ANOXIC SEDIMENT INCUBATIONS TO ASSESS THE METHYLATION POTENTIAL OF MERCURY CONTAMINATED SOLIDS

Nicolas Bloom and Eve Preus, Aquatic Geochemistry Group, Frontier Geosciences, Seattle Washington, USA.

ABSTRACT
Although Hg contamination enters the environment in an inorganic form, CH_3Hg is responsible for most of it's environmental risk. Because methylation usually occurs as a result of sulfur-reducing microbial activity, we developed an anoxic sediment bioassay to assess the relative bioavailability of Hg contaminated solids. Test solids were mixed with low Hg anoxic sediments, and incubated with constant agitation for 7 days at 20-23^oC, in sealed glass vials. CH_3Hg was analyzed by aqueous ethylation, and GC-CVAFS quantification. Over one week, the relative hierarchy of Hg compound bioavailability was as follows: $Hg(II)_{aq}$ > $Hg(II)_s$ > $HgSO_4$ > Hg^o >> *m*-HgS > HgS. When incubations were extended for 1 year, we found that methylation of the more reactive Hg species increased until all were equally bioavailable, while both HgS forms remained only slightly methylated.

RÉSUMÉ
Bien que la contamination par le Hg entre dans le milieu sous forme inorganique, le CH_3Hg est responsable de la plupart des ses risques environnementaux. Puisque la méthylation arrive habituellement comme conséquence d'une activité des microbes soufre-réduisants, nous avons développé un bioessai avec un sédiment anoxyque pour vérifier la biodisponibilité du Hg des solides contaminés. Des échantillons solides ont été mélangés avec des sédiments anoxyques à basse teneur en Hg et incubés dans des fioles en verre scellées, avec une agitation constante pendant 7 jours à 20-23°C. Le CH_3Hg a été analysé au moyen d'une éthylation aqueuse et d'une quantification par GC-CVAFS. Pour une incubation de plus d'une semaine, la hiérarchie relative de biodisponibilité du mercure a été la suivante: $Hg(II)_{aq}$>$Hg(II)_s$>$HgSO_4$>Hg^o>>*m*-HgS>HgS. Lorsque l'incubation a été étendue à un an, nous avons trouvé que la méthylation de l'espèce de Hg la plus réactive est augmentée jusqu'à ce que toutes les espèces soient également biodisponibles, tandis que les deux formes de HgS ont été faiblement méthylées.

1. INTRODUCTION

Mercury contamination typically enters the environment in an inorganic form, such as Hg(II) or Hg^o, but, because of it's greater toxicity, and the ability to bioaccumulate, CH_3Hg is responsible for most of the environmental risk (Davis, et. al, 1997). Thus, in assessing Hg contaminated sediments and soils, rather than focusing on the total Hg concentration present, it is important to understand the bioavailability of Hg with respect to methylation (Bloom, et. al, 2000; Bloom and Lasorsa, 1999; Barnett, et. al, 1995). Since most environmentally relevant Hg methylation occurs as a result of anaerobic microbial activities in sediments and wetlands (Gilmour, et. al, 1992), we sought to develop a simple sediment methylation bioassay to determine the relative bioavailability of Hg contaminated solids once they are introduced to the environment. To maximize the relative signal-to-noise ratio, contaminated site soils were mixed in a slurry with natural anoxic sediments which are low in total Hg and high in methylating capacity, and incubated with constant agitation for 7 days at room temperature, and then analyzed for CH_3Hg by solvent extraction, aqueous ethylation, and GC-CVAFS quantification (Bloom, et. al, 1997). Because the procedure only measures relative bioavailability, incubations are always performed with the same three control samples for comparison: unspiked, $HgCl_2$ spiked (maximum bioavailability), and HgS spiked (minimal bioavailability) sediment. We have recently used this incubation technique to assess the methylation potential of mine tailings (Bloom, et. al, 2000), residues from alumina extraction (Bloom, et. al, 2002b), and solid sludge from a wastewater treatment process. Estimated bioavailabilities were compared to inorganic Hg speciation determined using sequential selective extractions (Bloom, et. al, 2002), and found to correlate with either the F1 (water soluble) or F3 (KOH soluble) fractions.

