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Disclaimer:

Thermal Techniques for the In-Situ Characterization and Remediation of Mercury: Insights From Deployment of the Membrane Interface Probe

Enclosed is the oral presentation and speaker notes that was presented at the 12th International Conference on Mercury as a Global Pollutant (ICMGP) held July 28th – August 2nd, 2013 in Edinburgh, Scotland. The ICMGP conference has been running every 2-3 years since the first meeting in Gävle, Sweden in 1990. The conference is recognized as the pre-eminent international forum for formal presentation and discussion of scientific advances concerning environmental mercury.

While attending the conference this oral presentation was given by Mr. Dennis Jackson from Savannah River National Laboratory. Co-authors on this work include Brian B. Looney and Carol A. Eddy-Dilek, also with SRNL. The presentation focuses on how thermal energy can effectively be used to enhance characterization, promote the remediation, and aid in delivering a sequestering agent to stabilize elemental mercury in subsurface soils.

The accompanying slides and speaker notes are assembled to allow conference delegates future access to the information as wells as access to the information by others.

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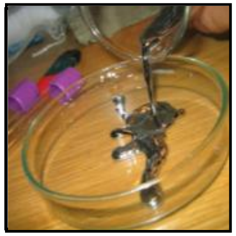
Thermal Techniques for the *In-Situ* Characterization and Remediation of Mercury: Insights From Deployment of the Membrane Interface Probe

Dennis Jackson P.E., Brian Looney PhD. and Carol A. Eddy-Dilek:

Savannah River National Laboratory

Aiken, South Carolina USA

80
Hg
Mercury
200.59



ICMGP Edinburgh 2013

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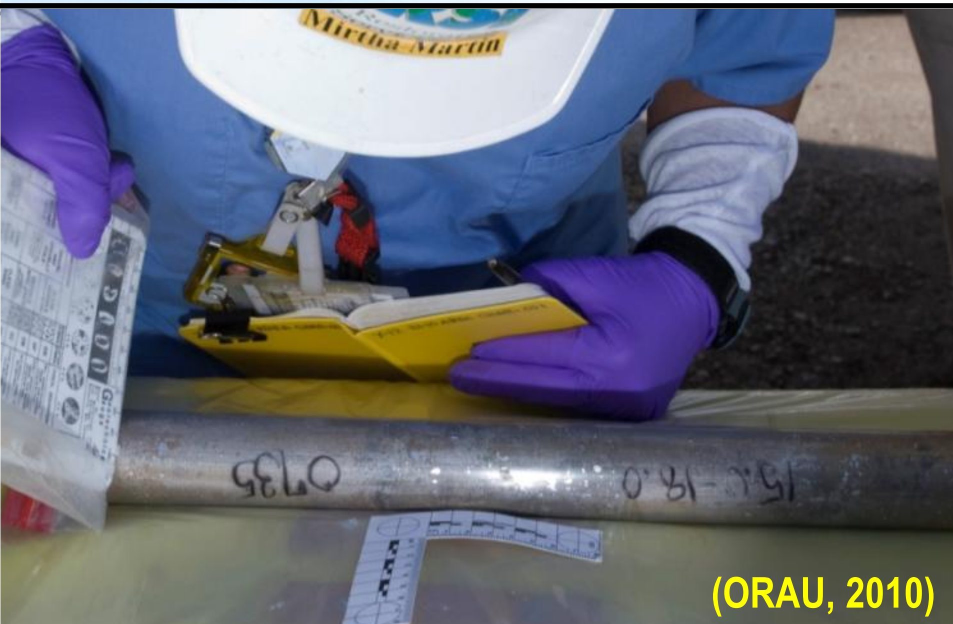
Presented at The 11th International Conference on Mercury as a Global Pollutant
July 28th – August 2nd, 2013. Edinburgh, Scotland

Delineation of Elemental Mercury in the Subsurface



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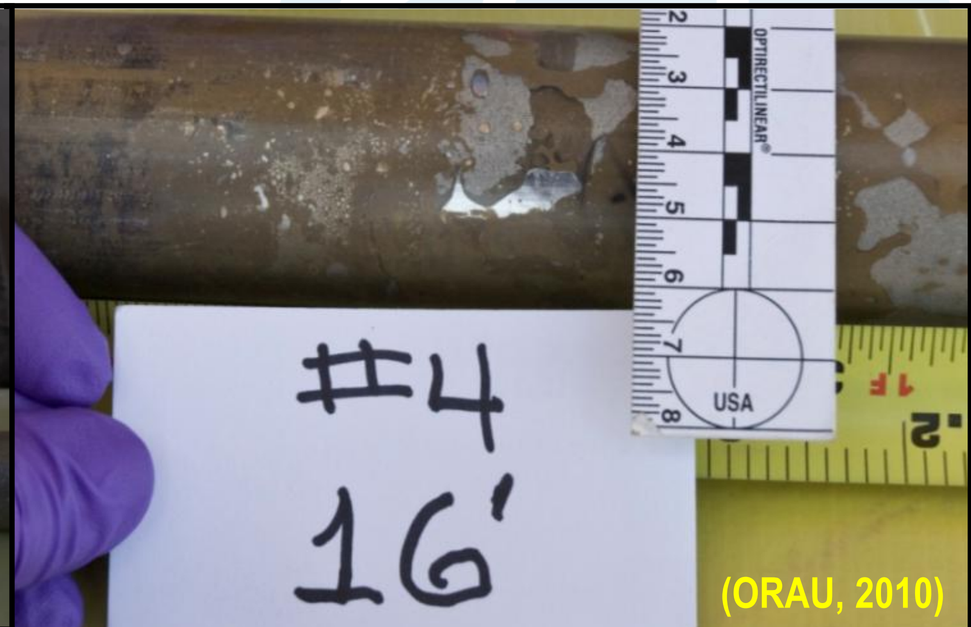

