Emerging Contaminants – SRP-Funded Research in Remediation Technologies

Heather Henry
Superfund Research Program, NIEHS

National Institute of Environmental Health Sciences
Research Triangle Park, NC
NIH Research Mission

Fundamental Knowledge

...of living systems
...with environmental exposures
...including health effects, risk assessment, detection and remediation

National Institutes of Health (NIH)

Health Outcomes

...reduced illness & disability
...caused by hazardous substances
...relevant to Superfund stakeholders

National Institute of Environmental Health Sciences (NIEHS)

Superfund Research Program (SRP)
SRP Mandates under SARA

University-based basic research program established in 1986 under Superfund Amendments Reauthorization Act (SARA)

Mandates Call for the Development of:

- Advanced techniques for the detection, assessment, and evaluation of the human health effects of hazardous substances
- Methods to assess the risks to human health presented by hazardous substances
- Methods and technologies to detect hazardous substances in the environment
- Basic biological, chemical, and physical methods to reduce the amount and toxicity of hazardous substances

Health Effects

Assessing Risks

Detection

Remediation

Biomedical and Risk Research

Environmental Science and Engineering Research
NIEHS Superfund Research Program Highlights

• Since 1987, The Superfund Research Program (SRP) has:
  – Conducted work at 217 hazardous waste sites
  – Patented approximately 98 inventions
  – Produced approximately 8105 peer-reviewed publications, which makes it one of the most productive programs ever funded by the federal government

• The SRP currently provides support to over 1400 professionals and more than 680 trainees involved in research
Where We Work…

15 Multi-Project Grants
6 SBIR/STTR
5 Bioavailability Assay Grants

Map also shows: Study Sites and Partnering Institutions
How SRP Defines Emerging Contaminants

- High Production Volume Information System (HPVIS)
- Rare Earth Elements (REEs)
- Provisional Peer Reviewed Toxicity Values (PPRTV)
- ATSDR emerging contaminants would include extremely data poor contaminants that ATSDR or National Center for Environmental Health (NCEH)
- Federal Facilities Restoration and Reuse Office (FFRRO)

**Emerging Compounds**: FFRRO
**SRP Emerging Contaminants**

Currently, SRP research of emerging contaminants includes:

<table>
<thead>
<tr>
<th>Remediation and fate and transport studies</th>
<th>Health effects and exposure studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 1,4-dioxane</td>
<td>• Environmentally persistent free radicals</td>
</tr>
<tr>
<td>• Nanoparticles</td>
<td>• Nanomaterials</td>
</tr>
<tr>
<td>• Perchlorate</td>
<td>• Perchlorate</td>
</tr>
<tr>
<td>• Perfluorooctonic acid (PFOA)</td>
<td>• Phthalates</td>
</tr>
<tr>
<td>• Phthalates</td>
<td>• Polybrominated flame retardants, including PBDE</td>
</tr>
<tr>
<td>• Polybrominated flame retardants, including PBDE</td>
<td>• Triclocarban and triclosan</td>
</tr>
<tr>
<td>• Triclocarban and triclosan</td>
<td></td>
</tr>
</tbody>
</table>
Groundwater Bioremediation of 1,4-dioxane
Lisa Alvarez-Cohen, UC Berkeley SRP (P42ES004705)

- Identifying and studying microbial communities (anaerobic and aerobic), that can remediate TCE and 1,4 dioxane
  - Degradation by both metabolic and cometabolic pathways
  - Identified signature genes that predict success in groundwater bioremediation
  - Studies on dioxane degradation pathway of *Pseudonocardia dioxanivorans* CB1190
Degradation of Dioxane in Superfund Site Soil

- Alvarez-Cohen applied her bioremediation work to soil from a Superfund site in CA with dioxane and other organic contaminants
- Researchers observed dioxane degradation by cometabolism with tetrahydrofuran (THF) or propane amendments

<table>
<thead>
<tr>
<th>Environmental sample</th>
<th>Growth substrate</th>
<th>Dioxane degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater sample (MW-1)</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Groundwater sample (MW-1)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Groundwater sample (MW-1)</td>
<td>Propane</td>
<td>+</td>
</tr>
<tr>
<td>Groundwater sample (MW-2)</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Groundwater sample (MW-2)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Groundwater sample (MW-3)</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Groundwater sample (MW-3)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Groundwater sample (MW-4B)</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Groundwater sample (MW-4B)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Soil sample (close to MW-2)</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Soil sample (close to M-2)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Activated sludge (from another site [site A])</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Activated sludge (site A)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Activated sludge (site A)</td>
<td>Propane</td>
<td>+</td>
</tr>
<tr>
<td>Activated sludge (site A)</td>
<td>Toluene</td>
<td>-</td>
</tr>
<tr>
<td>Activated sludge (from waste water facility [site B])</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>Activated sludge (site B)</td>
<td>THF</td>
<td>+</td>
</tr>
<tr>
<td>Activated sludge (site B)</td>
<td>Propane</td>
<td>+</td>
</tr>
<tr>
<td>Activated sludge (site B)</td>
<td>Toluene</td>
<td>-</td>
</tr>
</tbody>
</table>
Bioremediation of 1,4-dioxane

