Determining elemental mercury in soils by selective volatilization

Background

Goal - Determination of Hg^0 content in mercury contaminated soils

- Difficulty:
  - total mercury ≠ elemental mercury
  - soil chemistry is complex
- How it's been done before: 5 step sequential extraction is non-specific
- Solution: Selective volatilization of Hg^0 to separate it from other mercury species

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1. Anal. Methods, 2017, **9**, 2159–2167

Common mercury species in soils

Mineral (Cinnabar HgS)

- Naturally occurring
- Mercury is sequestered

Ionic mercury

- Like $HgCl_2$
- Includes chelated ions

Organo-mercury complexes

- Like CH_3Hg^+

Elemental Mercury

- Main target for remediation

TABLE 2. Sequential Chemical Extraction Method for Determining Hg Speciation As Developed by Bloom et al. (6)[a]

step	extractant	description	typical compounds removed
F1	DI water	water soluble	$HgCl_2$
F2	pH 2 HCl/HOAc	"stomach acid"	HgO, $HgSO_4$
F3	1 N KOH	organocomplexed	Hg humics, Hg_2Cl_2, CH_3Hg
F4	12 N HNO_3	strong complexed	mineral lattice, Hg_2Cl_2, Hg^0
F5	aqua regia	mercury sulfides	HgS, HgSe

[a] Listed are the extraction steps, the general category of Hg-containing phases removed in each step, and specific Hg-containing compounds that are typically removed in that step.

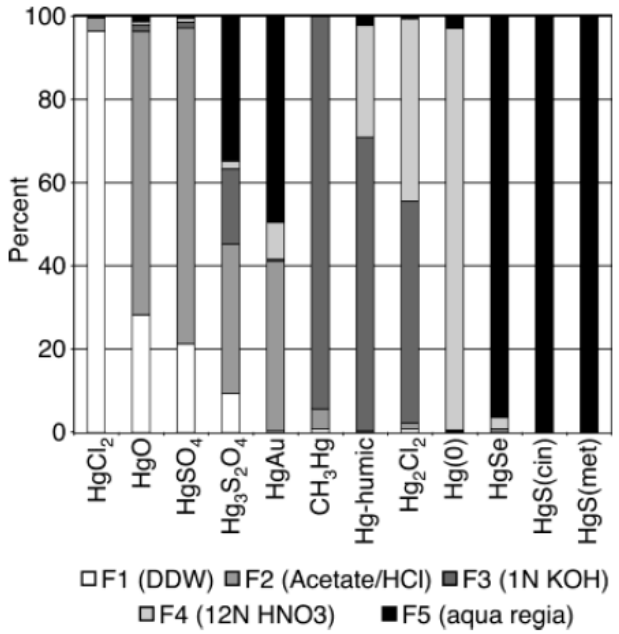

FIGURE 3. Sequential chemical extraction profiles for individual Hg compounds as developed by Bloom et al. (6).

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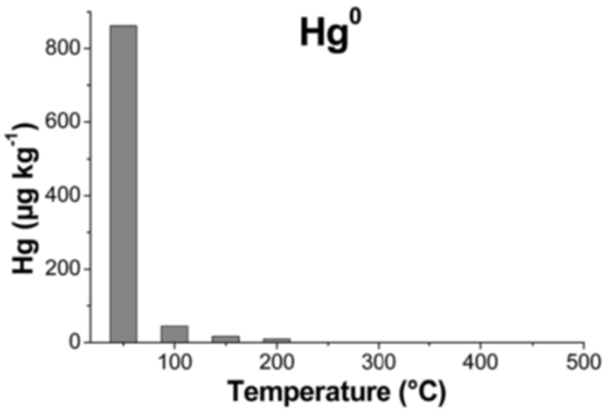
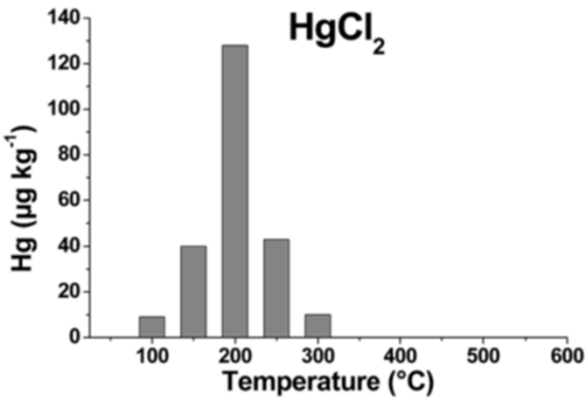
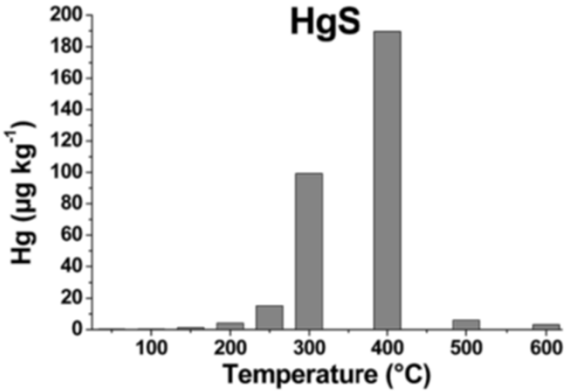
Direct mercury analysis for selective volatilization[1]







- Used to heat reference material in discrete steps
- Gives a temperature range for volatilization of different mercury species
- Small sample aliquot (50 mg) therefore not ideal for soil samples

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1. Anal. Methods, 2017, **9**, 2159–2167

