Mercury Source Zone Identification & Characterization

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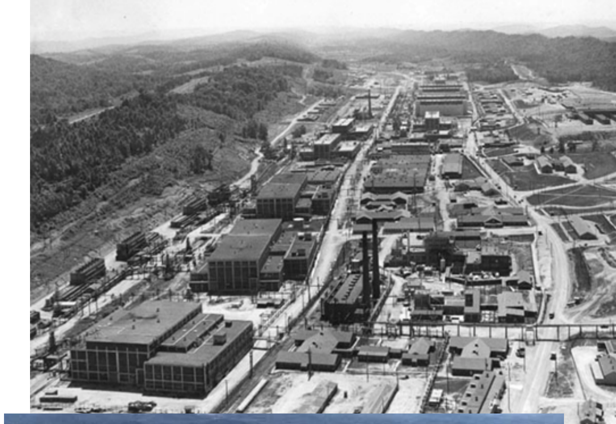
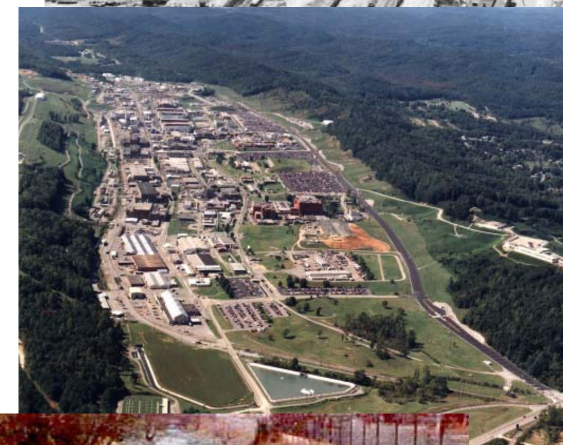




U.S. DEPARTMENT OF ENERGY

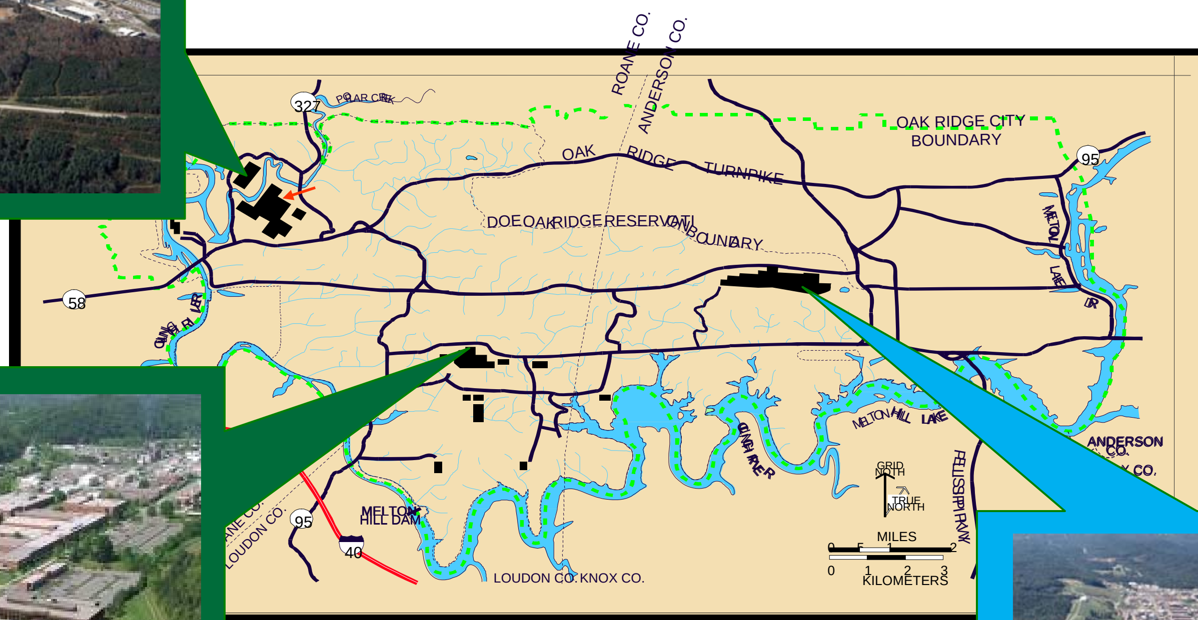
OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

DOE EM30 Applied Field Research Initiative (AFRI)
Remediation of Mercury and Industrial Contaminants

Objective: develop and demonstrate new tools and approaches for the characterization, remediation, and prediction of mercury and other contaminants in complex subsurface and surface water environments.

Goal: reduce remediation cost and risk

ETTP

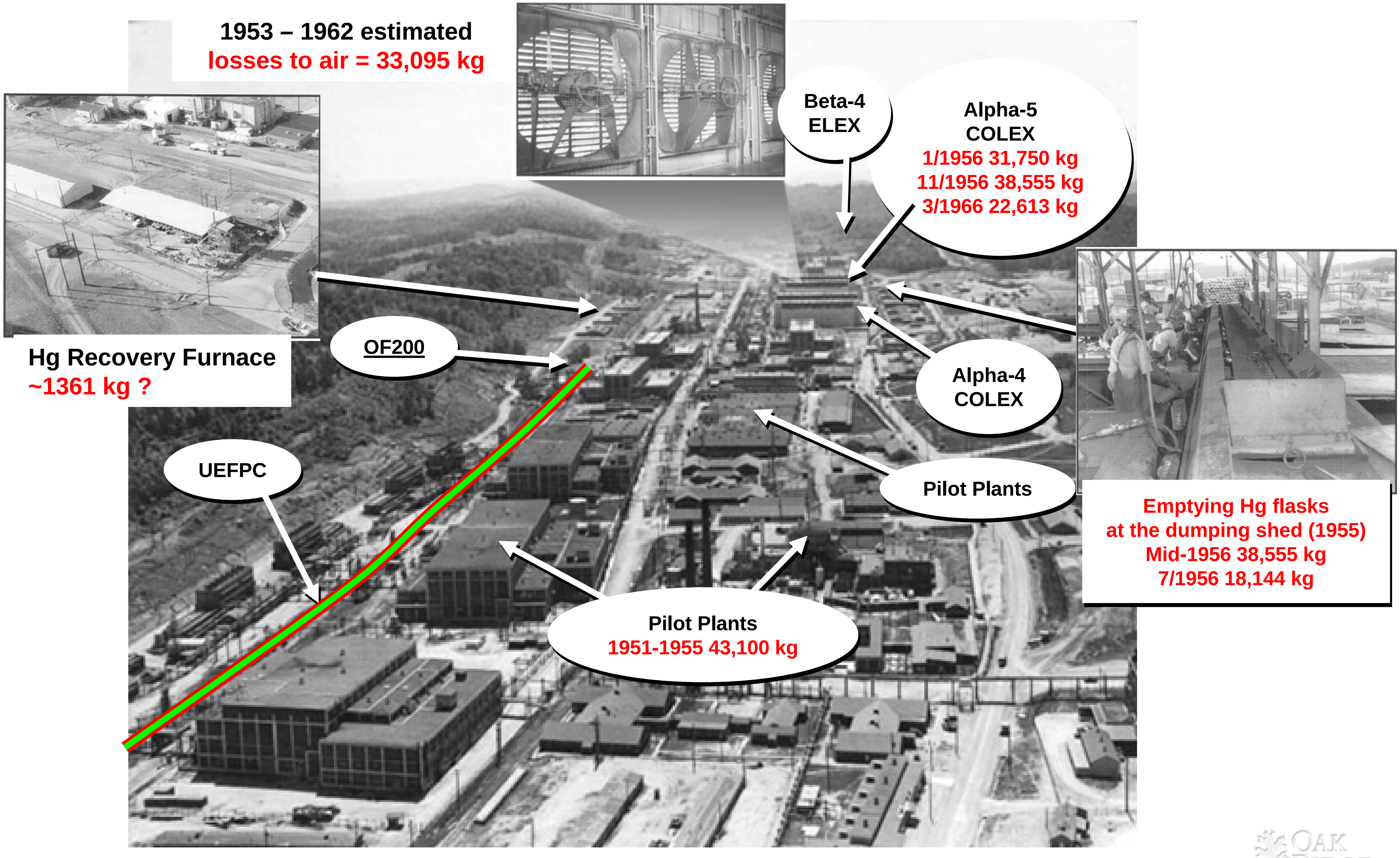


ORNL

Y-12 National Security Complex

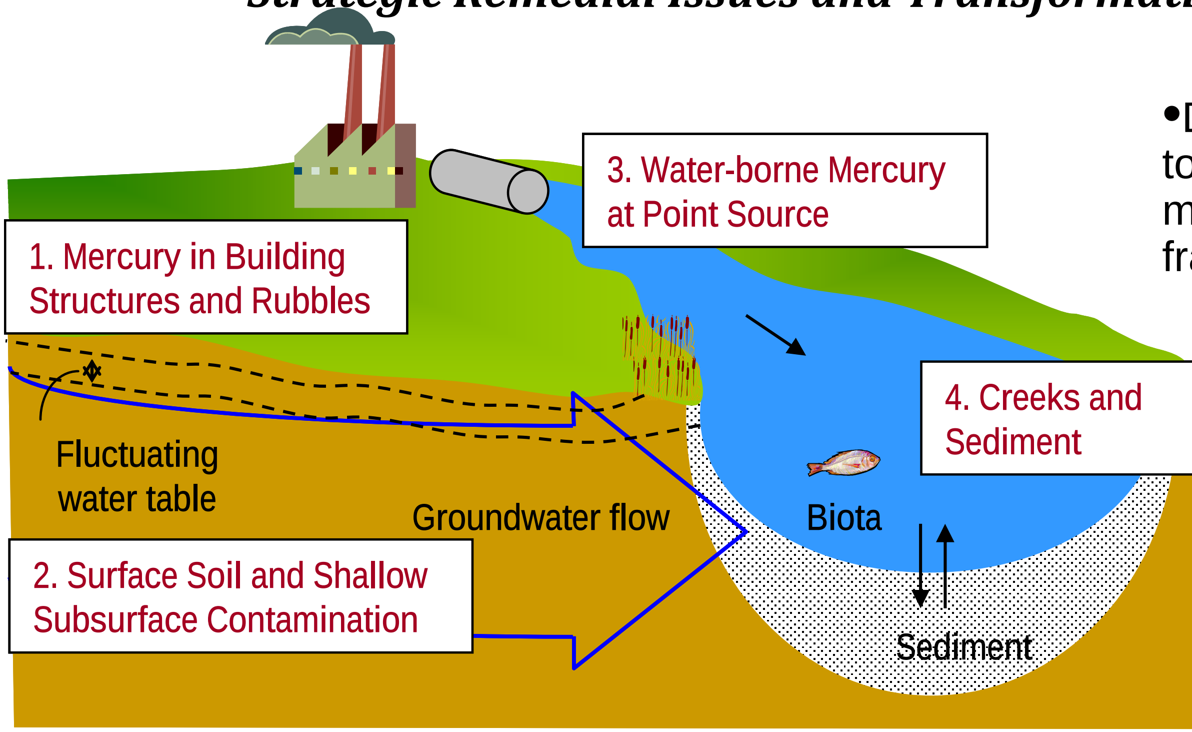
Managed by UT-Battelle
for the U.S. Department of Energy

Mercury use and accidental losses to ground at Y-12
Total known ~194,100 kg



Mercury Characterization and Remediation

Strategic Remedial Issues and Transformational Applied Science



- Develop and demonstrate reliable tools to detect and quantify mercury in soil, rubble, and fractured rock

  Goals: Efficient, economical waste segregation, treatment, and disposal. Improved prediction of mercury contamination, speciation, and transport in complex subsurface systems.