Microvi Technologies, Joseph Salanitro (R43/R44 ES022123)

- Remediation of **1,4-dioxane** from water resources via a biological treatment pathway
- SBIR investigators are developing an engineered bioreactor called the MB-DX bioreactor
- High density of Rhodococcus sp. N21 fully integrated within the bioreactor material matrix

Map of the PLS Site and dioxane plume

Scanning Electron Micrographs shows cross section of one biocomposite matrix (A), microbial integration throughout the pores and cavities of the material (B), and a high cell density contained within the matrices (B-D)
ISCO with Persulfate/Iron for 1,4 Dioxane and PFOA

David L Sedlak, Fiona M. Doyle, UC Berkeley (P42ES004705)

- Testing new approaches for oxidizing contaminants that are difficult to treat with existing technologies like PCBs, 1,4-dioxane, and perfluorooctanic acid (PFOA)

- Applying these approaches to create treatment systems and develop kinetic models with persulfate and iron-containing solids

- Currently working with aquifer sediment collected from a series of different hazardous waste sites to understand the relationship between geochemistry and persulfate activation rates.

- Anticipated Outcome: Model that will predict the efficiency of systems used for in situ chemical oxidation of organic contaminants with hydrogen peroxide
Direct-Push Oxidant Candles with Pneumatic Circulators

Mark Christenson, Airlift Environmental (R41ES022530)

- To remove chlorinate solvents and petroleum products from contaminated aquifers – potential use for 1,4 Dioxane

On a simple burner, purple permanganate granules are mixed with paraffin to create candles

Mark Christenson shows how paraffin-based permanganate candles are prepped for lowering down a borehole at a Cozad landfill site.

(Photos by Steve Comfort)
Biochar Amendments for TCC/TCS Remediation

Kate Scow, UC Davis (P42ES004699)

- Investigating how biochar application in soil may provide benefits through reduced contaminant mobility
- Biosolid land applications applications: TCC/TCS
- Wood and walnut shell biochar soil amendments effectively sequesters
- Also working with Ian Kennedy on NZVI for remediation.

![Chemical structures of Triclosan and Triclocarban]
Nanomaterial-based Remediation of Contaminated Sediments

Mark Weisner, Duke University (P42ES010356)

- Focus on polybrominated flame retardant decabrominated diphenyl ether, BDE-209, among other contaminants
- Researchers are studying nano-bio remediation using zero valent iron (ZVI) and titanium dioxide (TiO2) nanomaterials for contaminant degradation by:
  - Investigating the use of nanomaterials as catalysts for direct treatment of contaminated sediment and water
  - Assessing microbial degradation of the target contaminants by sediment microorganisms with and without nanomaterials
  - Uncovering possible synergies of nanoparticle-based remediation with natural microbial degradation processes
Detection Technologies to Improve Remediation of Perchlorate in Food and Water Supplies

Advanced Microlabs, Philippe Dekleva (R44ES017200)

• Online perchlorate analyzer to facilitate remediation efforts, allowing ion-exchange resin bed reactors to operate more cost effectively and with greater public safety

• Online device taken to Southern CA to test remediated water

• Bench instrument taken to a hazardous waste site in Mississippi to test perchlorate
  – More amendable to field work and quickly assessing many wells within a short time
  – Requires less sample volume
Detection and Exposure Assessment Tools
Northeastern University, Roger Giese, (P42ES017198)

- “Tea Bag” contains adsorbent(s)
- Concentrates analytes from large biological and environmental samples to make detection of the analytes easier.
- “Non-targeted” adsorbent collects suite of compounds (including phthalates) for later analysis.

Goal: Provide small, stabilized sample for long term storage and future testing of aliquots.
Bioavailability Assay
Arizona State University and University of Florida
Rolf Halden and Nancy Denslow, (R01ES015445)

- Multi-analyte Sensor: in situ sampling/bioavailability determination (IS2B) tool
- Analytes: triclosan, triclocarban, fipronil, ppDDE, dieldrin
- Sites: Lake Apopka, FL Superfund Site
Environmentally Persistent Free Radicals (EPFRs)
Louisiana State University (P42ES013648)

• LSU researchers have discovered chlorinated aromatic hydrocarbons and substituted phenols chemisorb to the surfaces of particulate matter where they reduce the metal and form a free radical

• LSU formed an interdisciplinary collaboration to explore the impacts of these emerging pollutant particle systems
  – EPFRs were shown to generate ROS, oxidative stress, and cardiopulmonary dysfunction in rat pups exposed by inhalation
  – Studies provide evidence that just measuring PM without considering EPFRs may lead to erroneous conclusions concerning toxicity of environmental PM
Discovering EPFRs in Soil at Hazardous Waste Sites

Detection at a Superfund Wood Treating Site

• Analyses of former wood treating facility containing pentachlorophenol (PCP) as a major contaminant revealed a 30x higher EPFR concentration in the PCP contaminated soils than in the non-contaminated soil.

