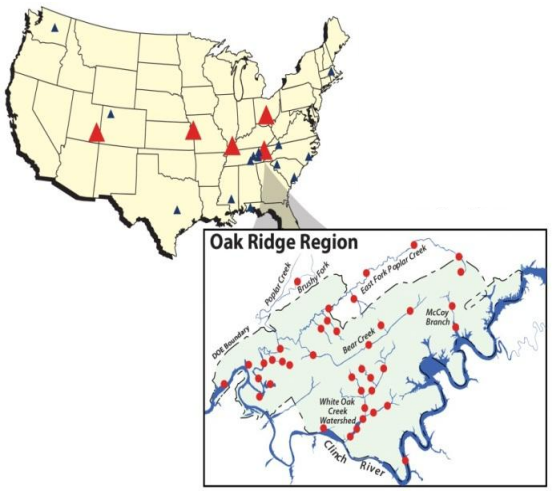
Biological Monitoring Programs – Aquatic Ecology Laboratory

Principal Investigator: Mr. Mark Peterson

Project Title:
Evaluation of ecological recovery at contaminated sites

Research Goal:
Develop and apply effective approaches for assessing, managing, and restoring ecosystems

Scope and Objectives:
•ORNL's Biological Monitoring and Abatement Program (BMAP) utilizes multidisciplinary and quantitative biological monitoring techniques to provide a rigorous assessment of remedial performance.
•Evaluate site-specific biological impacts of facility operations and legacy contamination in nearby waters
•Identify potential causal mechanisms and sources
•Apply knowledge gained to development of management strategies and remedial options for controlling inputs of pollutants or ameliorating their effects
•Evaluate the effectiveness of implemented strategies through assessments of spatial and temporal trends in biological conditions.
•Development of robust characterization tools and sensor development
•The program and associated laboratory provides rapid response (e.g., to TVA fly ash spill), and is the only aquatic research facility in the region.



Funded by:
Primarily the DOE, DoD, TVA, and numerous associated government contractors (including B&W, UCOR, Honeywell)

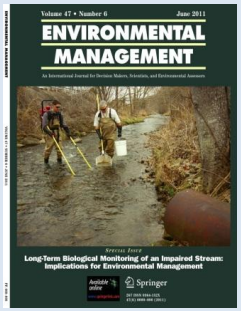
Education:
200+ university students supported by monitoring programs:

University of Tennessee, TN; University of the South, TN; Carlton College, MI; Midland Technical Community College, SC; University of Puerto Rico, Puerto Rico; University of Tulsa, OK; Georgia Perimeter Community College, GA; University of Georgia, GA; College of Charleston, SC; Ripon College, WI; Pacific University, OR; University of North Alabama, AL; Lawrence University, WI; Oral Roberts University, OK; Roane State Community College, TN; Shaw University, SC; Mountain Empire State College, VA; Emory University, GA; US Naval Academy, MD; Vanderbilt University, TN; Albion College, MI; Baylor University, TX; Stanford University, CA; Tennessee Technological University, TN; University of Delaware, DE; Earlham College, IN; Rockefeller Institute, NY; Southeastern Oklahoma State University OK; Salish Kootenai College, MT; East Tennessee State University, TN; Santa Fe Community College, FL; Lincoln Memorial University, TN; University of New Hampshire, NH; Juniata College, PA; Salish Kootenai College, MT; Depauw University, IN; Robert Woodward University of Southern Missouri, MO.

