Determination of Methylmercury Levels in Mercury-contaminated Soils from Oak Ridge TN by Cold Vapor Generation

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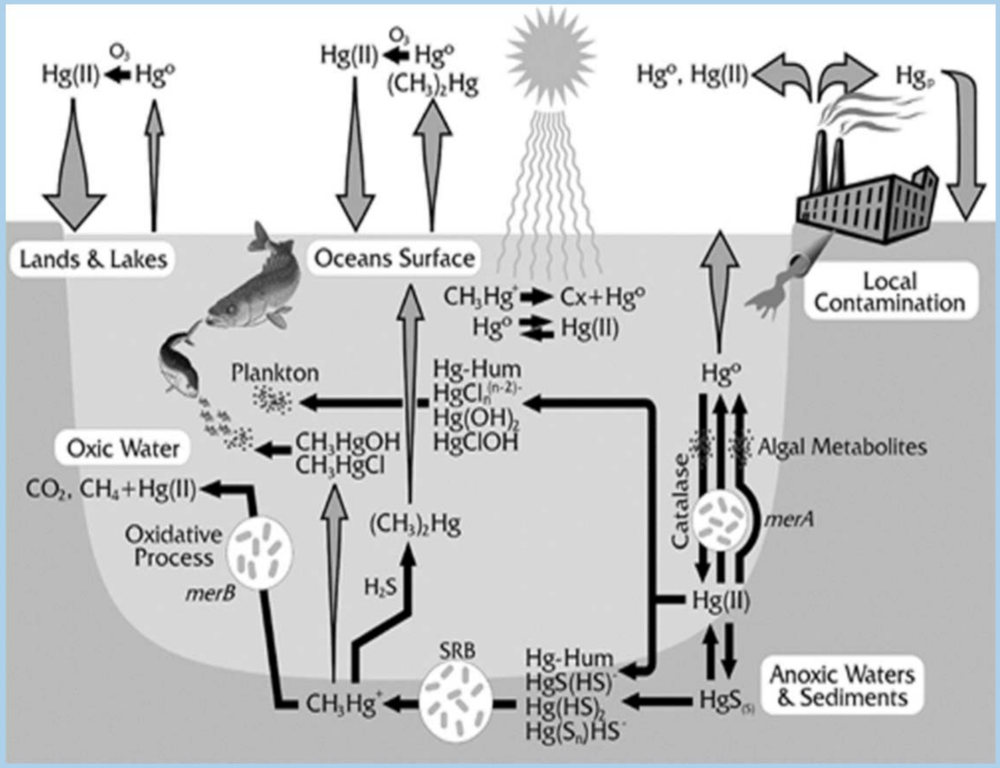
Mercury

- Released into the atmosphere from natural sources, such as volcanic eruptions and ocean emissions, as well as from anthropogenic sources

- Distributed throughout the environment in various inorganic and organic forms, including elemental (Hg^0), mercurous (Hg_2^+), mercuric (Hg^{2+}) and alkylated compounds (methylmercury and ethylmercury).

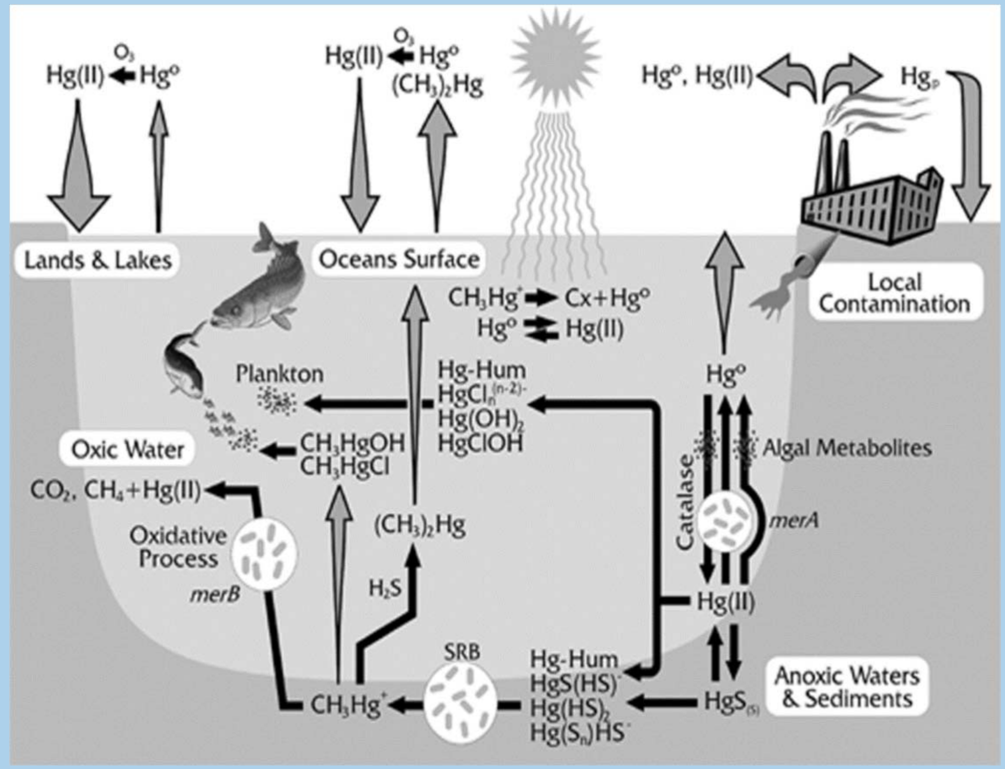
- Strong neurotoxin impacting the central and peripheral nervous system. Organomercury species bioaccumulate in many different environments.



- Mineral cinnabar (HgS) is the most insoluble (4.65×10^{-25} g/L at 25 °C) form. HgO and $HgCl_2$ are relatively soluble Hg species in water, with solubilities of 0.051 g/L at 25 °C and 69 g/L at 20 °C, respectively.

Methylmercury

- Methylmercury (CH_3Hg) is the most toxic form of mercury that bioaccumulates compared to other forms of mercury.
- Impairs the central nervous system, as well as genetic and enzymatic information.
- CH_3Hg represents the predominant form of mercury in the aquatic food chain.



Methods for Mercury Determination

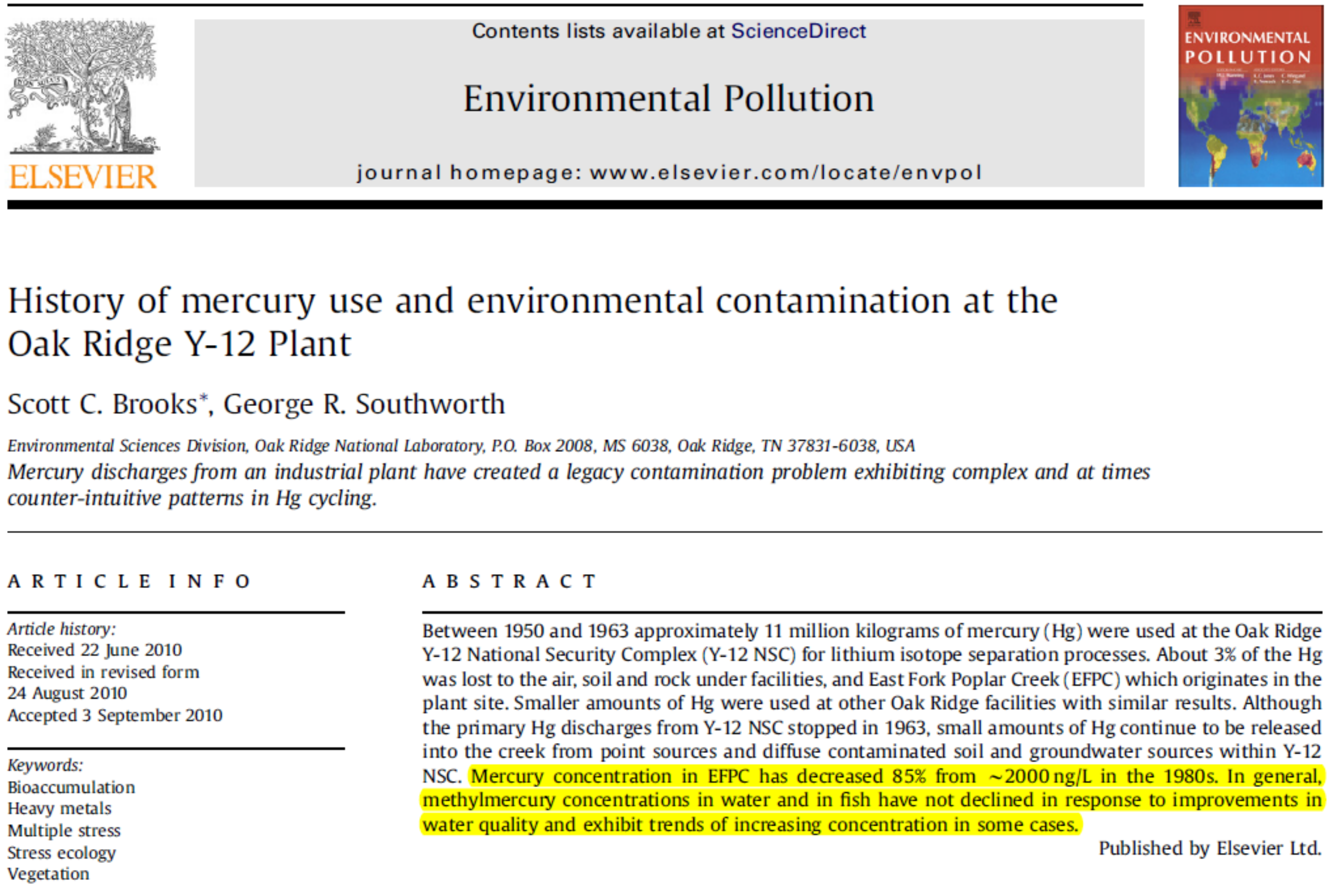
- **Gas Chromatography (GC)**
  - Volatilization of analyte and detection via GC.
  - Westoo's method is popular for sample prep to determine organic mercury species.
- **HPLC**
  - Preferred over GC because of no volatilization step.
  - Column preconcentration is still necessary.
  - Reversed-phase HPLC is preferred for organomercury detection due to hydrophobic stationary phase, ideal for organic compound detection.
- **Cold vapor generation (CVG)**
  - Ideal for trace Hg analysis
  - Allows speciation of Hg.
  - Popular for determination of Hg in blood, hair and urine.
- **ICP-MS**
  - Favored for isotopic Hg determinations
  - Low LOD and multi-sample analysis in short amount of time.