- Develop and validate physical and chemical amendments to stabilize mercury in soil, sediment, and stream banks

  Goal: Long-term mercury immobilization to reduce release and risk

- Demonstrate and optimize novel treatment methods for mercury in water

  Goal: Prevention of mercury release to surface water and ecosystems

- Improve the understanding of biochemical and environmental controls on mercury methylation and food-chain transfer (collaboration with Office of Science)

  Goals: Biogeochemical manipulations to suppress mercury methylation, bioavailability, bioaccumulation

Characterization of Hg source Areas

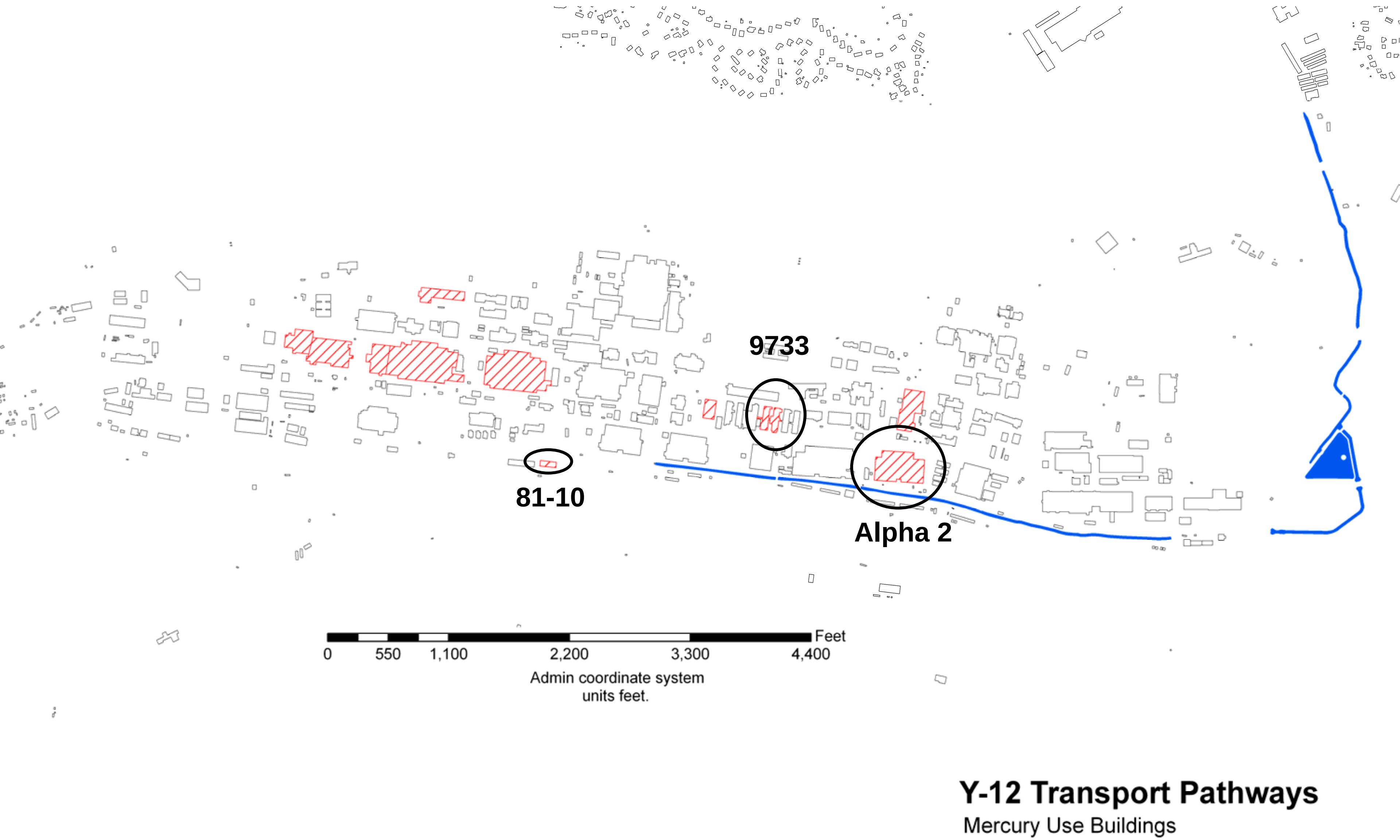
Task Objectives

- Test soil gas sampling and analysis techniques and Membrane Interface Probe (MIPs) (SRNL) to locate Hg onsite source areas
- Characterize nature of onsite Hg sources
  - Lithologic associations
  - Sequential extractions for Hg speciation
  - XRF comparison
  - Mineralogical associations & changes (oxides, clays)
  - Thin sections, SEM, XPS, XRD
- Assess and determine pathways and conditions needed for Hg mobilization
- Evaluate treatment technologies

Field characterization approach

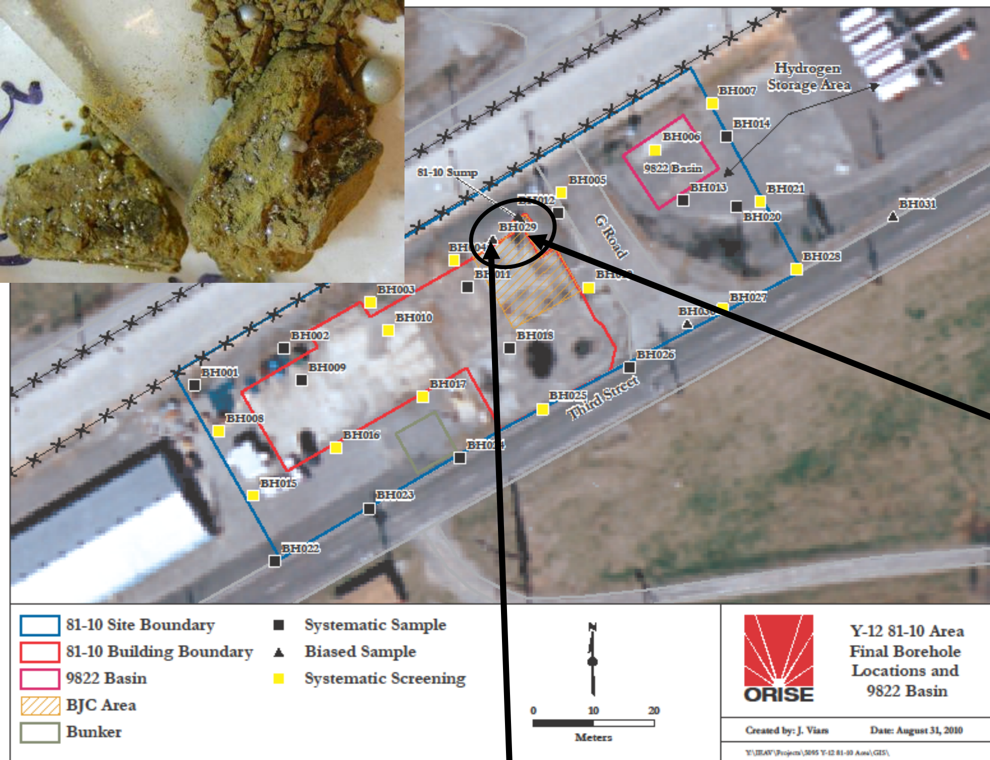
- Initial soil gas survey with pushprobe to less than 1' (to avoid penetration permit issues) at all areas
- Geoprobe pushprobe soil gas collection at depth discreet intervals Alpha 2, 9733 & 81-10
- Characterization & Hg speciation
  - Get splits of soil samples from ORAU for Hg speciation from 81-10 retort building
  - Bucket of Hg contaminated waste soil from 9733
  - More controlled collection of core and install groundwater wells at Alpha 2

Study Areas at the Y-12 NSC

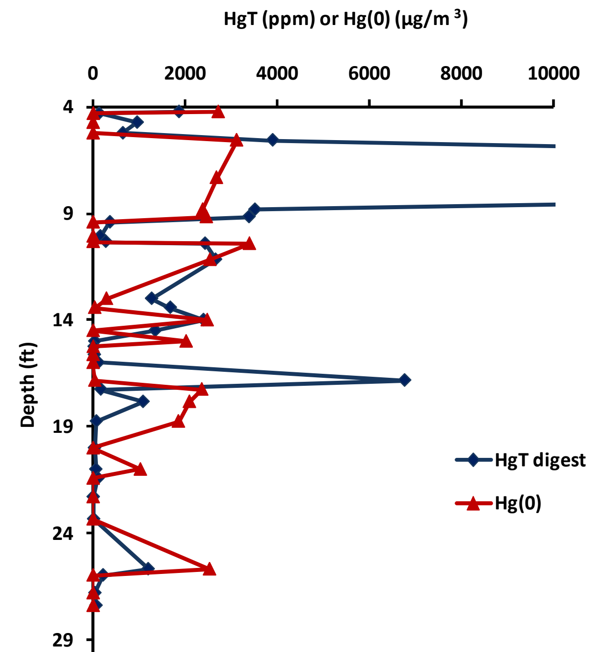


81-10 Hg Retort Building Core analysis results

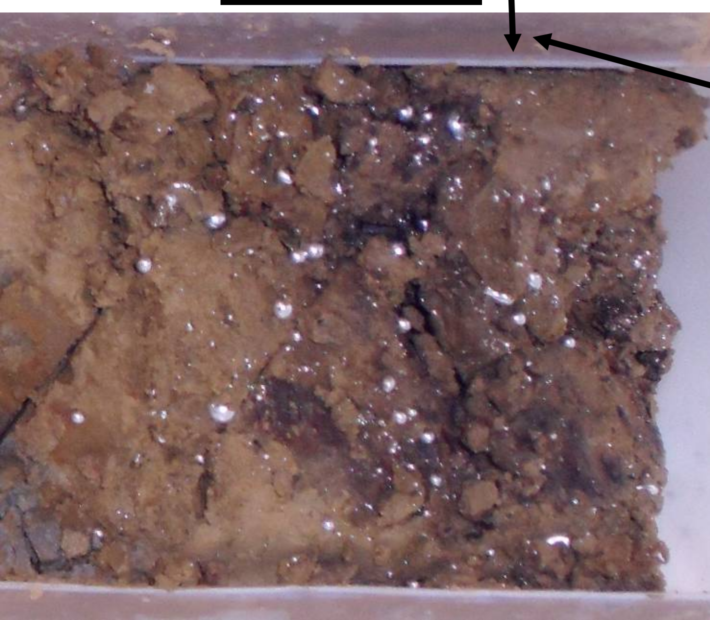
- Pools of Hg detected @15'
- Associated with gravelly material overlying clay

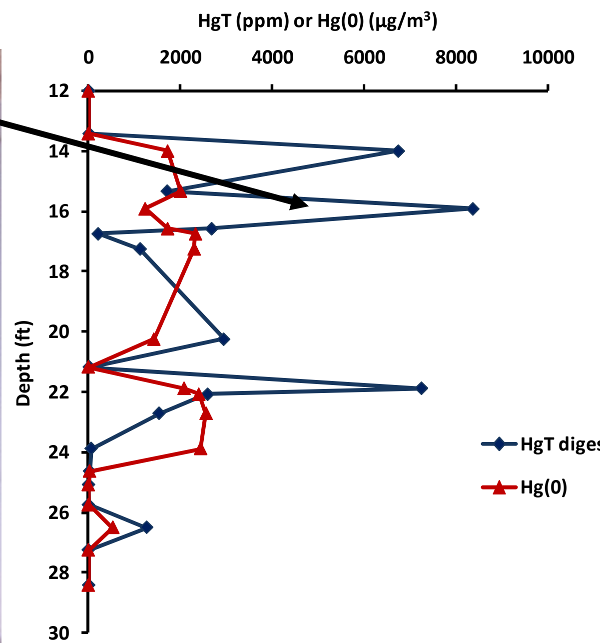


Core 29



Core 4 (15')