Science to Application

http://www-esd.ornl.gov/comic_atrc/index.html

Summary of Biological Monitoring Accomplishments

Research Products	**161 Publications** **~300 Technical reports and scientific presentations** **Staff routinely interviewed for print and television** **Presentations at public meetings, universities** **Student education** 
Recent Scientific Highlights	• Special Issue of Environmental Management (10 papers, June 2011): "Long-term Biological Monitoring of an Impaired Stream; Implications for Environmental Management". • The 2011 "State of the Creek Address; Long-Term Biological Monitoring of East Fork Poplar Creek". December 2011 public meeting highlighting stream improvements and challenges. • Ecological Management and Enhancement strategy, first of its kind approved by EPA, reduces PCB concentrations in fish and saves DOE 25 million relative to sediment removal option. • Paper and oral presentation for the 2012 Waste Management Symposia: "Benefits of a Biological Monitoring Program for Assessing Remediation Performance and Long-Term Stewardship". • Biological monitoring results and interpretation are a key part of two major CERCLA documents currently under regulatory review: the Oak Ridge Reservation's 2012 "Remediation Effectiveness Report" and the third reservation-wide "CERCLA Five Year Review".
New Developments	• **Paper to soon be submitted is getting significant local press: "Decreasing aqueous mercury concentrations to achieve safe levels in fish: examining the water-fish relationship in two point-source contaminated streams".** • **Four talk lecture series, July- August, 2012. Oak Ridge Institute for Continued Learning**

Science to Application

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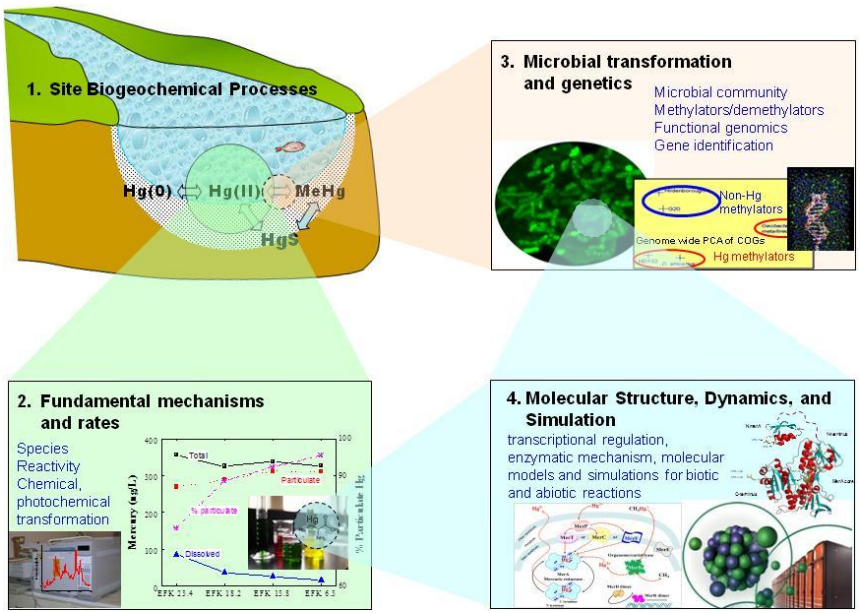
Mercury Science Focus Area

Principal Investigator: Dr. Liyuan Liang

Project Title:
Geochemical and molecular mechanisms controlling mercury transformation in the environment.

Research Goal:
Provide scientific understanding of the rates and mechanisms of net methylmercury production in mercury contaminated environment

Scope and Objectives:
- Elucidate the rates, mechanism, and controls of abiotic and microbial processes affecting mercury speciation and transformation
- Resolve what and how critical mercury precursors are produced and subsequently passed into cells and become methylated
- Understand fundamental microbial subcellular mechanisms by studying the structure and dynamics of biological macromolecules involved in the acquisition, transfer, and transformation of major mercury species and methylmercury
- Determine the net balance of methylation and demethylation



Collaborators:

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The University of Tennessee UT
Princeton University
Mizzou University of Missouri
Smithsonian Institution
Pacific Northwest National Laboratory
Tennessee Tech University
Argonne National Laboratory
UCSF University of California San Francisco
The University of Georgia
south river SCIENCE TEAM

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Oak Ridge National Laboratory

