Mercury and the GSI: A Dynamic CSM Uniroyal East Parcel, Detroit River

A Joint Effort Between MDEQ-RRD and AECOM, with Support of the City of Detroit and the Riverfront Conservancy

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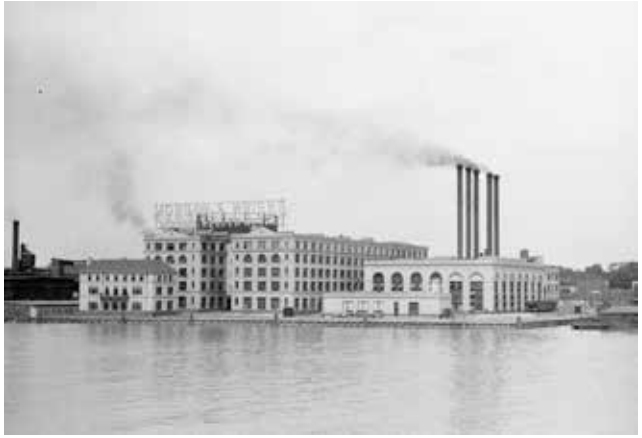
Project Team

- Steve Hoin, Senior Geologist, DEQ Warren District
- AECOM Team
  - Leslie Hartig, Project Manager
  - Barry Harding, Technical Leader
  - Anne Lewis-Russ, Principal Geochemist
  - Mike Wolf, Senior Hydrogeologist
  - Glenn Hendrix, Senior Ecologist
  - John Yanchula, Field Oversight
  - Aaron Humphrey, Geotechnical Engineer
- Dan Cassidy, WMU

Introduction

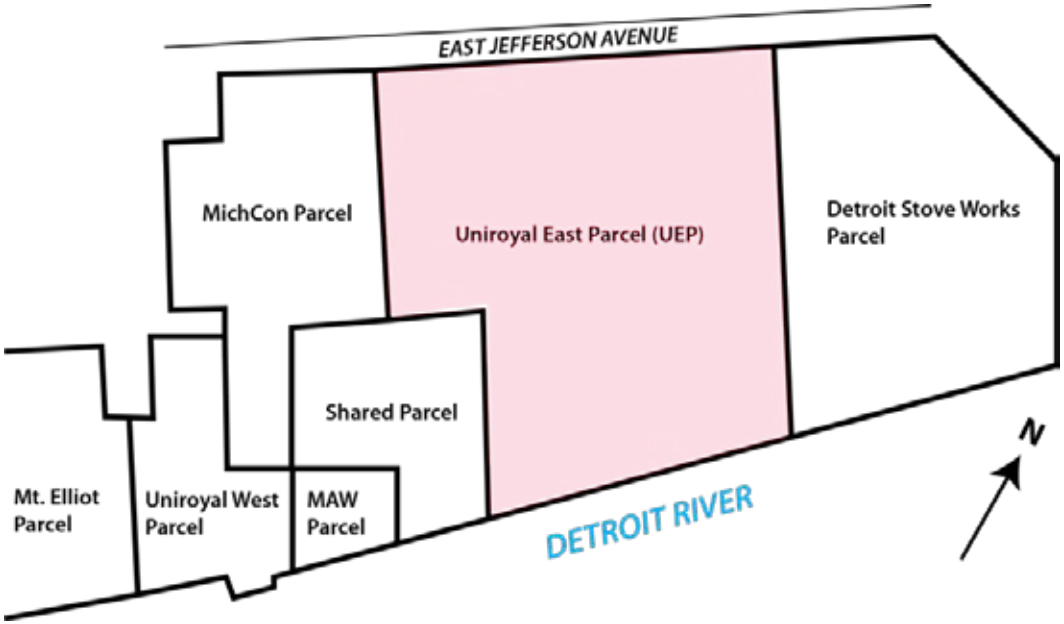
- State Funded Project (SWQIF)
- Large scale project with multiple owners, properties and challenges
- GSI and mercury driving decisions (big $$ at stake)
- Cooperative effort
- Interesting results



Historical Morgan & Wright Detroit Rubber Works Plant on the Detroit River, circa 1910. Image Source: Detroiturbex.com.

Source: Detroit News.
Date: April, 1930.

Uniroyal East Parcel



- Industrial usage from 1860 to late 1970's.
- Iron smelting, coal and ore storage. Rubber processing from 1905 to approximately 1977.
- Mercury "hotspots" identified in 2003. Mercury in fill.
- Settlement in 2014 with subsequent SWQIF.
- Response Action to be determined.

Suspected Sources of Mercury

- Catalyst in vulcanizing synthetic rubber?
- Coal?
- Ballast in laboratory equipment?
- Unknown fill?