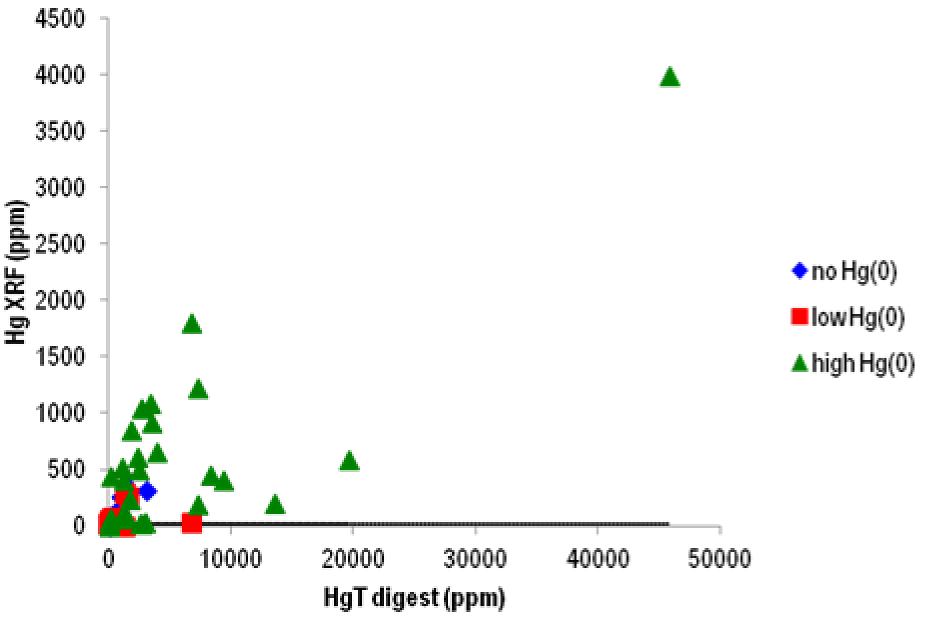


“Best” analysis techniques depends on the question

- Analyzed >85 samples using three techniques
  - X-ray Fluorescence (XRF): quick, easy to use in field but underestimates concentration of Hg
  - Total Hg (HgT) Digest: Standard method used by analytical labs; if Hg(0) present measured concentrations highly variable due to heterogeneity
  - Hg(0) headspace analysis: Good for determining presence of Hg(0)

Sample	Average (ppm)	Standard deviation	Range (ppm)
1	10876	7223	3115-19605
2	1153	881	628-2701
3	1558	316	1107-1992
4	2550	552	1907-3392
5	3.3	0.39	2.79-3.62

Measured Hg concentration highly variable when Hg(0) present



XRF underestimates Hg present in soil

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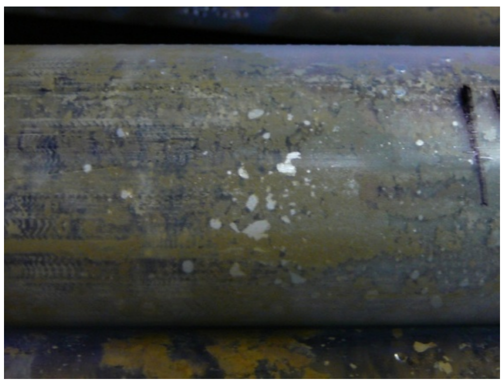

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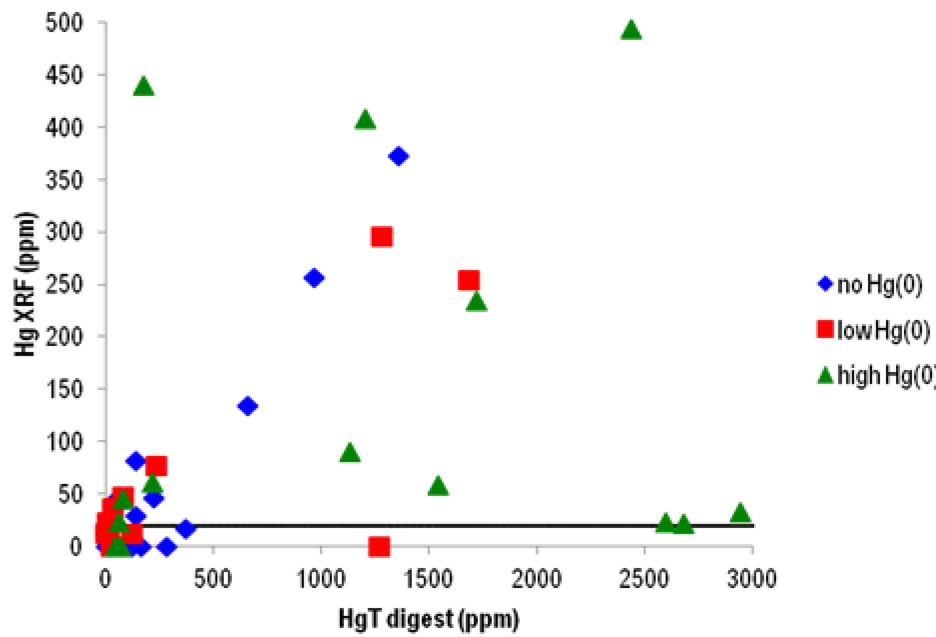


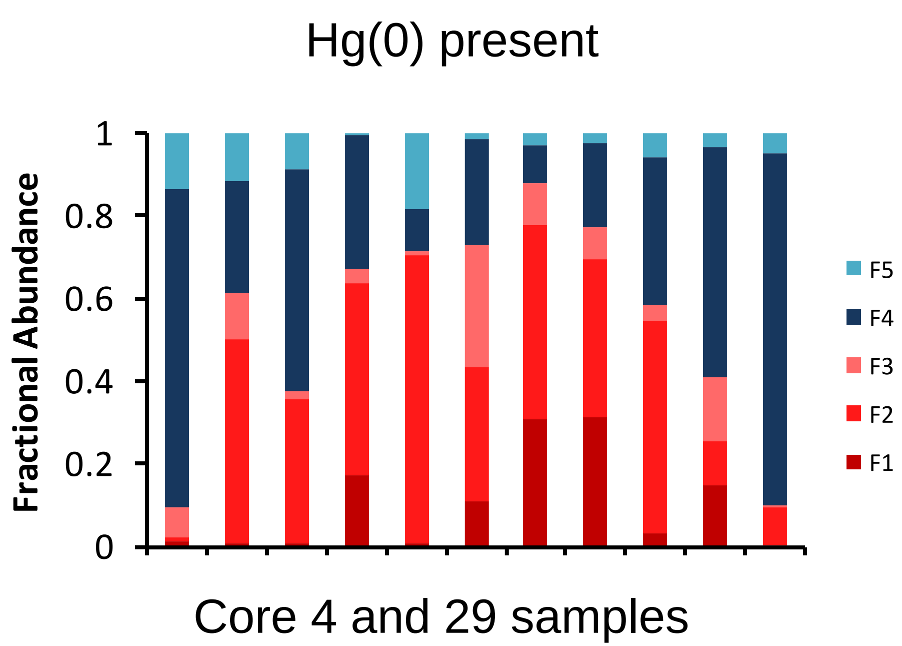
XRF underestimates Hg present in soil

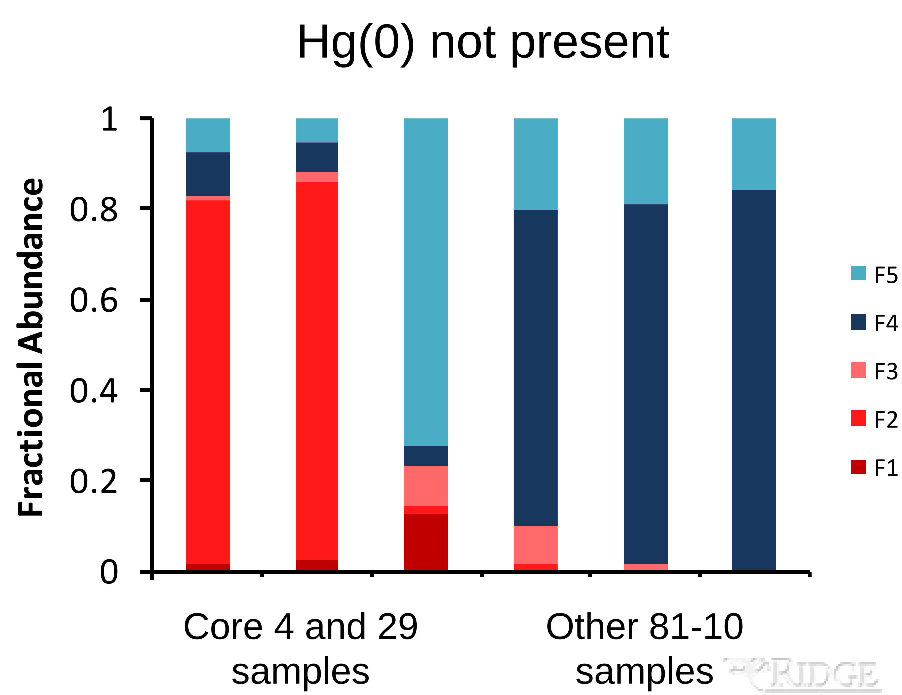
Hg reactivity is 81-10 soils: Sequential Extractions

- Hg in "mobile" fractions when Hg(0) present
- Hg in areas not containing Hg(0) "unreactive"
- In samples not containing Hg(0) but from areas close to Hg(0) contamination reactivity variable

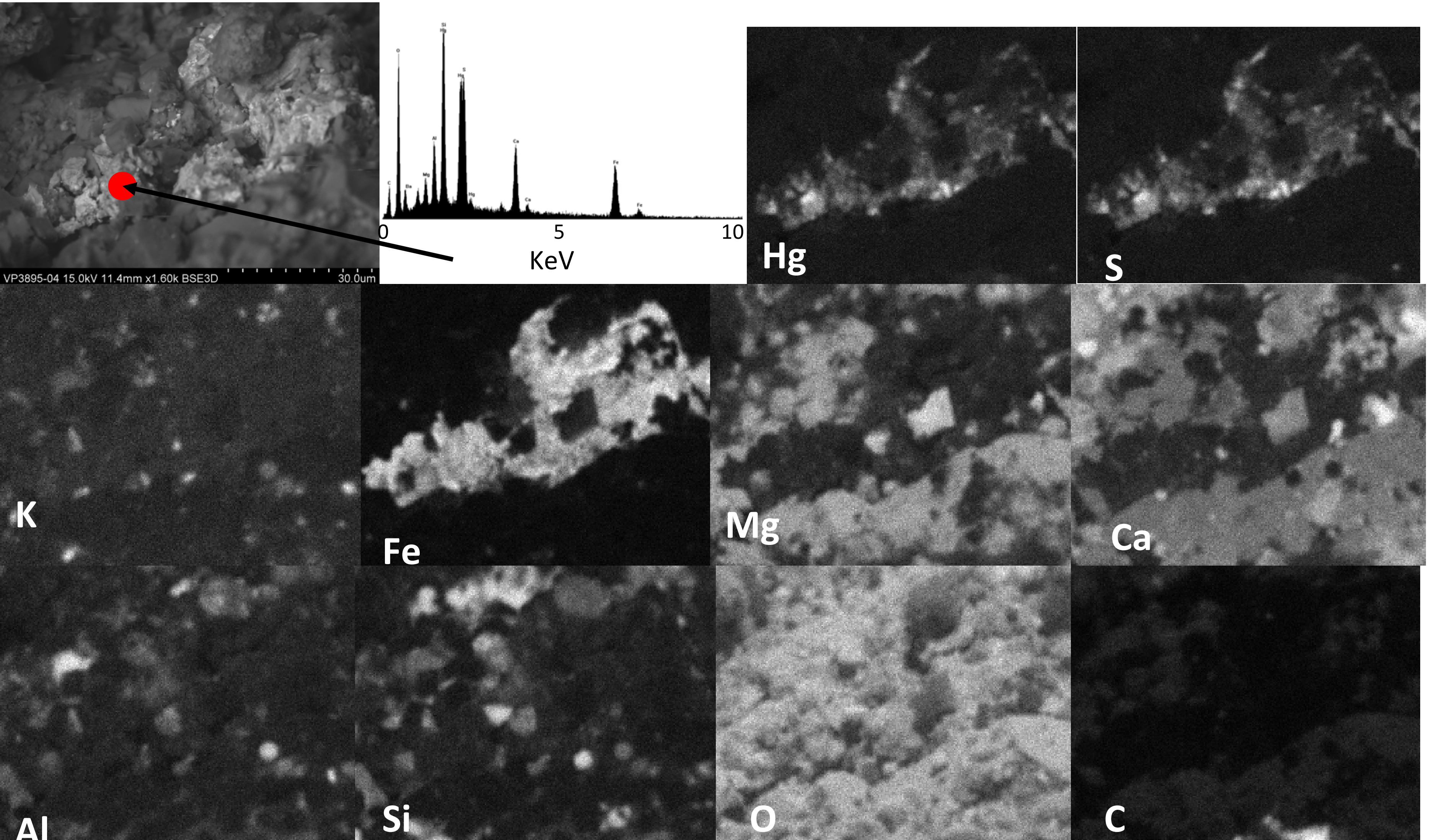
Fraction	Extracting solution	Potential Hg species
F1	DI water	$HgCl_2$, $HgSO_4$
F2	Hydrochloric acid/Acetic acid (pH 2)	HgO, Hg-oxides (Fe, Mn)
F3	1 N potassium hydroxide	Hg-organic, Hg_2Cl_2
F4	12 N nitric acid	Hg(0), Hg_2Cl_2
F5	Aqua regia (3:1 mix hydrochloric/nitric acids)	HgS, m-HgS