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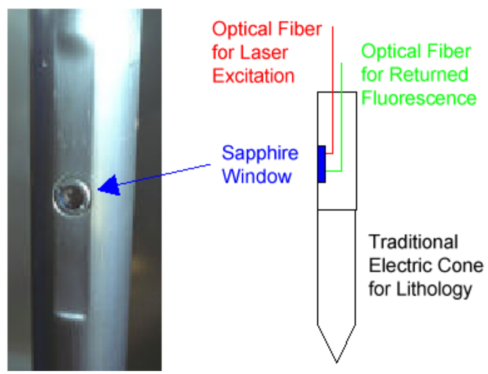
(ORNL, 2010)

Philosophy of Direct Push Characterization…

Direct Push Equipment & DNAPL Characterization Tools

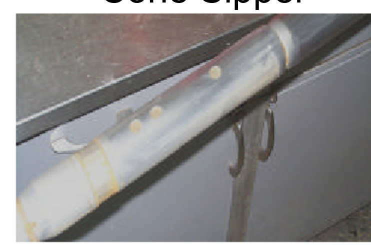
Wireline CPT Soil Sampler



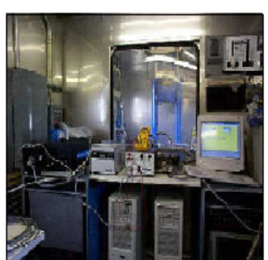
Laser Induced Fluorescence

GeoVis (video)

Cone Sipper



Cone Permeameter



Raman Spectroscopy

In Situ Gamma Detector

GeoProbe® MIP + Mercury Vapor Analyzers

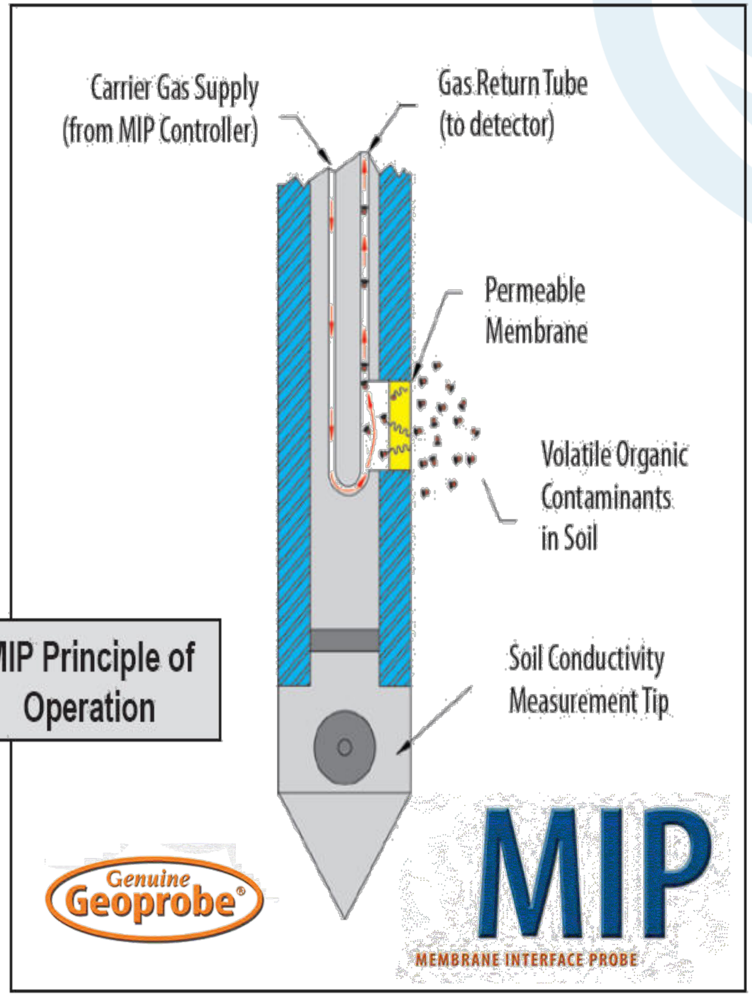
Jerome®

Gold Film Sensor
J431-X: 3- 999 ug/m3
J405: 0.5-999 ug/m3

BROOKS RAND LABS
MEANINGFUL METALS DATA

Model III

Cold Vapor Atomic Fluorescence
LDL: < 0.1 pg Hg(0)