Summary of Mercury SFA Accomplishments

Research Products	**17 Published articles—2 in PNAS** **29 Presentations or posters** **5 Invited presentations or talks** **5 Conferences/workshops attended** **3 Television, Print, and Radio articles** **2 National/international leadership planning activities**
Scientific Highlights	• DOM plays a dual role in Hg chemistry. It reduces Hg(II) to Hg(0), but it also oxidizes Hg(0) depending on the concentrations of both Hg and DOM. Ligand-induced oxidative complexation of Hg(0) with DOM is proposed as a new mechanism that controls Hg(0) oxidation and sequestration in anoxic environments. • Hg(II) uptake is an active transport process requiring energy; not a passive process as commonly perceived; Hg(II) uptake and methylation is highly dependent upon the chemical characteristics of the complexing thiols in Geobacter sulfurreducens, but less so in Desulfovibrio sp. ND132; MeHg is exported out of the cell immediately upon its production • The 3.8 Mb genome of *Desulfovibrio desulfuricans* ND132 and the 4.2 Mb genome of *Desulfovibrio africanus* are sequenced
New Developments	• **SFA External Scientific Advisory Committee visits March 3-4, 2011** • **Hosted special sessions for ICMGP at Halifax, Summer 2011**

Science to Application

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  - BMAP – DOE ORO Funded

Present Y-12 End State

Science to Application http://www.esd.ornl.gov/romic_afrc/index.shtml

Backups

National and International Collaboration and Leveraging

http://www.blm.gov/ak/st/en/fo/ado/hazardous_materials/red_devil_mine.html. **Red Devil Mine** (RDM) - is an abandoned mercury mine and production facility in southwestern Alaska that is the subject of a number of major environmental restoration projects. The Department of Interior's Bureau of Land Management is responsible for the Environmental Restoration of RDM.

http://www.southriverscienceteam.org/. **South River Science Team (SRST)** - South River a portion of the Shenandoah River in Waynesboro, Virginia is contaminated with mercury as a result of the mercury being used as a catalyst in the manufacturing process of Rayon fiber. **SRST** was established in 2000 consist of VA state departments (Environmental Quality, Health, Fish & Game), Dupont Company, and University Researchers. Purpose was to serve as a focal point for technical and scientific issues concerning mercury in the South River and downstream waterways.

Mercury 2011: 10th International Conference on Mercury as a Global Pollutant (ICMGP) – Holifax, Nova Scotia. **Session Chair:** Liyuan Liang (ORNL) – *Mechanism of microbial mercury methylation and resistance.*

Biogeochemical Controls on Mercury Transformation and Global Cycling. Goldschmidt 2010: Earth, Energy, and Environment. Session Chairs: **Baohua Gu (ORNL)**, Kathryn Nagy (Univ. of Illinois at Chicago), Xinbin Feng (Chinese Academy of Sciences), **Liyuan Liang (ORNL)**, and Thorjorn Larssen (Norwegian Institute for Water Research)

International Workshop on Mercury in Contaminated Sites: characterization, impacts, and remediation. (2010). Location: Republic of Slovenia at the Jozef Stefan Institute. **Title:** *Flow alteration and chemical reduction: experimental manipulations to reduce subsurface discharges of mercury to surface water*. **ORNL team:** Carrier Miller, S. Brooks, G. Southworth, MA Bogle, and L. Liang

Mercury Challenges in the Environment: A Technical Summit. **(2008). Location:** Vanderbilt University. **ORNL Organizers:** L. Liang, M. Peterson, G. Southworth, and M. Bogle.

