Development of a More Robust Method for the Determination of Reactive Mercury [$Hg(II)_R$] in Sediment Samples

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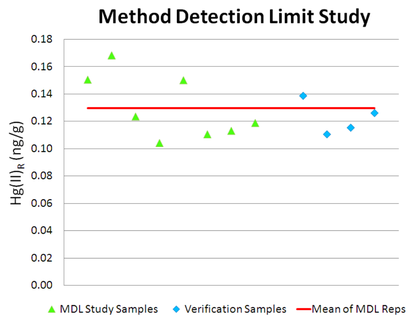
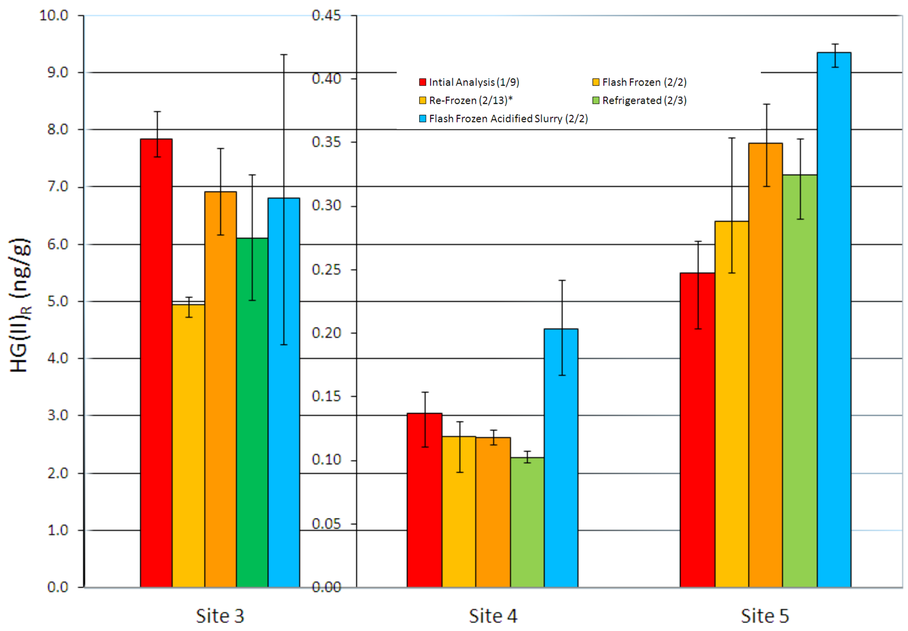
Summary

Reactive mercury [$Hg(II)_R$] is a variety of inorganic mercury complexes in the Hg(II) state. These less toxic inorganic mercury species are converted to monomethylmercury (MMHg) by biotic processes, most commonly by sulfur reducing bacteria (SRB).[1] Several factors affect the rate of MMHg production in an area, but one important factor is the amount of $Hg(II)_R$ available for methylation.[2] This study looks at storage and analytical techniques for reliably measuring the concentration of $Hg(II)_R$ in sediment samples.

The analysis technique for $Hg(II)_R$ used in this study was developed by Mark Marvin-DiPasquale.[3,4] The method involves the treatment of the sediment samples with a 0.5% (v/v) HCl solution, followed by reduction of the entire sediment slurry with stannous chloride. The volatile mercury species are purged from the slurry and concentrated on a gold sand trap before desorption to an atomic fluorescence detector. This analytical method has shown excellent accuracy and precision. Comparison between this method and other operationally-defined mercury speciation methods indicates good recoveries of inorganic mercury and no collection of non-target mercury species, including MMHg.



Graph 1: The graph shows the sample replicates used to calculate the method detection limit (MDL) and a verification of the results with a larger sample volume. The MDL was determined by taking the standard deviation multiplied by the student-t value (n = 8). An MDL of 0.070 ng/g was achieved.