2. EXPERIMENTAL METHODS

2.1 Incubation Protocol

Incubations were performed under anoxic conditions, in 40 mL or, in some cases, 250 mL borosilicate glass vials with Teflon lined caps. An amount of fresh sediment approximately equal to 10% solids when the vial was filled with water was weighed into each vial. Overlying water from the site where the incubation sediments was collected was used to dilute the slurries. For experiments conducted under strictly anoxic conditions, all steps in the procedure were carried out in a N_2 purged glove-box, while experiments requiring 'oxic' conditions were performed in the lab atmosphere until the vials were sealed, after which they rapidly became anoxic. All incubations were conducted at room temperature (19-23^oC) with continuous end-over-end rotation to keep the solids in suspension.

2.2 Incubation Sediments

Most incubations were carried out using 2 mm seived sediments from a cattail marsh in Greenlake (Seattle, WA). These sediments were selected because of thier low ambient total Hg concentration (about 100-200 ng/g dry

basis) and high total organic carbon content (60% loss on ignition, LOI). After exposure to air, once Greenlake sediments are sealed into an air-tight vial they rapidly (<24 hours) re-establish anoxic conditions due to thier high carbon content. Because these sediments are low in total Hg and are very microbiologically active, they generate a high methylation response per unit mass Hg(II) added, making them a very sensitive indicator of methylation potential. Usually these sediments were employed within a week of collection, unless the experiment aimed to investigate the effect of freezing or other storage conditions. For comparison with different sediment types, several experiments were conducted using low organic carbon (<1% LOI) sediments collected from Capay Dam on the lower Cache Creek (CA).

2.3 Test Samples and Controls

Incubations were spiked with pure Hg compounds or test solids immediately before sealing the vials for end-over-end rotation. Mercuric chloride ($HgCl_2$), the model compound for maximal bioavailability (Davis, et. al, 1997) was added in one of two ways: either as a direct injection of dissolved $HgCl_2$ in 0.5% HCl (only 2.5-25 μL of stock solution were added, so the matrix did not measurably change the pH or pCl of the incubated sediments), or by the addition of a pre-weighed quantity of kaolin which had been impregnated with approximately 2,600 μg/g of powdered $HgCl_2$ solid (Bloom, et. al, 2000). All other pure Hg compounds (HgS, *m*-HgS, Hg^o, etc.) were added as the finely divided solid suspended in kaolin. Contaminated site test solids, such as cinnabar mine tailings, were added as 100μ seived solids or slurries at thier ambient water content. These samples (except the gold mine tailings, a reference material in our lab) were not dried or ground, to avoid oxidation reactions which might increase thier bioaccessibility (Willett, et. al, 1992).

2.4 Analytical Protocols

To avoid cross contamination of the samples or the lab, samples were processed and analyzed using established ultra-trace clean sample handling procedures (Bloom, 1995). Samples were analyzed for total Hg after room temperature aqua regia digestion, $SnCl_2$ reduction, purge and trap on gold coated sand, and cold vapour atomic fluorescence spectrometry (CVAFS) (Bloom and Fitzgerald, 1988; Bloom and Crecelius, 1983). To avoid the positive artifacts observed when extracting CH_3Hg from sediments using distillation, sediments were extracted from an $HBr/CuSO_4$ solution into CH_2Cl_2, and back extracted into deionized water prior to analysis by aqueous phase ethylation, purge and trap onto Carbotrap, isothermal GC separation, and CVAFS quantification (Bloom, et. al, 1997). Sediments were always centrifuged and then extracted within 4 hours of the end of an incubation, or frozen immediately after centrifugation, at –20°C until they could be analyzed.

Inorganic solid phase Hg speciation was estimated using a 5-step sequential selective extraction (SSE) procedure designed specifically for Hg (Bloom, et. al, 2002; Bloom and Katon, 2000). In this SSE scheme, inorganic Hg is separated by its solubility into DI water (F1), pH 2 HCl/CH_3COOH (F2), 1N KOH (F3), 12N HNO_3 (F4), or aqua regia (F5). In previous studies, *in situ* CH_3Hg was found to be positively correlated with the F3 fraction, which measures the humic-bound Hg, and inversely correlated with the F5 fraction, which represents the sum of HgS, *m*-HgS, and other recalcitrant Hg species, if present (Bloom and Katon, 2000). All Hg concentrations are reported on a dry weight basis, calculated from the measured wet samples and an independent determination of the percent moisture (weight loss at 105°C).