Bloom et al. 2003

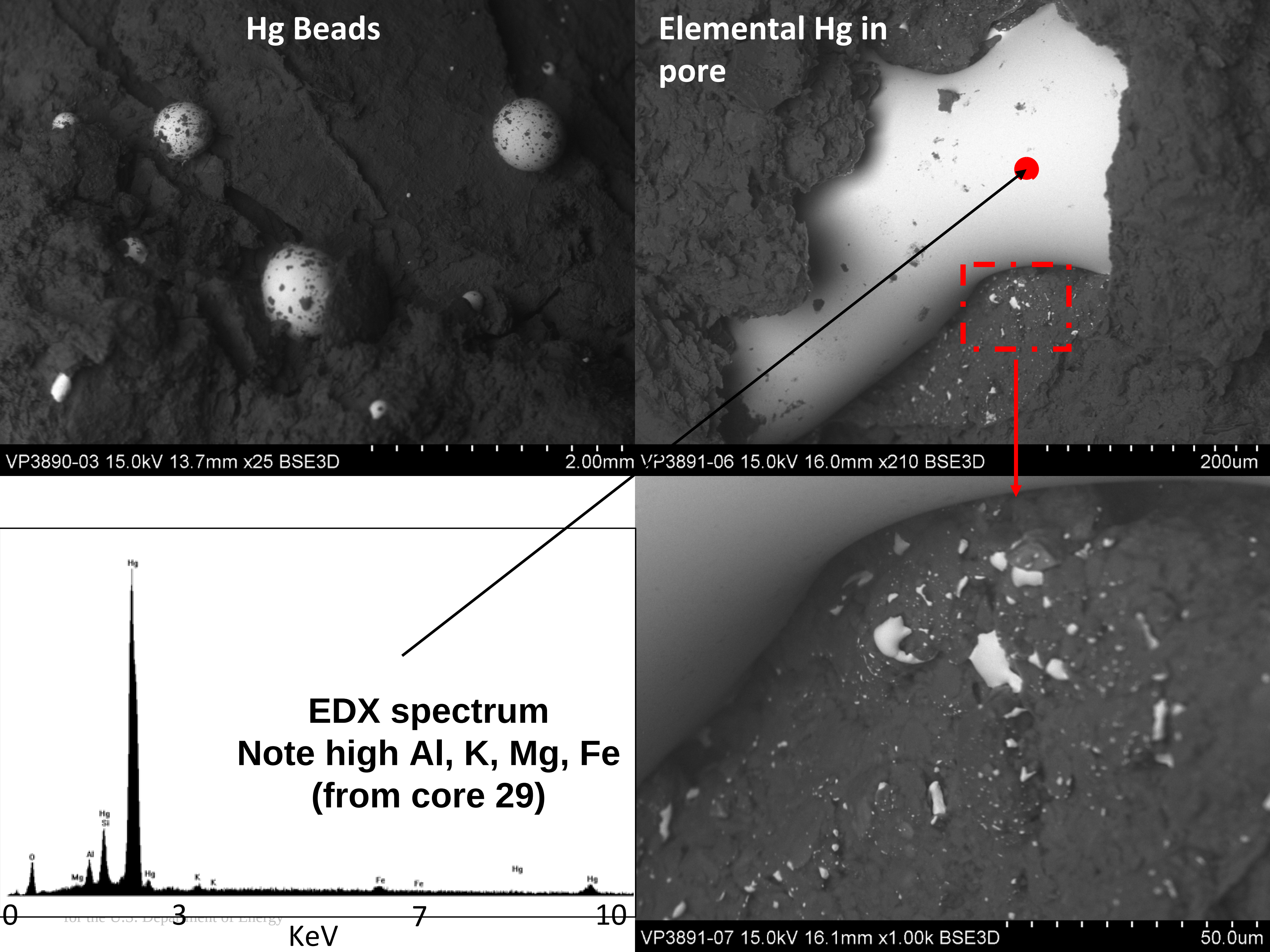


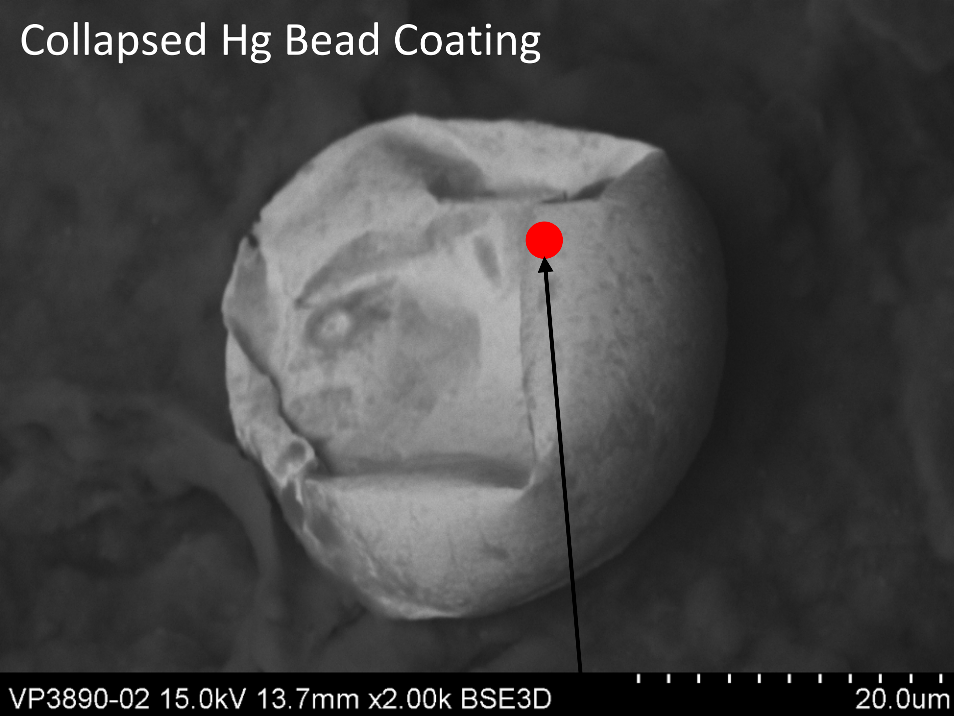


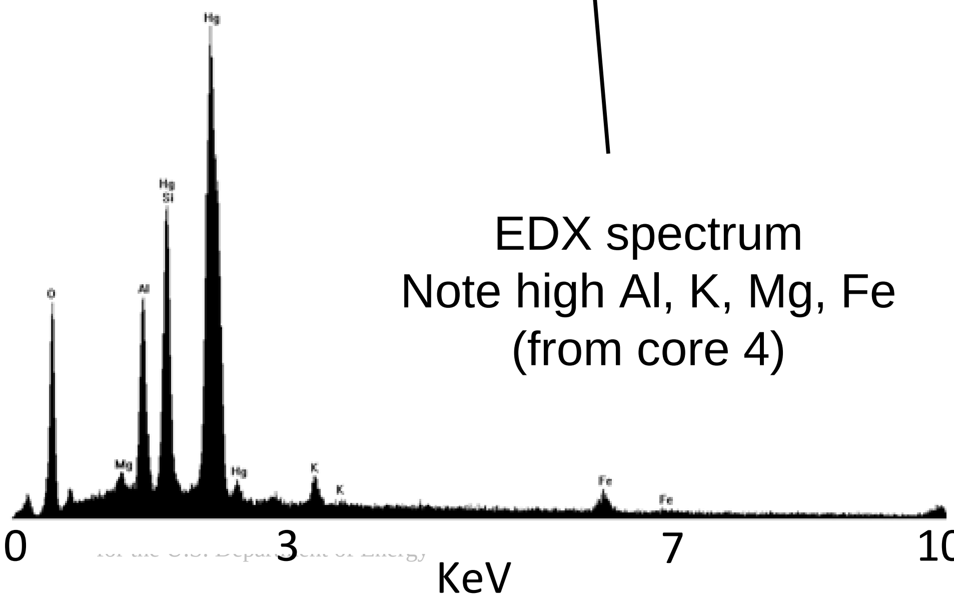
Identifying Forms of Hg in Source Area - SEM Analysis



Hg mineral associated with Fe and S


Hg Beads
Elemental Hg in pore
VP3890-03 15.0kV 13.7mm x25 BSE3D
2.00mm
VP3891-06 15.0kV 16.0mm x210 BSE3D
200um
VP3891-07 15.0kV 16.1mm x1.00k BSE3D
50.0um
EDX spectrum
Note high Al, K, Mg, Fe
(from core 29)
Hg
Hg Si
O
Al
Mg
K
Fe
0
3
7
10
KeV

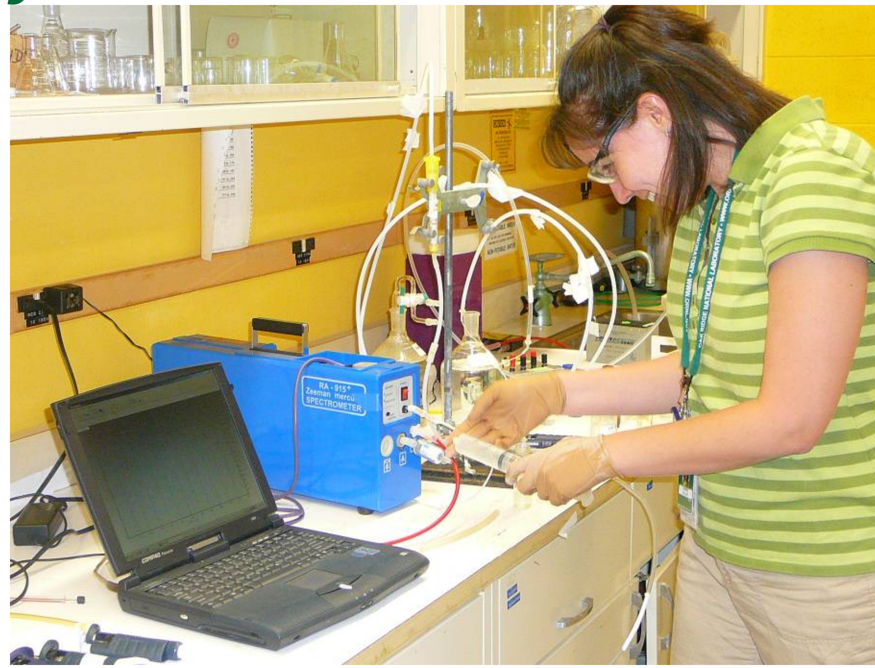




EDX spectrum
Note high Al, K, Mg, Fe
(from core 4)