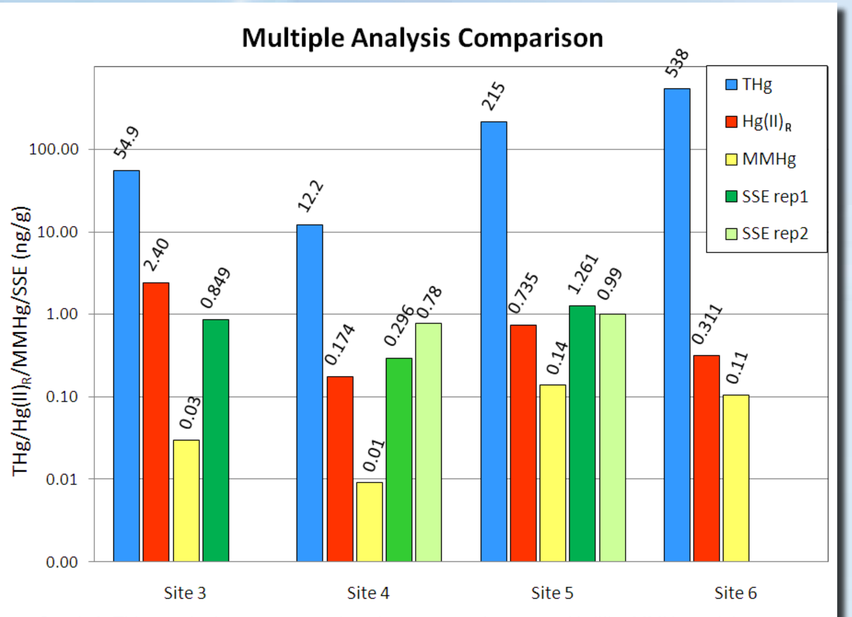
Graph 5: For the first collection dates, the initial analysis was performed without a full rinse of the sample container to remove the residual sediment. An additional collection and analysis was performed to confirm that the lost particulate matter did not cause significant low bias to the initial analysis. The results confirmed the previous storage analysis method procedures. For all further analyses, all sediment was thoroughly rinsed from the sample container.

Multiple Analysis Comparison

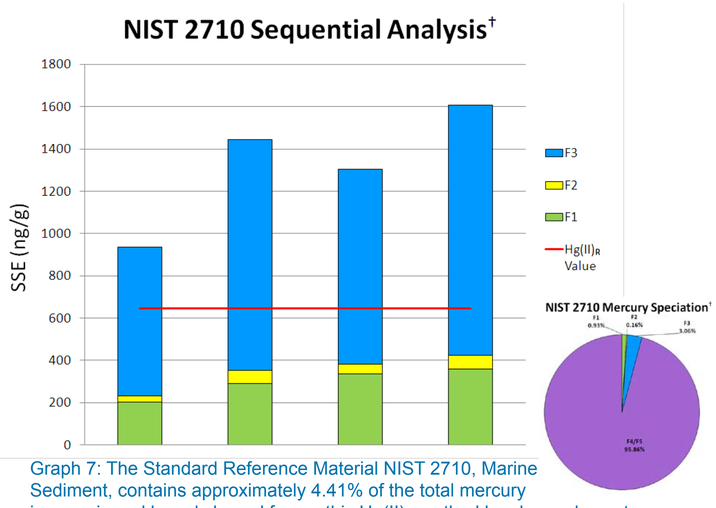
A series of comparisons were made between the $Hg(II)_R$ analysis and other speciation methods to confirm that the $Hg(II)_R$ method recovers all of the bioavailable mercury without recovering other species such as MMHg.

Comparisons are made to a five-step selective sequential extraction (SSE) procedure, which uses sequential reagent extractions to measure mercury species in solid samples.[5] Only the first three sequential steps are compared, as they include the inorganic and weakly-complexed mercury, the species in $Hg(II)_R$, as well as MMHg, which is not reactive.

Five replicates fortified with 500 pg MMHg were analyzed using the $Hg(II)_R$ method. Negligible recoveries were produced, demonstrating MMHg is not recovered in significant quantities by this analysis.

