

Field and Laboratory Characterization of Mercury Contaminated Soils: Implication on Mercury Transformation and Remediation

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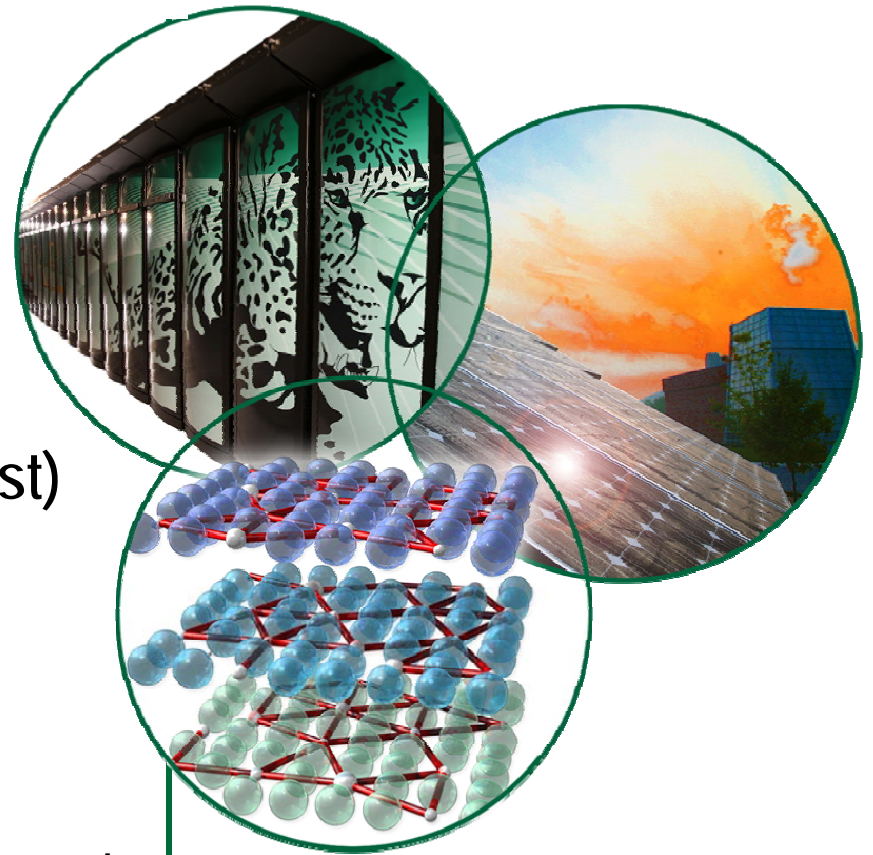
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History of Hg contamination

- Elemental Hg was used at the Y-12 facility in Oak Ridge, TN, USA between 1950-1963
 - > 10 million kg used, ~194,100 kg lost to the ground
 - Hg(0) present in the soils, groundwater and creek water



Research Objectives

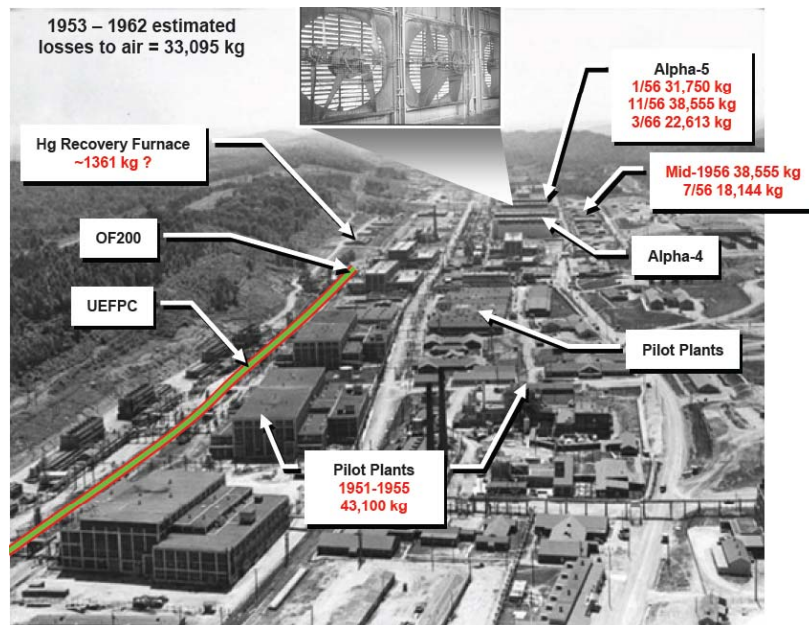
- Characterize Hg in the soils to help direct remediation efforts
 - What are the best techniques for examining Hg in contaminated environments?
 - Method comparison: HgT digest vs. XRF
 - What is the solid phase speciation in Hg in contaminated soils at Y-12?
 - Headspace analysis for Hg(0)
 - Sequential Extractions
 - SEM/WDS spectroscopy



Soil core with visible Hg(0)

Sample locations

- Building 81-10: Historic site of Hg retort facility
 - ~0.9 acre
 - 32 boreholes (34 composite samples) and 2 partial cores (intact)
- Alpha-2: Pilot scale studies resulted in Hg(0) spills
 - 2 intact cores
- Both sites potential Hg sources to East Fork Poplar Creek