In the end, no definitive source but mercury is present in the fill and groundwater.

Initial (Starting) CSM

Based on:

- Review of 30 years of data
- Site-specific conditions
- Postulated mercury behavior

Mercury is leaching into groundwater and migrating into the Detroit River above GSI criterion at distinct but unknown locations.

Part 201 Criteria

MDEQ Policy Number: 09-014 - If Mercury is venting to surface waters at less than 200 ng/l, then it is considered *De Minimis*.

GROUNDWATER: PART 201/213 RISK-BASED SCREENING LEVELS					MDEQ Rule 57 WQV
Hazardous Substance	Residential Drinking Water Criteria	Nonresidential Drinking Water Criteria	Groundwater Surface Water Interface Criteria	Quantification Level	Final Acute Value
Mercury (Total) (B,Z)	2.0 (A) ug/L	2.0 (A) ug/L	1.3 ng/L	200 ng/L	2.8 (D) ug/L

SOIL: PART 201/213 RISK-BASED SCREENING LEVELS				
		Groundwater Protection		Contact
Hazardous Substance	Statewide Default Background Level	Residential Drinking Water Protection Criteria	Groundwater Surface Water Interface Protection Criteria	Direct Contact Criteria
Mercury (Total) (B,Z)	130 ug/Kg	1700 ug/Kg	50 (M) 1.2 ug/Kg	160000 ug/Kg

A State of Michigan drinking water standard, Section 5 of 1976 PA 399, MCL 325.1005.

B Background, as defined in R 299.1(b), may be substituted if higher than the calculated cleanup criterion. Background levels may be less that criteria for some inorganics.

D Measured as dissolved.

M Calculated criterion is below the analytical target detection limit, therefore, the criterion defaults to the target detection limit.

Z Generic cleanup criteria for mercury is based on data for different species of mercury. Data for methyl mercury serve as basis for the GSI Criterion. Data for mercuric chloride serve as basis for remaining criteria.

Mercury (Hg)

- Mercury is a unique transition metal: liquid, solid or gas at room temperature.
- Uses: catalyst, chemical reagent, electrical components, dental amalgams….
- Combines with natural organic matter; can form highly toxic organic compounds. Reacts with sulfur to form stable HgS.
- Neurotoxin - Bio-accumulative; serious risk, especially to the top of the food chain.
- Mercury GSI criterion is very low (1.3 ng/L); hard to achieve.
- Specialized and potentially confusing sampling and analysis requirements (Mercury Lab Methods: 6010, 6020, 6200, 6800, 7470, 7471, 7472, 7473, 7474….)

Mercury Geochemistry

- Oxidizing Conditions
  - Oxygen present
  - Hg^{2+} or complexes with Cl or OH
  - Hg adsorbed or iron or manganese minerals
- Reducing Conditions
  - Oxygen not present
  - Elemental Hg or complexes with S or organic matter
  - Mercury sulfide solid