Basic procedure

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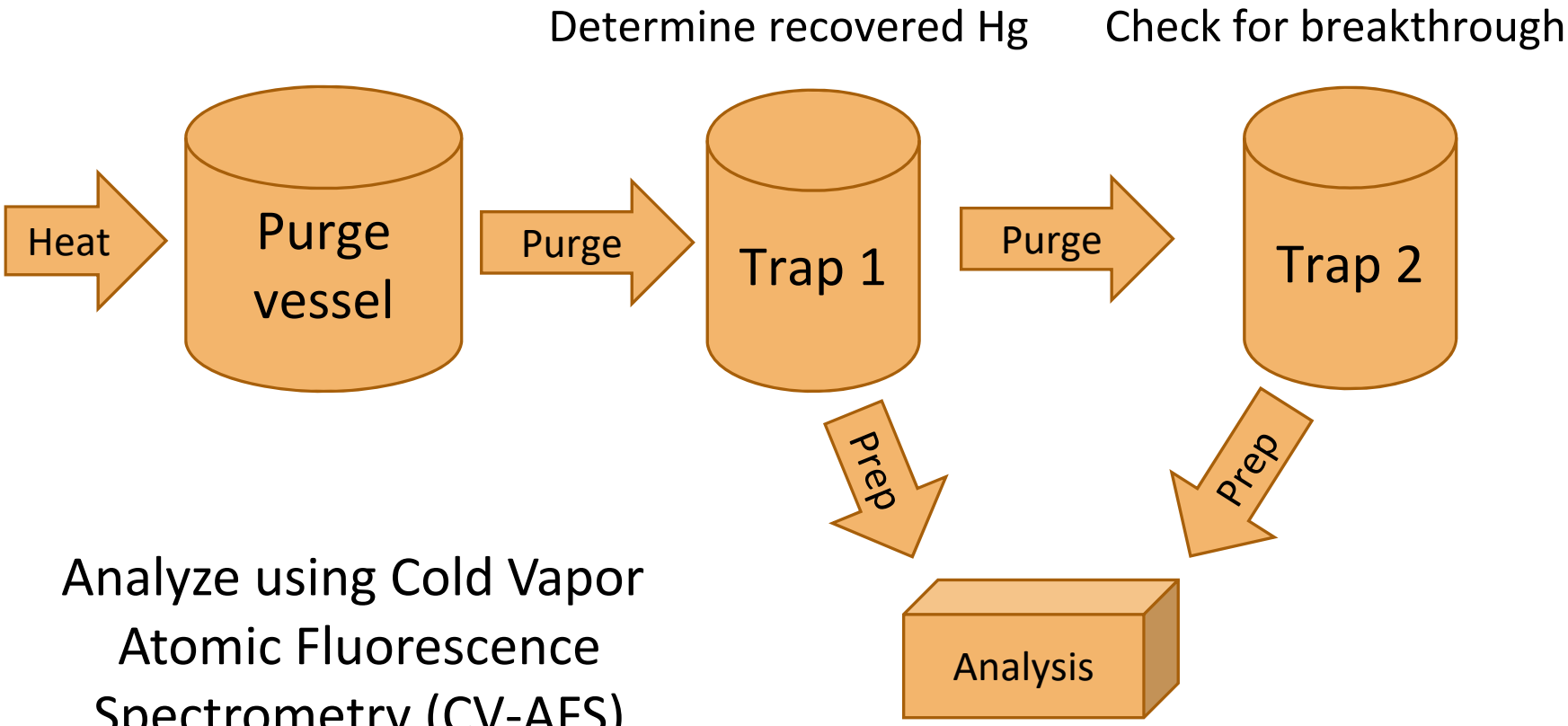
Basic apparatus



Analyze using Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS)

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RM results

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Selectivity studies

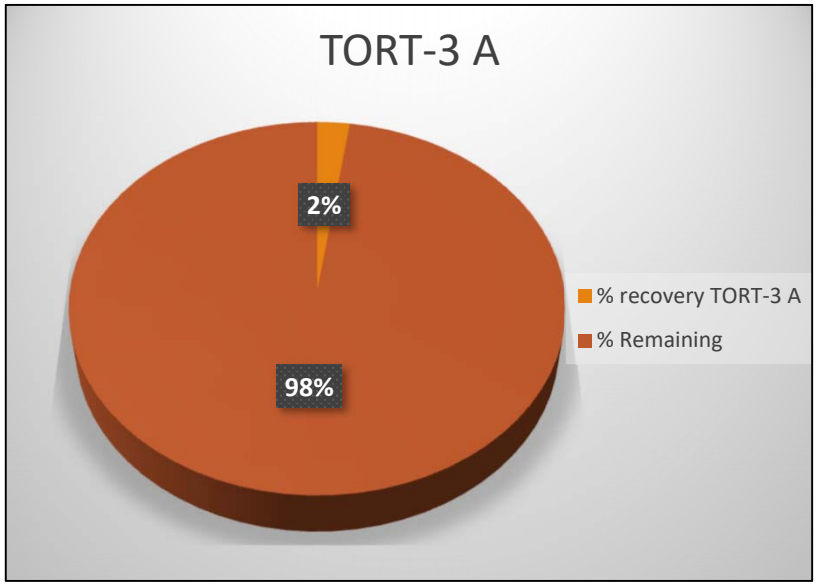
Tested method against three reference materials:

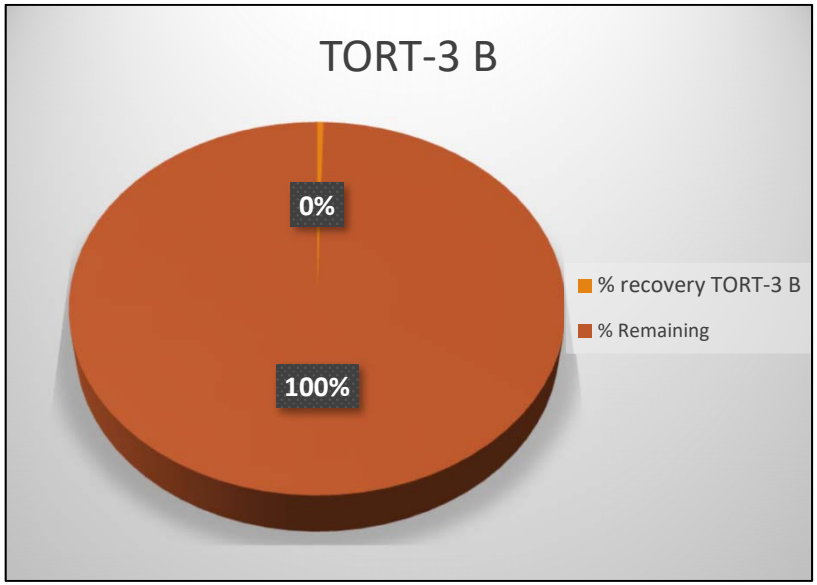
$HgCl_2$, HgS, Hg^0 in Kaolin with total values certified by a round robin study

Tested against 2 certified reference materials for methyl mercury recovery:

DOLT-5, TORT-3, the matrices are not soil but do have certified methyl mercury and total mercury values

Hg^0 recovery of TORT-3 RM





Reference material concentrations:

MeHg = 0.1370 mg/kg

Hg_{total} = 0.2920 mg/kg

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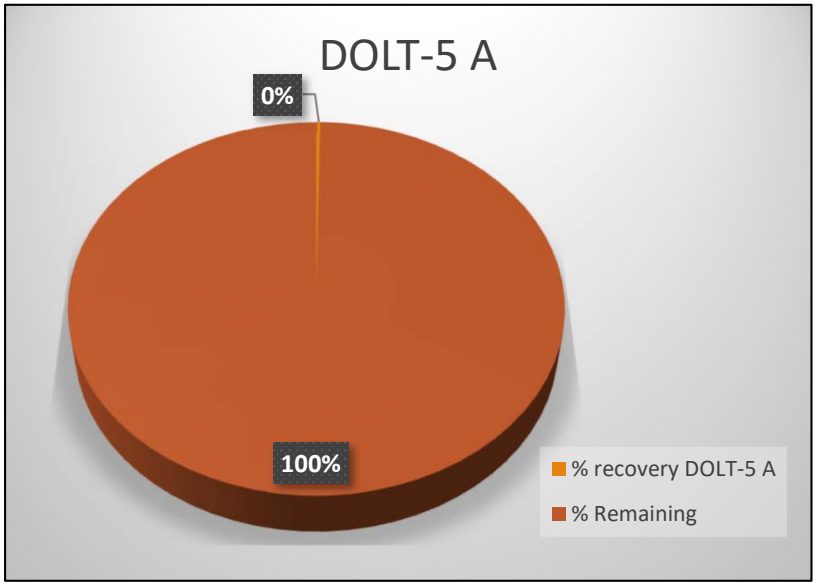
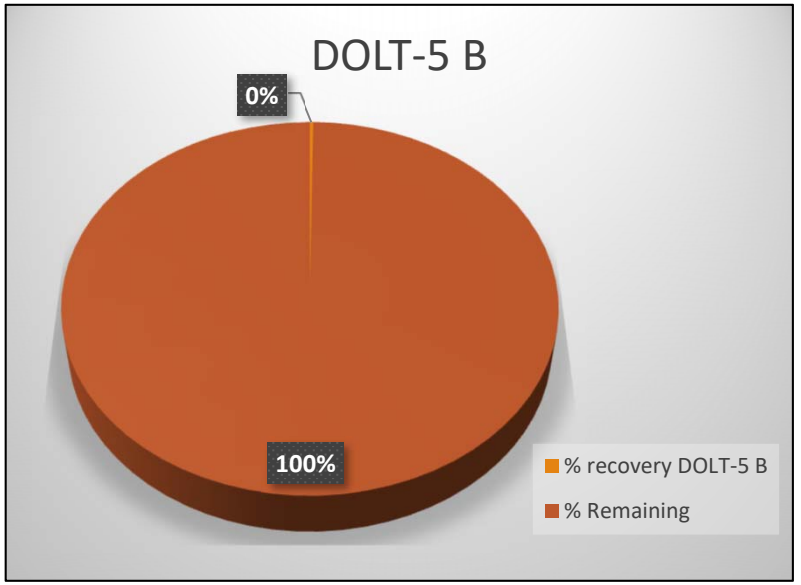
Hg^0 recovery of DOLT-5 RM