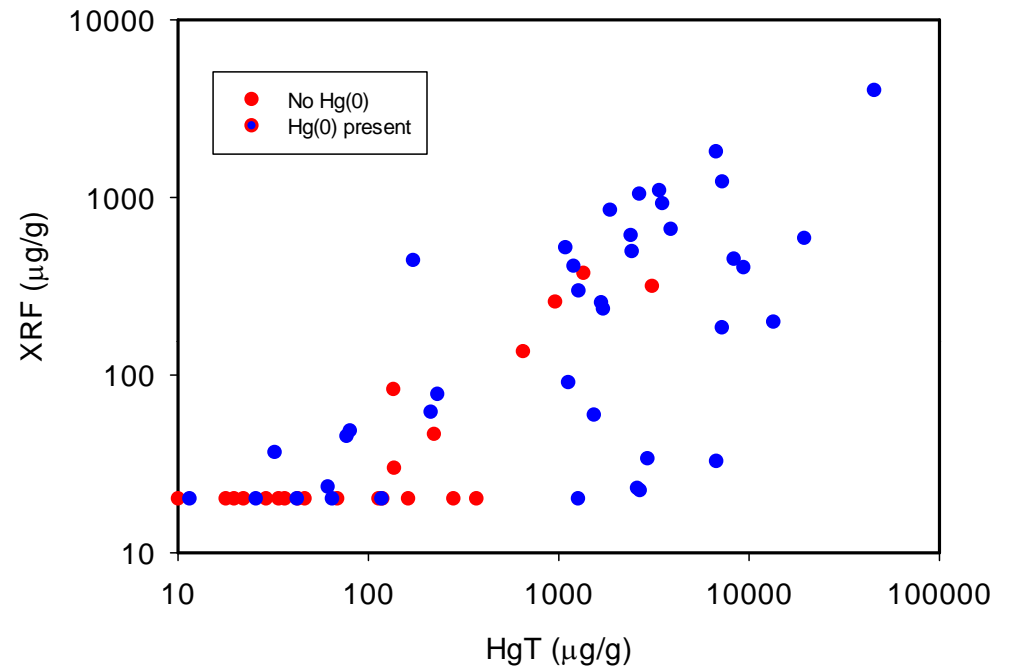


Brooks and Southworth, 2011



Comparison X-ray fluorescence (XRF) and total Hg digest

- Techniques:
 - HgT acid digest
 - X-ray fluorescence: fast, field friendly instrument; limited validation work with Hg
- Analyses done on same subsample of soil
- XRF 0.5 – 50% of concentration measured with HgT digest

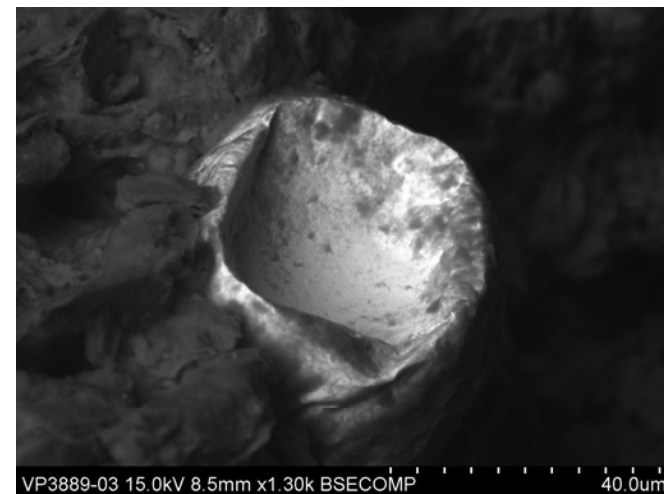
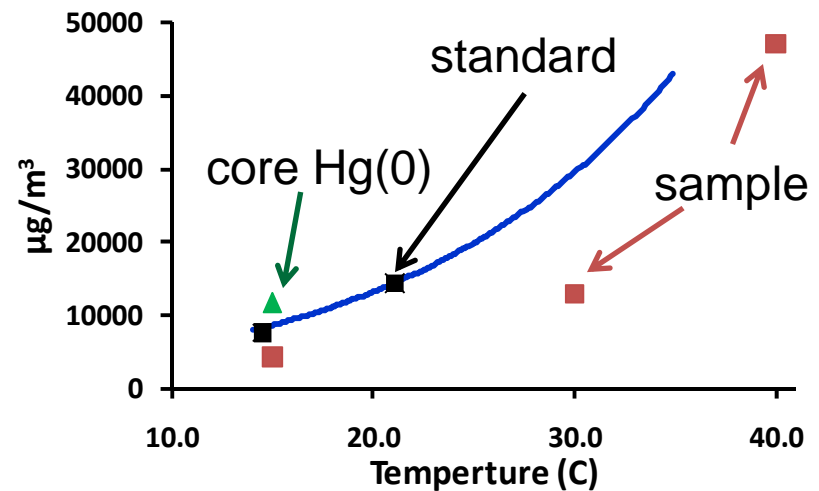


Sample Heterogeneity

- High variability in replicate samples
 - Analytical reps: 4.3%
 - Digest reps: 49%