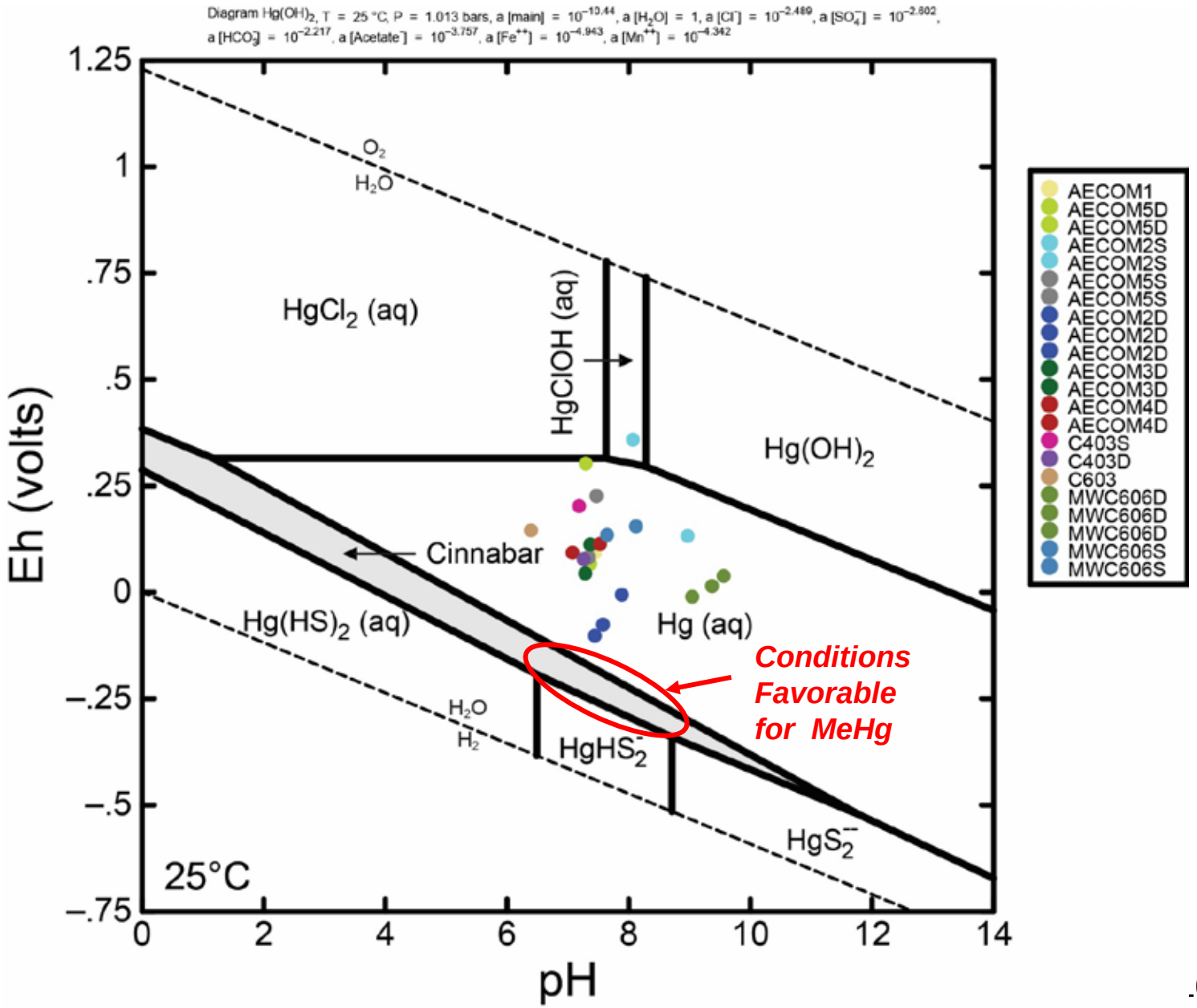
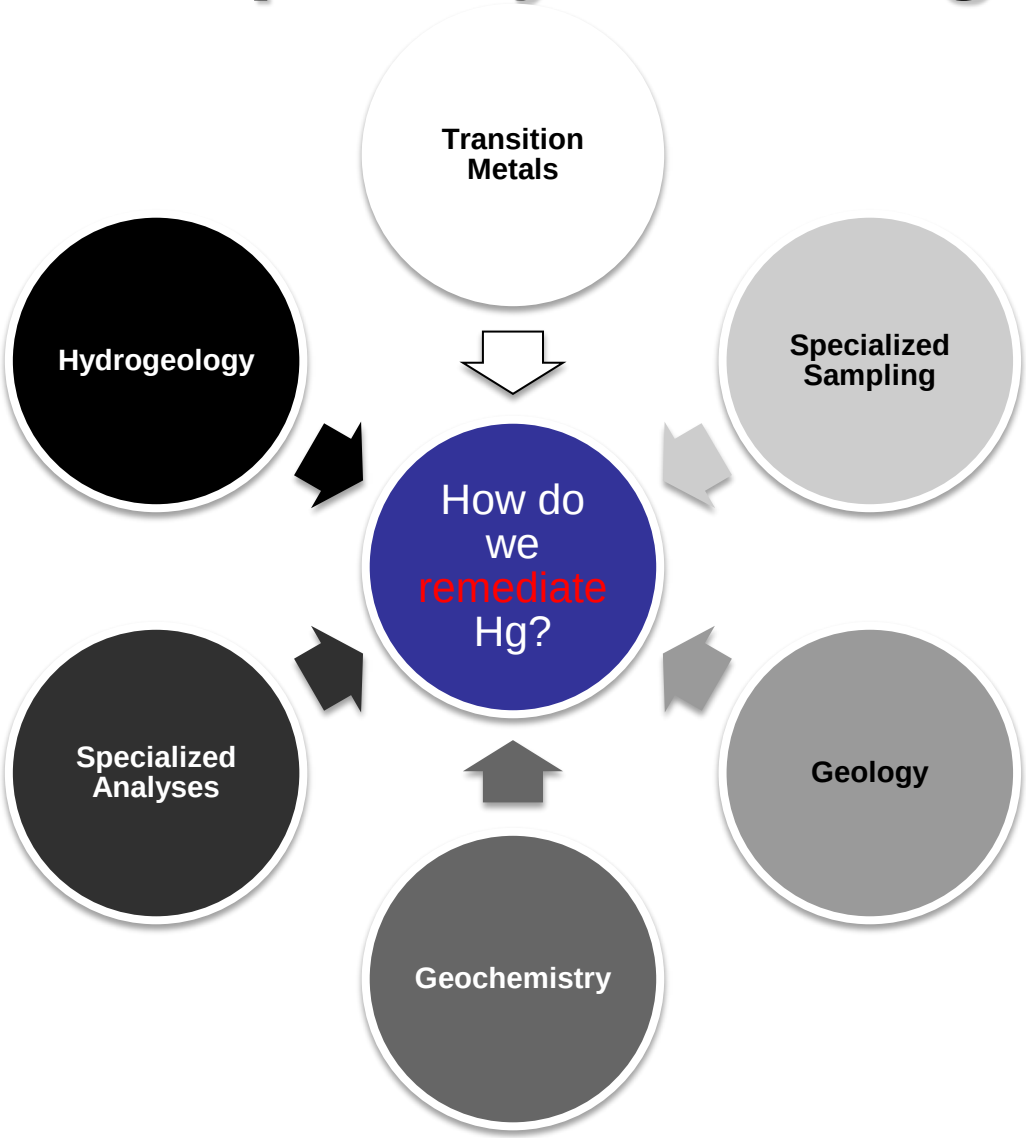