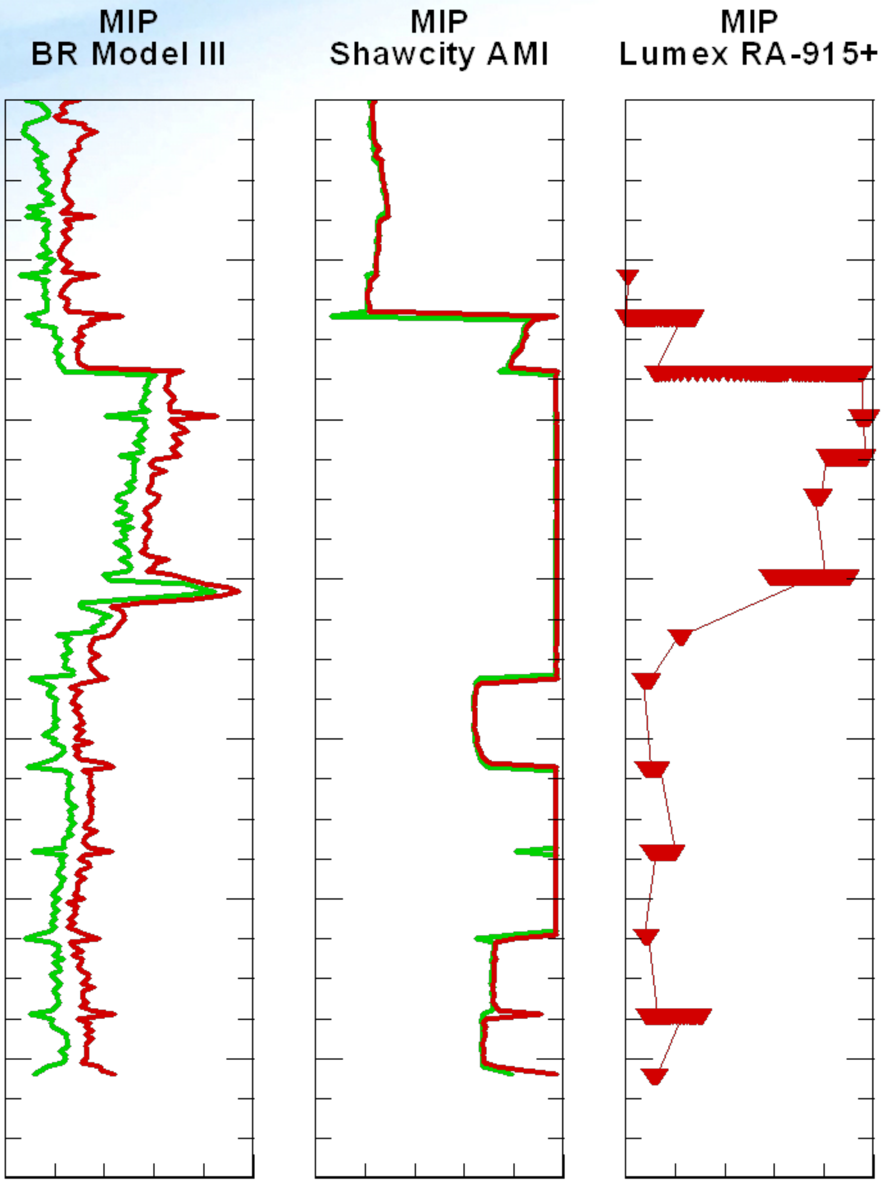


Dual Beam UV Absorption
MVI Low: 0.1 – 200 ug/m^3
MVI High: 1 – 1999 ug/m^3
AMI: 1 – 200 ug/m^3

LUMEX

Atomic Absorbance with Zeeman Effect
Single-Path: 500-200,000 ng/m^3
Multi-Path: 2-20,000 ng/m^3

MIP Development and Testing – Key Points:



- System responsive to Hg(0) consistent with vapour pressure
- Hg(0) permeates membrane and is detectable at surface
- Effective in delineation of “Free” Mercury in subsurface
- Results consistent with Depth-Discrete Soil Samples
- MIP + Model III configuration considered most versatile
- Provide high resolution delineation in subsurface.

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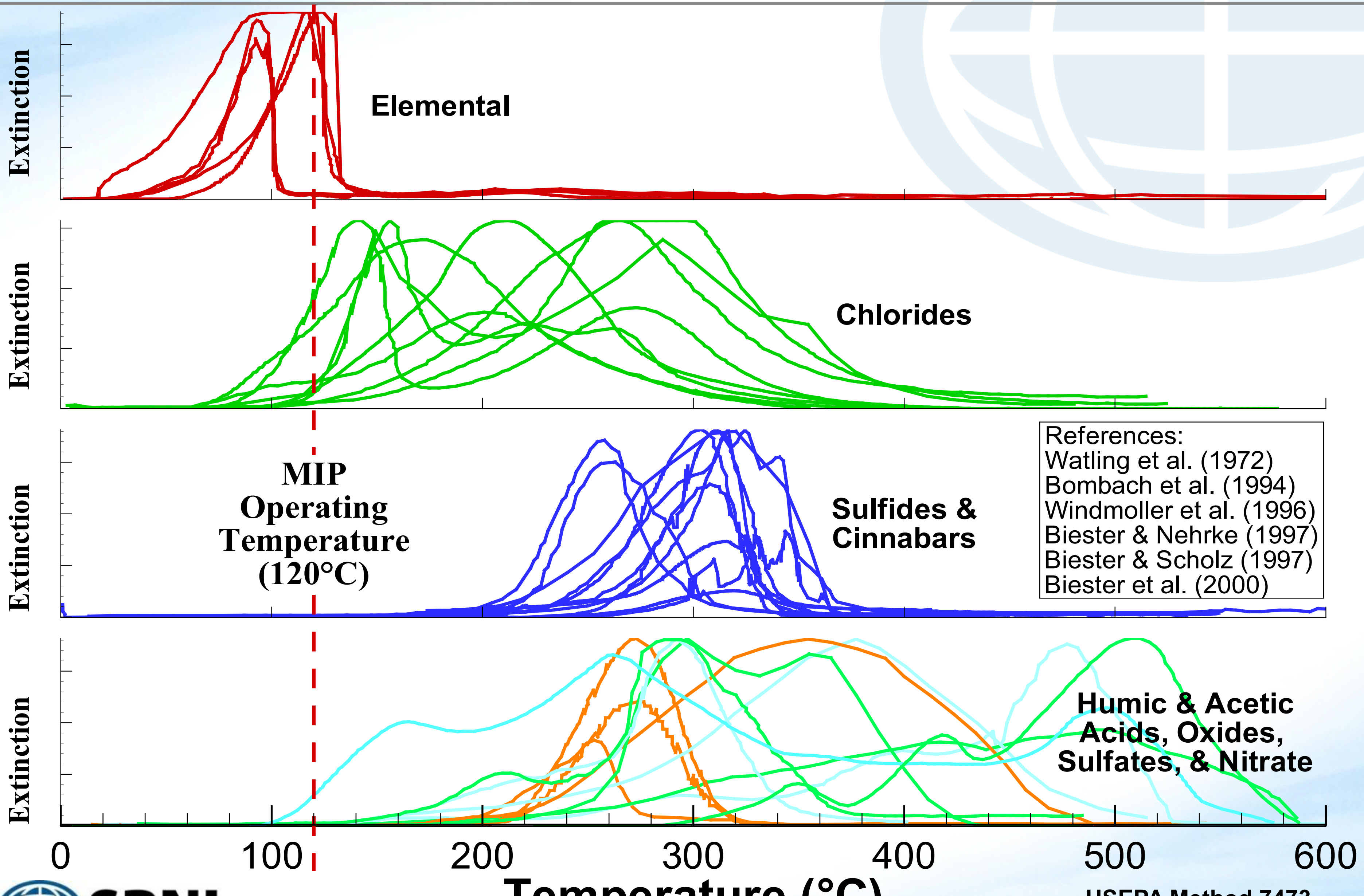
Mercury Removal (Speciation) from Soils during Heating