Hg(0) headspace analysis

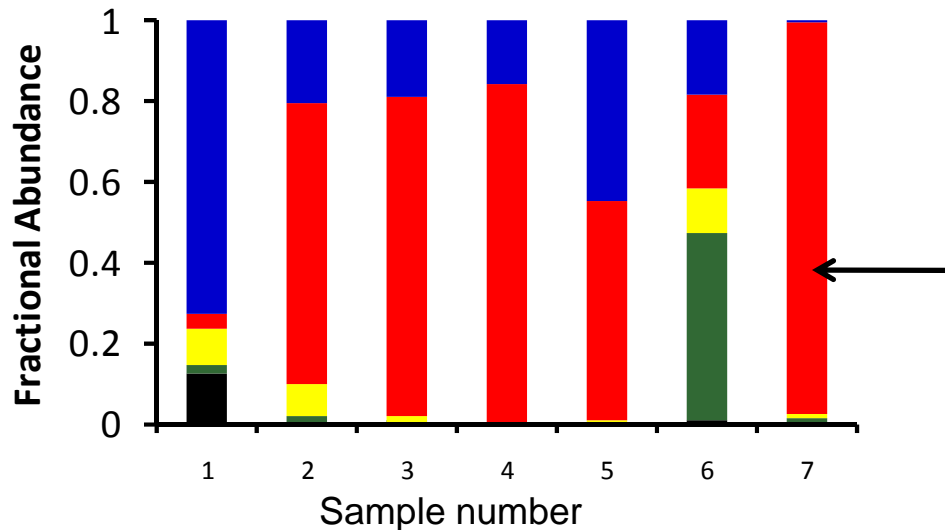
- Headspace concentration is a function of temperature not soil Hg concentration
- Hg(0) detected in 39 of 84 samples
 - Lower than predicted
- Increase in Hg(0) concentration with temperature suggests Hg(0) is present
- Evidence of coating on beads of Hg could explain lower than expected measurements



Hg speciation: Sequential Extraction

Fraction	Extracting solution	Operationally defined fraction	Potential Hg species
F1	DI water	Water soluble	HgCl ₂ , HgSO ₄
F2	Hydrochloric acid/Acetic acid (pH 2)	"human stomach" acid soluble	HgO, Hg sorbed to oxides (Fe, Mn)
F3	1 N potassium hydroxide	Organo-chelated	Hg-organic, Hg ₂ Cl ₂
F4	12 N nitric acid	Elemental Hg, mineral lattice	Hg(0), Hg ₂ Cl ₂ m-HgS w/ impurities
F5	Aqua regia (3:1 mix hydrochloric/nitric acids)	HgS	HgS, m-HgS

Bloom et al. 2003

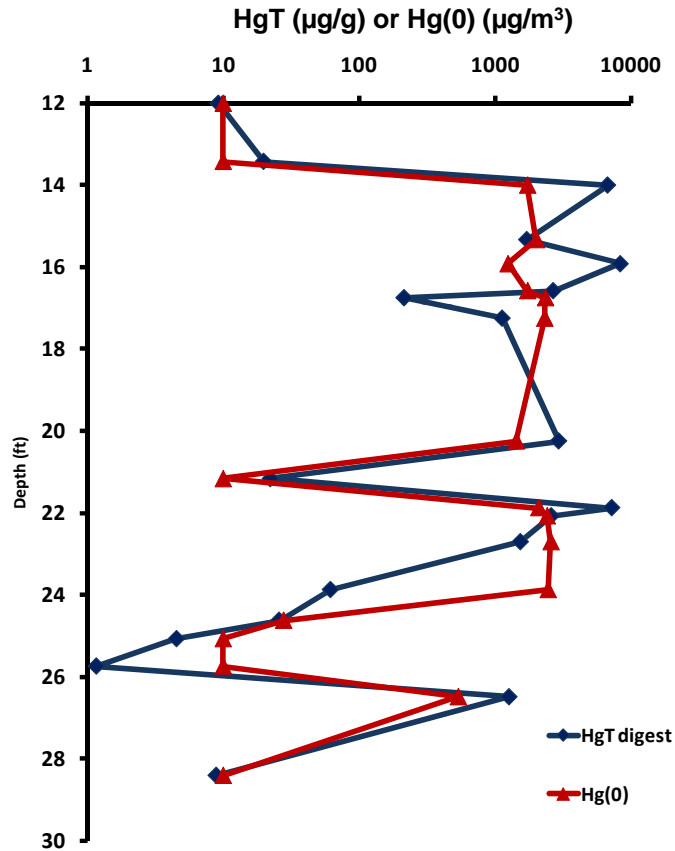


- Samples from 7 locations; collected at different depths
- Headspace: Hg(0) only detected in one sample
- Sequential Extractions:
 - Hg(0) present in samples without detectable headspace Hg(0)
 - HgS present
 - Organic complexed Hg not a dominant species