3. RESULTS AND DISCUSSION

It was necessary to investigate the sensitivity of the incubation procedure to a variety of experimental conditions, including sample handling protocols, Hg concentration, incubation time, and type of receiving sediment (bioactivity) before the procedure could be reliably used. The percentage of Hg methylated was particularly sensitive, in complex and interactive ways, to the Hg concentration, amount of organic matter in the receiving sediment, and incubation time. These findings ultimately mandate that the incubation experiment must be carefully designed such that all the above mentioned parameters are held constant if it is to be successfully used as a comparative tool for ranking the Hg bioavailability of different soils. Similarly, if the incubation is used to rank the relative methylation potential of various receiving sediments within an ecosystem, then the Hg concentration and species added must be uniform.

3.1 Effect of Hg Concentration

The concentration of bioavailable Hg in the incubation was found to have a particularly strong effect on the percentage of Hg methylated (Figure 1). At low Hg concentrations (typically less than 3-5 μg/g) the fraction of Hg methylated is highest and relatively constant. As the concentration of Hg increases, the absolute concentration of CH_3Hg continues to increase, sometimes to surprisingly high levels (over 1,000 ng/g), but at a diminishing rate compared to the increase in added Hg(II). This results in a dramatic decrease in the percentage of Hg in the methylated form, similar to the general relationship seen amongst ambient sediment samples (Figure 2).

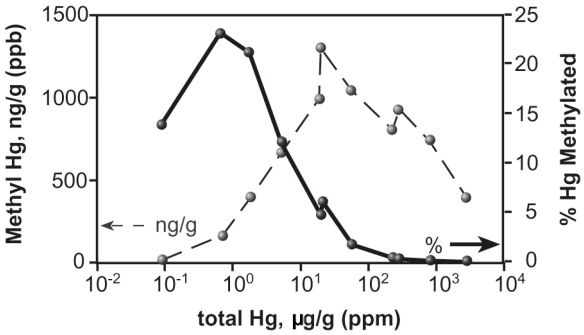

Figure 1. Relationship between concentration of methyl Hg (light) in $HgCl_2$ spiked Greenlake sediment and the percent methylated (dark) after a 7-day anoxic incubation.

The decrease in the fraction methylated could be due to saturation of the microbial community's ability to methylate Hg. Alternatively, at high levels of inorganic Hg, there may be enough to form a stable solid such as cinnabar, effectively taking it out of the pool available for methylation. This idea has not been supported, however, in lab experiments by the observation of a dramatic increase in F5 (aqua regia) soluble Hg as the percentage CH_3Hg decreases. As the added Hg(II) levels increase even more, the absolute concentration of CH_3Hg begins to decrease, reducing the fraction of Hg in the methylated form even more dramatically, possibly due to toxic effects on the microbial community.

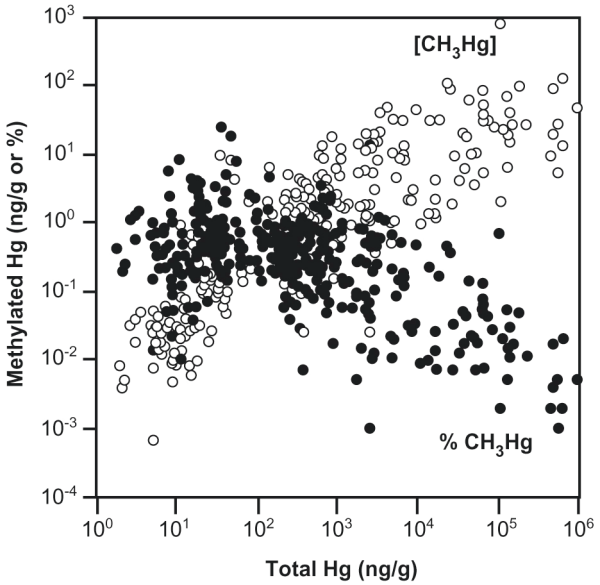

Figure 2. Relationship between methyl Hg concentration (open) and percent methylated (closed) in 365 opportunistically collected surficial sediment samples.