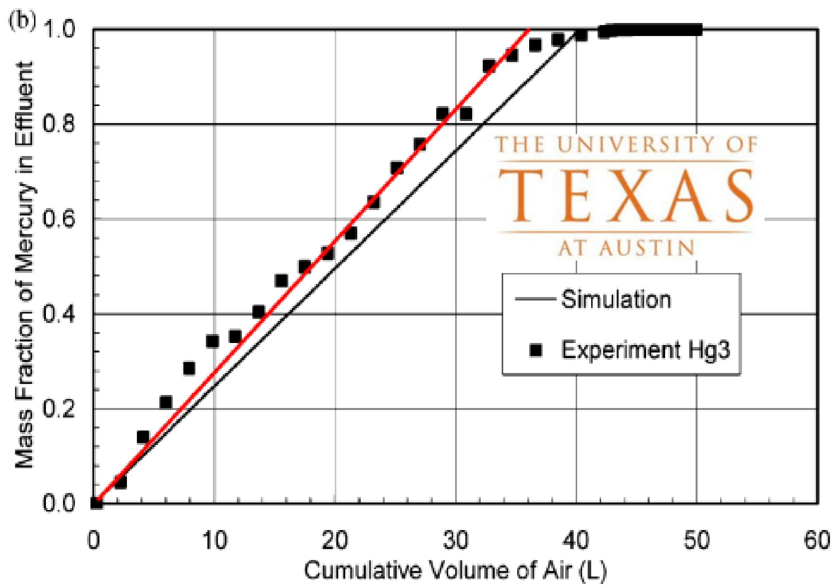


USEPA Method 7473
T ≥ 750°C

Use of Heat during Mercury Production: California (1955)

In-Situ Thermal Remediation - Removal Rates

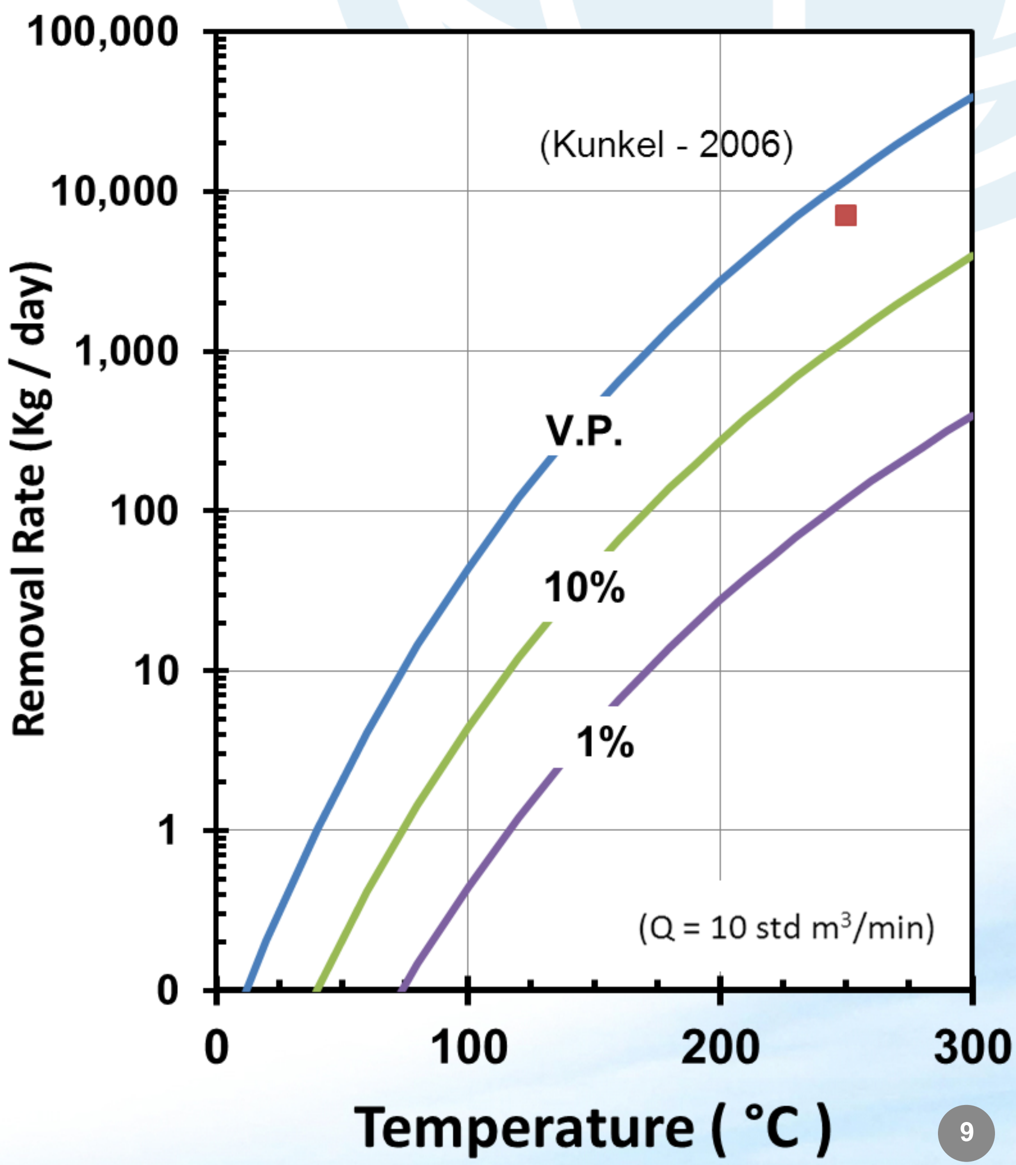
Lab Study (Kunkel et al., 2006):