Reference material concentrations:

MeHg = 0.1190 mg/kg

Hg_{total} = 0.4400 mg/kg

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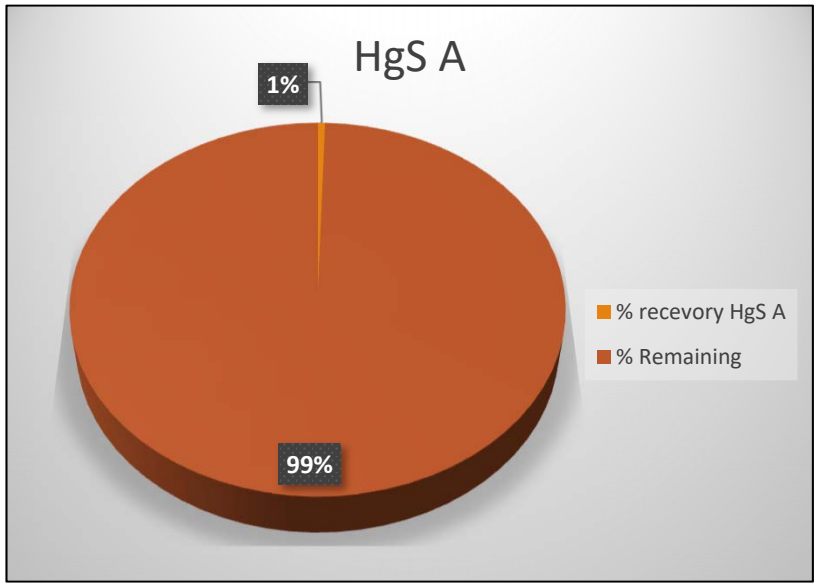
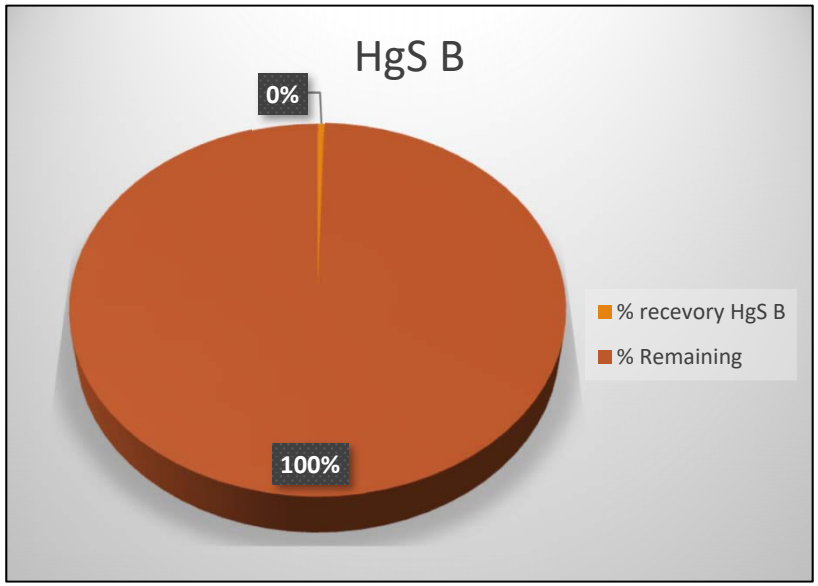
Hg^0 recovery of HgS RM





Reference material concentrations:

Hg_{total} = 2150 mg/Kg

- Recovers at blank levels (below MDL)

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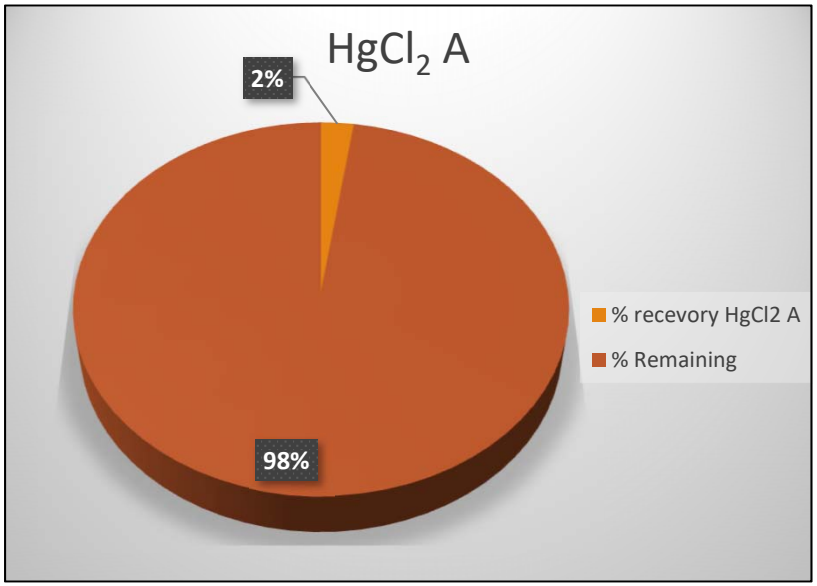
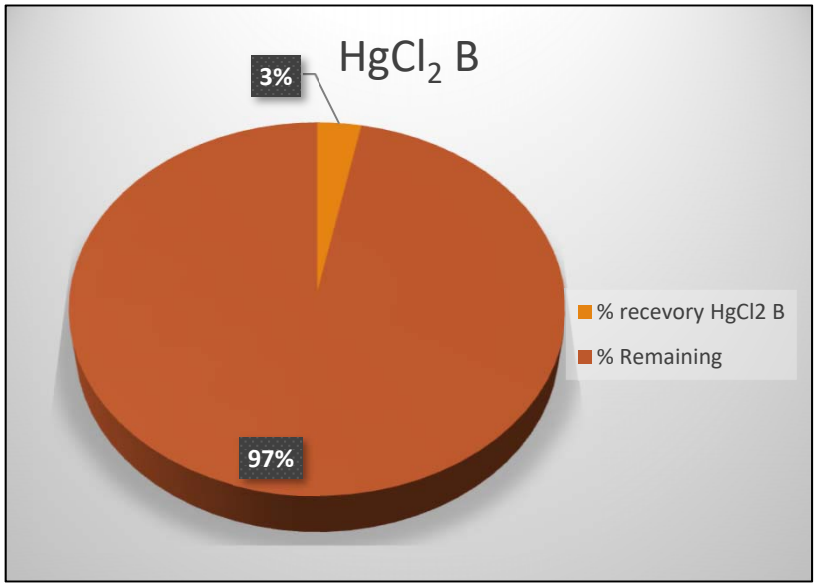
Hg^0 recovery of $HgCl_2$ RM





Reference material concentration:

Hg_{total} = 1900 mg/Kg

- Some recovery
- At higher temperatures recovery increases.