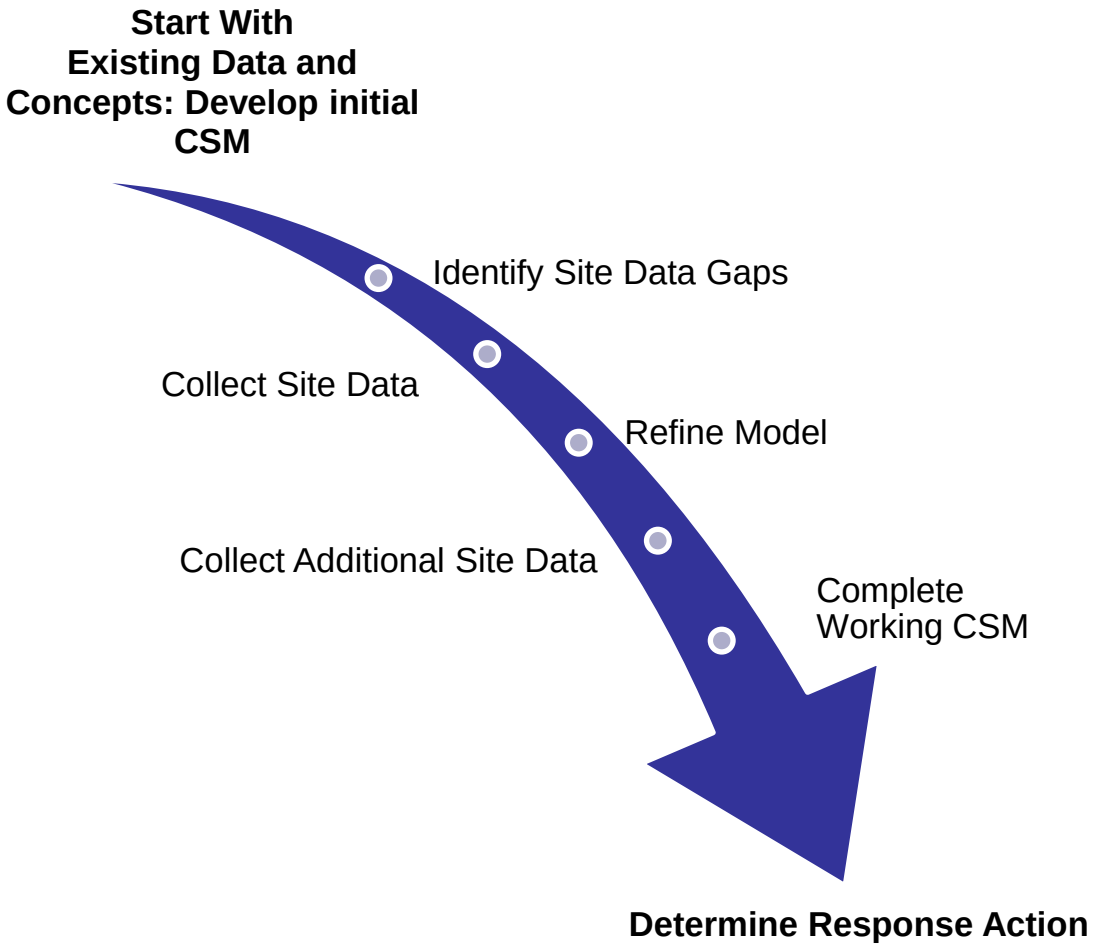