Data point extrapolated from a treatability study evaluating thermal removal of mercury. In this study a sand column containing a heterogeneous mercury source was remediated (circa 244° C) with extracted gases approximately 0.6X vapor pressure (■).

Significant vapor phase removal using thermal based treatments.

Mercury Removal Scenario



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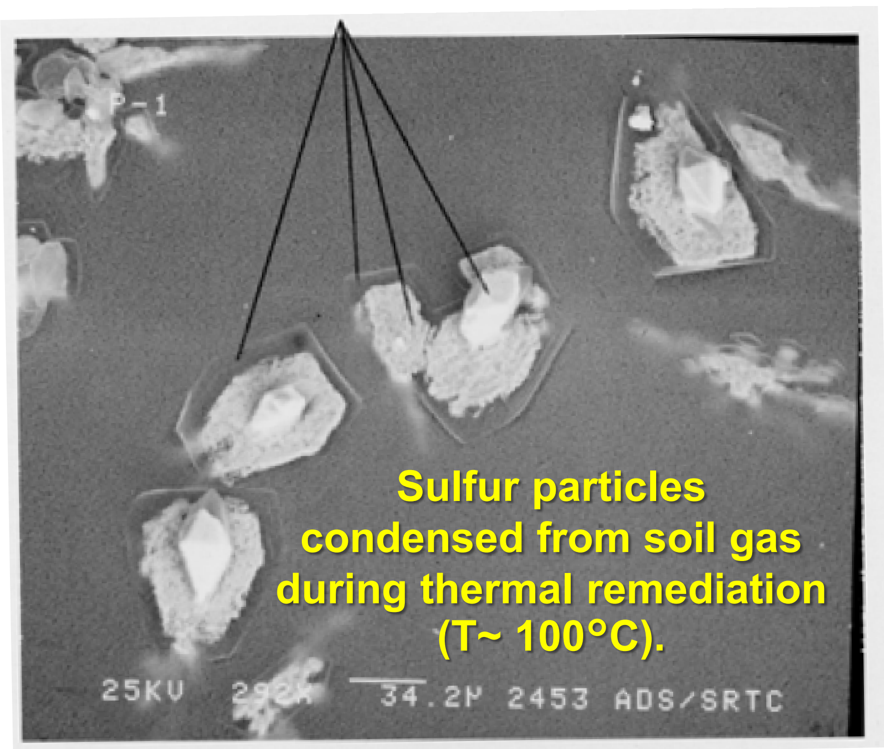
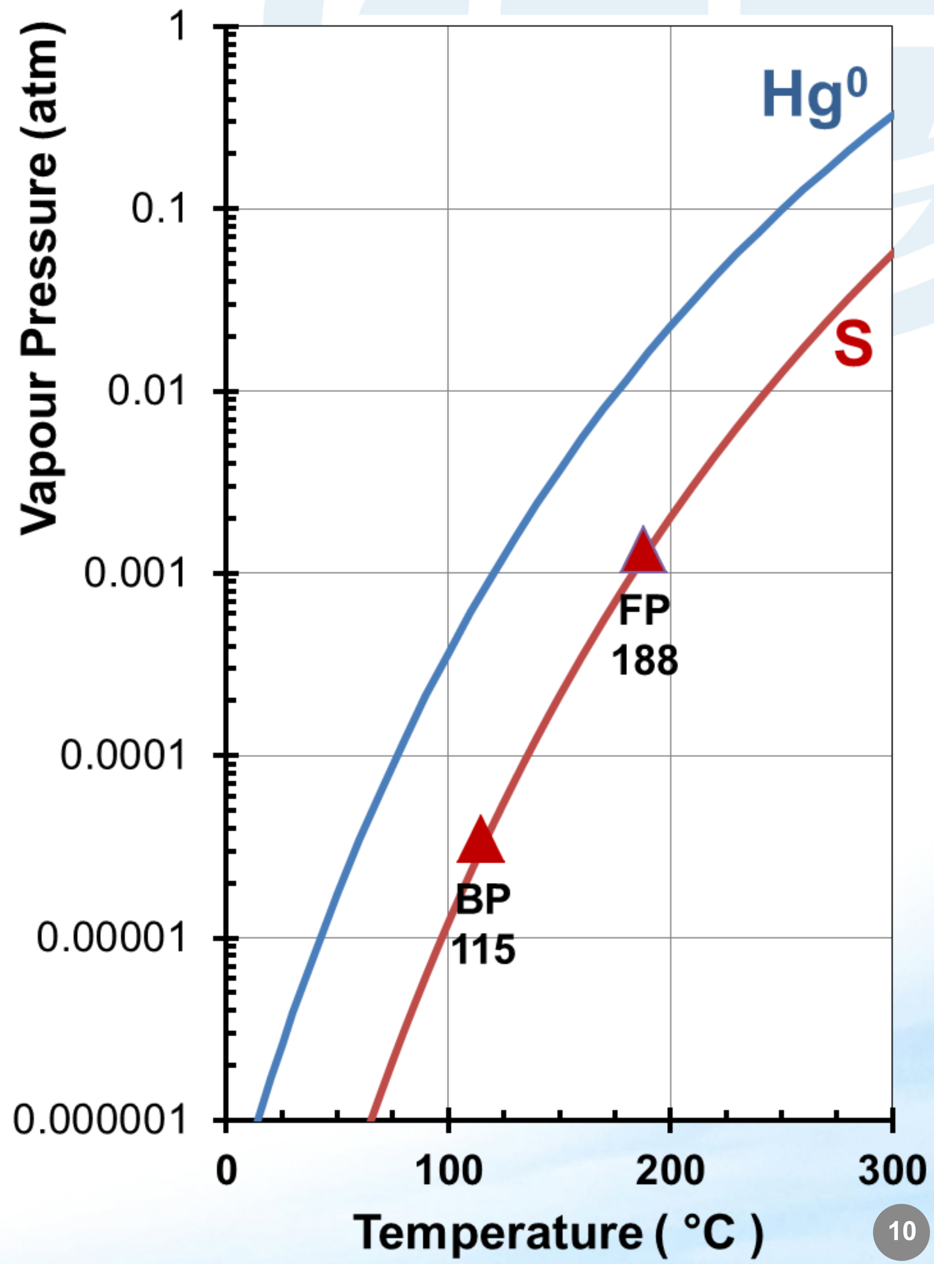
Stabilization of Residual Elemental Mercury