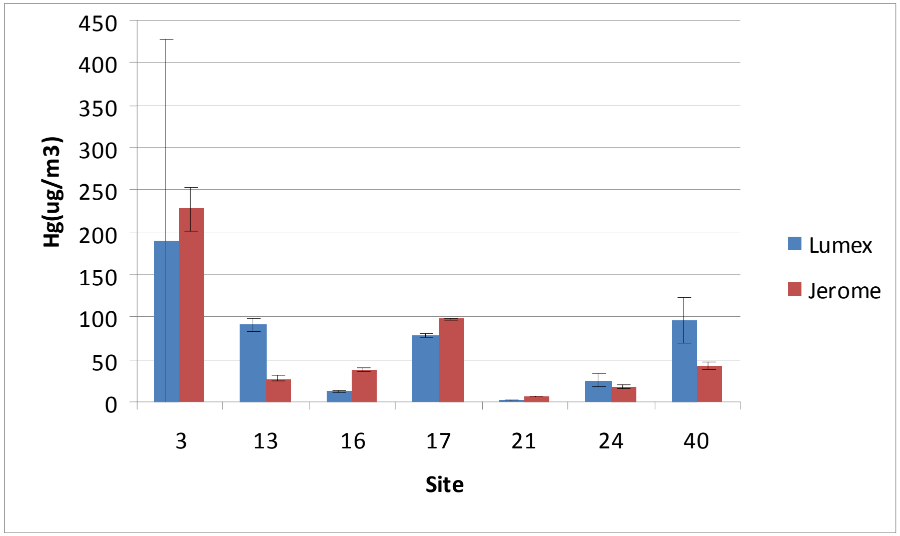
Soil Gas Collection and Mercury Analyses

Hand driven 1’ probes

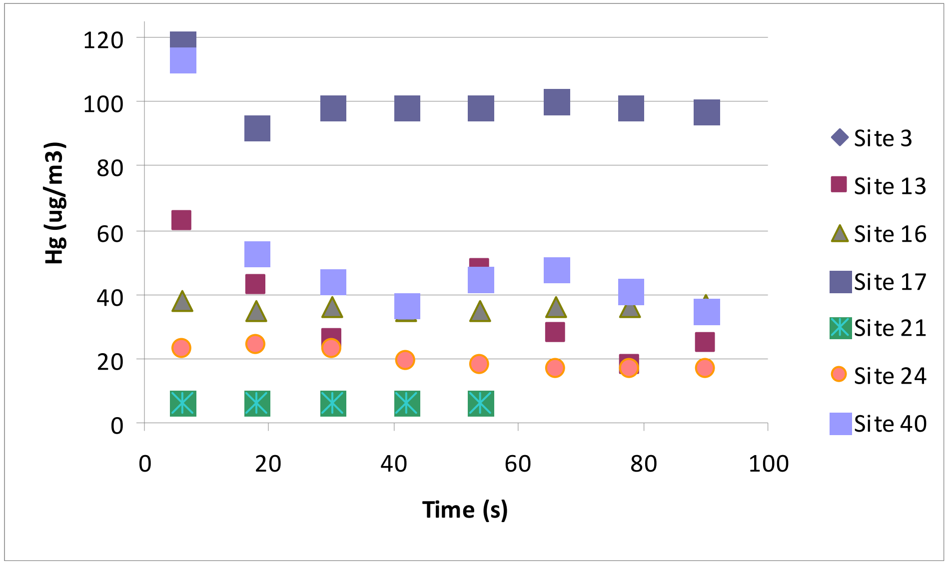


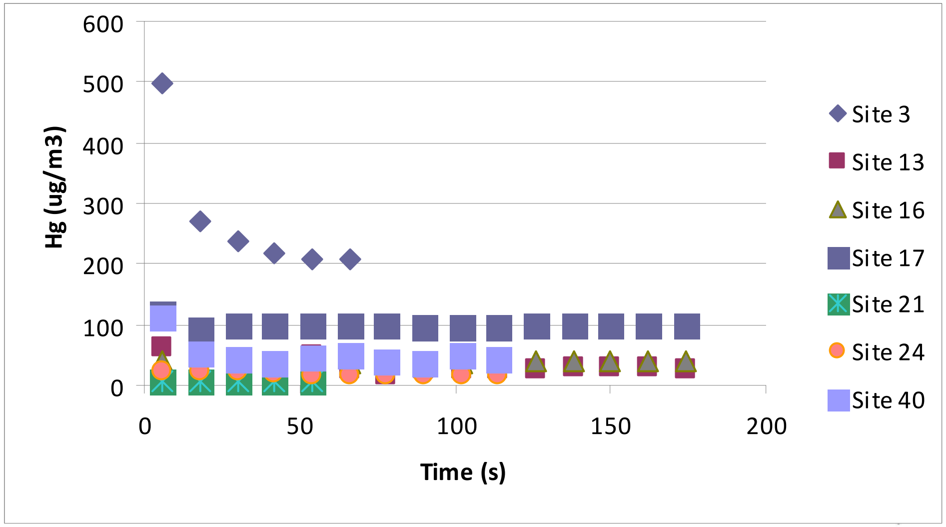
Lumex and Jerome analysis

Soil gas measurements using Jerome meter reached steady state as seen in time series data



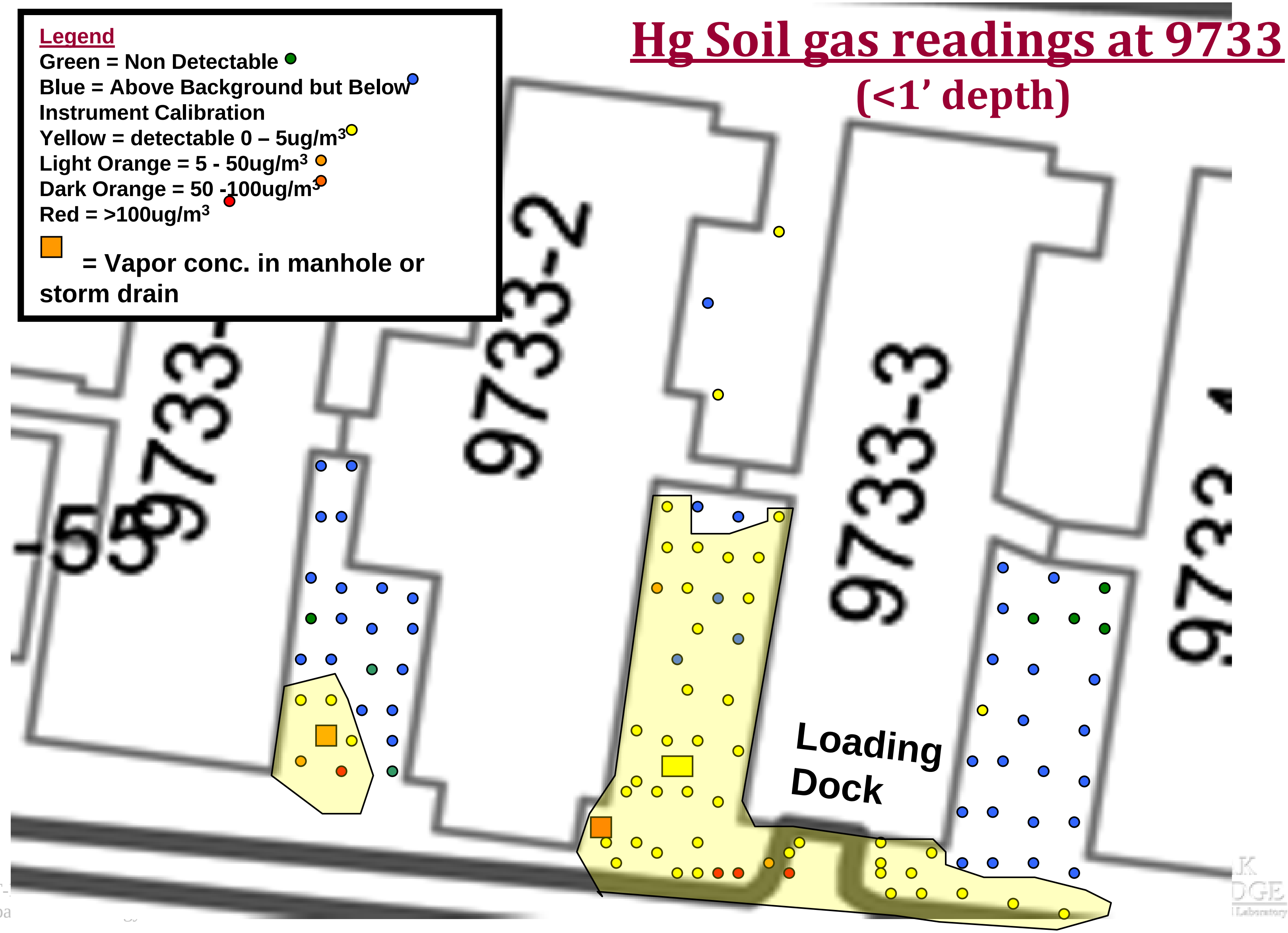
Comparison Lumex to Jerome



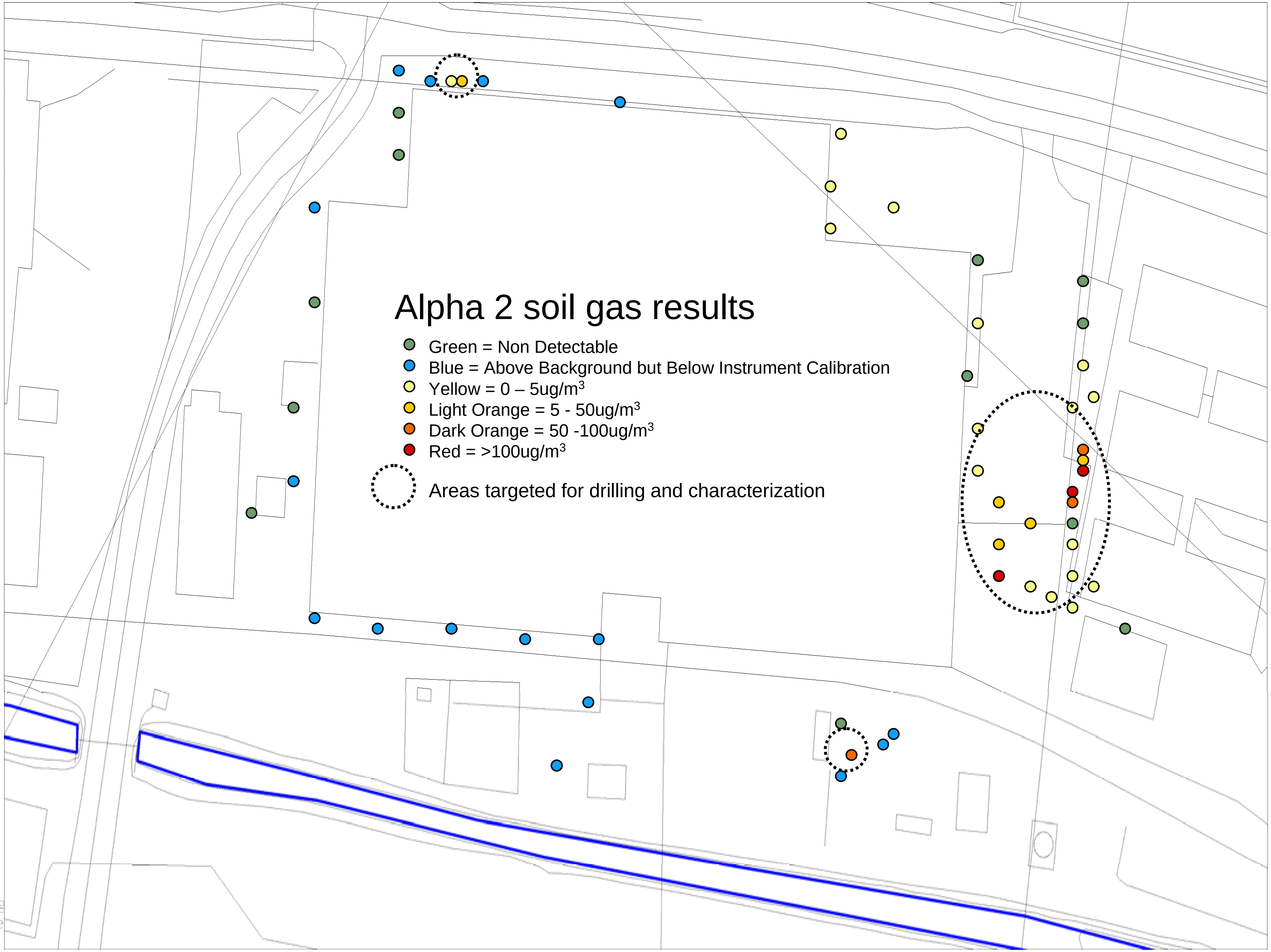


Hg soil gas measurements used to locate source zones at 3 sites

Hg Soil gas readings at 9733
(<1' depth)