Coupled Methods for Mercury Determination

- Cold Vapor Generation Atomic Fluorescence Spectroscopy (CVG-AFS)
- Cold Vapor Generation Atomic Absorption Spectroscopy (CVG-AAS)
- Gas Chromatography -Atomic Fluorescence Spectroscopy (GC-AFS)
- HPLC-Cold vapor generation Atomic Absorption Spectroscopy (HPLC-CVG-AAS)
- Cold Vapor Generation Electrothermal Atomic Absorption Spectroscopy CV-ETAAS
- Cold Vapor generation - Optical Emission Spectrometry (CVG-ICP-OES)
- Microwave Induced Plasma Atomic Emission Spectroscopy (MIP-AES)
- HPLC Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS)
- Gac chromatography Inductively Coupled Plasma Mass Spectrometry (GC-ICP-IDMS)

Legacy Hg Contamination in Oak Ridge, TN

- In 1960's, elemental Hg was used at Y-12 National Security Facility for manufacturing components of nuclear weapons.
- It is estimated that 350 tons of Hg was released to environment.
- Hg distributed through run-off by the East Fork Poplar Creek (EFPC) which ran through the Y-12 complex, flowing into the surrounding community and terminating at the Clinch River.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History of mercury use and environmental contamination at the Oak Ridge Y-12 Plant

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Mercury discharges from an industrial plant have created a legacy contamination problem exhibiting complex and at times counter-intuitive patterns in Hg cycling.

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ABSTRACT

Between 1950 and 1963 approximately 11 million kilograms of mercury (Hg) were used at the Oak Ridge Y-12 National Security Complex (Y-12 NSC) for lithium isotope separation processes. About 3% of the Hg was lost to the air, soil and rock under facilities, and East Fork Poplar Creek (EFPC) which originates in the plant site. Smaller amounts of Hg were used at other Oak Ridge facilities with similar results. Although the primary Hg discharges from Y-12 NSC stopped in 1963, small amounts of Hg continue to be released into the creek from point sources and diffuse contaminated soil and groundwater sources within Y-12 NSC. Mercury concentration in EFPC has decreased 85% from ~2000 ng/L in the 1980s. In general, methylmercury concentrations in water and in fish have not declined in response to improvements in water quality and exhibit trends of increasing concentration in some cases.

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Statement of Problem

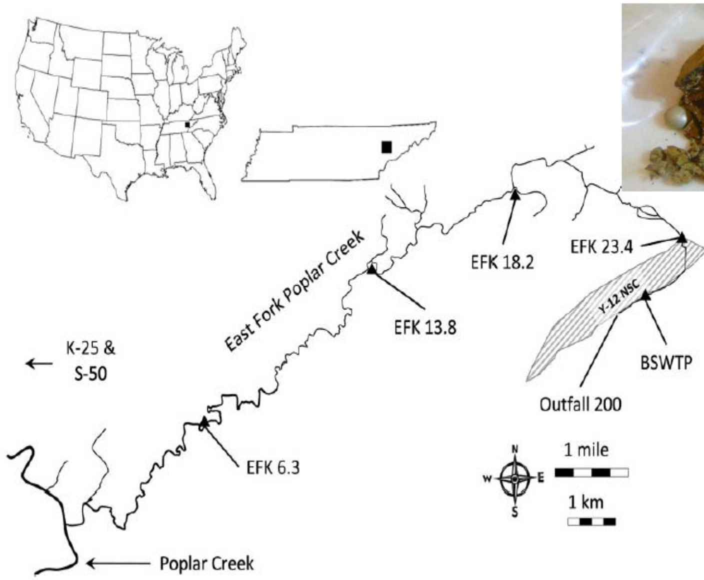
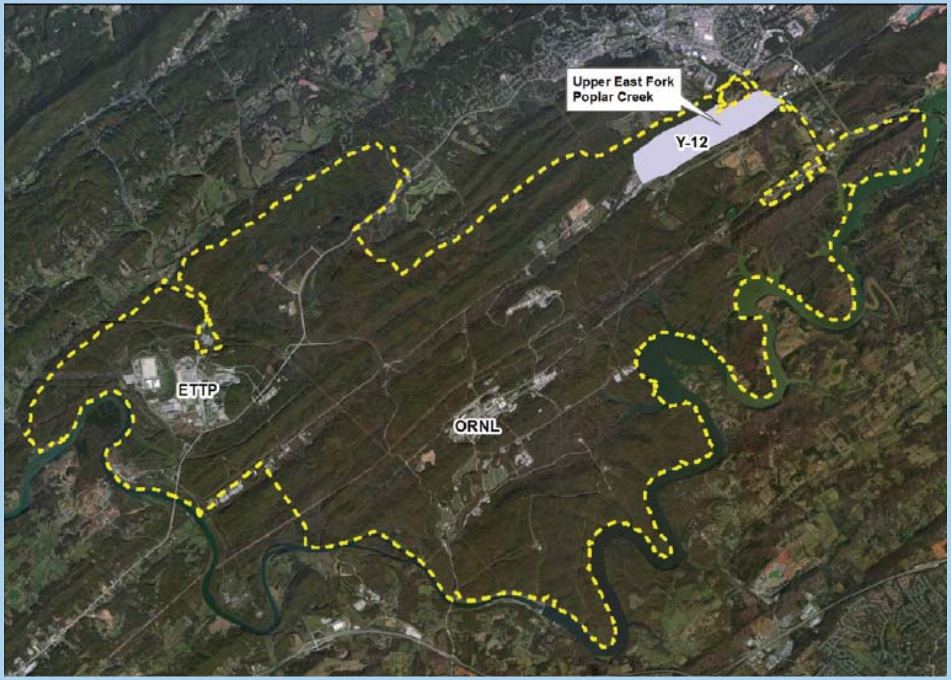


Fig. 2. The Y-12 National Security Complex and East Fork Poplar Creek. The former K-25 and S-50 plants are farther to the west, rescaling to include them obscures more relevant features of East Fork Poplar Creek. BSWTP = Big Springs Water Treatment Plant.