Diagram Hg(OH)2, T = 25 °C, P = 1.013 bars, a [main] = 10^-10.44, a [H2O] = 1, a [Cl-] = 10^-2.489, a [SO4--] = 10^-2.802, a [HCO3-] = 10^-2.217, a [Acetate-] = 10^-3.757, a [Fe++] = 10^-4.943, a [Mn++] = 10^-4.342
Eh (volts)
pH
1.25
1
.75
.5
.25
0
–.25
–.5
–.75
0
2
4
6
8
10
12
14
O2
H2O
HgCl2 (aq)
HgClOH (aq)
Hg(OH)2
Cinnabar
Hg(HS)2 (aq)
Hg (aq)
H2O
H2
HgHS2-
HgS2--
25°C
Conditions Favorable for MeHg
AECOM1
AECOM5D
AECOM5D
AECOM2S
AECOM2S
AECOM5S
AECOM5S
AECOM2D
AECOM2D
AECOM2D
AECOM3D
AECOM3D
AECOM4D
AECOM4D
C403S
C403D
C603
MWC606D
MWC606D
MWC606D
MWC606S
MWC606S

Multi-Disciplinary Challenges



Evolution of [our] CSM

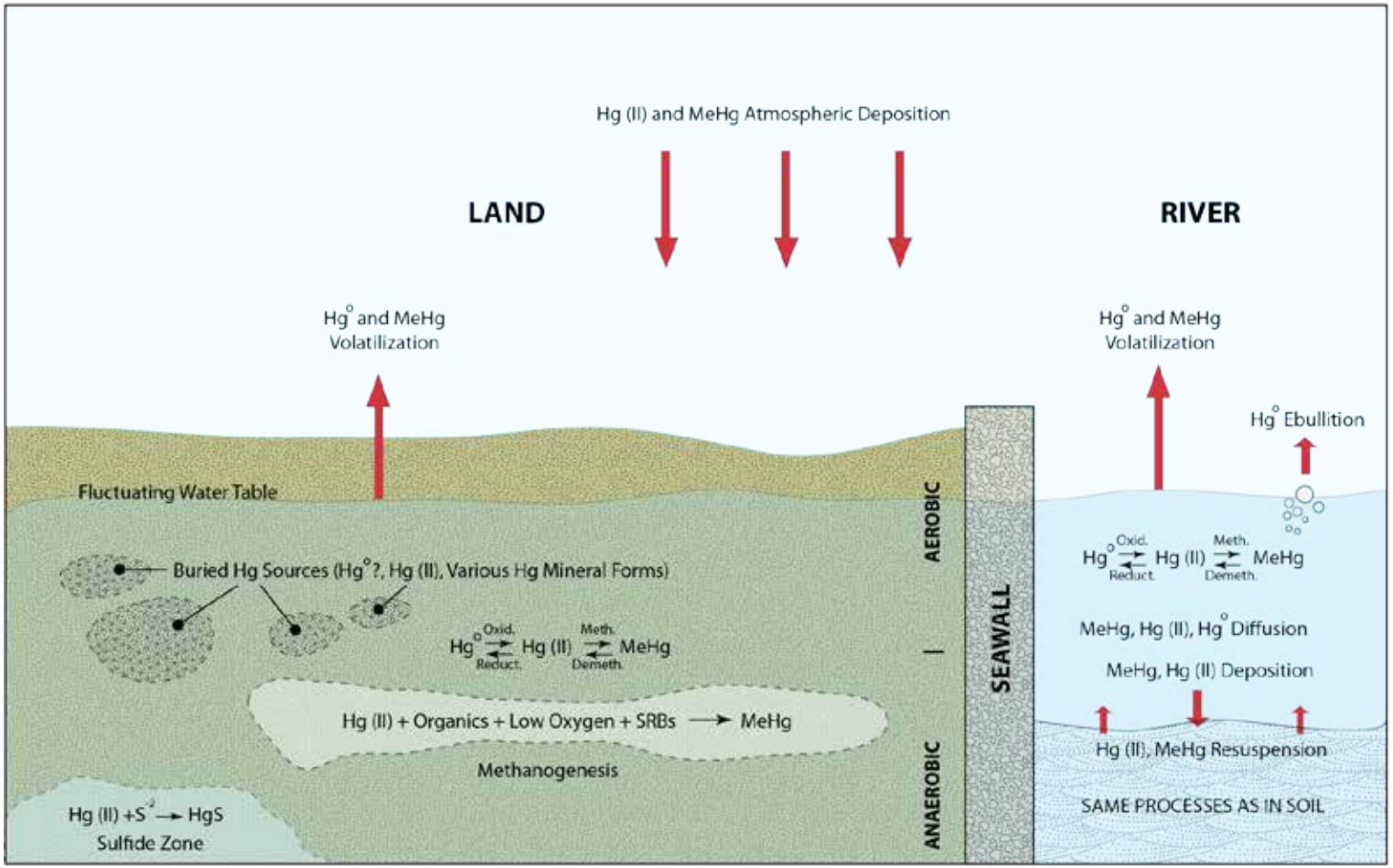


Interesting Things We Did

- Groundwater Gridding
  - to focus in on hot spots
- Low Colloid Well Installation
  - Sonic Installed/Pre-Pack Wells
- Mercury Eh-pH Phase Modeling
- Mercury Sequestration Evaluation
  - XRD Suspended Fractions - Mineralogy
- Mercury Conversion Evaluation
- GSI Discharge Point Evaluation (On-Going)
  - Specific Conductivity Mapping
  - Thermal Imaging of Sheet Pile