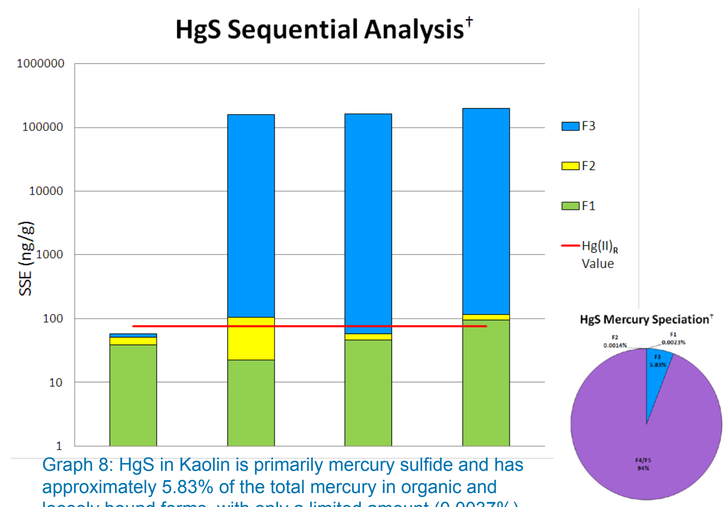


Graph 6: This graph shows a comparison between total mercury, $Hg(II)_R$, MMHg and the relevant SSE speciation results for mercury. The $Hg(II)_R$ concentration is most closely related to sum of the SSE steps 1-3, and appears to be unrelated to the amount of total mercury present in the samples. The results for the SSE fractions may be biased low because the total mercury results are low enough to allow re-absorption of the mercury to the sediment particles, as discussed in the initial SSE publication. *Please note: logarithmic scale.*



Graph 7: The Standard Reference Material NIST 2710, Marine Sediment, contains approximately 4.41% of the total mercury in organic and loosely bound forms; this $Hg(II)_R$ method has been shown to recover 2.73% of the total amount of mercury. The pie chart demonstrates the division of the total mercury content into all five sequential extraction fractions.