Science to Application

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Capabilities/Resources/Acknowledgments

- ORNL Capabilities/Resources:
  - Current and Former Staff
  - Facilities and Equipment
- Environmental Sciences Division
  - Current Staff: L. Liang, B. Gu, M. Peterson, S. Brooks, MD Cheng, C. Miller, A. Johs, D. Watson, F. He, T. Mathews, K. Lowe, and J. Terry
  - Former Staff: S. Lindberg[1,2], M. Adams[2], G. Southworth[2], M. Bogle[2] R. Turner[2], J. Ellwood[2], and S. Hildebrand[2]
  - Variety of post doctoral students and visiting scientist
- Other ORNL Divisions
  - T. Palumbo (BSD), D. Graham (BSD), J. Parks (BSD), C. Mattus (ETSD), P. Taylor (FCID), W. Hermes (FCID), and T. Conely (NSED)

ESD has over 20000 sq. ft. of lab space dedicated to mercury-related research

[1]ORNL Corp. Fellow, Emeritus
[2]ORNL Retired Staff Member

Science to Application

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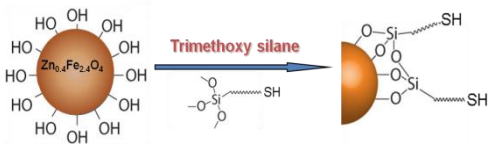
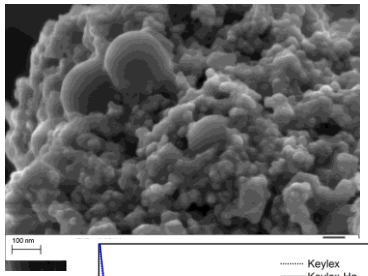
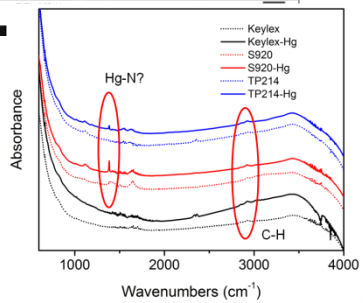
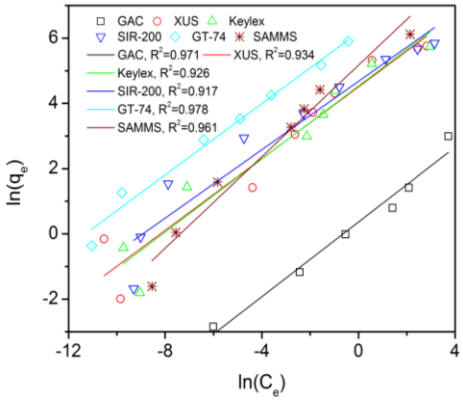
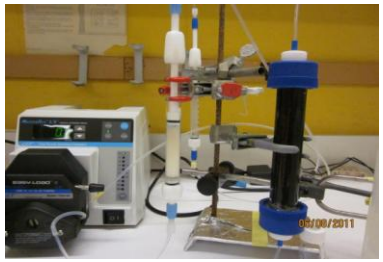
Example: Science/Engineering to Application







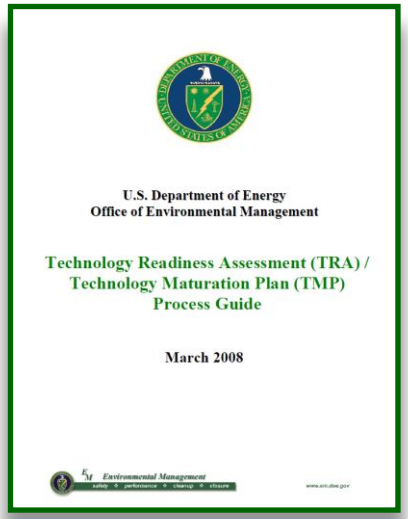




Scale-up Testing and Design

Full-scale Design/Implementation by EM Site Contractor

aerial photo of water treatment system at Hanford Site



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Technology Readiness Assessment (TRA) / Technology Maturation Plan (TMP) Process Guide

March 2008

- **Commercial and Novel Sorbents previously evaluated:**
  Carbon based materials, Thiol-based resins, Other reducing sulfur-based resins, and Other sorbent material
  - **Developed mechanistic understanding of Hg capture and conducted scale-up testing and design of a small treatment system**
- **EM Technology Development targets concepts to engineering-scale demonstration (TRL 1 – 6) – not the old EM 50**

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