I: Start with a Known Model

CONCEPTUAL MERCURY CYCLING IN A TERRESTRIAL ENVIRONMENT NEAR A RIVER

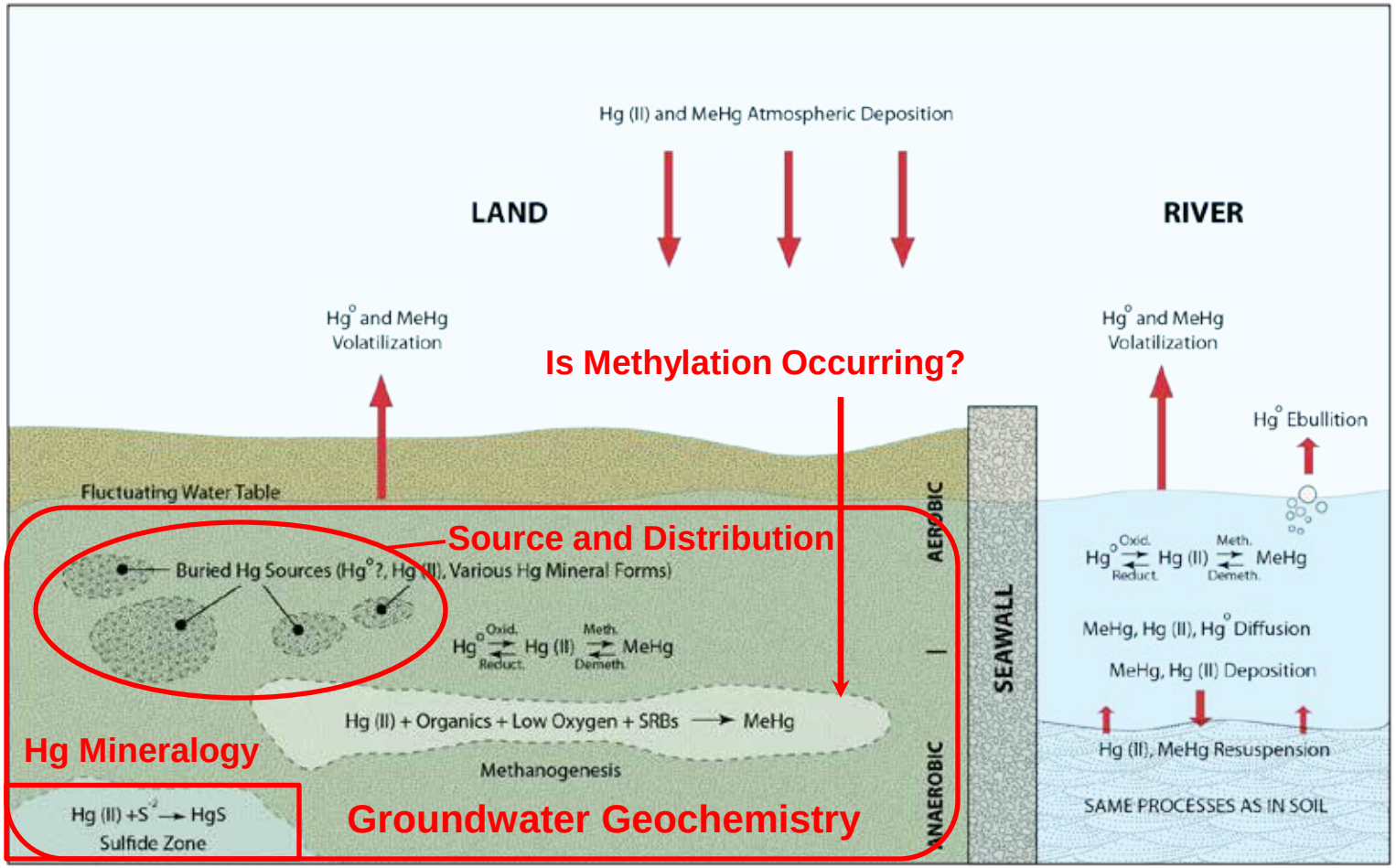


Adapted from South Florida Water Management District, Everglades Consolidated Report (2000)
South Florida Water Management District, West Palm Beach, Florida.