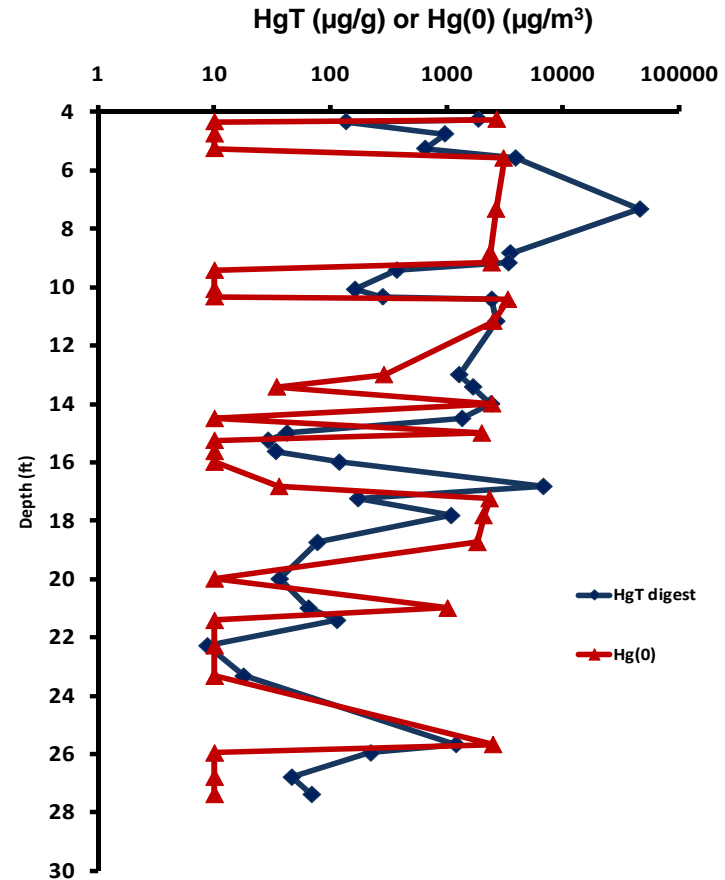
Only sample with detectable headspace Hg(0)

Area 81-10: Headspace analysis provides good indication of zones of high Hg

Core 4



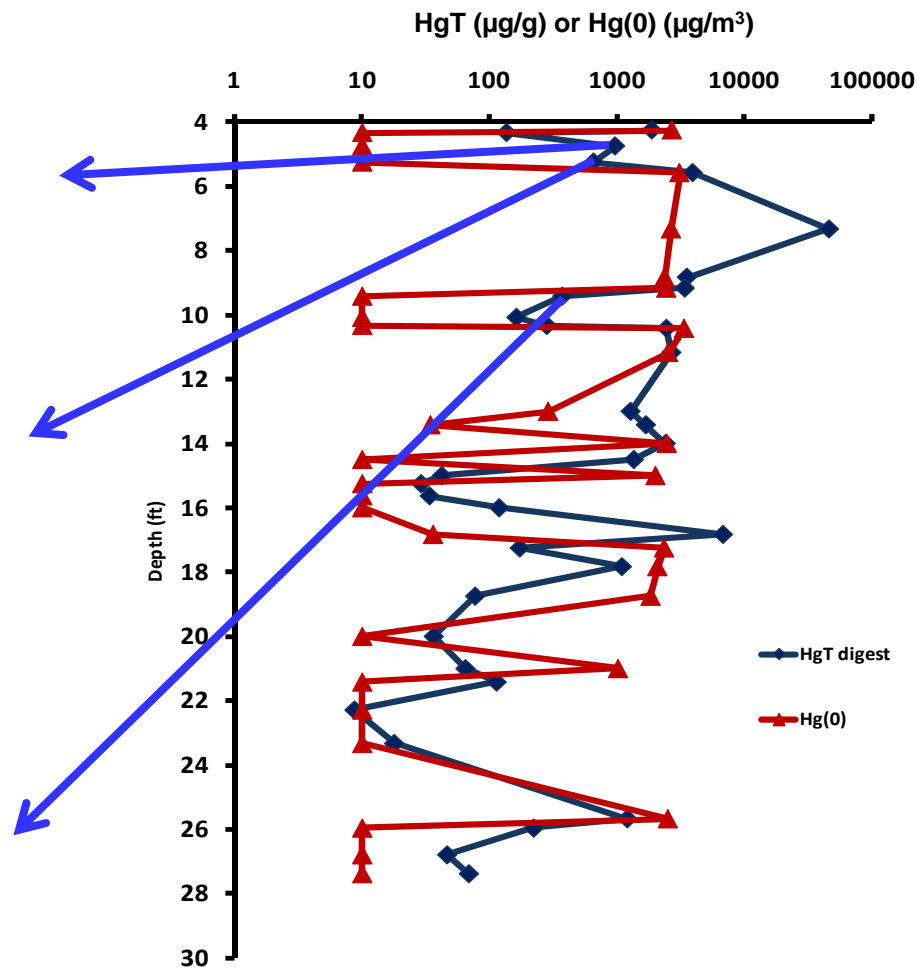
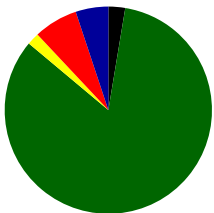
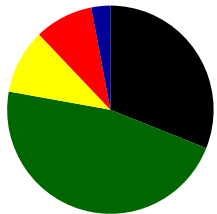
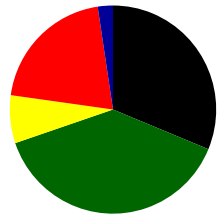
Core 29