$Hg_{(g,\ell)} + S_{(g)} \rightarrow HgS$

Sulfur





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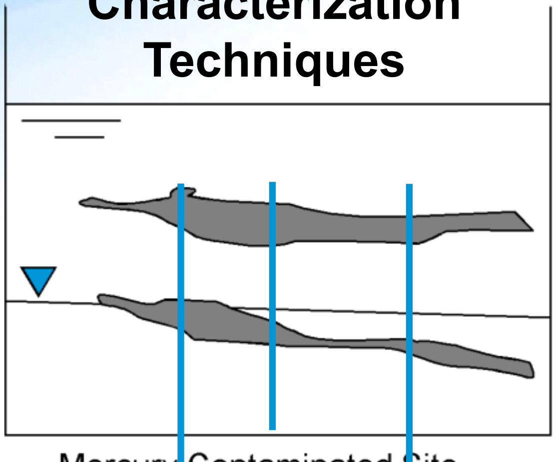
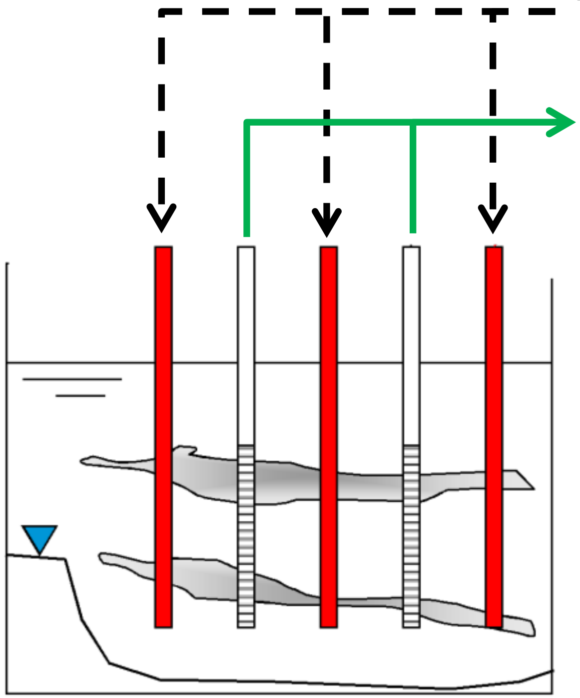
Strategy for Sites Containing Elemental Mercury