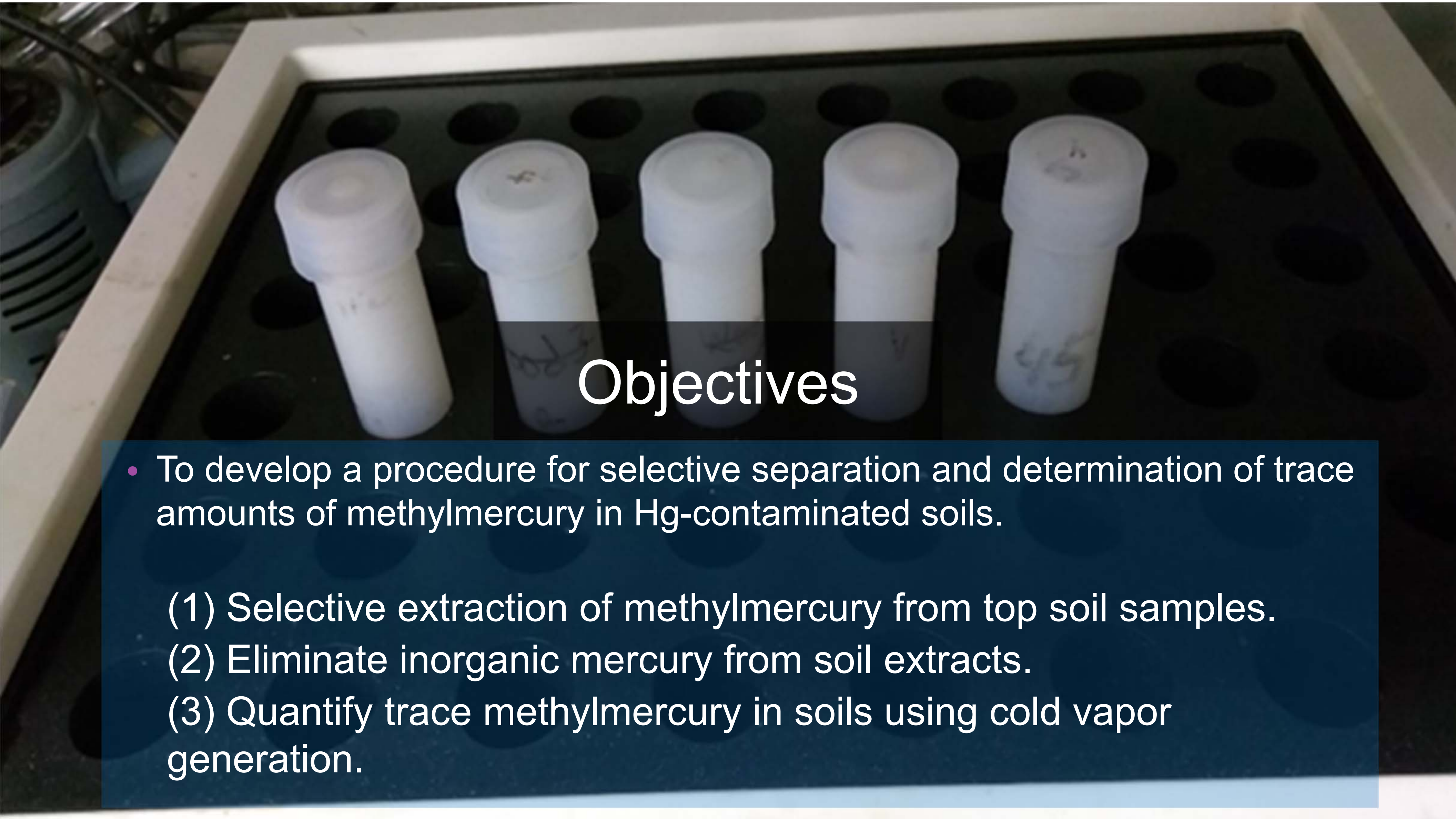
Through remedial actions over the last 25 years, Hg concentrations and fluxes have been reduced, but Hg levels in water at the Y-12 Complex boundary continue to exceed both the regulatory limit (51 ng/L) and the remediation goal (200 µg/L) (Brooks and Southworth 2011). Commensurate reductions in the fish tissue concentrations (to achieve the EPA criteria of 0.3 µg/g) have not been observed (Peterson et al. 2011).

Hypothesis



Mercury contaminated soil from the Y-12 Complex. Adopted from the Knoxville News Sentinel.

- Methylmercury is water-soluble and thus could directly affect contamination in water and wildlife.
- It is hypothesized that Hg-contaminated soils in Oak Ridge TN contain significant levels of methylmercury that is responsible for elevated Hg contamination in soil and water.



Objectives

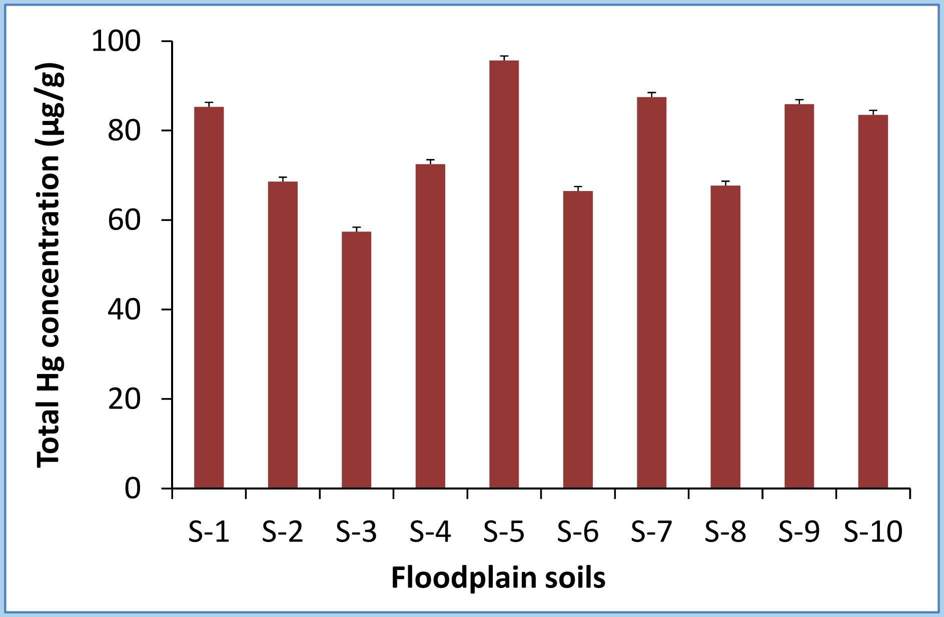
- To develop a procedure for selective separation and determination of trace amounts of methylmercury in Hg-contaminated soils.

(1) Selective extraction of methylmercury from top soil samples.
(2) Eliminate inorganic mercury from soil extracts.
(3) Quantify trace methylmercury in soils using cold vapor generation.

Results: Total Mercury Levels

- Total Hg analysis were made by acid digestion of the soils. About 0.1 g soil samples (n=3) was digested on a Graphite Digestion Block at 140 °C in 5 mL HNO_3 and then treated with H_2O_2 to oxidize organic material.

- Montana soil (SRM 2710) and Domestic Sludge (SRM 2781) from National Institute of Standards and Technology (NIST, Gaithersburg, MD) were used for verification of total mercury analysis.



ICP-MS analysis showed that contaminated top soil contained about 57 to 95 mg/kg Hg.

Selective extraction: Sample Preparation

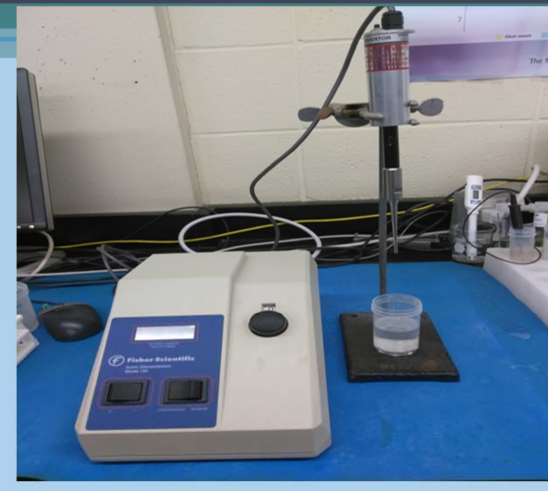
- Extraction of CH_3Hg from soil matrix is carried with template soils collected from Biloxi, MS. They were ground and sieved through 0.25 mm apertures. Samples were analyzed by ICP-MS for Hg content before utilizing in any experimental work.

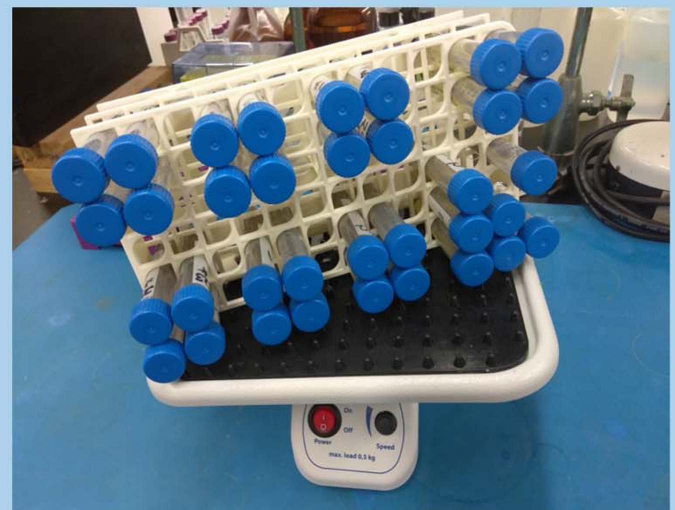
- Samples of template soils (0.5 g) were contaminated with 0.2 mL of 100 μg/mL Hg(II) or CH_3HgCl. Dried at room temperature for at least 48h to simulate the soil matrix from Oak Ridge, TN.

- 20 μg Hg or CH_3HgCl spiked into 0.5 g soil (40 mg/kg)

Extraction

- Extraction with HCl and HNO_3 was attempted for selective extraction of MeHg from the soils.
- Extractions were performed via shaking of soil suspensions up to 24 h in HCl or HNO_3.
- Similar suspensions were subjected to ultrasounds using a sonic dismembrator equipped with Titanium probe for time intervals up to 6 minutes.