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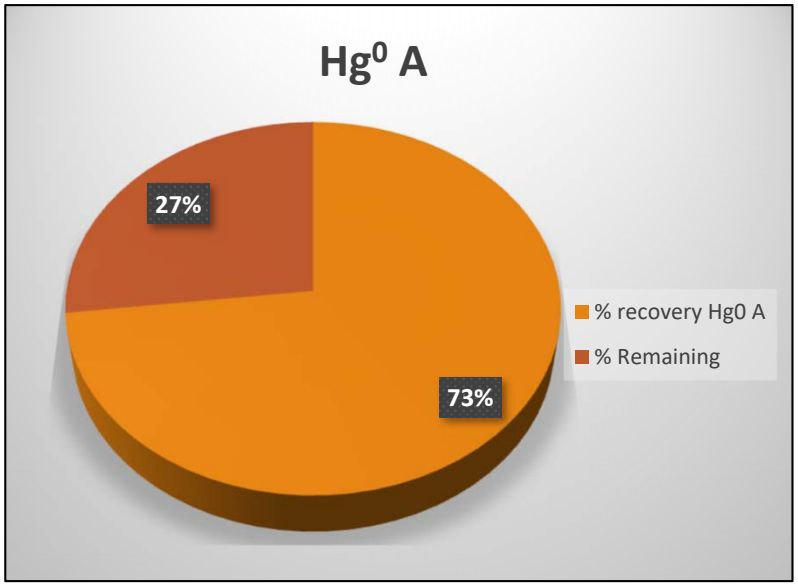
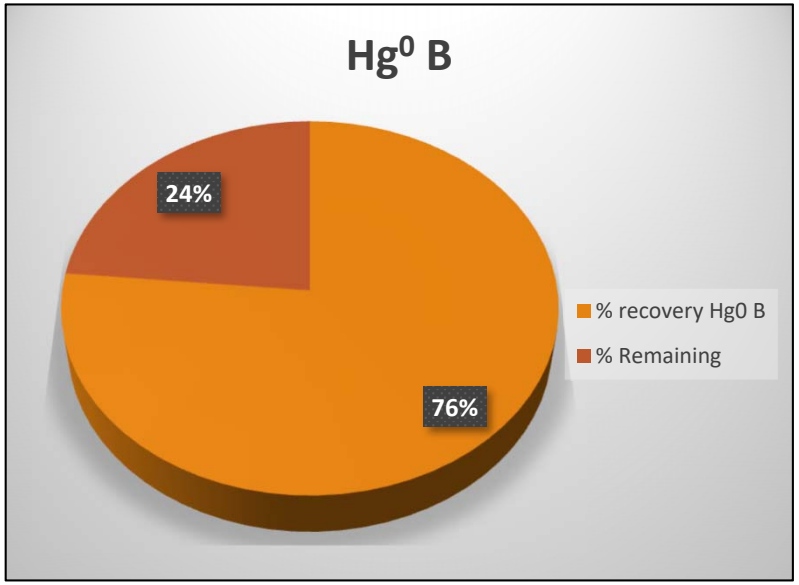
Hg^0 recovery of Hg^0 RM





Reference material concentration:

Hg_{total} = 5861 mg/Kg

- As we optimized temperature to reduce Hg(II) recovery the Hg^0 recovery also dropped
- Why?

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Speciation analysis of Hg^0 RM by IP-CV-ICP-MS

Refence Hg concentration

Hg_{total} = 5861 mg/kg

Recovery low compared to expected total concentration

Rep	Recovery Hg mg/kg	Hg % Recovery
1	4295	73.1
2	4483	76.7
3	4424	75.4
4	4406	75.2
Avg = 4399 ± 82.8 mg/kg		

So we ran speciation analysis to determine Hg(II) content

Rep	Recovery Hg(II) mg/kg	Hg(II) % Recovery
1	1752	29.9
2	1679	28.6
3	1742	29.7
Avg = 1724 ± 39.7 mg/kg		

Refence material Hg^0 concentration

Hg^0_{calc} = 4137 mg/kg

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Hg^0 recovery from selective volatilization

Rep	% Recovery (Hg^0)
1	103.6
2	108.3
3	106.9
4	106.3

Reference material Hg^0 concentration

Hg^0 = 4137 mg/kg

- Total Hg value determined by round robin study, Hg^0 speciation determined in house
- Hg^0 Recovery is over 100% most likely due to recovery of some Hg(II) species
- Good reproducibility

Effect of water on RM

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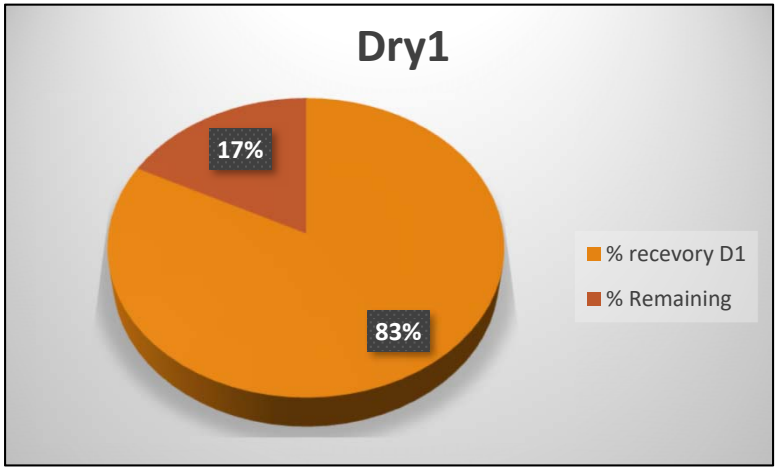
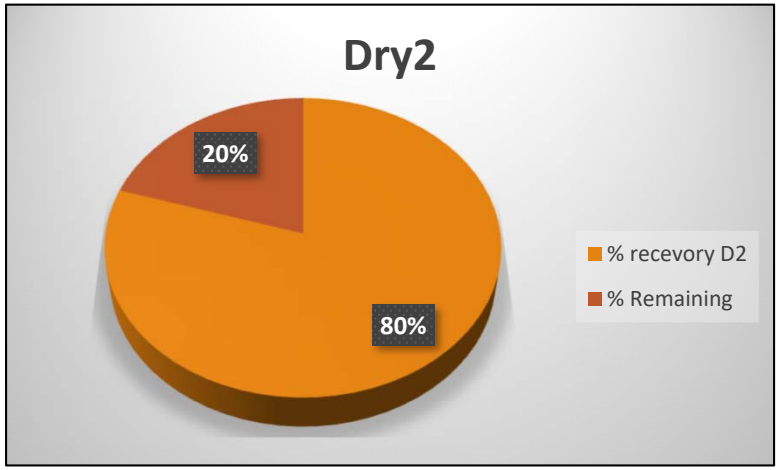
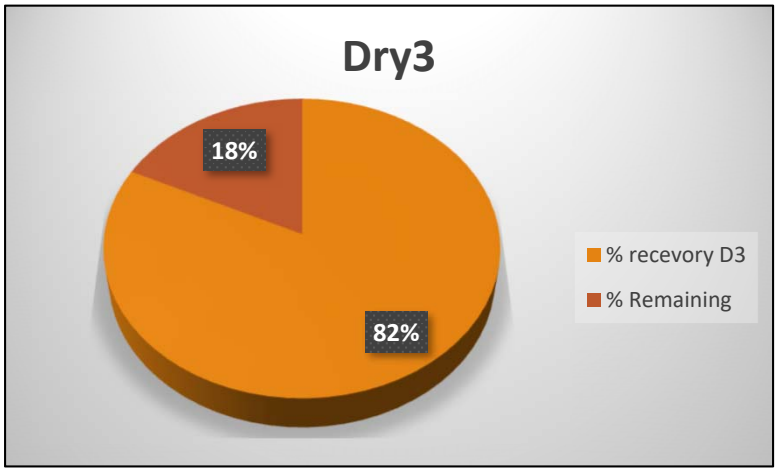
What about soil that's wet?