DNAPL Characterization Techniques



Mercury Contaminated Site

Thermal Treatment for Mass Reduction

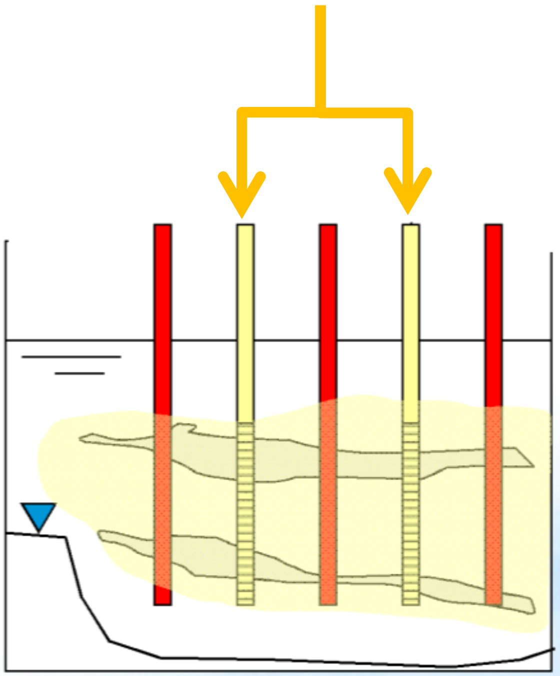


During Thermal SVE
site is heated and mercury vapors are removed

THE UNIVERSITY OF TEXAS AT AUSTIN

TERRATHERM

Gas Phase Amendment for Stabilization



Gas Phase Sulfur Injection
heated gas saturated with sulfur vapor injected into the site

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Summary & Conclusions

- **Hg(0) should be treated as a DNAPL source zone.**
- **Traditional DNAPL Tools can exploit unique properties to provide high resolution delineation in subsurface.**
- **Existing *In-Situ* Thermal Methods (T~250°C) should remove significant fraction of source material.**
- **Complete Remediation will likely require the combination of remedies (heat + stabilization).**
- **Sulfur in the gas-phase will provide consistent delivery of reagent within the source zone.**

Questions & Acknowledgements

Funding from the U.S. Department of Energy Office of Environmental Management's Soil & Groundwater Remediation Program

Select Illustrations – John Tenniel

TECHNIQUES IN-SITU CHARACTERIZATION & REMEDIATION

Good afternoon my name is Dennis Jackson and I'm with Savannah River National Laboratory. We are an applied Research & Development facility located at the Savannah River Site in South Carolina. In our role as the Corporate Laboratory for the US Department of Energy's Office of Environmental Management we have an active applied mercury research program that supports issues within the DOE complex.

Over the past several years we have been investigating the use of direct-push tools for the characterization of elemental mercury in the subsurface.

This afternoon I wish to share with you the results from this work and provide our insights on implementing an overall strategy for the characterization & remediation of sites containing elemental mercury.

Before going to far I wish to acknowledge my co-authors Brian Looney & Carol Eddy-Dilek both of Savannah River National Laboratory.

Delineation of Elemental Mercury in the Subsurface

Our objection was to improve techniques for identifying elemental mercury in the subsurface. We wanted to identify methods that would improve on baseline characterization techniques.

For the most part, baseline techniques involve the depth-discrete collection of soil samples, followed by laboratory analysis. Generally this is a total mercury analysis using either chemical reduction or pyrolysis and subsequent quantification – sometimes adding speciation to the analysis.

While effective this approach has a high potential for exposure to hazardous vapors.

Our strategy was to approach delineation of elemental mercury in the subsurface from a DNAPL perspective. Under this approach we sought to identify direct-push technologies that would be applicable for elemental mercury.

PHILOSOPHY OF DIREST PUSH CHARACTERIZATION

For those unfamiliar with Direct-Push methods – this illustrates the concept in the context of our surroundings – the beautiful city of Edinburgh.

In this illustration we observe the March Hare and Hatter using Dormouse to check first if there is any tea in the teapot.

In addition to checking for presence of tea Dormouse can also provide important information on temperature or if one lump or two lumps of sugar are required.

DIRECT PUSH EQUIPMENT & DNAPL CHARACTERIZATION TOOLS

Direct-push platforms have gained widespread acceptance in the environmental industry over the past decade because of their versatility, relatively low cost, and mobility.

Direct-push units use either hydraulic pressure, percussion hammering, or vibrational energy to advance sampling devices and/or sensors into the subsurface. The sensors incorporated onto the string are tailored to perform specific downhole measurements or gather a soil, water, or vapor sample at a specific depth

When sensors are tailored to measure unique properties of DNAPL then a robust, cost-effective system emerges for high profile delineation of these materials in the subsurface.

GeoProbe MIP + Mercury Vapor Analyzers

The MIP is a direct push tool developed to log the relative concentration of VOCs with depth in soil. The system has been used extensively in the U.S. and Europe for mapping the extent of VOC contamination in the subsurface. For site investigators the system is:

- Able to detect contaminants in both coarse and fine grained soils,
- Works in both saturated and unsaturated soils,
- The MIP can be either pushed or driven to depth,
- Readily combined with other sensors for lithology or permeability,
- Real time screening information allows field adjustment.

The membrane serves as an interface to a detector at the surface. Volatiles in the subsurface diffuse across the membrane and partition into a stream of carrier gas where they can be swept to the detector. The membrane is heated so that travel by VOCs across this thin film is almost instantaneous. MIP acquisition software logs detector signal with depth.