3.2 Effect of Sediment Type

It is well understood that sediment type has a profound effect on the fraction of Hg in the methylated form (Bloom, et. al, 1999). This difference is essentially due to the degree of sulfur reducing bacterial activity in the sediment (Gilmour, et. al, 1992), which is in turn determined by the levels of organic carbon and sulfate which sustain these bacterial populations. To gauge the impact of substrate sediment type on the degree of methylation during 7 day anoxic incubations, we spiked three types of sediment (sandy open water sediment from Greenlake, organic rich marsh sediment from Greenlake, and sandy marine sediment from Puget Sound) with $HgCl_2$, HgS (red cinnabar), and Hg contained in gold mine tailings. Selective extraction profiling indicates that these tailings contain approximately 70% cinnabar and 30% more soluble compounds. The type of receiving sediment was found to have a profound effect on the degree of methylation (Figure 3), especially with respect to the $HgCl_2$ and mine tailings. Even though more HgS was methylated in the organic-rich sediment, the absolute level of methylation was still very low.

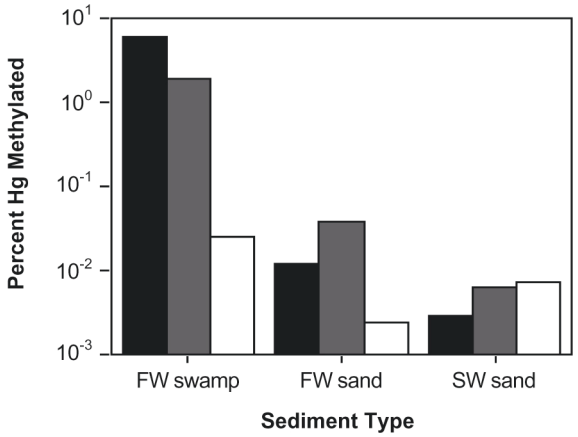

Figure 3. Methylation of solid substrates in three different sediment types. Black bars are $HgCl_2$, grey are gold mine tailings, and white are HgS.

3.3 Effect of Hg Species Added

We investigated the degree to which the chemical form of Hg affected methylation. Several compounds and physical forms of Hg were incubated with anoxic sediments from Capay Dam, a low-organic carbon (<1% LOI) and mildly Hg contaminated impoundment located down stream of Cache Creek, in the Coast Range of California. The ambient sediments behind this dam showed a rather high *in situ* level of Hg methylation (2.4% of THg), making it difficult to see low-level methylation of some spiked Hg compounds. We found negligible methylation of Hg in the form of cinnabar, meta-cinnabar, or Hg^o amalgamated with micron-sized gold dust (Table 1). In fact, the addition of the gold dust appeared to diminish methylation to below the unspiked levels, perhaps by amalgamating labile Hg species in solution, and so removing them from the pool available for methylation.

Table 1. Methylation of Hg compounds by anoxic Capay Dam Sediments. Except aq-$HgCl_2$, all species were suspended in kaolin (mean of 2 incubations each).

Added Hg Species	[Hg] ng/g	[MHg] ng/g	Net %-MHg
control	407	9.9	2.43
Hg(II)/goethite	1,345	111	10.82
aq-$HgCl_2$	2,625	122	5.07
$HgCl_2$	2,162	66.3	3.22
$HgSO_4$	1,314	33.8	2.62
Hg^o	844	18.2	1.91
HgS	1,287	10.0	0.02
m-HgS	843	9.9	0.02
Hg/Au	1,667	7.6	-0.18

The more biologically available Hg compounds ($HgCl_2$, $HgSO_4$, and Hg^o) all showed levels of methylation similar to the ambient Hg (2-3%), when suspended in kaolin clay, but

$HgCl_2$ was twice as available when added as an aqueous solution, and four times as available when added pre-adsorbed to synthetic goethite (*am*-FeOOH). We speculate that although Hg(II) added directly to the sediment is initially maximally bioavailable, it is also rapidly complexed by organic matter and sulfides which may diminish it's long term bioavailability. Hg(II) adsorbed to iron hydroxide, on the other hand, may be released more slowly over time, as the Fe(III) hydroxide is reduced to soluble Fe(II), hence providing a sustained dose of Hg(II) to the microorganisms over the length of the experiment.