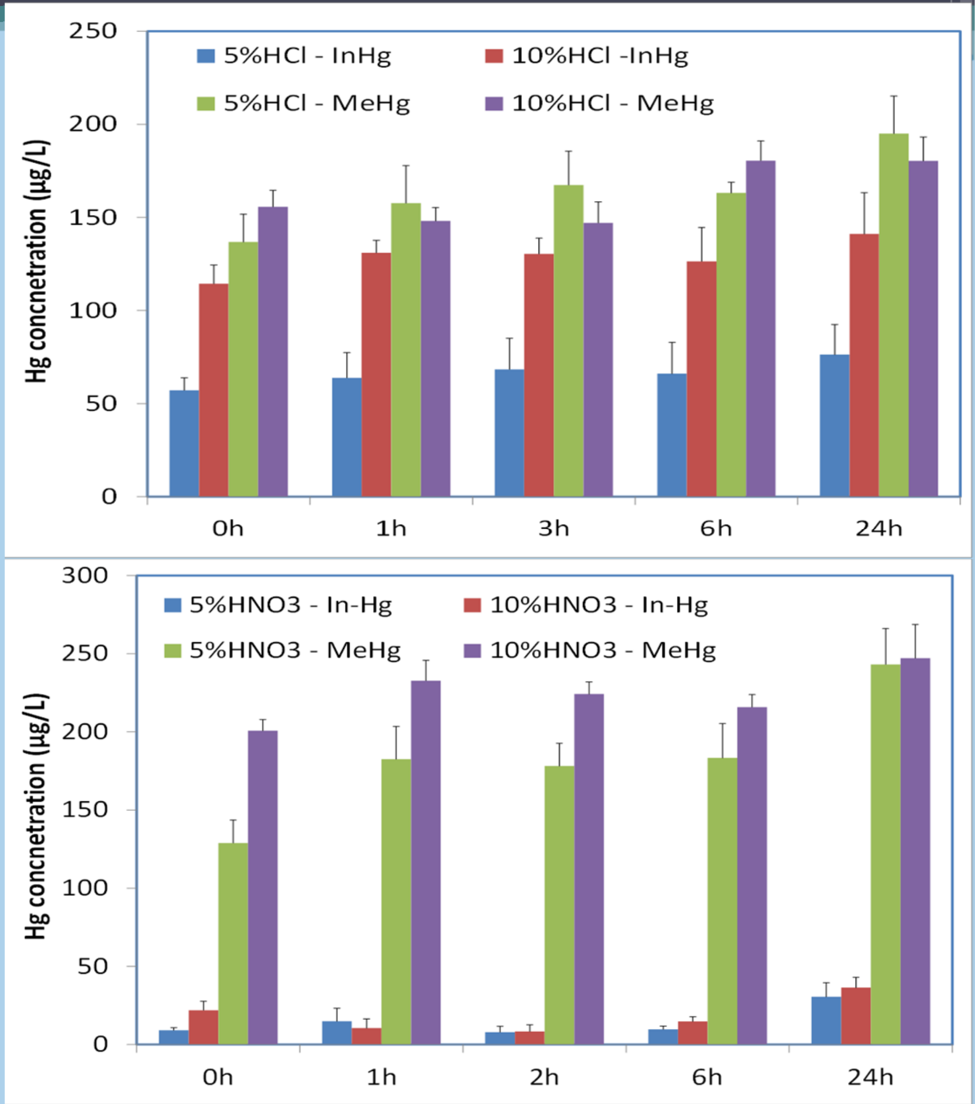
Effect of shaking

HCl extraction

- In-Hg was extracted substantially in dilute HCl with shaking. However, it was not extracted fully within 24-h of shaking in HNO_3.
- MeHg was extracted from soils in 5% HCl within 3-h shaking.

HNO_3 extraction

- Spiked MeHg was extracted in HNO_3 in 1 h of shaking into solution.
- In-Hg extraction was minimal in HNO_3.



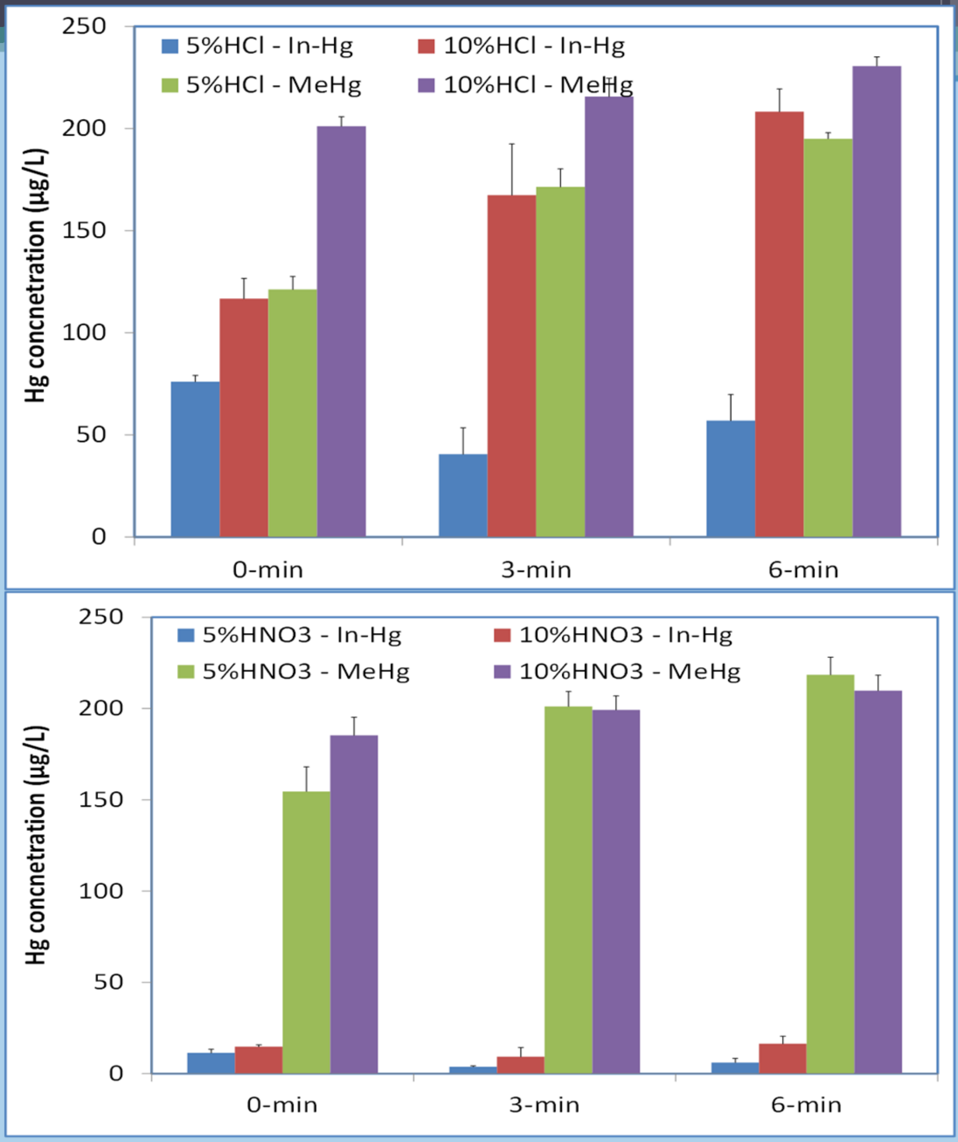
Effect of ultrasounds

HCl extraction

- Ultrasound sonication in HCl and HNO_3 yielded similar results with shaking.

HNO_3 extraction

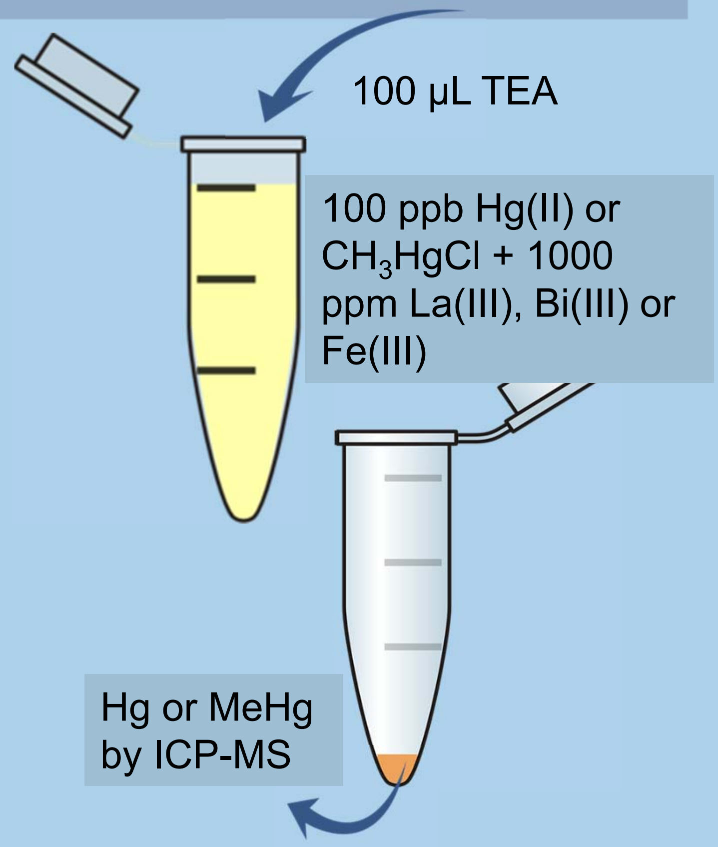
- Extraction was much faster. In 3 min sonication, all MeHg extracted into solution with 5% HNO_3.