GeoProbe MIP + Mercury Vapor Analyzers (continued)

There are several instruments available for detection of Hg(0) vapors. The instruments that we evaluated included:

- Jerome J431/J405 Gold Film Sensor
- Brooks Rand Model III
- Ion Science/Shawcity AMI
- Ohio Lumex RA-91

MIP DEVELOPMENT & TESTING – KEY POINTS

- In our investigation we determined that the MIP is responsive to Hg(0) and that the response is consistent with temperature:vapor pressure relationships.
- We determined that Hg(0) readily permeates the membrane of the probe and the vapor can be readily detectable at surface using any of the instruments previously identified.
- The integrated system of MIP Probe and Hg(0) analyzer provides an effective system for the delineation of “Free” Mercury in the subsurface.
- The results are available “real-time” and are consistent with Depth-Discrete Soil Sampling that involves offsite analysis by a laboratory.
- In our experience the configuration of the MIP with the Brooks Rand Model III provided the most versatile configuration. This was due to adjustable sensitivity and signal outputs (0-1V) of the Model III.
- The system provide high resolution delineation of Hg(0) in subsurface.

MERCURY REMOVAL (SPECIATION) FROM SOILS DURING HEATING

So why is the MIP approach ideal for the delineation of elemental mercury in subsurface?

For the answer we look at analytical methods that use pyrolysis to provide information on mercury speciation. During this technique a soil sample is slowly heated. During heating various mercury species are converted to Hg(0) and this species is quantified using mercury vapor analyzer.

For our application we observe that elemental mercury desorbs from soils at temperatures below 140°C which corresponds well with the operating temperature of the MIP system.

We also note in these "thermograms" that other species require higher temperatures before they are thermally reduced and released from soils.

So how would this effect an in-situ thermal remediation project? To answer this let's first review mining and processing of cinnabar.

Use of Heat during Mercury Production: California (1955)

Important Observations from Mining Industry:

- "Quicksilver" is extracted from cinnabar ore (HgS).
- Crushed ore is heated in rotary kiln.
- 450°C for 30 minutes drives all Hg into the off gas.
- Vaporized mercury (elemental) extracted as gas and collected.

This and thermograms provide base design paradigm for thermal remediation of mercury in soils and indicate the temperatures are analogous to semivolatile organic compounds (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons, high molecular weight hydrocarbons, etc.) and that such remediation could be performed in-situ (using an In Situ Thermal Desorption approach) or ex situ (performed in batches/piles, or in a continuous feed system).

IN-SITU THERMAL REMEDIATION – REMOVAL RATES

Data from University of Texas support the viability of thermal remediation for elemental mercury and document that the process removes mercury consistent with tabulated physical-chemical properties

Controlled pyrolysis studies and the resulting thermograms for different mercury species indicate that relatively low temperatures are required for removal of elemental mercury (80 to 150°C) and labile mercury chlorides (100 to 300°C).

More recalcitrant (i.e., less soluble and bioavailable) mercury species such as sulfides require higher temperatures for removal (e.g., 200 to 350°C).

Most mercury species are effectively removed below the boiling point of elemental mercury (357°C) and well below the 750°C used for pyrolysis in EPA Method 7473.

STABILIZATION FOR RESIDUAL ELEMENTAL MERCURY

Because mercury is such a reactive element and has very low environmental thresholds any type of *in-situ* remedy will need to incorporate a mechanism for managing residual material.

We are investigating use of gas phase amendments following in-situ thermal treatment. Sulfur can be deployed as a gas in the subsurface using heat. Sulfur reacts spontaneously with Hg(0) to from more recalcitrant mercury sulfides.

A number of factors such as secondary reactions (e.g., sulfur oxidation and soil acidification) need to be considered and additional study is needed to support full scale deployment.

CHARACTERIZATION, REMEDIATION, & STABILIZATION STRATEGY

Our approach for elemental mercury (DNAPL) sites:

1. High resolution characterization using direct-push sensors: We have demonstrated the MIP can provide the same versatility for characterizing elemental mercury as it does for traditional DNAPLs.
2. In-Situ Thermal heating (T = 250°C) to removal majority of mass: TerraTherm has patented technology that allows for in-situ thermal heating of the subsurface. This technology has been successfully deployed to remediate sites with high molecular weight compounds such as PAHs & coal tars.
3. Brief cooling with residual mass extraction followed by gas-phase sulfur injection (T < 150°C): The gas-phase sulfur injection will sequester any residual elemental mercury forming cinnabar. This is a solid species and will not migrate with groundwater to sensitive receptors in aquatic systems.

SUMMARY & CONCLUSIONS

Hg(0) should be treated as a DNAPL source zone in subsurface and characterization and remediation should utilize proven DNAPL techniques.

Traditional DNAPL Tools can exploit unique properties to provide high resolution delineation in subsurface. One such tool is the Membrane Interface Probe. Our experience is that this tool can be readily coupled with mercury vapor analyzer to provide high resolution delineation of Hg(0) in the subsurface.

Once delineated existing In-Situ Thermal Methods ($T \sim 250°C$) should remove significant fraction of source material.

As mercury has a large bio-availability potential, a complete remediation strategy should incorporate a combination of remedies (heat + stabilization) to ensure success and long-term environmental protection.

SUMMARY & CONCLUSIONS (*CONTINUED*)

We advocate that sulfur in the gas-phase can be effectively delivered using residual thermal energy following an initial thermal treatment. The mercury:sulfur reaction is spontaneous and produces the less biologically available species of mercury – cinnabar. Right now we have only accomplished the characterization component of this approach. Future research will focus on heating and removal aspects of elemental mercury in soils and associated responses.

Questions & Acknowledgements

Prior to taking any questions we would like to acknowledge the U.S. Department of Energy Office of Environmental Management's Soil & Groundwater Remediation Program for funding this work.