MeHg	Methylmercury
Hg (II)	Divalent Mercury
Hg°	Elemental Mercury
HgS	Mercury Sulfide
SRB	Sulfate Reducing Bacteria

II: Identify Data Gaps

CONCEPTUAL MERCURY CYCLING IN A TERRESTRIAL ENVIRONMENT NEAR A RIVER



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III: Design Field and Lab Approach

Water

- Total and Dissolved Hg
- Methyl Hg
- Total and Dissolved Fe and Mn
- Geochem Parameters
- CENSUS: Biological
- Mineralogy: XRD

Reduce Turbidity
Pre-Packed Well Screens
Sonic-Drilled Boreholes

Sulfate, Sulfide,
Nitrate, Nitrite, Chloride

SRBs,Methanogens,
Geobacter, Total Eubact.,
Sulfate Reduction Assay

Colloid/Clay Fractionation
X-Ray Diffraction

Soil

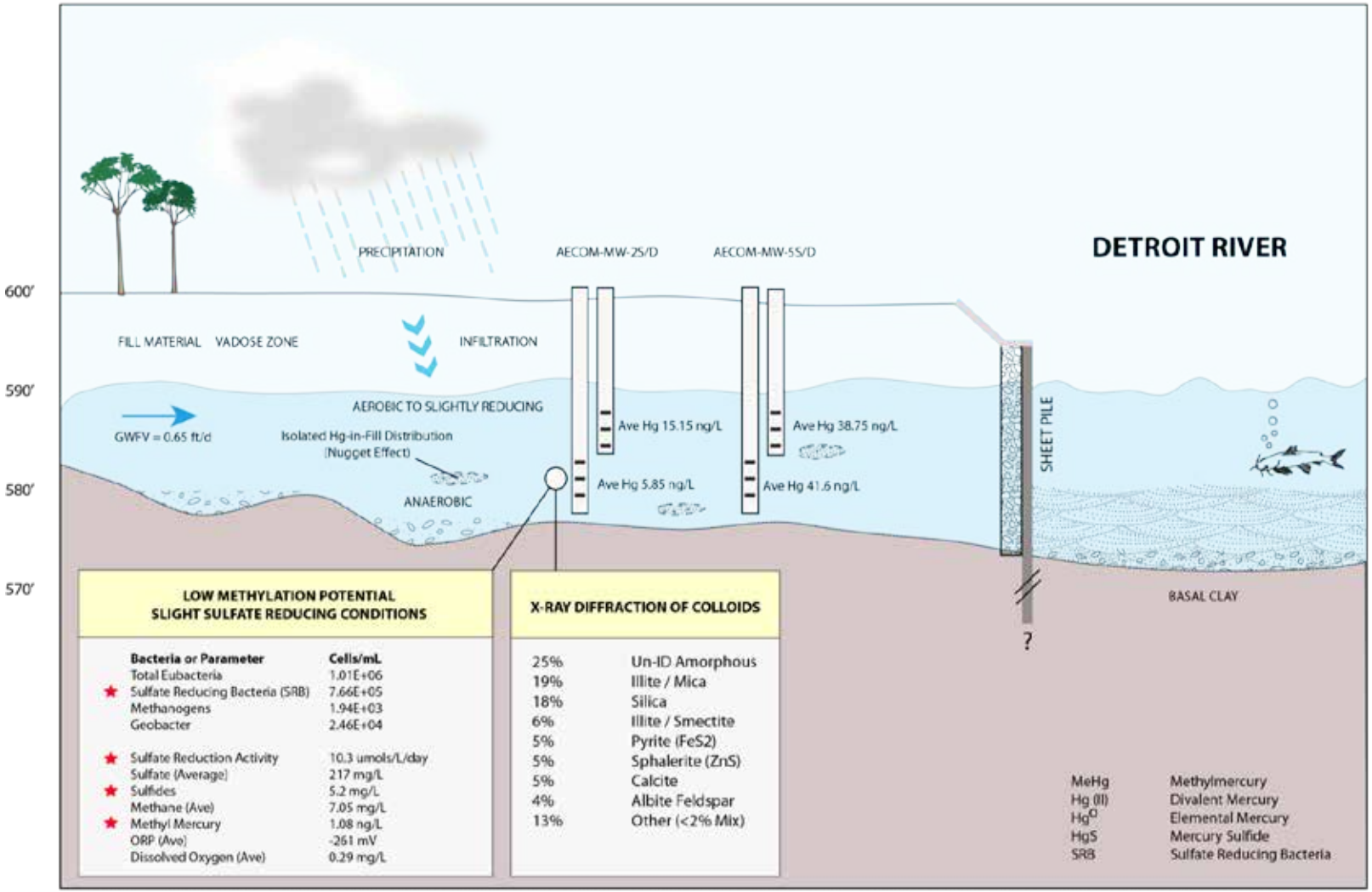
- Hg, Fe and Mn
- Total Organic Carbon
- Geotechnical
- Benchscale Treatability

Grain-Size, Porosity
Bulk Density and Perm.