More optimization needed for removal of extracted Hg(II)

Coprecipitation was attempted to remove residual Hg(II) from soil extracts

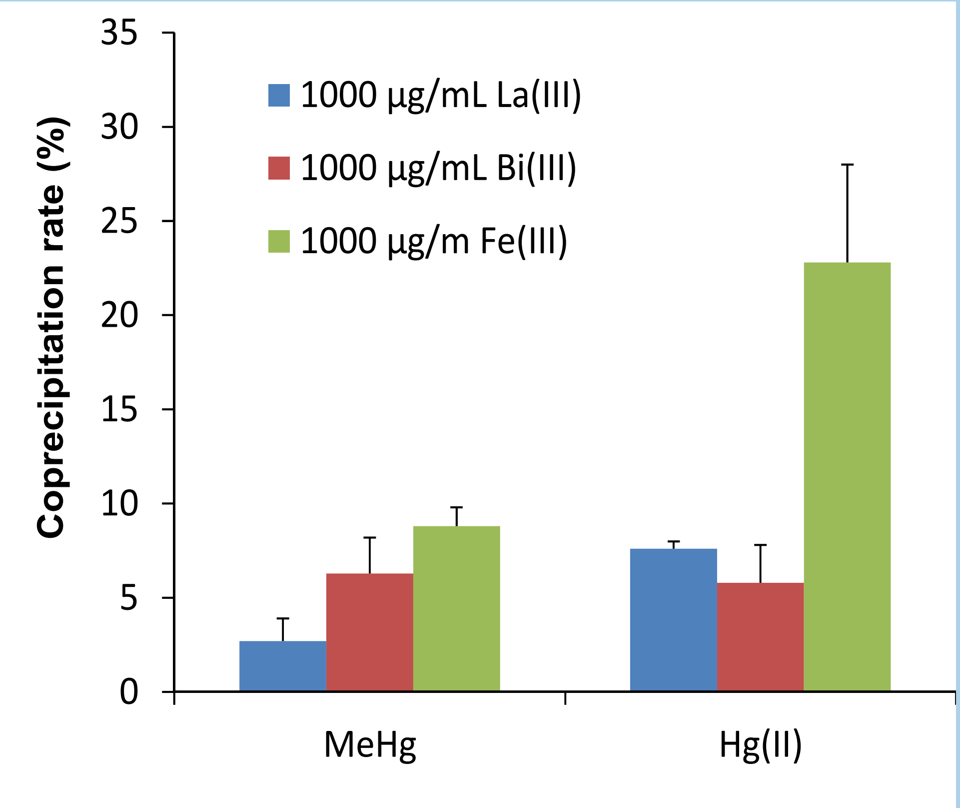
- Coprecipitating agents: bismuth (III), lanthanum (III), iron (III) and ammonium sulfide
- Complexing agents: L-cysteine and thiourea
- Precipitation of 100 ppb Hg(II) or CH_3HgCl was made in 1000 ppm La(III), Bi(III) or Fe(III) with or without L-cysteine and thiourea. Metal hydroxides were precipitated with triethylamine (TEA)
- Separate coprecipitations were made with ammonium sulfide, $(NH_4)_2S$.



Coprecipitation trials without ligands

Matrix/Precipitant	Recovery (%)	
	MeHg	Hg(II)
1000 µg/mL La(III)	2.7 ± 1.2	7.6 ± 0.4
1000 µg/mL Bi(III)	6.3 ± 1.9	5.8 ± 2.0
1000 µg/m Fe(III)	8.8 ± 1.0	22.8 ± 5.2

Fe(III) removed the most Hg(II) from solution without impacting CH_3HgCl concentration. Coprecipitation of Hg(II) with $Bi(OH)_3$ and $La(OH)_3$ provided very little Hg(II) recovery.

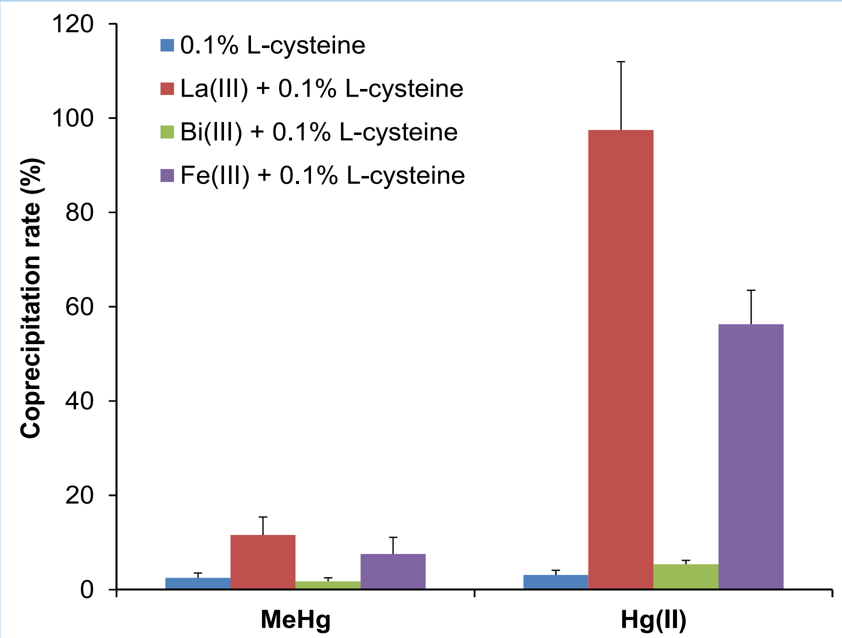


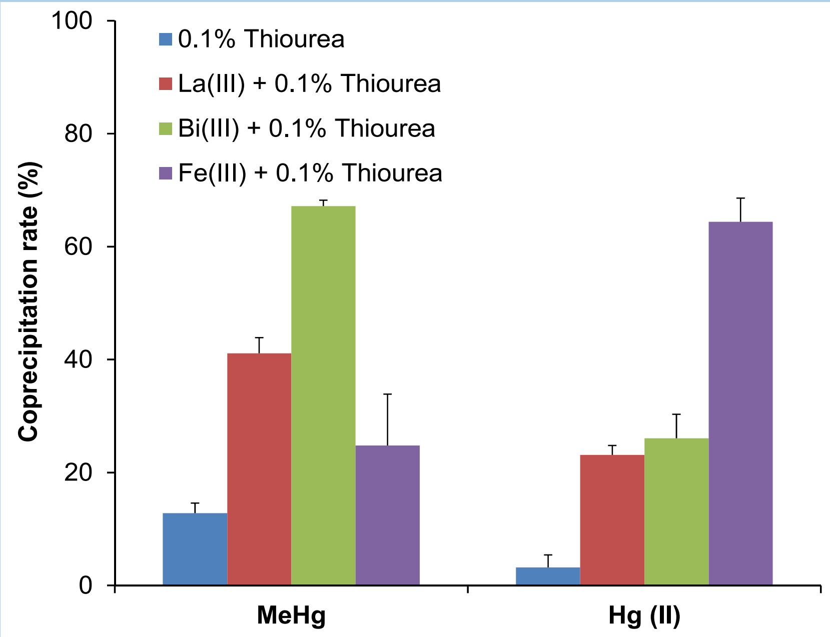
Coprecipitations with Ligands

Thiourea and L-cysteine were made to 0.1% (m/v) in 2 mL solution of 100 µg/L CH_3HgCl or Hg(II) and 1000 µg/mL La(III), Bi(III) or Fe(III). The contents were precipitated with 0.2 mL TEA.