† Studio Geochimica Reference Material and certified results

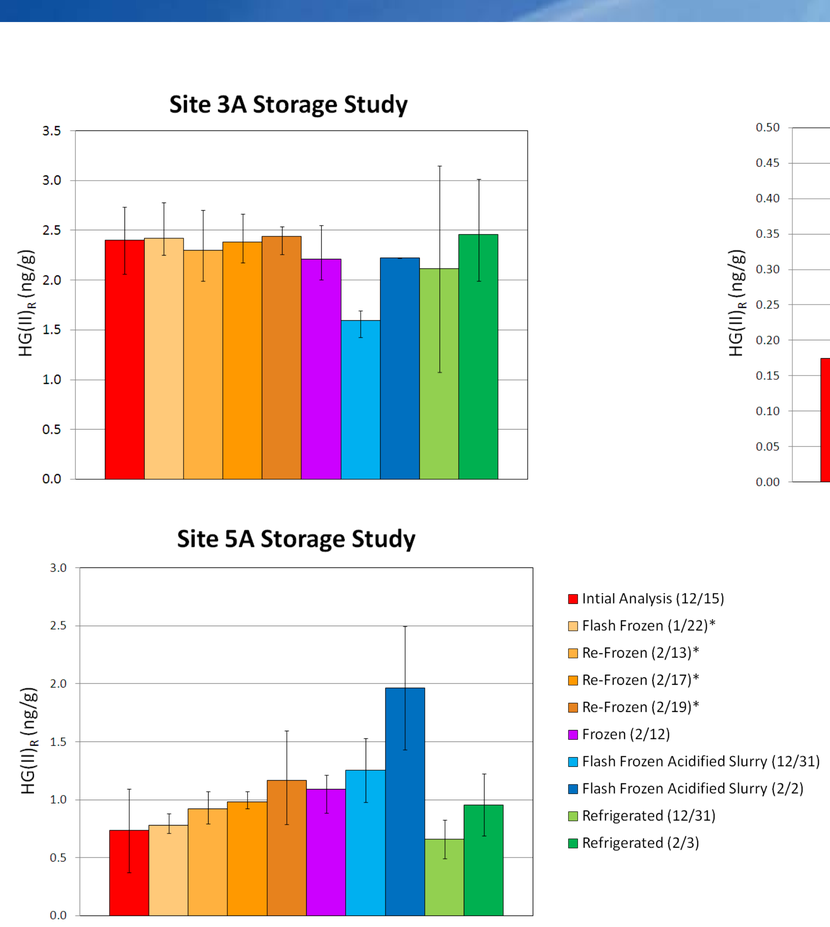


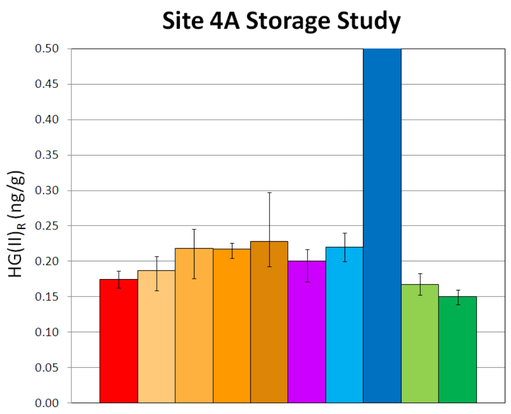
Graph 8: HgS in Kaolin is primarily mercury sulfide and has approximately 5.83% of the total mercury in organic and loosely bound forms, with only a limited amount (0.0037%) as weak acid leachable mercury. The $Hg(II)_R$ analysis recovered 0.0034% of the total mercury. The pie chart demonstrates the division of the total mercury content into all five sequential extraction fractions.

Storage Study

- *Initial* samples were aliquotted, mixed with 10 mL of 0.5% (v/v) anoxic HCl, and analyzed using stannous chloride within four hours of collection.
- *Refrigerated* samples were stored at 4 ± 2 ºC after collection.
- *Flash Frozen* samples were frozen using liquid nitrogen within 4 hours of collection. *After initial defrosting, *Flash Frozen* samples were not re-frozen with liquid nitrogen, but were instead placed in a freezer at -18 ºC and handled as frozen samples.
- *Frozen* samples were placed in a freezer at -18 ºC immediately following collection.
- *Flash Frozen Acidified Slurry* samples were divided into pre-weighed aliquots, mixed with 10 mL of 0.5% anoxic HCl, and flash frozen using liquid nitrogen.

Site	Sample Characteristics
Site 3	Even, coarse, black sand 60% Dark, fine silt 30% Fine and medium gravel 10% Small pieces of dark woody material in sample Moist; sample collected at or below the water line
Site 4	Even, light brown, medium grain sand 95% Fine light brown silt 5% Few roots and vegetation mixed in sample Damp; sample collected just above the waterline
Site 5	Light brown clay 60% Light brown fines 35% Sand 5% Slightly moist; no visible water

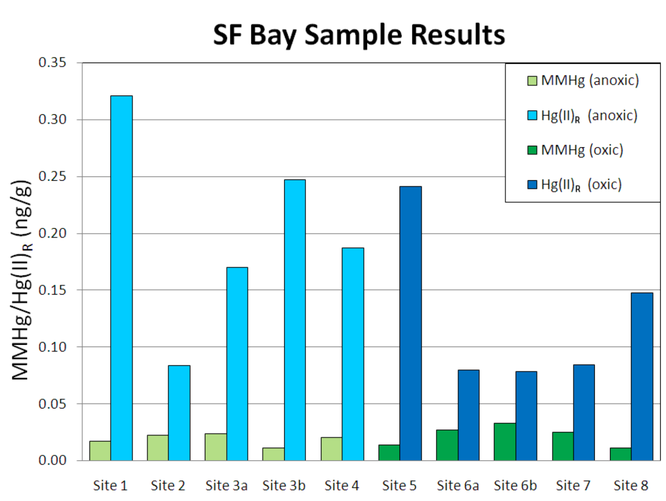




Graph 2-4: These graphs represent the concentrations of the samples following various storage methods. Both *Flash Frozen* and *Frozen* sample results compared well to the initial analysis results; there was no significant difference between the two storage methods. The *Flash Frozen Acidified Slurry* and *Refrigerated* samples showed too much variation over time for these methods to be appropriate for samples storage. An additional analysis showed no variation between *Frozen* samples and those stored at 4 ºC for 48 hours before freezing.

San Francisco Bay Samples

For this research project, the San Francisco Bay Estuary Institute (SFEI) generously collected and provided samples from both oxic and anoxic conditions. The samples were analyzed for MMHg, $Hg(II)_R$, and total mercury. The sample results showed very little variation for total mercury, with an average recovery of 40.2 ng/g (wet) and an RSD of 7.0%. The other concentrations were more varied, with slightly higher $Hg(II)_R$ in the oxic samples and slightly higher MMHg in the anoxic samples. This shift is not unexpected, as most methylation occurs under anoxic conditions by sulfur-reducing bacteria; however, more data is needed to draw a clear conclusion.



Graph 9: Reactive and MMHg results for oxic and anoxic sediments.

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References

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