Elemental Hg present at depth which make excavation difficult

Area 81-10: Speciation variable

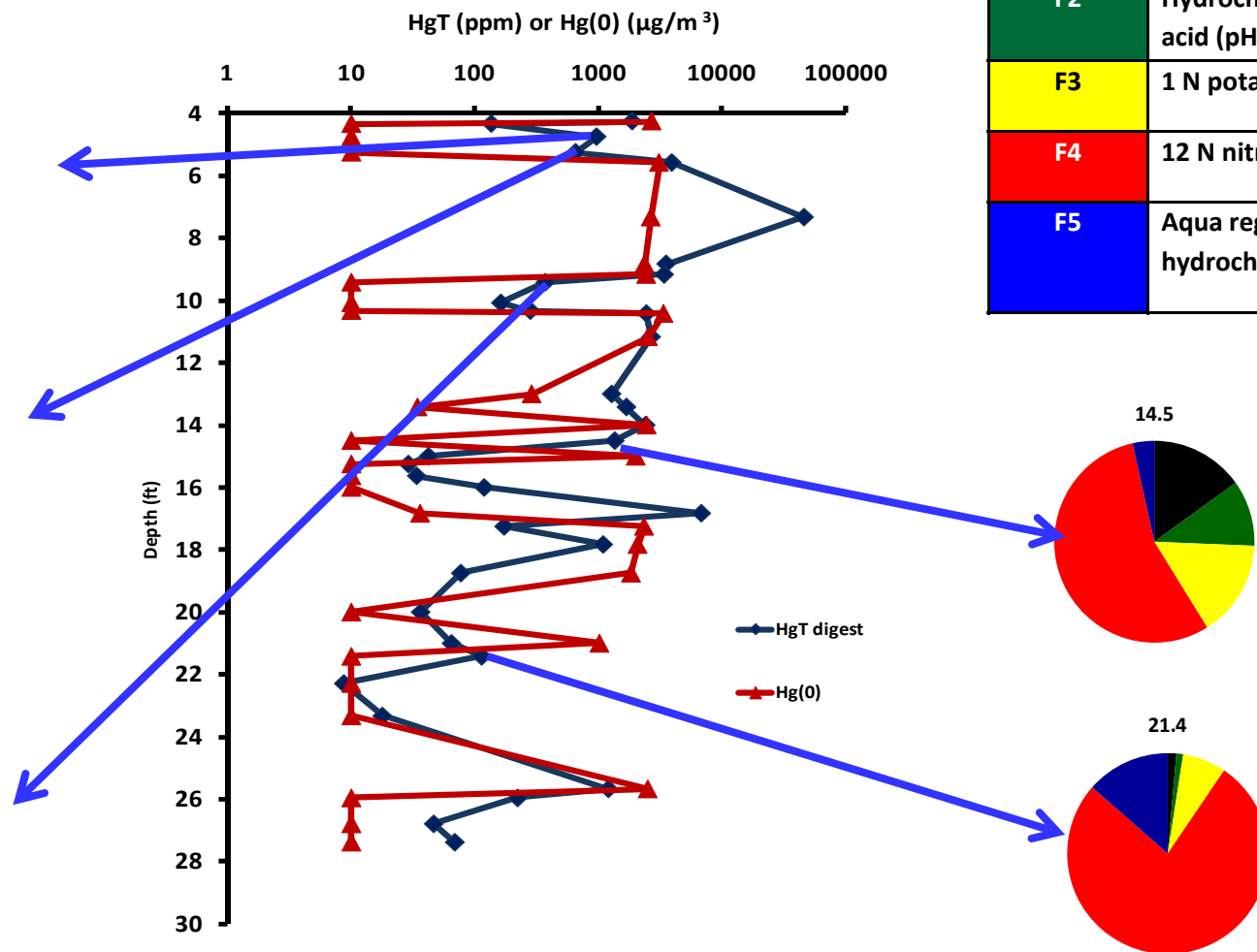
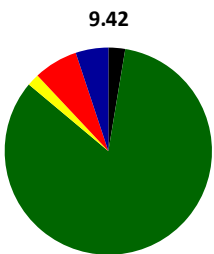
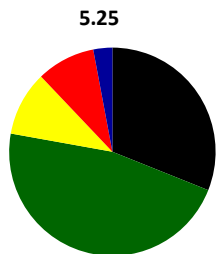
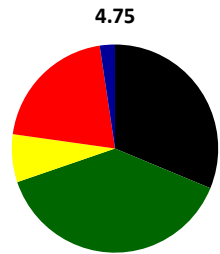
Fraction	Extracting solution
F1	DI water
F2	Hydrochloric acid/Acetic acid (pH 2)
F3	1 N potassium hydroxide
F4	12 N nitric acid
F5	Aqua regia (3:1 mix hydrochloric/nitric acids)



Samples w/o detectable Hg(0)