3.4 Effect of Sample Handling and Incubation Time

Because sediment collection under anoxic conditions and immediate use of natural sediments for incubations can be inconvenient for routine application, experiments were undertaken to compare the methylation rates of fresh sediments collected under rigorously anoxic conditions to the same sediments after an initial exposure to oxygen (by stirring vigorously in an open bowl in ambient air), and anoxic sediments which were frozen at –20°C for a week prior to thawing, spiking and the start of incubation. The receiving sediment, from a small unnamed fresh water marsh (Kingston, WA) had a mean total Hg concentration of 192±24 ng/g (dry weight basis), and was spiked with on average 3,280 ± 476 ng/g added as dissolved $HgCl_2$. Each incubation condition was set up in 15 replicate 40 mL vials. At various time periods up to three weeks, three vials from each test condition were randomly selected for analysis of Hg and CH_3Hg.

This set of results (Figure 4) indicated that rigorously anoxic and oxygen impacted sediments behaved rather similarly over the course of the experiment, achieving a peak level of methyl Hg production of about 10% after one week, and then dropping steadily thereafter. The sediment that had been frozen reached a peak of only about 6% methylated, and that peak occurred a few days later than the peaks for the unfrozen sediments. Over the three week period, the unspiked control sediment slowly decreased in the fraction methylated from about 8% to 3.5%, with small fluctuations probably resulting from analytical variability. Although the frozen sediments never methylated Hg to the same levels as the fresh sediments, all of the handling conditions resulted in very high methylation rates, suggesting that if the incubation is applied as comparative tool (i.e., where test samples are compared to "maximal" Hg methylation of Hg(II) spikes), then the use of previously collected and frozen sediments is an acceptable choice. It also appears as though the selection of a seven-day incubation time was appropriate, resulting in the highest signal-to-noise ratio.

In a related experiment, we compared two other sediments, one an organic-rich marine sediment from the Nisqually River Delta (Puget Sound, WA), and the other a low organic carbon silty lacustrine sediment (Lake Sammamish, WA), under similar conditions, except that all samples were incubated for only 7 days. This experiment generally supported the previous time course study, with the additional observation that the low TOC sediment seemed to be much more sensitive to oxygen pre-exposure. Results from this sediment fluctuated wildly, generally, but not always, yielding diminished methylation in the oxygen exposed samples. This suggests that highly organic sediments have a stronger "reductive buffering capacity" that enables them to be handled with less caution prior to incubation and yet still give results which mimic the sediments handled anoxically. Because highly organic sediments also show the strongest methylating potential they should be used in cases where relative methylatability information is required.

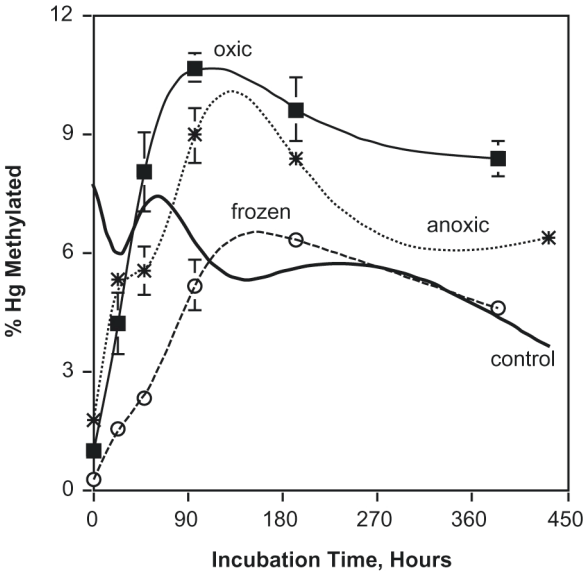

Figure 4. Time course incubation of spiked Greenlake sediment under various treatment conditions. Control sediment was anoxic at all times. Each point is the mean ± SD of three incubations.

3.5 Bioavailability of Contaminated Soils

The anoxic incubation assay was evaluated with real-world samples using Hg-contaminated samples from historic cinnabar mines that operated during the gold rush (1848-1912). Sieved (100μ) tailings from three of the biggest mine sites in the upper Cache Creek watershed (the Abbott, Manzanita, and Turkey Run mines), as well as the suspended iron-sulfide floc from a natural geothermal vent ("Jones Fountain of Life") were incubated with both Capay Dam (low organic carbon) and Greenlake swamp (high organic carbon) sediments. These samples were incubated in the same set, under exactly the same conditions as the pure substances reported in Table 1.