Hg hot spots are identified at Alpha 2

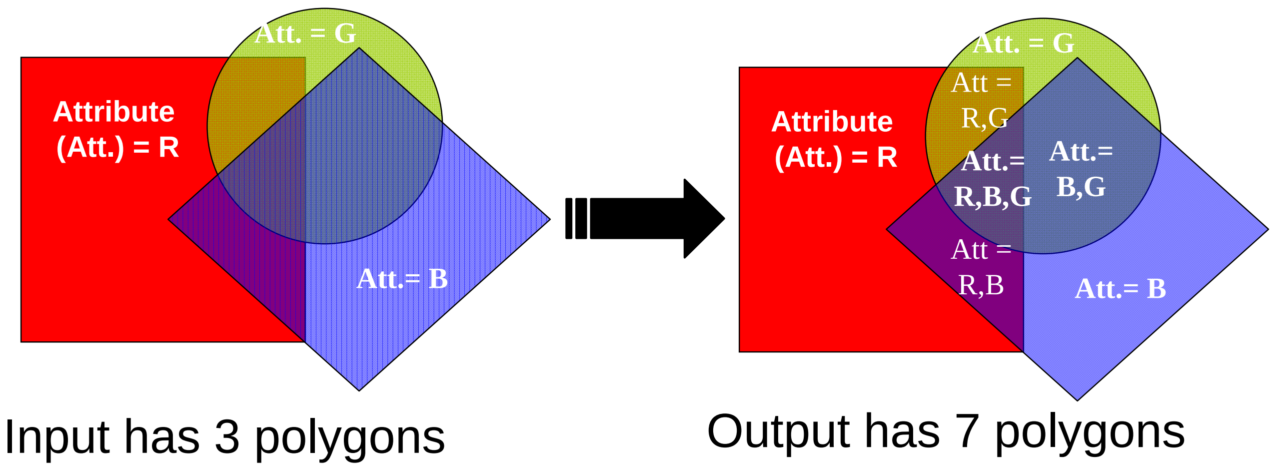


81-10 Soil gas data correlates well to core data

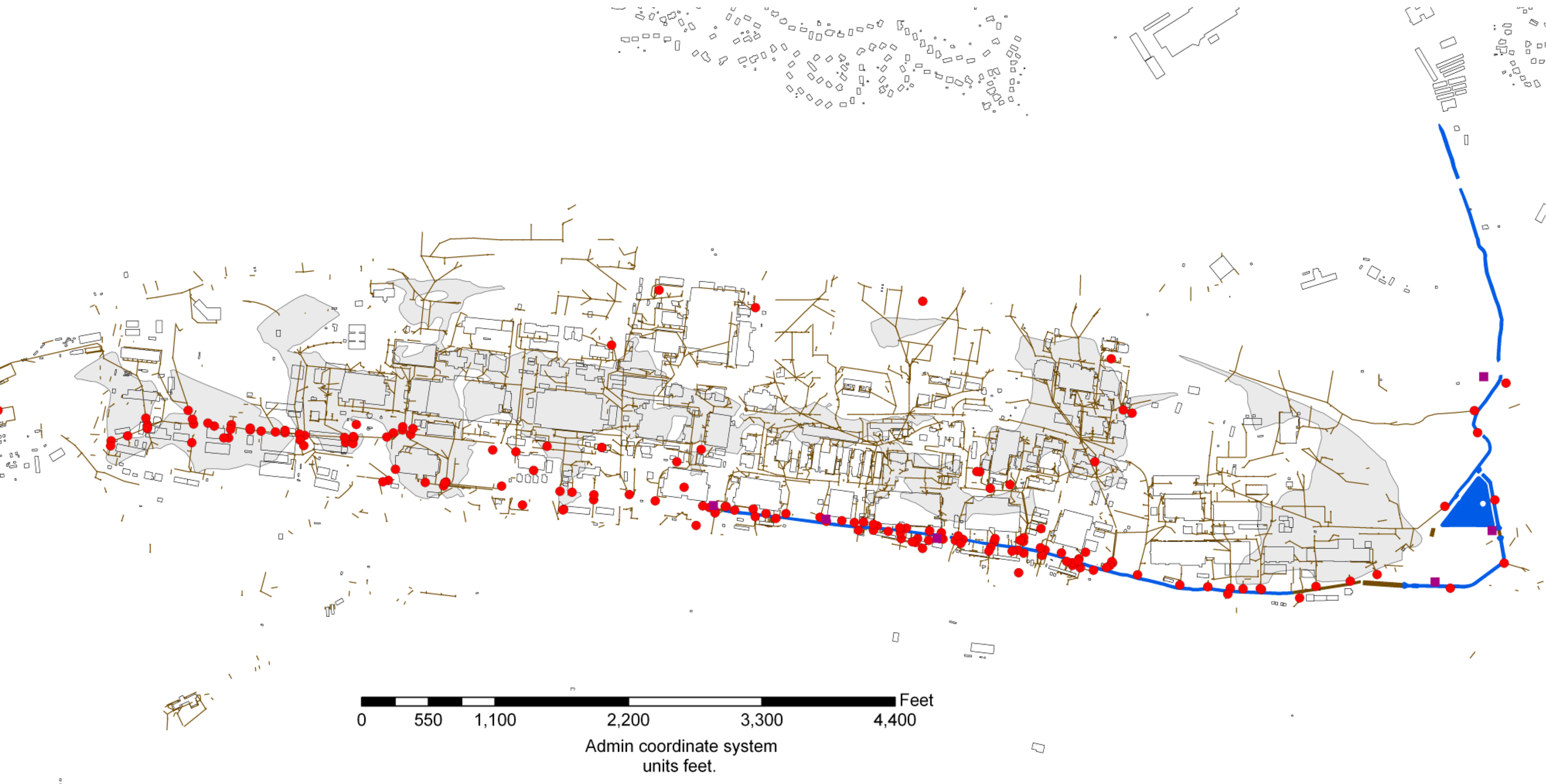
Lateral extent to the north is not well constrained

Systems analysis to assess pathways

- Gather site-specific data regarding potential preferred transport pathways
  - e.g., storm drains, sump pumps, old stream channels, fill areas, important geologic units, proximity to creeks, contaminants etc.
- Create GIS layers
- Use site-specific knowledge to assign vulnerability values, distance weighting, etc and join pathway layers in GIS (ESRI® ArcMap V9.2)
- Overlay or join with contaminants and IFDP activities to help plan monitoring, interception, modeling and contingency activities



Transport pathways – Storm drain inverts

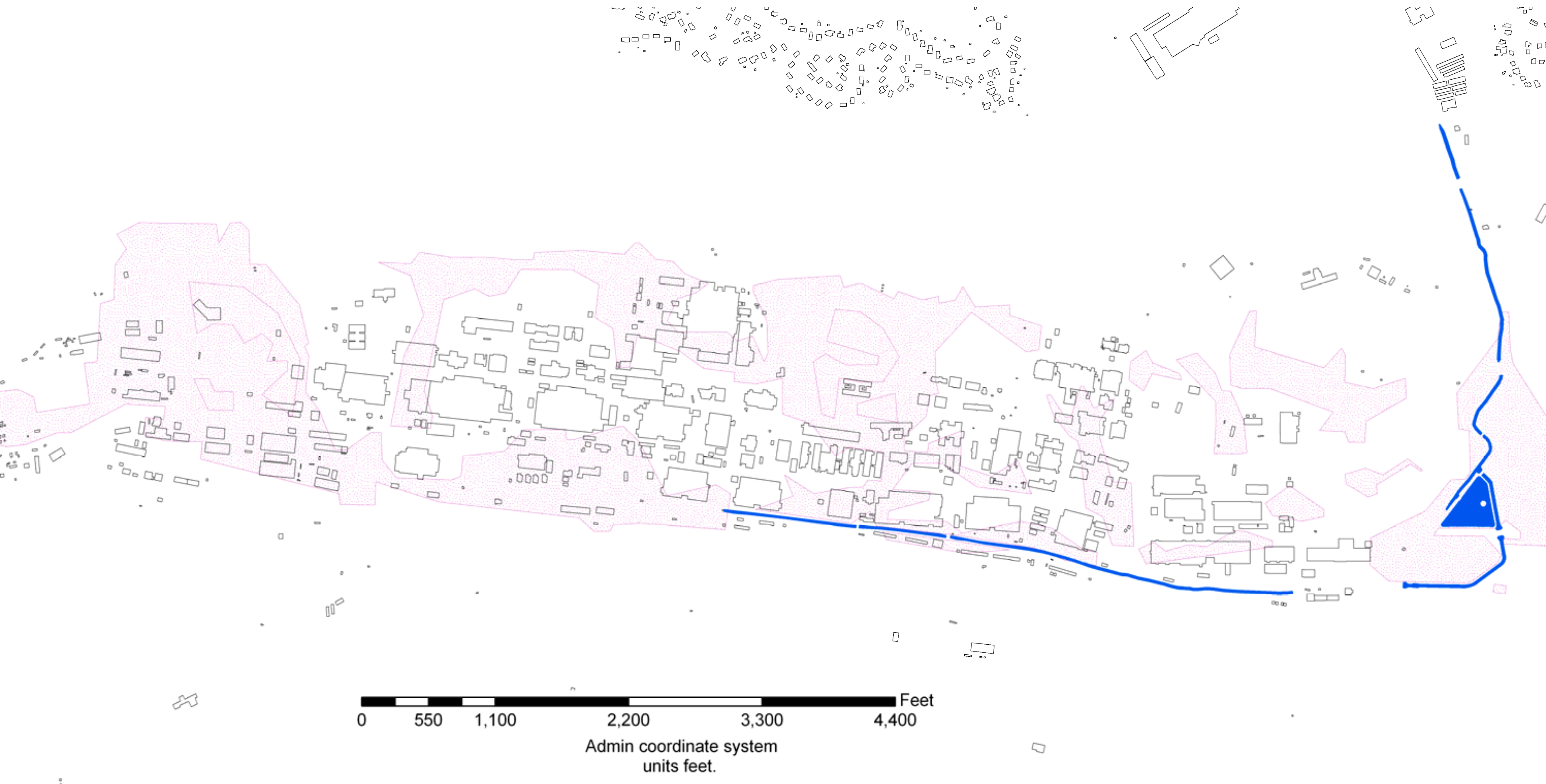


Upper East Fork Poplar Creek	Streams
Storm Drain lines	Outfalls
Buildings	
Areas with storm drain inverts below high ground water levels	