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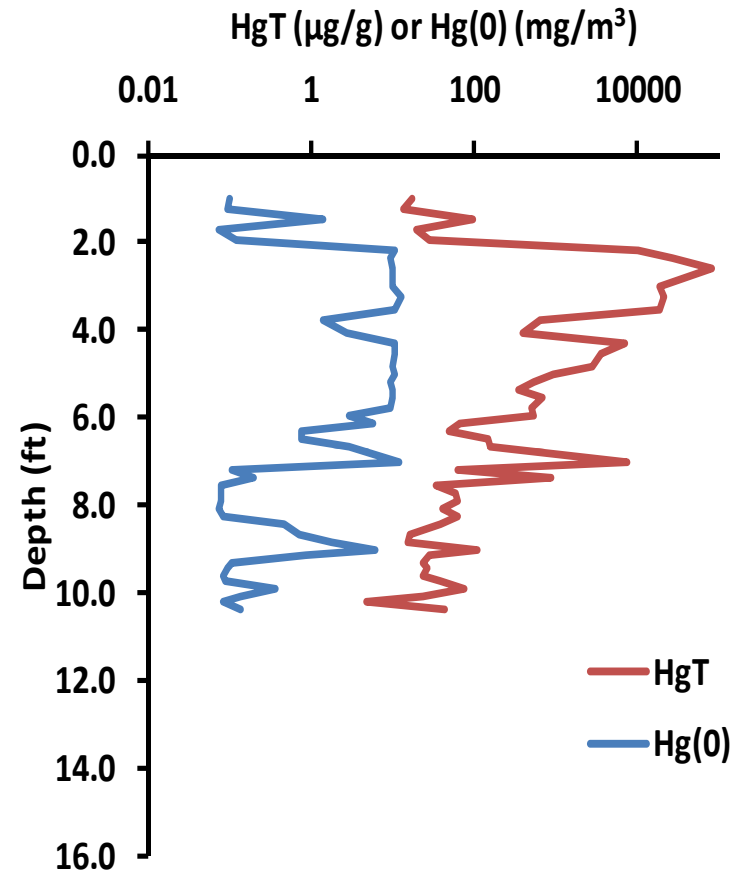
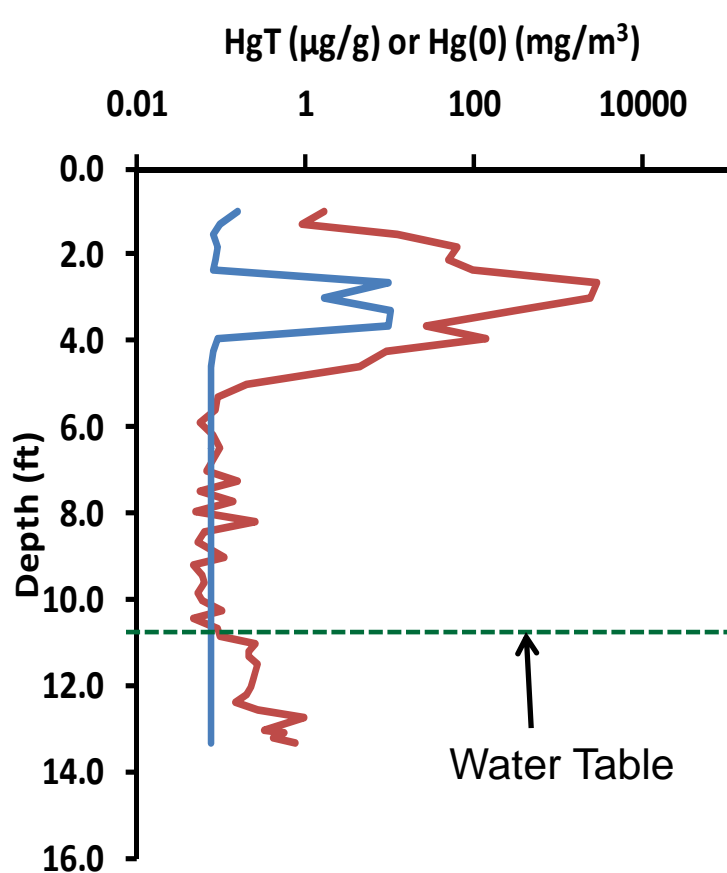
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Samples w/o detectable Hg(0)

Samples w/ detectable Hg(0)