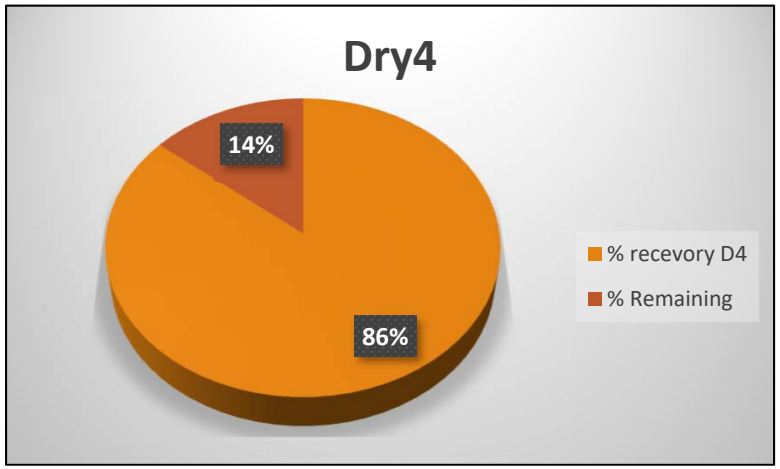
- Most samples come in wet
- But the act of drying them may also release the elemental mercury we want to measure
- Moisture from drying the sample in the system may interfere with Hg adsorption on the traps
- Tested the reference materials with the addition of 0.250 mL of water to see how it affected recovery

Wet vs Dry recovery for the Hg^0 RM









Average recovery = 83%

RSD = 3.1%

recovery based off Hg_{total} concentrations

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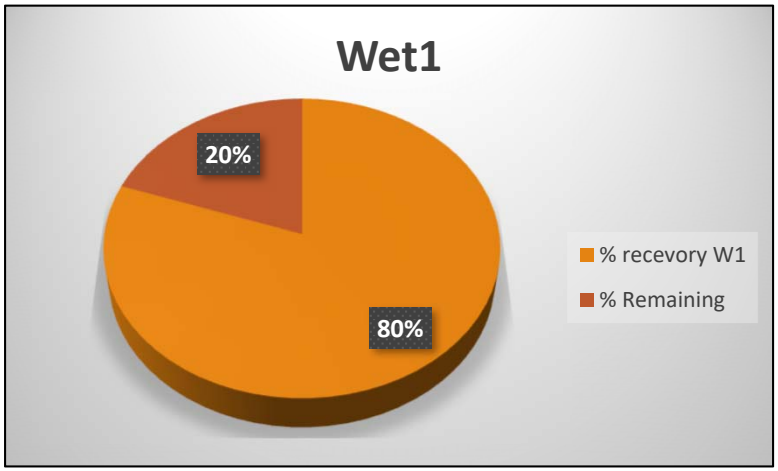
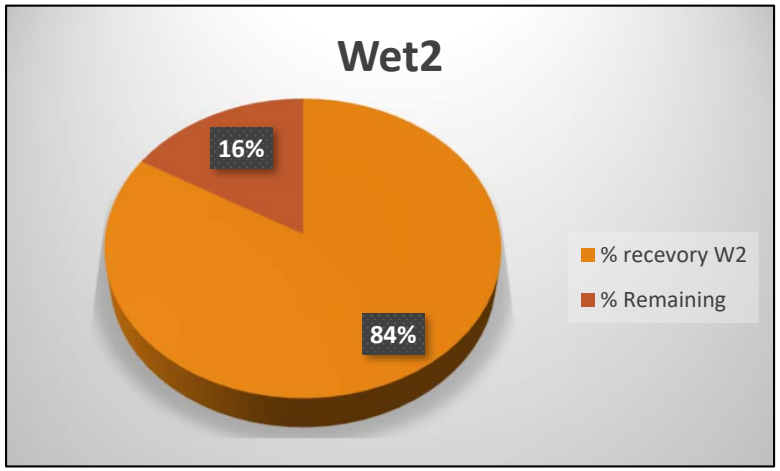
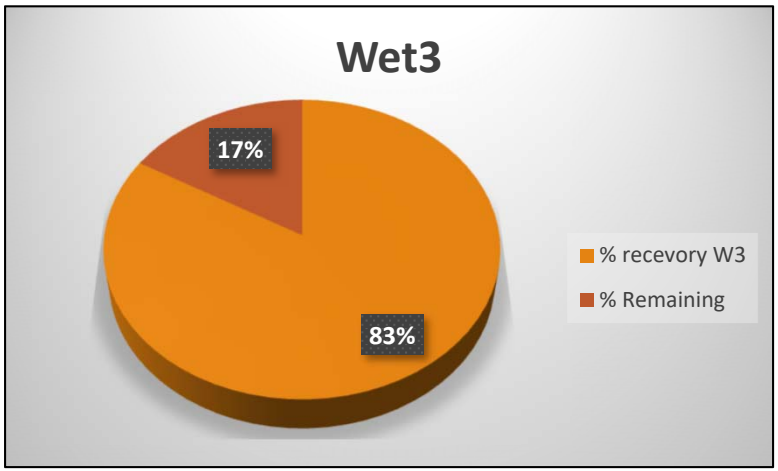
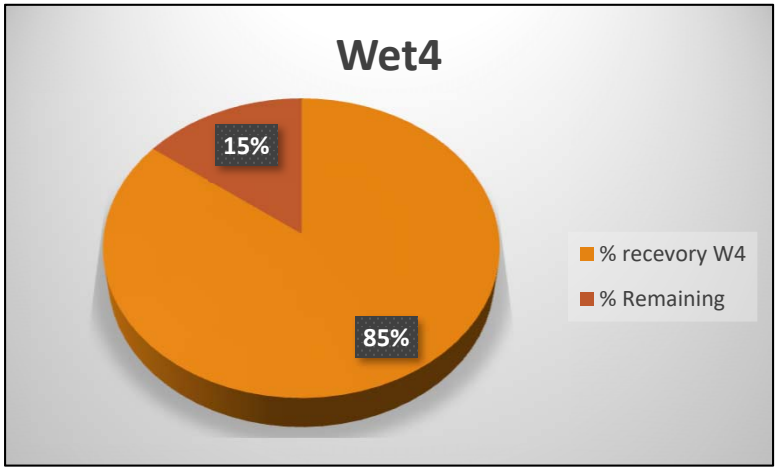
Wet vs Dry recovery for the Hg^0 RM