Y-12 Transport Pathways

Storm Drain Lines, Outfalls and Inverts below high ground water table

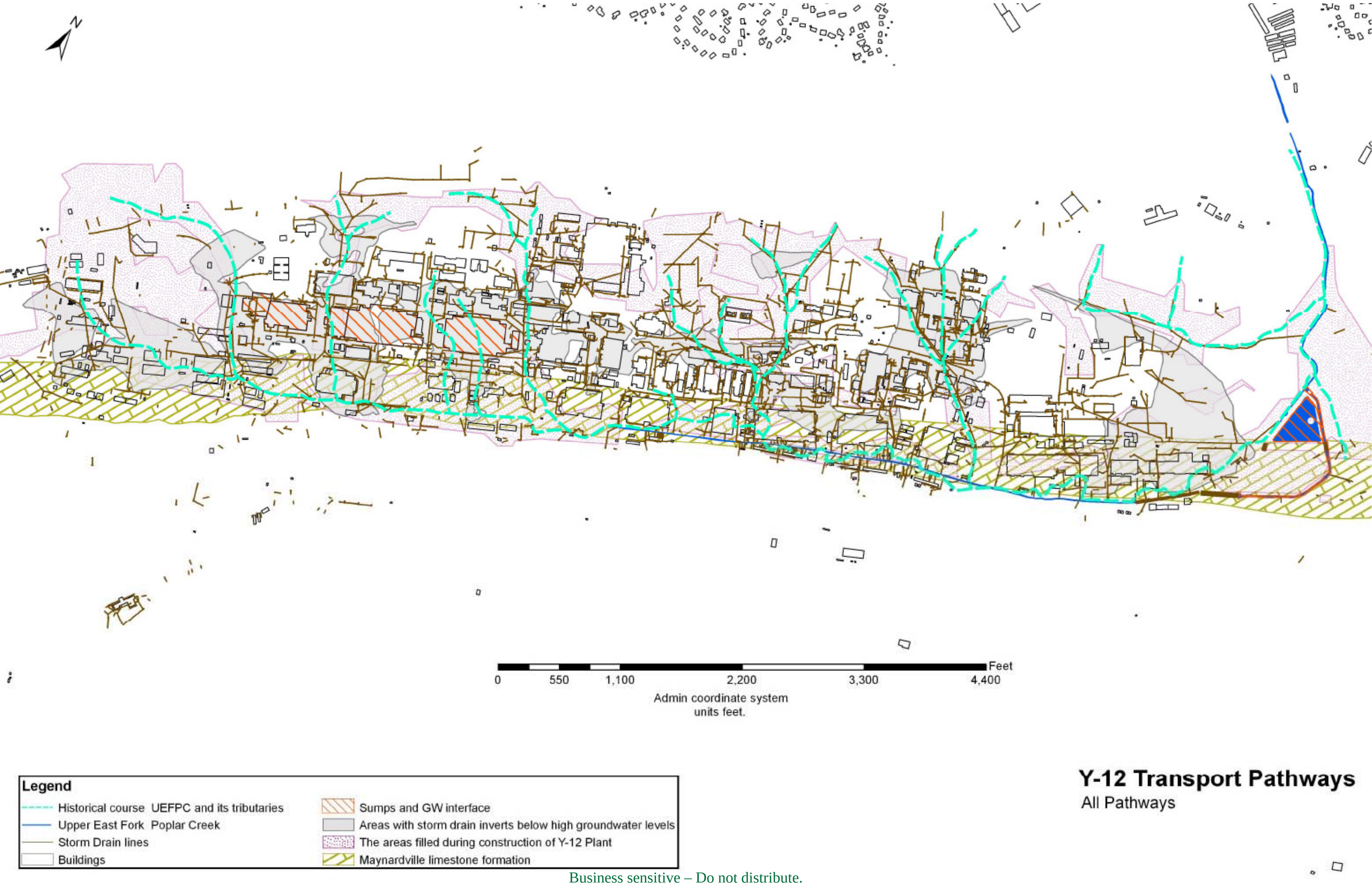
Transport pathways – Fill areas



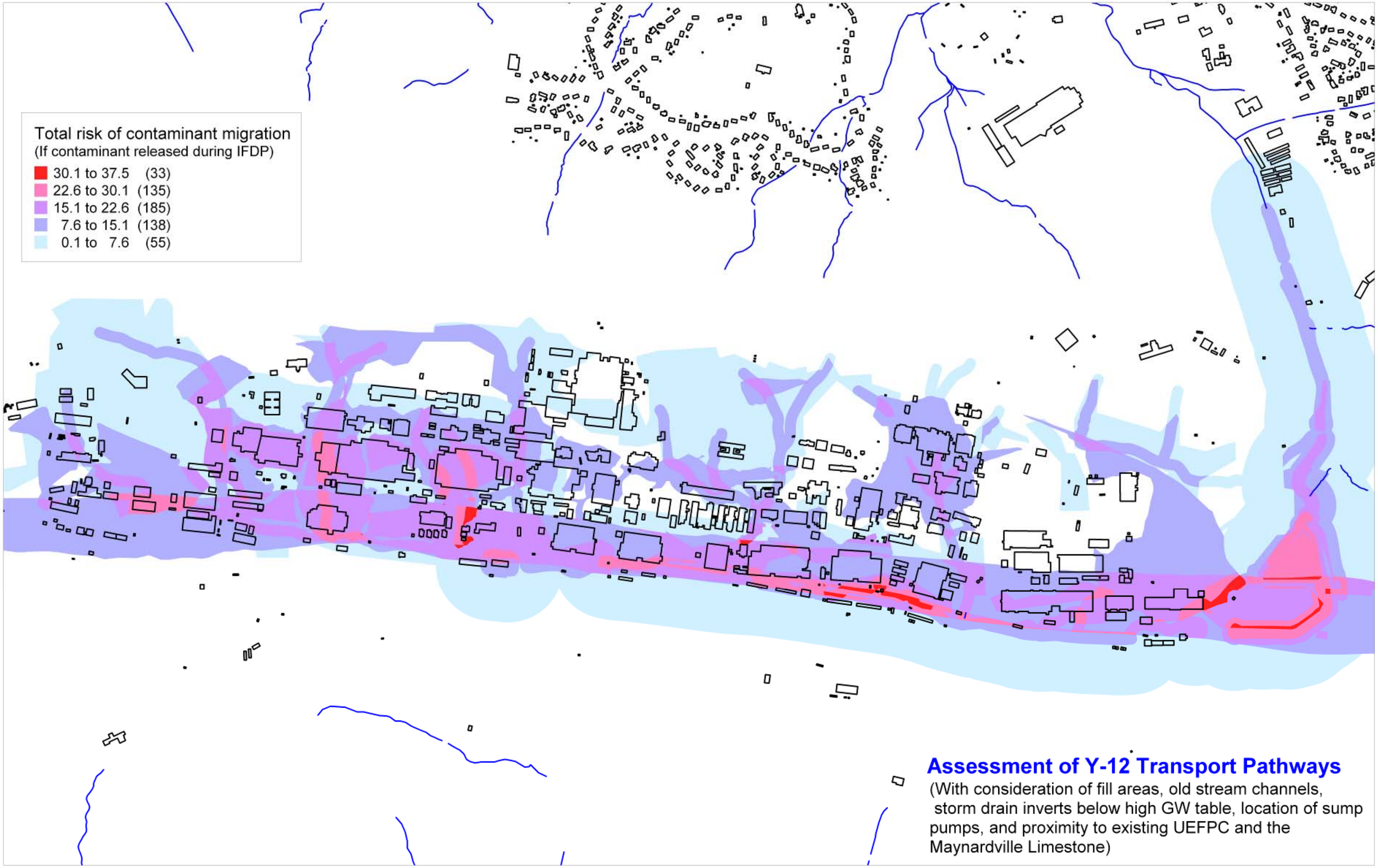
Y-12 Transport Pathways

Areas filled during construction
of the Y-12 Plant

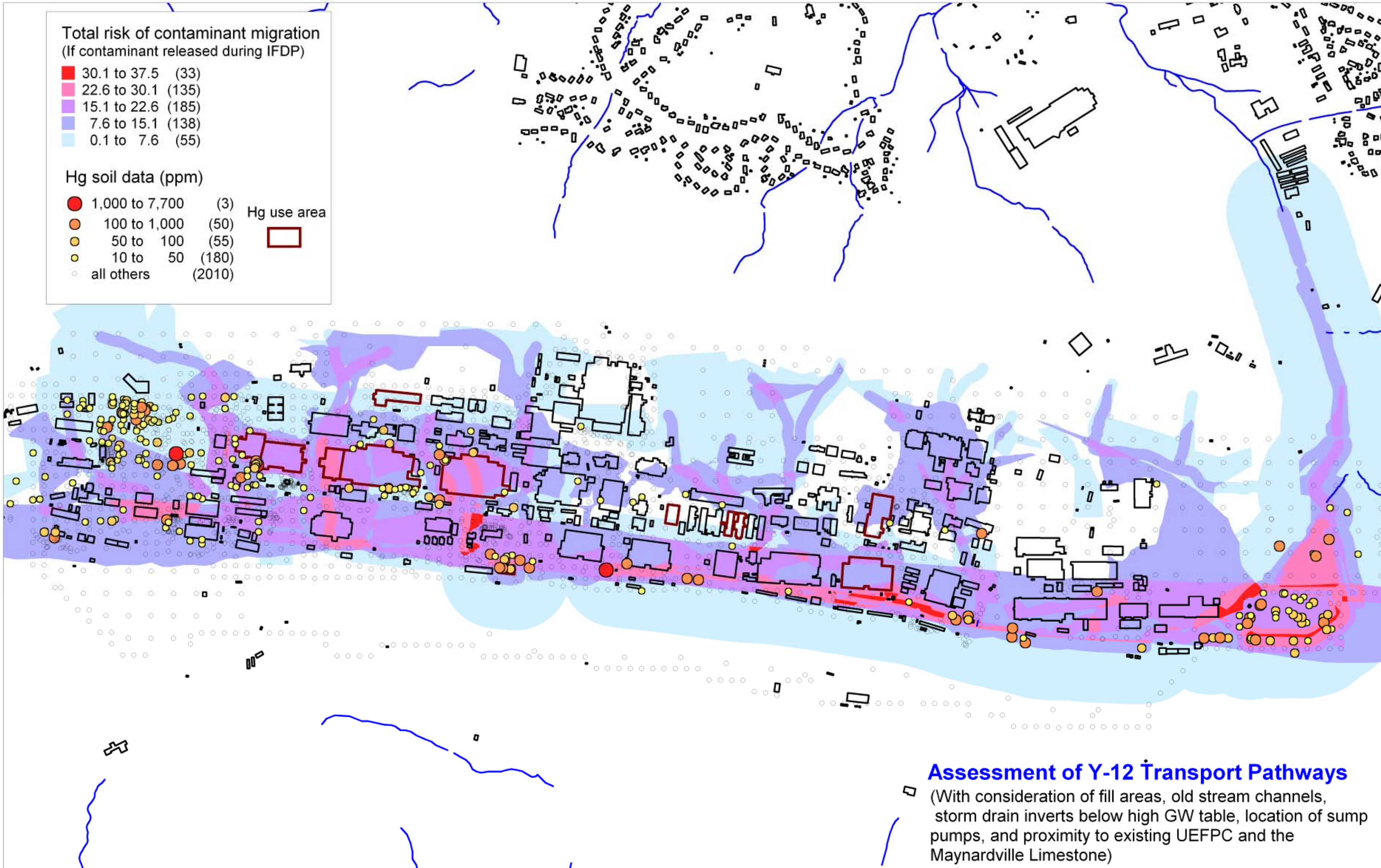
Overlay of all transport pathways considered in evaluation