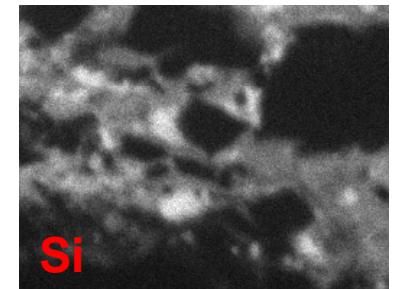
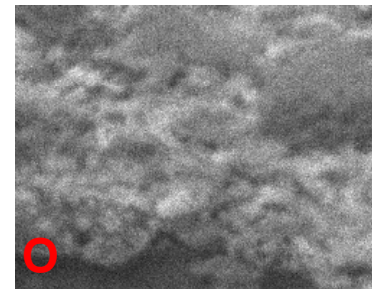
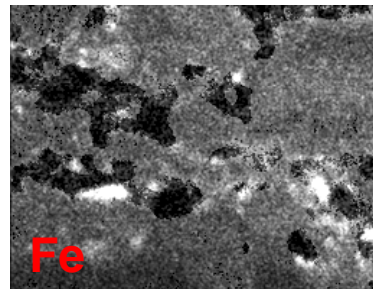
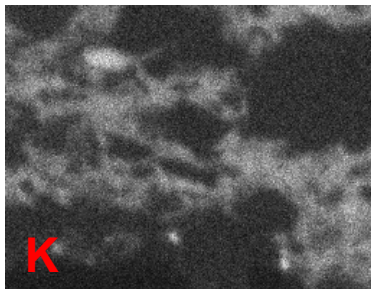
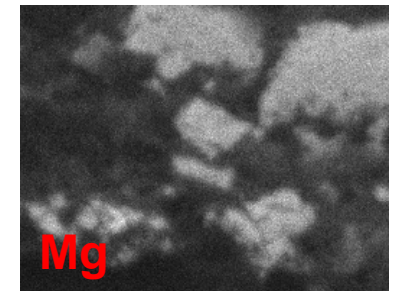
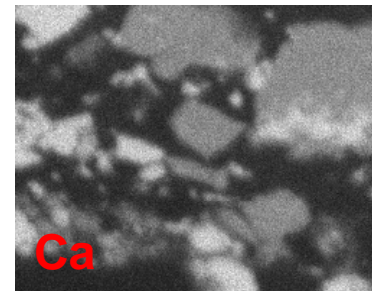
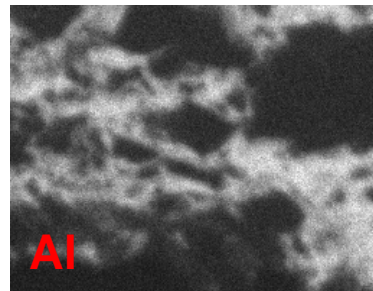
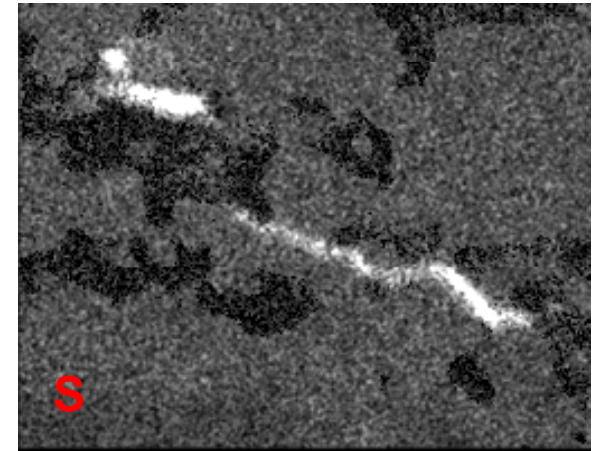
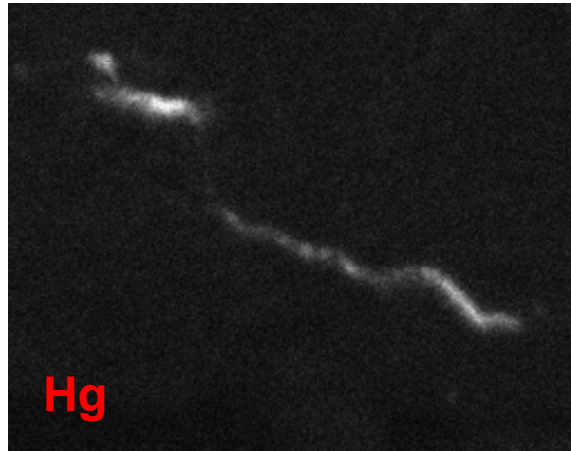
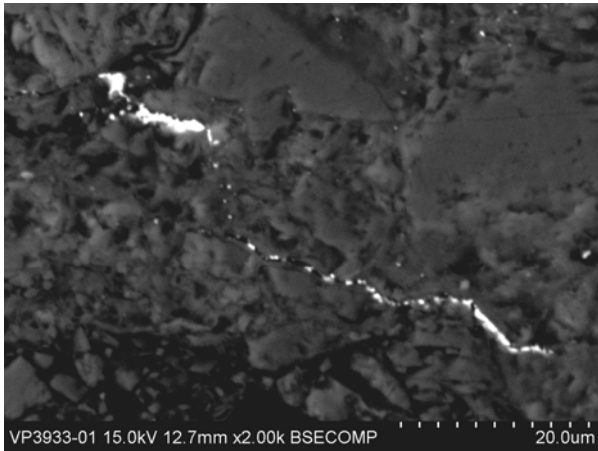
Alpha-2 Area:



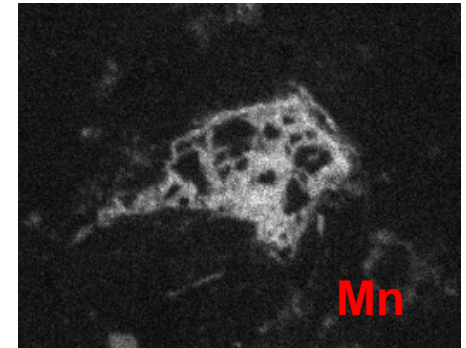
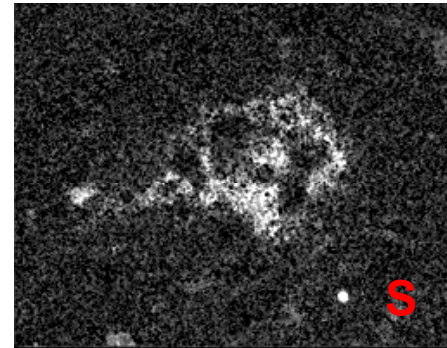
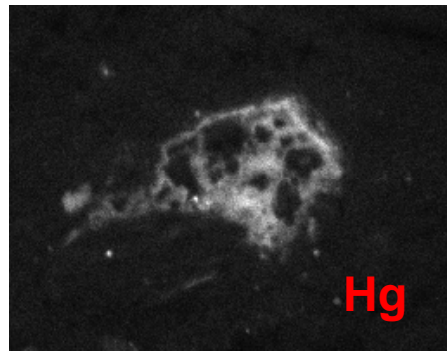
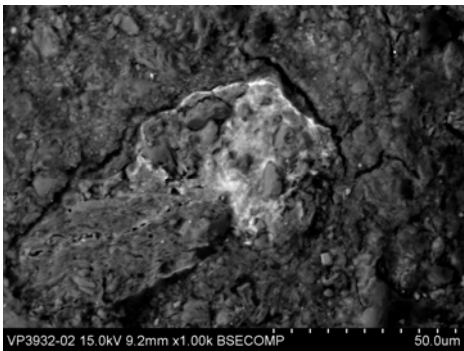
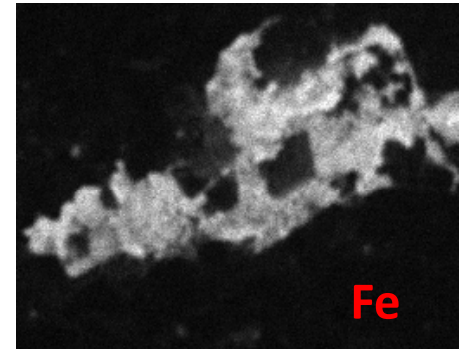
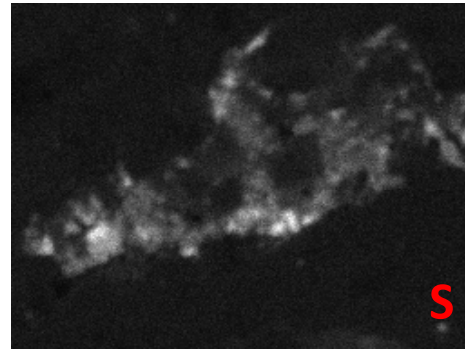
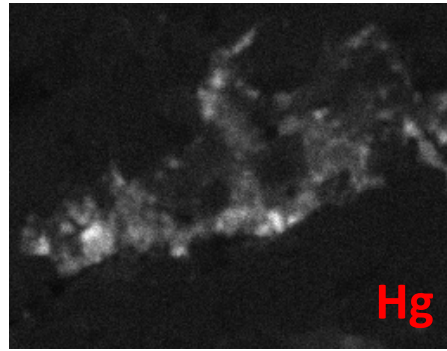
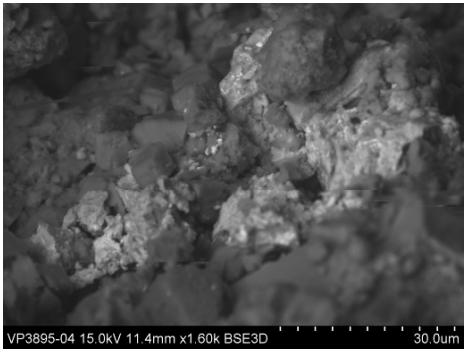
- Distribution of Hg(0) varies both with core location and with depth
- Increase Hg concentration within zone of water table fluctuation

Scanning Electron Microscopy(SEM)- Wavelength Dispersive Spectroscopy (WDS)

- 81-10 Core 29 gravel layer
 - Hg associated with sulfur

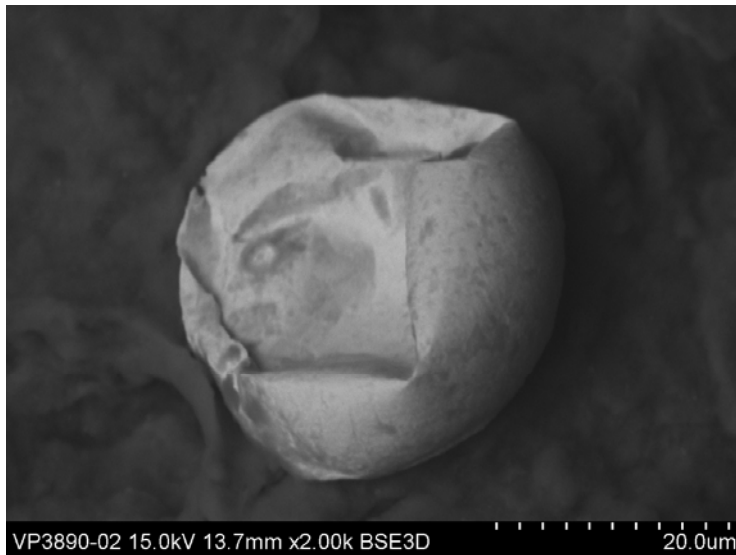


Core 29: polished section



Hg mineral associated with Fe, Mn and S

Coating on Hg(0) beads



Summary

- Analytical Techniques
 - XRF not a good screening tool for Hg in soils
 - Sample heterogeneity results in variable HgT results
- Solid phase speciation
 - Hg present in “reactive” fractions in samples not containing Hg(0)
 - Both Hg(0) and HgS appear to be present in contaminated soils at Y-12
- Implications for remediation
 - Depth of Hg will make soil excavation difficult
 - In situ treatment option will need to take into account the different Hg speciation

Questions?