Matrix/precipitant	Recovery (%)	
	MeHg	Hg
0.1% L-cysteine	2.5 ± 0.7	3.1 ± 0.6
1000 µg/mL La(III) + 0.1% L-cysteine	11.6 ± 3.8	97.5 ± 14
1000 µg/mL Bi(III) + 0.1% L-cysteine	1.8 ± 0.7	5.4 ± 0.8
1000 µg/mL Fe(III) + 0.1% L-cysteine	7.6 ± 3.5	56.3 ± 7.2
0.1% Thiourea	12.8 ± 1.8	3.2 ± 2.2
1000 µg/mL La(III) + 0.1% Thiourea	41.1 ± 2.8	23.1 ± 1.7
1000 µg/mL Bi(III) + 0.1% Thiourea	67.2 ± 1.0	26.1 ± 4.2
1000 µg/mL Fe(III) + 0.1% Thiourea	24.8 ± 9.1	64.4 ± 4.2
0.005 M Ammonium sulfide*	102 ± 3	3.3 ± 1.9

Coprecipitations with Ligands



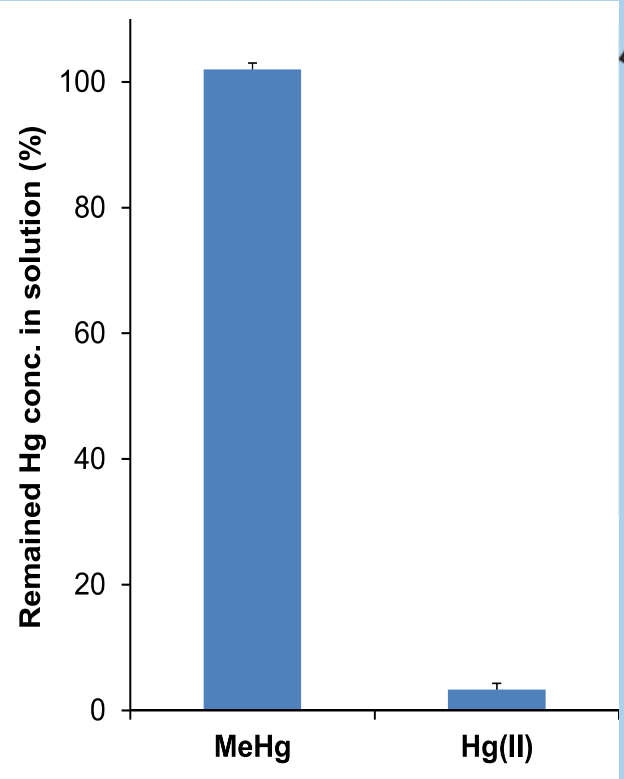


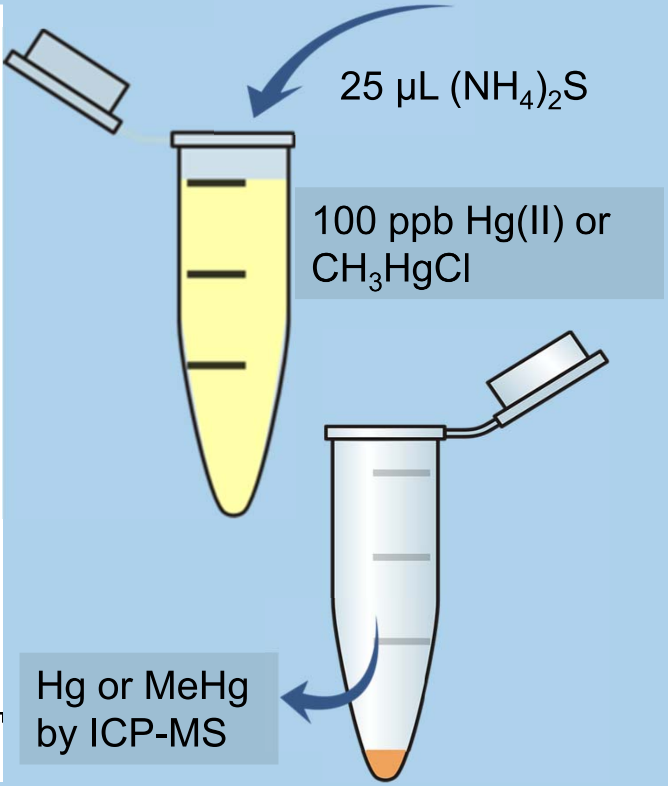
La(III) + L-cysteine yielded the most effective for separation of CH_3Hg from Hg(II). However, CH_3Hg concentration in solution was reduced by about 12%.

Thiourea gave very sporadic recoveries with Fe(III), Bi(III) and La(III). Highest and most selective precipitation enhancement being with that of Bi(III).

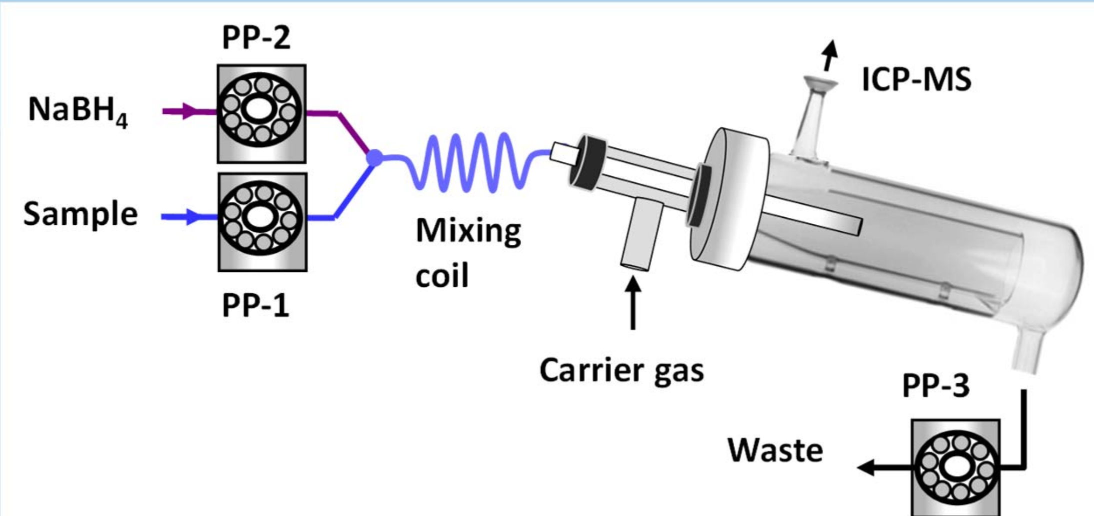
Coprecipitation with Ammonium Sulfide

- Attempts were made to selectively remove Hg(II) from soil with ammonium sulfide, $(NH_4)_2S$.
- 25 to 30 µL of 0.35 M $(NH_4)_2S$ was added to 2 mL test solutions that contained 100 µg/L CH_3Hg or Hg(II).
- After centrifugation, supernatant was analyzed by ICP-MS because HgS is very insoluble, even in concentrated acids.
- Recovery of MeHg was quantitative. Hg(II) was effectively eliminated.