Average recovery = 83%

RSD = 2.5%

recovery based off Hg_{total} added 0.25 mL H_2O

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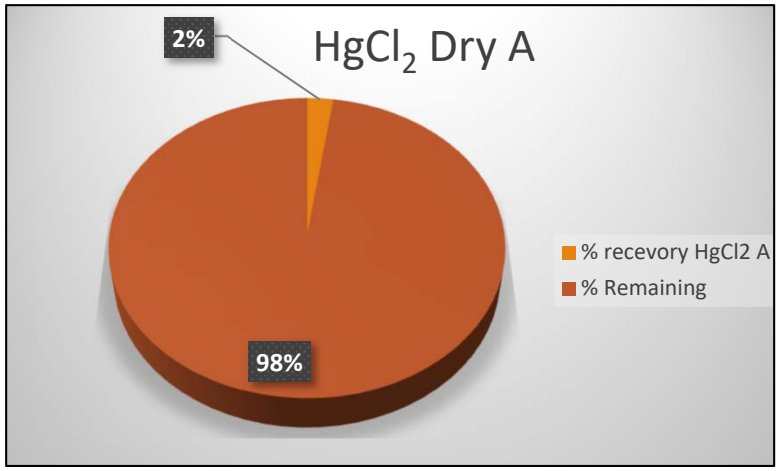
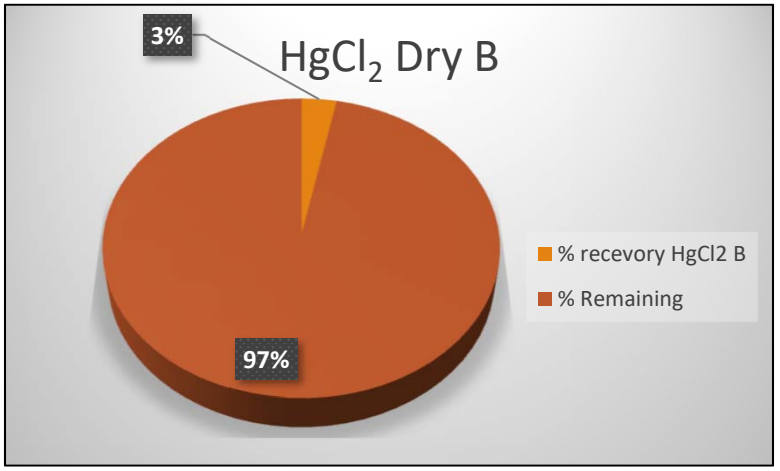
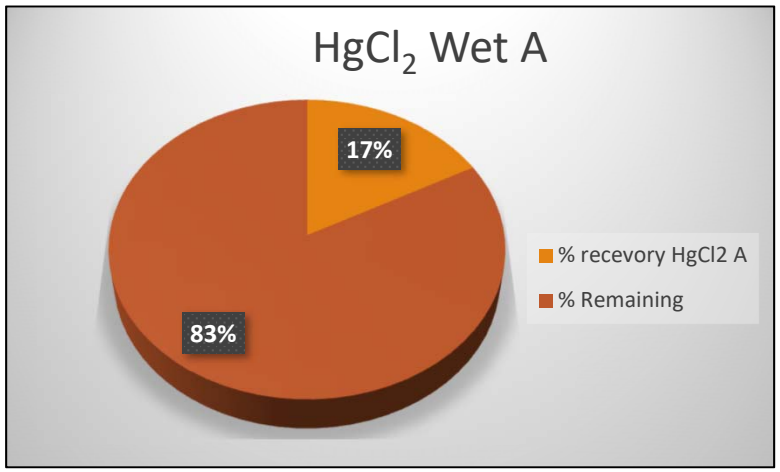
Wet vs Dry recovery for the Hg^0 RM

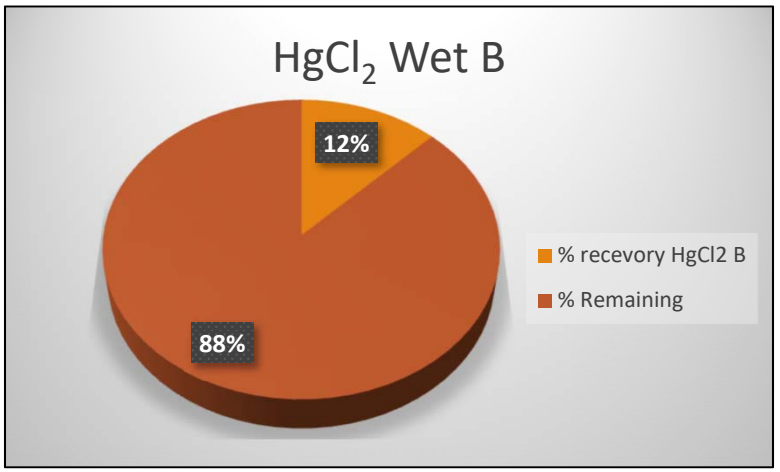
- RSD between the wet and dry runs is 2.8%
- This indicates that moisture does not hinder recovery of Hg^0
- Most real samples will come wet and drying them beforehand risks losing Hg^0

Wet vs Dry recovery for the $HgCl_2$ RM









Increased recovery of $HgCl_2$ when wet

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Soil sample results with comparison to F step results

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Sequential extraction comparisons:

Selective volatilization appears to separate elemental mercury from other species in reference materials but what about actual soil samples?

Another way we characterize samples is through sequential extractions (5 steps)[2]

The 5 step process separates mercury species through different extraction conditions

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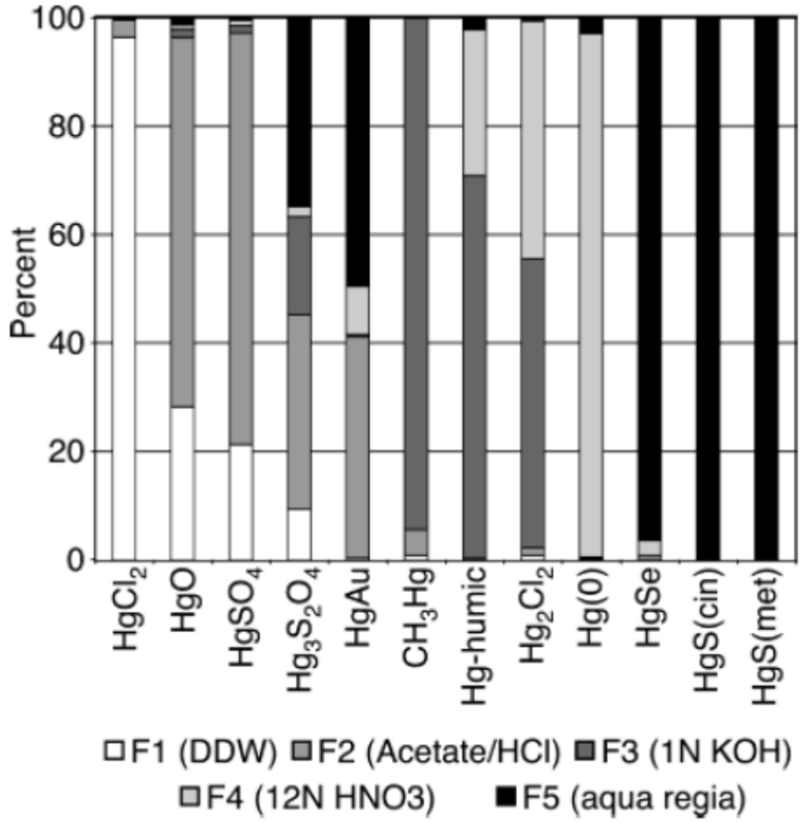
2. Environ. Sci. Technol. 2003, **37,** 5102-5108