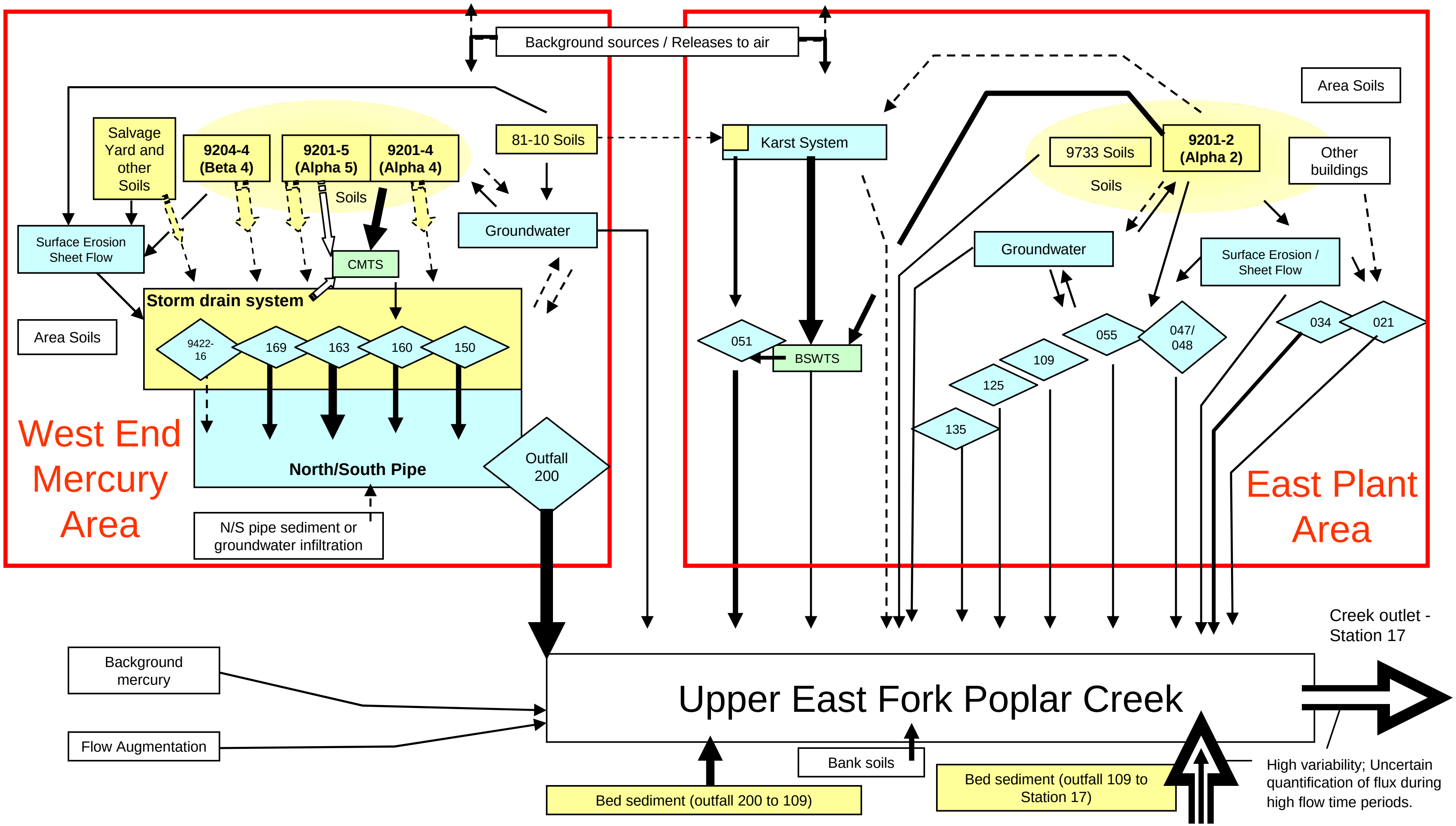


Result of assigning risks and joining layers



Result of assigning risks and joining layers
Hg use areas and soil sampling results overlain





Y-12 Mercury Conceptual Model

Title: Conceptual model for mercury showing primary source areas, transport pathways, and flux (grams/day) at the Y-12 Complex.
Model Version: 03/09/2011.

[1]*To the exent possible, longer-term average fluxes used in model, reflecting dry and wet weather conditions.*

Legend

- Primary Source Areas
- Secondary Source Areas
- # Transport paths (sampling locations)
- Treatment systems

 # - Numbers refer to SD outfalls, basins

Flux in grams/day[1]

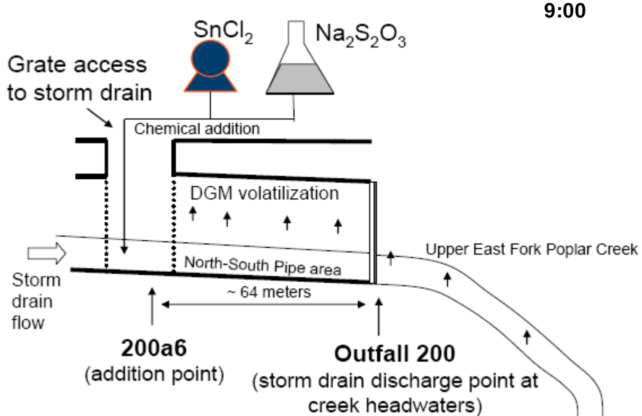
- 15-25
- 6-15
- 2-6
- 0.5-2
- 0.1-0.5
- < 0.1
- Potential, but unknown
- Flux no longer treated

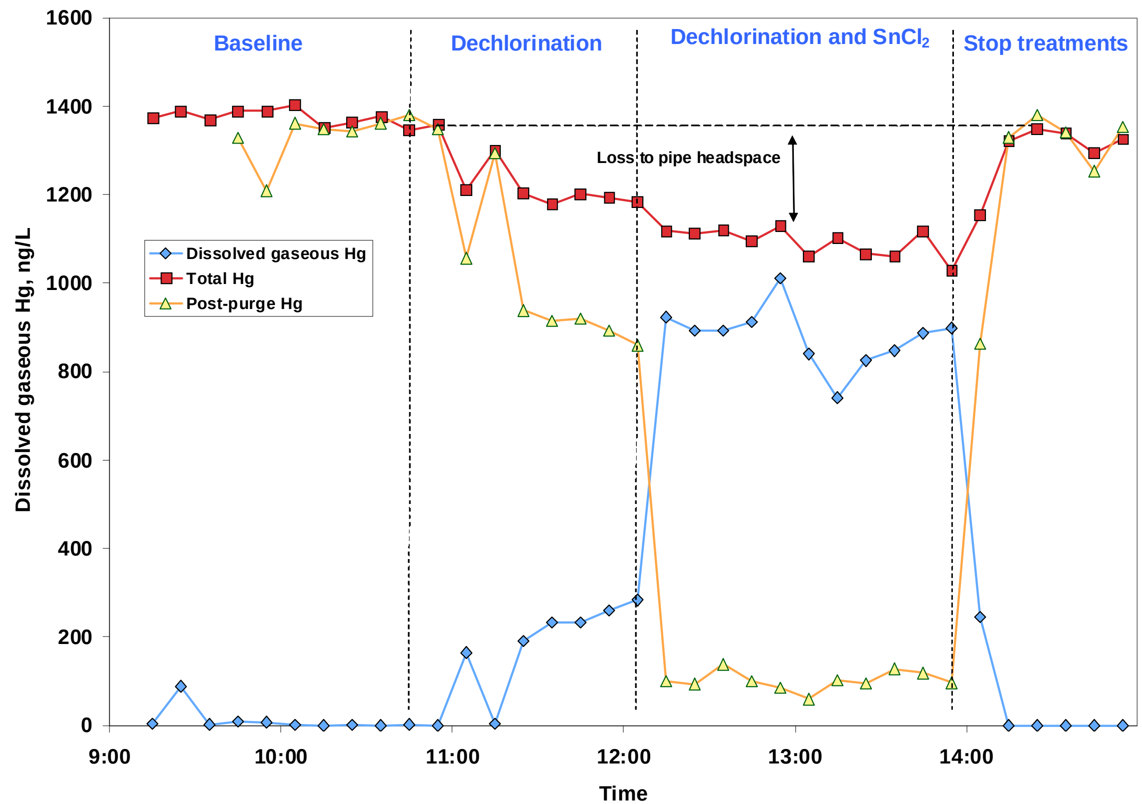
Laboratory and field tests are successful for waterborne Hg removal

Next step: optimization and pilot-scale

- In-Situ chemical reduction of mercury for high flow, low level sources

-Sorption technology for source area where mercury level is high and flow is low





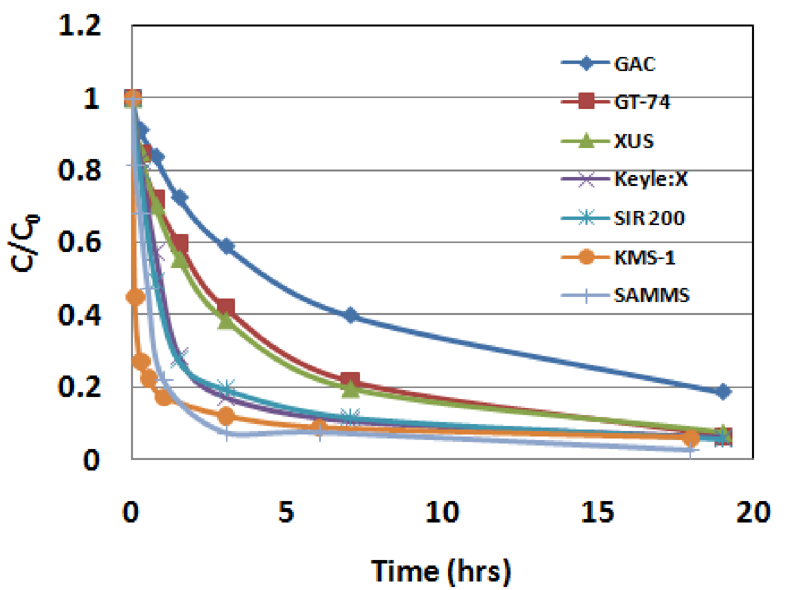
Up to 90% of the mercury is Hg(0) in the treated water via chemical reduction, after removal of residual chlorine (89 g tin/d, 25.3 kg/d ascorbic acid)

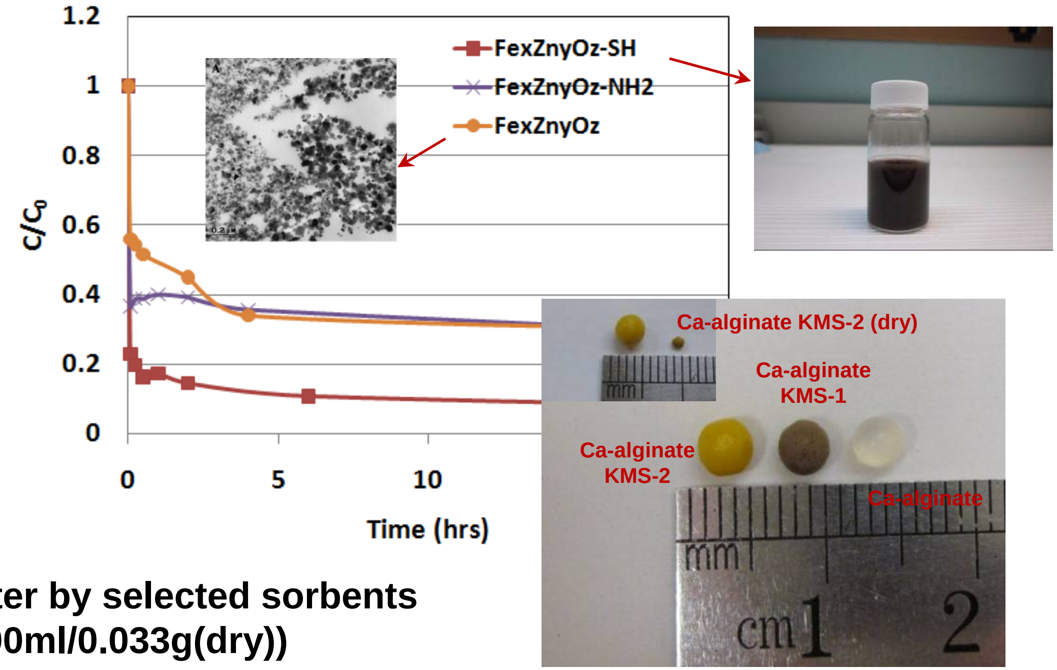
Sorbents Tested for Sorption Kinetics

Source zone water treatment

- Promising sorbents include SIR-200 (low cost) and SAMMS from batch results.
- Engineering micro-scale KMS-1 and KMS-2 mercury sorbents (developed in Northwestern University) into calcium-alginate beads for column treatment.
- Developing thiol-functionalized Zn-doped magnetite nanoparticles

Feng He, Liyuan Liang, Carrie Miller, 2010. Technology Evaluation for Waterborne Mercury Removal at the Y-12 National Security Complex, ORNL/TM-2010/268





Sorption kinetics of Hg(II) in source water by selected sorbents
(Hg = 23.5 µg/L, pH = 8.0, L/S=100ml/0.033g(dry))

Rapid Removal of Treatment Media with Magnet

thiol-functionalized Zn-doped magnetite nanoparticles