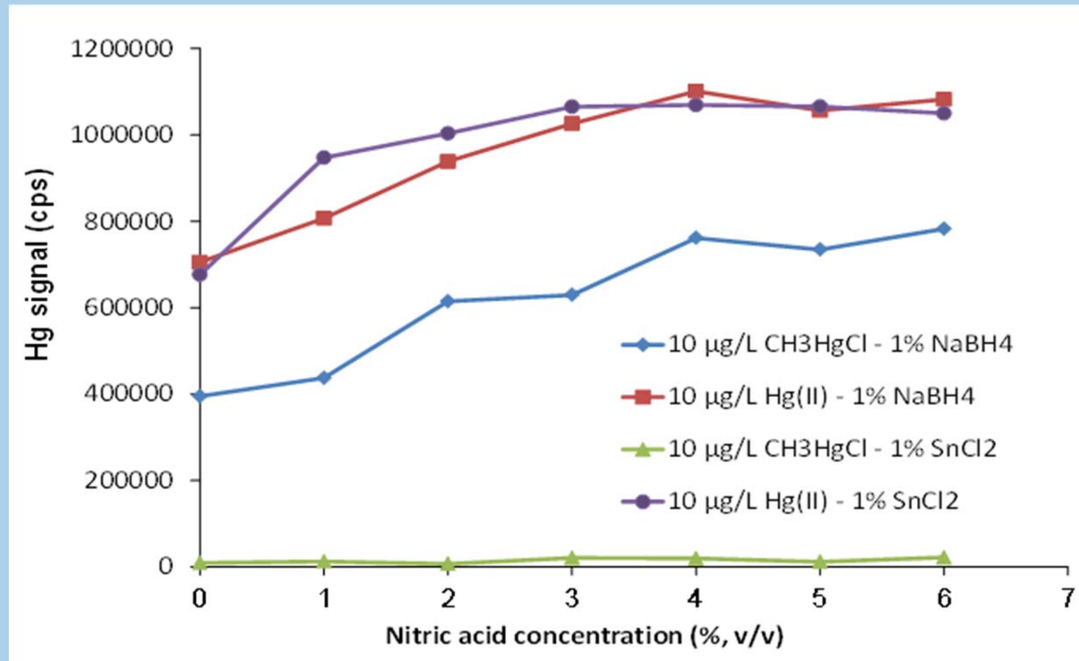
Optimization of cold vapor generation



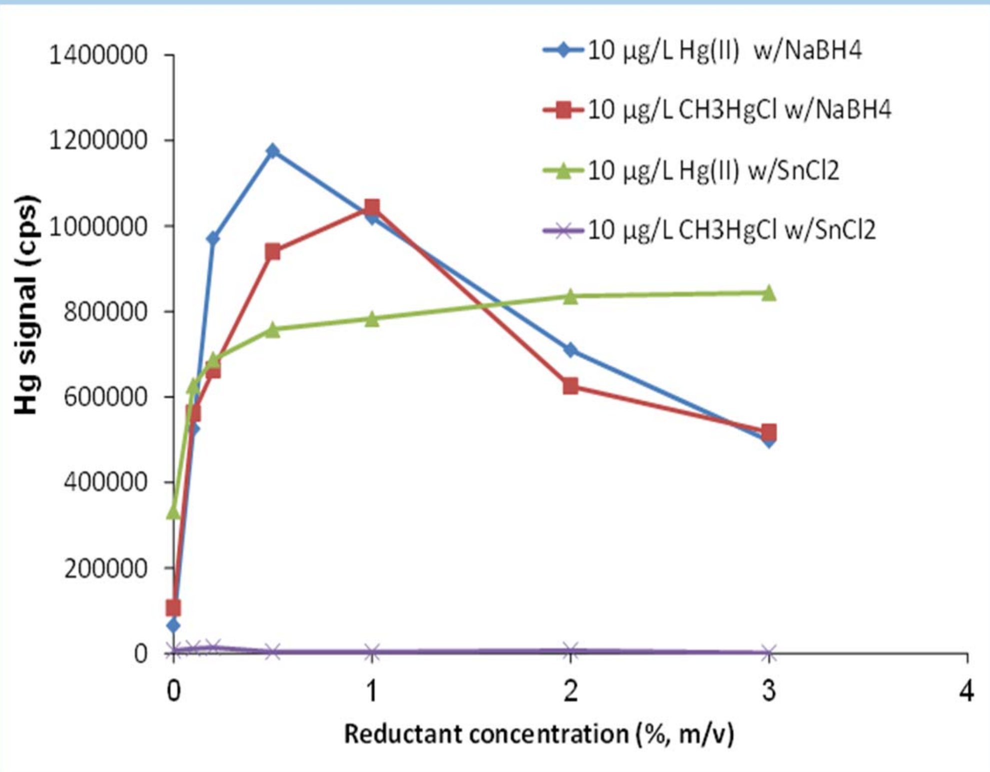
Cold vapor generation manifold and ICP-MS instrument for determination of CH_3Hg

Examining Acid Concentration in CVG System

- For both CH_3HgCl and Hg(II), CVG signals increased with HNO_3 concentration, and gained consistency at around 4% HNO_3.
- This is an indication that no modifications need to be done to mercury suspensions prior to determination with CVG-ICP-MS.
- $SnCl_2$ did not affect CH_3Hg at all, but performed similarly to $NaBH_4$ for vapor generation from Hg(II).

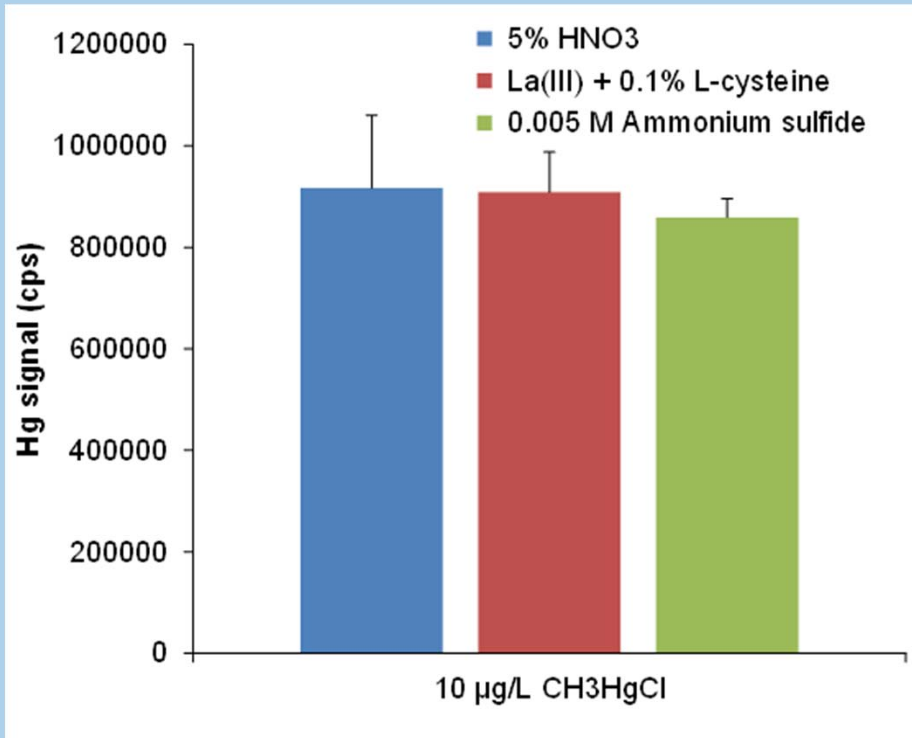


Examining reducing agent in CVG System



- $NaBH_4$ and $SnCl_2$ were examined on Hg(II) and CH_3HgCl in 5% (v/v) $HNO_{3,}$
- There was no notable vapor generation of CH_3HgCl, and none at all proceeding 3% of $SnCl_{2,}$ whereas Hg(II) signals showed a steady pattern at 0.5% (m/v) $SnCl_2$.
- 0.5 and 1% (m/v) $NaBH_4$ gave max readings for both CH_3HgCl and Hg(II).
- Signals decreased with increasing $NaBH_4$ levels which generates excessive H_2 that changed sampling position in the plasma.

Interference studies for $(NH_4)_2S$ and La(III) + L-cysteine



When compared to CH_3HgCl in 5% HNO_3 with 1% $NaBH_4$:

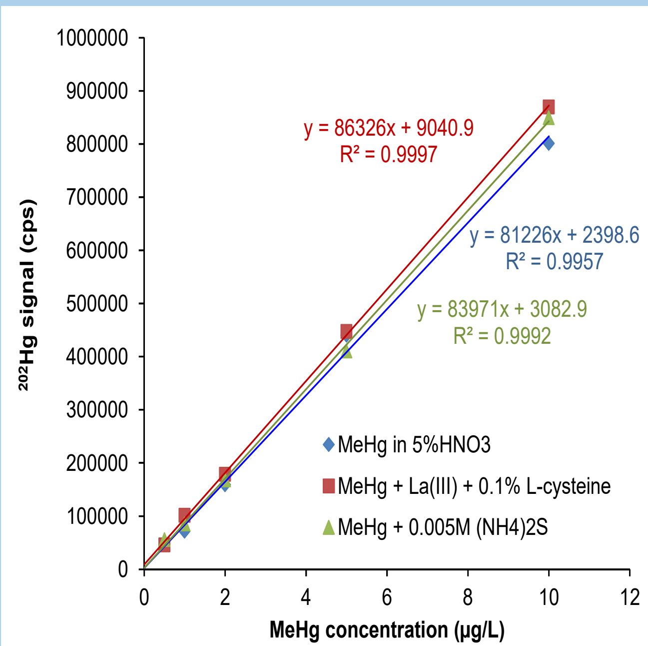
La(III) + L-cysteine showed no significnat interference on MeHg CVG system.

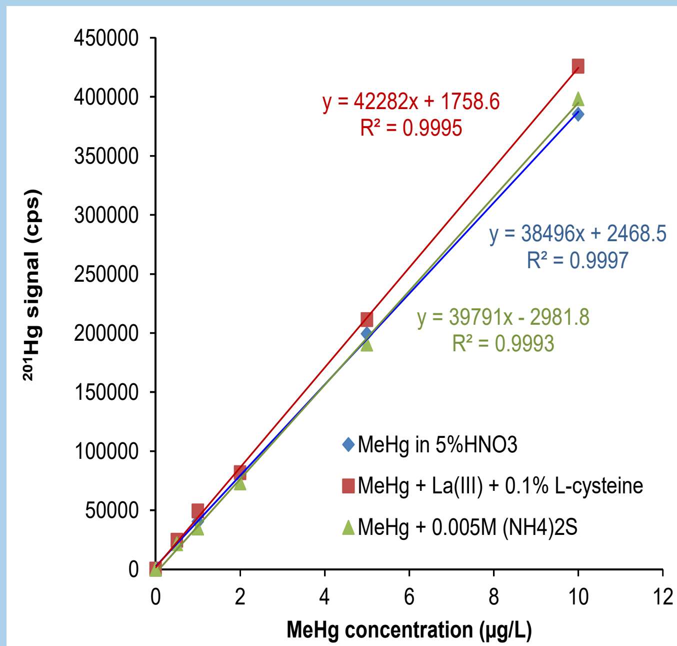
Ammonium sulfide showed some signal depression, but it was not significant .