Things to keep in mind about SSE

- Semi quantitative
- Each step corresponds to different mercury species and often more than one
- Step 4 is associated with elemental mercury but not selectively



2. Environ. Sci. Technol. 2003, **37,** 5102-5108

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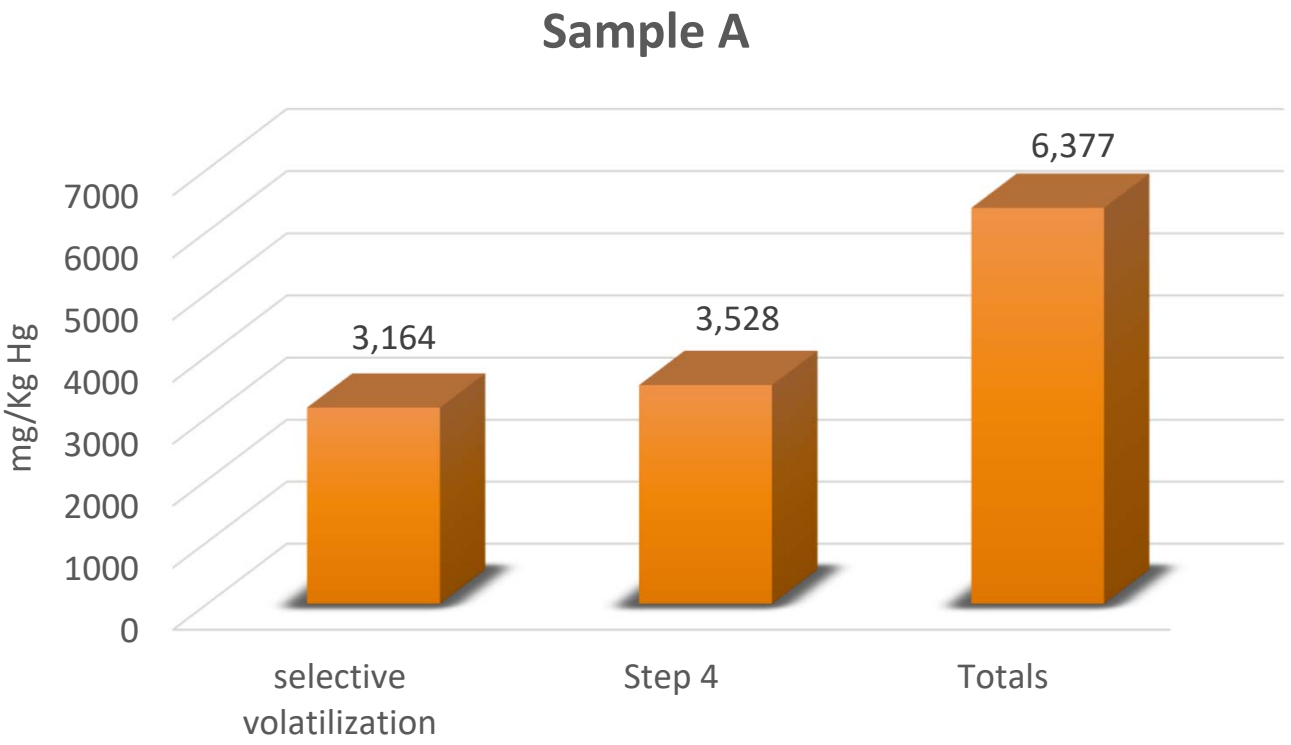
Soil samples from remediation sites



89.5% recovery compared to step 4

49.5% of mercury species likely elemental

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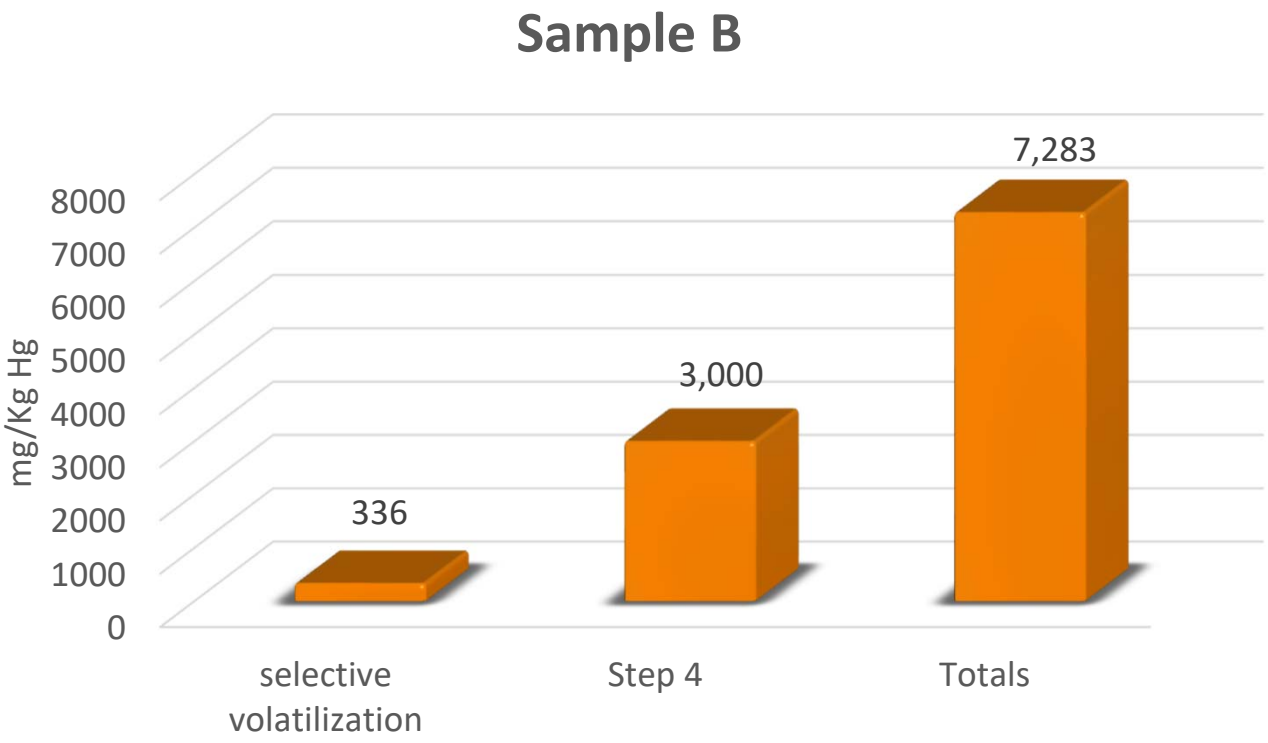
Soil samples from remediation sites