• Recognition that EPFRs can be formed in PCP contaminated soils indicates EPFRs are not confined to combustion-generated PM and are more environmentally prevalent than originally suspected.

• The existence of potentially toxic EPFRs questions the long held belief that sorption of an organic pollutant to a soil matrix is a method of mitigating its environmental impact.
Thank You!

Contributors:
Sara Mishamandani, Danielle Carlin,
Beth Anderson, Michelle Heacock, and Bill Suk

Heather Henry
henryh@niehs.nih.gov
919-541-5330
Searching for SRP Research

- **SRP Website:**

- **NIH RePORTer:**
  - [http://projectreporter.nih.gov/reporter.cfm](http://projectreporter.nih.gov/reporter.cfm)
There were 2 results matching your search criteria.
Click on the column header to sort the results.

<table>
<thead>
<tr>
<th>T</th>
<th>Act</th>
<th>Project Year</th>
<th>Sub #</th>
<th>Project Title</th>
<th>Contact PI/Project Leader</th>
<th>Organization</th>
<th>FY</th>
<th>Admin IC</th>
<th>Funding IC</th>
<th>FY Total Cost by IC</th>
<th>Similar Projects</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>P42</td>
<td>ES047055</td>
<td>26</td>
<td>PROJECT 4, META-OMICs OF MICROBIAL COMMUNITIES INVOLVED IN BIOREMEDIATION</td>
<td>SMITH, MARTYN T</td>
<td>UNIVERSITY OF CALIFORNIA BERKELEY</td>
<td>2013</td>
<td>NIEHS</td>
<td>$311,743</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SRP Funding Mechanisms

**Multi-Project Centers (P42)**
Designed for integration across disciplines: Biomedical and Non-Biomedical Research; Community Engagement, Research Translation, and Training. Basic and application-oriented. Request for Applications. Annual RFA.

**Small Business Research Grants**
**SBIR/STTR (R41-44)**
Foster the commercialization of technologies, relevant to hazardous substance clean-up and monitoring. Ongoing Funding Opportunity

**Conference Grants (R13)**
Provides funding for conferences related to SRP mandates. Ongoing Funding Opportunity

**Individual Research Project (R01)**
Designed to address specific issues to complement the multi-project research program; tackle issues of emerging concern for Superfund. Current solicitation:

- **Biogeochemical Interactions Affecting Bioavailability for in situ Remediation of Hazardous Substances (R01)**

**Occupational Training (R25)**
Emerging issues in EHS training. Closed.

**Supplement Awards**
Trainee externships/work exchanges, technology transfer opportunities.

Funding Opportunities: [http://www.niehs.nih.gov/research/supported/dert/cris/programs/srp/funding/index.cfm](http://www.niehs.nih.gov/research/supported/dert/cris/programs/srp/funding/index.cfm)
## SRP Scientific Topics and Approaches

### Contaminants Studied
- Dense non-aqueous phase liquids (DNAPL)
- Dioxins/Furans
- Fluoropolymers
- Metals
  - Arsenic
  - Cadmium
  - Chromium
  - Lead
  - Manganese
  - Metal Mixtures
  - Mercury
  - Nickel
- Nanoparticles
- Organobromides
- Organochlorides
- Organophosphates
- Persistent Free Radicals
- Phthalates
- Polycyclic aromatic hydrocarbons (PAH)
- Polychlorinated biphenyls (PCB)
- Triclosan and triclocarbon
- Volatile organic compounds (VOC)

### Disease Endpoints
- Cancer
- Bladder
- Brain
- Lung
- Skin
- Dermal Toxicology
- Developmental Toxicology
- Immunotoxicology
- Nephrotoxicology
- Neurotoxicology
- Pulmonary/Cardiology Toxicology
- Reproductive Toxicology

### Scientific Approaches
- Analytical Tool Development
- Animal Studies
- Bioavailability
- Biomarker Research
- Biomolecular Studies
- Community Engagement
- Data Analysis/Bioinformatics
- Ecology
- Epidemiology Studies
- Environmental Samples Studies
- Air
- Groundwater
- Soil and Sediment
- Surface Water
- Fate and Transport
- Human Studies
- Modeling
- Remediation Technologies
- Bioremediation
- Chemical/Physical Remediation
- Nanoparticles for Remediation
- Phytoremediation
- Research Translation
- Risk and Exposure Assessment
- Susceptible populations
- Training