- Hg Stabilization
- Hg Encapsulation
- Reactive Barrier

COLLECT DATA
TWO SAMPLING EVENTS

Refine the CSM



What Have We Learned?

- Site Hg is associated with non-native fill materials.
- Areal distribution of Hg in soil is variable. No confirmed hot-spots exist.
- Groundwater geochemistry, including Eh and pH varies across site and at different depths, and may change seasonally due to surface water infiltration/river fluctuations.
- Sulfate-reducing conditions limited in extent.
- Dissolved groundwater Hg well below 200 ng/L.
- Hg potentially bound in suspended colloids in groundwater (Total Hg).
- Methylation potential is low due to aged Hg source and geochemical conditions (not sufficiently reduced).

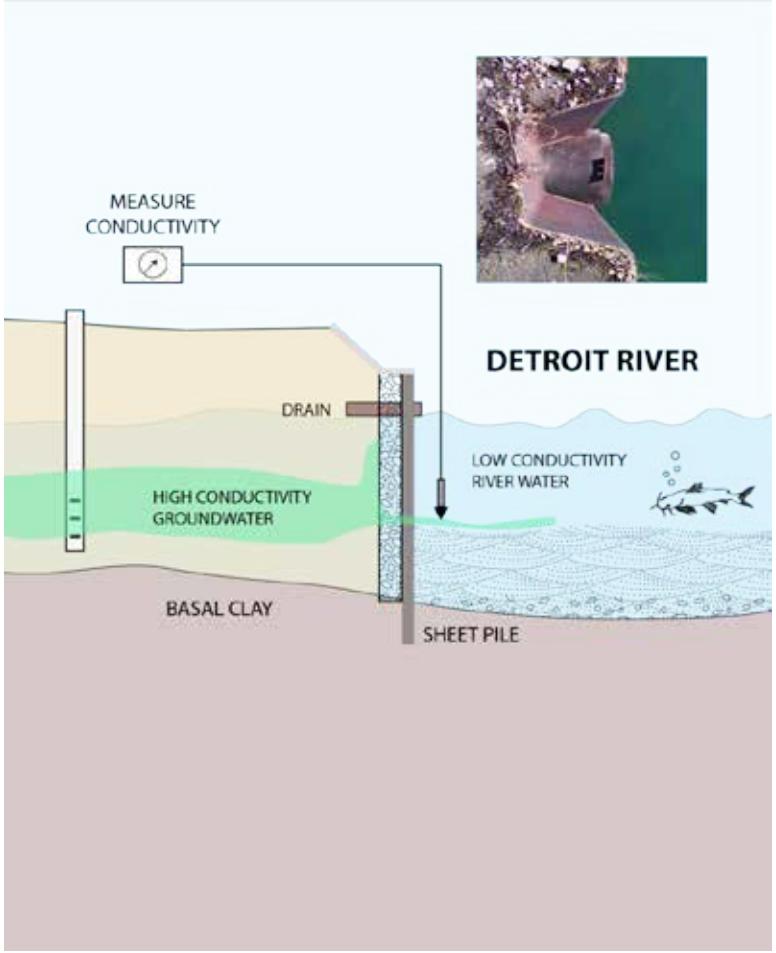
Refined CSM

Mercury is leaching from fill material but at lower levels than anticipated and in less toxic forms and is not reaching the Detroit River at levels above the target compliance number of 200 ng/l.

- We are still working to verify this….

Ongoing and Projected

- Fall 2015: Specific Conductance Study along seawall.
- Late 2015: Tracer Study (maybe).
- Late 2015: Complete White Paper on Mercury Geochemistry.
- Late 2015: DEQ decision.



Take Home Points

- Mine from legacy data and build an initial CSM (or two?).
- Identify data gaps in your CSM; the CSM is dynamic and will change.
- Develop a well-defined SOW with clear DQO's to test/refine CSM.
- Assemble a talented team with specialists well-versed in the issues (e.g., metal geochemistry).
- Allow your contractor/consultant to have a strong voice.
- Know what you don't know.

  Mercury mobility is greatly affected by its physical state and association with other constituents, as well as by geochemical conditions. These all affect the form of mercury and its transport.
- Stay collaborative, share ideas, listen and be open minded, but stay focused on the objectives.

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