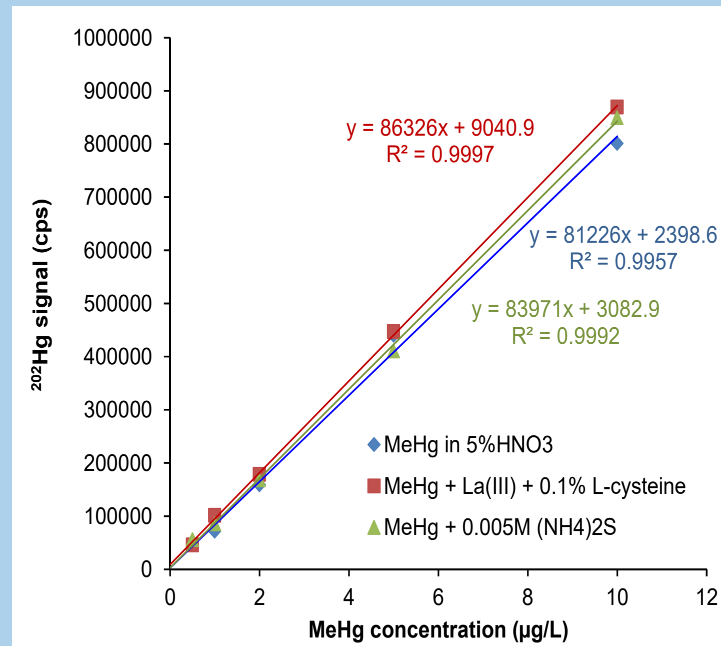
Calibration curves

Calibration curves constructed with CH_3HgCl solutions prepared in 5% HNO_3 with La(III) + L-cysteine and 0.005 M $(NH_4)_2S$ additives.

La(III) + L-cysteine and $(NH_4)_2S$ media showed similar calibration slopes to that of MeHg solutions in 5% HNO_3.



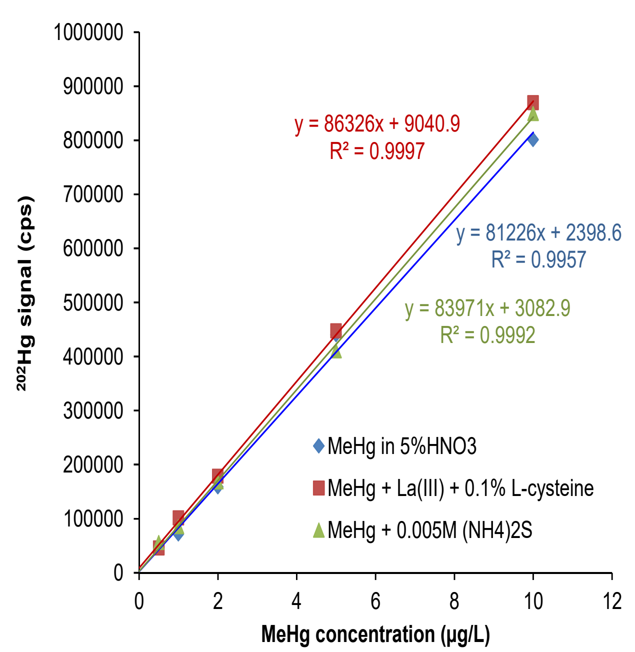


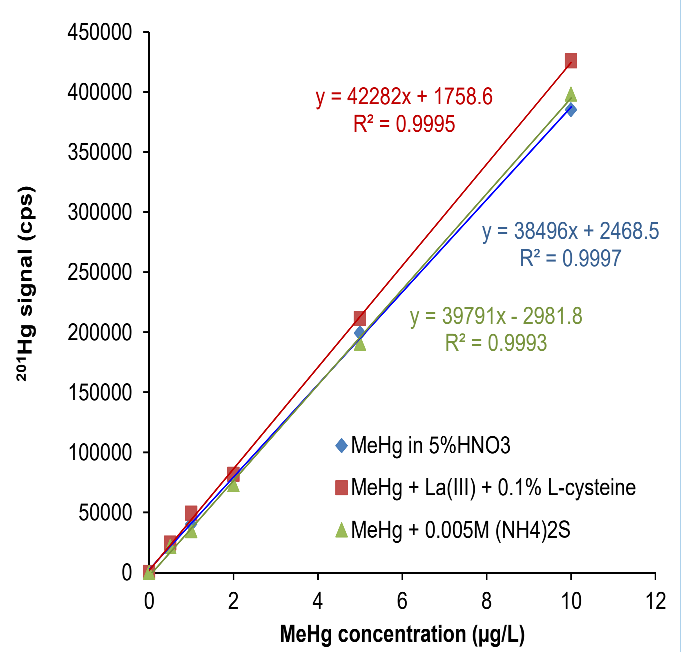


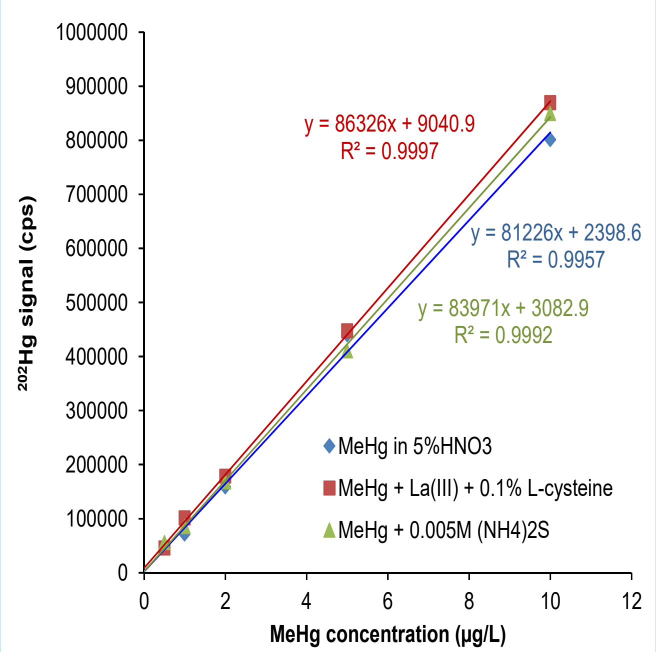
Limits of detection

- The highest LODs were from La(III) + L-cysteine system due to the high background blanks.
- LODs for ammonium sulfide were similar to those with 5% HNO_3.

Medium	LOD (µg/L)		
	^{200}Hg	^{201}Hg	^{202}Hg
5% HNO_3	0.082	0.09	0.085
La (III) + L-cysteine	0.41	0.38	0.42
Ammonium sulfide	0.12	0.1	0.1







Method validation

Sample	CH_3Hg concentration (ng/g)			Certified value (ng/g)
	^{200}Hg	^{201}Hg	^{202}Hg	
SQC1238	13.0 ± 3	13.2 ± 3	12.8 ± 4	10.00 ± 3
ERM – CC580	81 ± 7	79 ± 8	80 ± 4	75 ± 4

- **Reference materials SQC1238 (methylmercury sediment)**
  CH_3Hg = 0.01 ± 0.00291 µg/g
- **ERM – CC580 (estuarine sediment)**
  Total Hg = 132 ± 4 µg/g and CH_3Hg = 0.075 ± 0.004 µg/g

  - Samples (0.2 g for SQC1238 and 0.1 g for ERM-C580) were agitated via ultrasound for 3 min in 5% HNO_3 (5 mL).
  - 2 mL of the extract was then taken and treated with 30 µL of 0.35 M $(NH_4)_2S$ for removal of Hg(II).
  - Contents were centrifuged at 12,000 rpm for 20 min, then transferred to 2-mL micro-centrifuge tubes and analyzed by CVG-ICP-MS.

Analysis of soils for MeHg

- Soils from Oak Ridge TN were processed with optimized method, and analyzed along with SRMs.
- CH_3Hg levels ranged from 0.030 to 0.051 µg/g. CH_3Hg distribution in the floodplain soils were much lower compared with Hg(II) or total Hg levels.
- CH_3Hg concentrations are within the proximity of regulatory limit (0.051 µg/g).

Sample	CH_3Hg concentration (µg/g)		
	^{200}Hg	^{201}Hg	^{202}Hg
Soil 1	0.043 ± 0.006	0.043 ± 0.006	0.045 ± 0.006
Soil 2	0.040 ±0.008	0.040 ± 0.008	0.041 ± 0.008
Soil 3	0.040 ± 0.012	0.041 ± 0.013	0.040 ± 0.013
Soil 4	0.032 ± 0.003	0.032 ± 0.004	0.033 ± 0.04
Soil 5	0.032 ± 0.009	0.032 ±0.009	0.033 ± 0.009
Soil 6	0.050 ± 0.01	0.051 ± 0.012	0.051 ± 0.015
Soil 7	0.046 ± 0.005	0.047 ± 0.006	0.047 ± 0.005
Soil 8	0.029 ± 0.002	0.030 ± 0.002	0.031 ±0.0013
Soil 9	0.033 ± 0.009	0.032 ± 0.008	0.033 ± 0.008
Soil 10	0.042 ± 0.011	0.043 ± 0.012	0.042 ± 0.012

Conclusions

- The method developed for selective extraction of MeHg from contaminated sediments provides rapid extraction and high selectivity with effective removal of Hg(II) prior to determination.
- Ultrasounds extraction in HNO_3 and further sample treatment with ammonium sulfide precipitation allowed the highest selectivity for accurate determination of CH_3Hg with cold vapor generation.
- Results show that there is MeHg in the contaminated soil from the Y-12 National security complex.
- The distribution of MeHg in the topsoil in the contaminated regions are at the threshold of regulatory limits of 0.051 µg/g.

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