All test samples showed extremely low methylation in both the Capay Dam (Table 2) and Greenlake Swamp incubations (Table 3), despite the fact that these incubations are set up to maximize the potential observable methylation. In all except the case of Abbott Mine tailings incubated in Greenlake sediments, the methylation of the mine site materials were about 2-5 times the degree observed for pure cinnabar, but 50-200 times less than the methylation of $HgCl_2$. Abbot Mine tailings were somewhat more strongly

methylated in the Greenlake sediment, possibly a result either of sample inhomogeneity or analytical variability, given that all of the observed net methylation rates were just a small fraction of the *in situ* control methylation percentage. This is consistent with previous SSE data that showed >99% of the Hg contained in these materials was in the F5 ("cinnabar") fraction.

As part of a field study of *in situ* methyl Hg levels in the upper Cache Creek, we had observed considerably higher levels of methylation (0.3-2.3%) in the sediments directly impacted by Abbott Mine. Although the geochemical processes at the site have not yet been investigated, we suspect that the higher methylation is due to inputs of dissolved mercury and sulfate as the result of weathering and run-off from the tailings heaps, in addition to the large quantities of relatively inert particulate HgS. The ambient sediments from these creeks contained 4-80 μg/g Hg, mostly in the F5 fraction.

Table 2. Methylation of Hg in cinnabar minesite materials by anoxic Capay Dam sediment. Net methylation is just that of the added material.

Added Hg Species	[Hg] ng/g	[MHg] ng/g	Net %-MHg
control	407	9.9	2.43
Jones FOL	1,427	11.6	0.18
Abbott Mine	2,039	12.6	0.17
Manzanita	1,234	10.7	0.11
Turkey Run	1,488	10.1	0.03

Table 3. Methylation of Hg in cinnabar minesite materials by anoxic Greenlake swamp sediments. Net methylation is just that of the added material.

Added Hg Species	[Hg] ng/g	[MHg] ng/g	Net %-MHg
control	193	31.1	16.2
Jones FOL	2,122	34.4	0.16
Abbott Mine	1,187	41.4	0.98
Turkey Run	1,749	32.0	0.04
aq-$HgCl_2$	2,462	267	10.4
HgS	968	31.7	0.05

3.6 Speciation Shifts Observed in Long-Term Incubations

Concurrent to the development of the simple anoxic incubation assay described above, we also conducted a one year long microcosm study in which pure Hg compounds and mine tailings from a Sierra (CA) gold mine were incubated in 4-litre beakers. These microcosms were somewhat more realistic than the incubations. They consisted of a layer of Greenlake sediments settled in lake-water, and were exposed to the normal outdoor lighting and temperature conditions of Seattle over a one year period. The sediments were thus oxic at the surface, although based upon sediment color, they appeared to become anoxic within the first 2 mm of sediment depth.

At each sampling interval, the entire contents of the beakers were thoroughly homogenized, sub-sampled, and then allowed to settle again. Midway through the experiment, additional organic carbon (1 gram of powdered dried leaves) and sulfate (10 ppm as $MgSO_4$) were added to each beaker. The Hg spiking levels were about 50-100 μg/g total Hg (dry weight basis), which is much higher than the values which gave maximal methylation (Figure 1), but not unlike the concentrations found in the sediments of ambient streams of the upper Cache Creek watershed.

The results of this long term microcosm study present an interesting contrast to the incubation studies, and may indicate the behavior of mine-site solids when they are discharged into the ambient environment (Figure 5). As expected, initially the $HgCl_2$ was most strongly methylated. As time passed, methylation of both the Hg^o and gold mine tailings increased, until, by the end of a year, all three of these added forms showed about the same high methylation percentage (3-5%) as the ambient sediments. This was surprising, given the inverse Hg concentration versus methylation dependence observed earlier (Figures 1 and 2). By the end of the experiment, these spiked sediments contained far higher high absolute concentrations of methyl Hg (up to 5,800 ng/g) than we have ever observed in nature. The much higher degree of methylation of the gold mine tailings in this experiment is supported at least partially by the SSE speciation, which showed only 70% of the Hg to be in the F5 ("cinnabar") before incubation (Table 4), leaving a significant pool of Hg from that spike available for methylation.