11.2% recovery compared to step 4

4.6% of mercury species likely elemental

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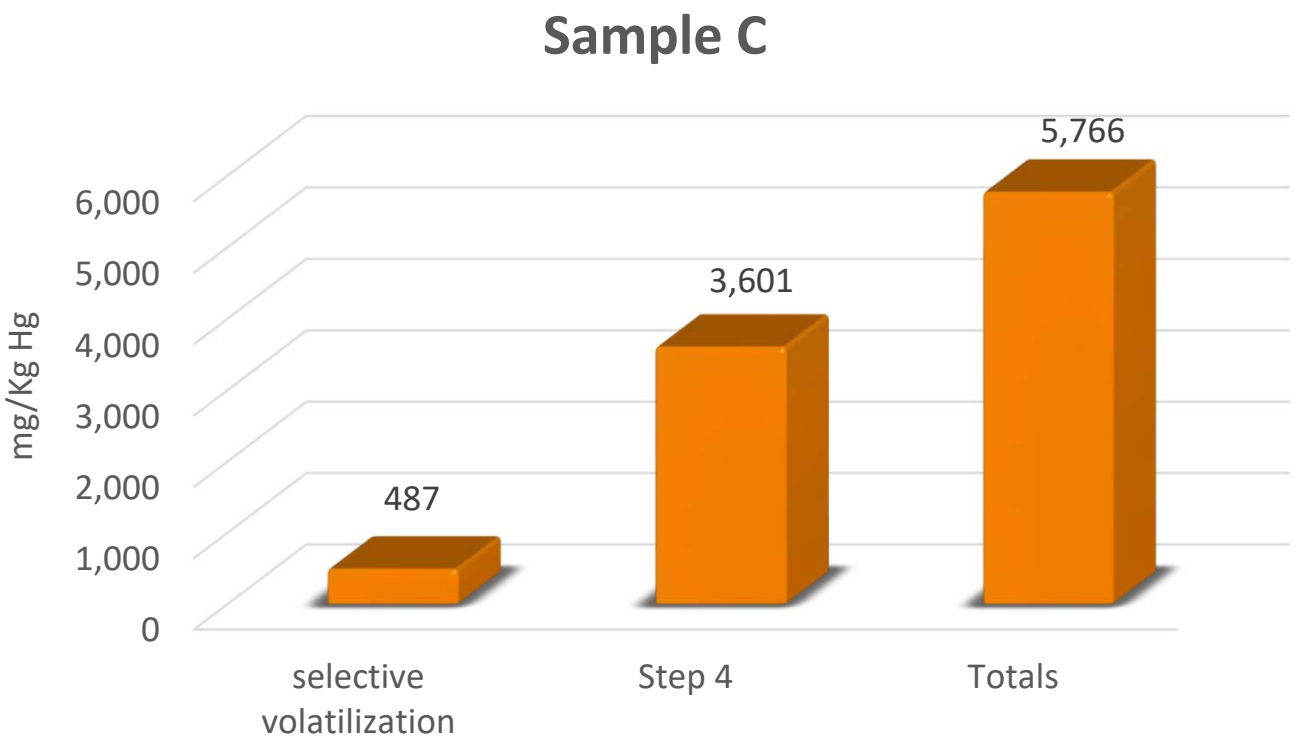
Soil samples from remediation sites



13.5% recovery compared to step 4

8.4% of mercury species likely elemental

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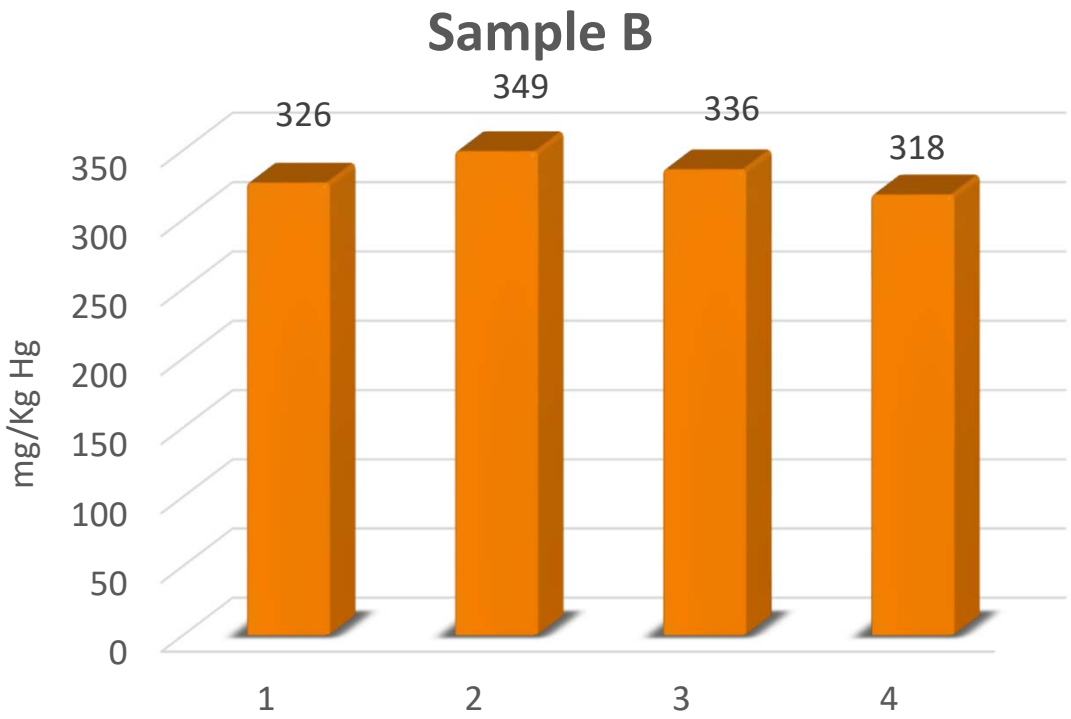
Reproducibility & Robustness



Average = 332 mg/Kg ± 13E mg/Kg

RSD = 4.0%

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Matrix spike test on sample B

Run	Sample result (pg)	Spike level Hg^0 (pg)	Sample + spike result (pg)	Recovery (%)
A	402	1047	1140	70.5
B	437	1031	1490	102.2

- Added Hg^0 reference material to sample B
- Gently mixed after vial sealed
- Good recovery but better reproducibility is desirable

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Conclusions

Conclusions:

- Good reproducibility seen in soil samples from actual remediation sites
- Apparatus is fully disposable and self contained, drastically reducing cross contamination risks
- Using selective volatilization we are able to separate elemental mercury selectively from HgS and $MeHg^{+}$
  - Good separation from Hg(II) species for dry samples
  - High bias to Hg^{0} results when samples are wet and contain significant concentrations of Hg(II) – research underway
- Method compares well to 5 step sequential extraction may be more selective than F4 for Hg^{0}

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Thank you and question slides

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Thank you for your time

Stephen Springer PhD

The Brooks applied team

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Questions?

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