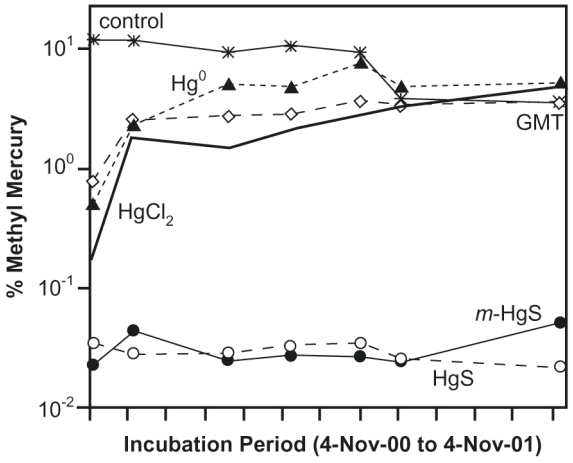

Figure 5. Change in Hg Speciation during one-year sediment microcosm incubations, after spiking with various Hg species (GMT is gold mine tailings).

By contrast, both HgS and *m*-HgS were only very slightly methylated over the entire course of the experiment (0.03-0.06%), with the most methylation occurring early. One explanation is that initially, traces of a more soluble oxidation product ($HgSO_4$ perhaps) contained on the cinnabar powder was methylated, and virtually none of the HgS compounds themselves were methylated. Curiously,

while the SSE speciation of the HgS spiked sediments showed 93% in the F5 fraction, only 51% of the *m*-HgS was found in the F5 fraction at the end of 1 year. By this time, 38% of Hg in the *m*-HgS spiked beaker was observed in the F3 ("organo-complexed") fraction, and yet the percentage of Hg that was methylated was still very small (about 0.06%, compared to 0.03% in the HgS spiked beaker).

By the time a year had passed, the SSE-based Hg speciation patterns of more labile species had been substantially altered from the initial patters expected for $HgCl_2$ (F1 predominance) or Hg^o (F4 predominance), to the same general distribution as the initial sediment matrix (F3 predominance). Mercury in the gold mine tailings was largely converted to the F3 form by the end of the experiment, with a significant amount still in the less bioavailable F4 and F5 fractions. The fact that 70% of this material was in the F5 fraction at the beginning of the experiment and only 18% at the end further suggests that the HgS in this material was largely present as metacinnabar. This finding was borne out by EXAFS evaluation of the Hg speciation in the materials from this mine site (Bloom and Katon, 2000).

Table 4. Change in inorganic speciation in sediments from the one-year sediment microcosm incubation (GMT is gold mine tailings).

	% of Hg in each fraction				
sample	F1	F2	F3	F4	F5
control	0.4	0.0	87.6	8.7	5.2
HgS, t-0	0.00	0.00	0.00	0.13	99.9
HgS, t-365	0.01	0.00	1.1	6.2	92.7
*m*HgS, t-0	0.00	0.00	0.00	0.13	99.9
*m*HgS, t-365	0.00	0.00	37.8	11.6	50.6
Hg^o, t-0	0.04	0.12	0.23	96.9	2.70
Hg^o, t-365	0.23	0.00	80.2	17.0	2.50
Hg(II), t-0	96.5	3.2	0.17	0.09	0.03
Hg(II), t-365	0.74	0.01	88.8	9.7	0.70
GMT, t-0	2.45	3.29	1.21	23.2	69.7
GMT, t-365	0.33	0.01	64.8	18.9	16.1

4. CONCLUSIONS

At low total Hg concentrations (<5 μg/g) the percentage of added Hg(II) methylated is highest, and relatively constant, but the percentage then decreases rapidly at higher total Hg concentrations, even as the absolute concentration of MHg continues to increase. This concentration dependence mandates that all incubations contain about the same total Hg concentration, chosen to be either in the low, linear response range, or at a level equivalent to the observed site concentrations. Over the one week incubation time, the relative hierarchy of Hg compound bioavailability is as follows: $Hg(II)_{aq}$ > $Hg(II)_s$ > $HgSO_4$ > Hg^o >> *m*-HgS > HgS. When incubations are extended for a very long time period (up to 1 year), we have found that methylation of the labile Hg species increases until all are equally bioavailable, and quite similar to the control sediment, while the mercuric sulfide forms remain only slightly methylated, and do not increase measurably in bioavailability over time.

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