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Bacterial Mercury Methylation at the Sediment-Water Interface of Mercury Contaminated Sediments

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Abstract

Bench scale experiments were conducted to improve our understanding of bacterial mediation of mercury transformation (methylation), specifically those factors which govern the production of methyl mercury (MeHg) at the sediment-water interface. The greatest cause for concern regarding mercury contamination is bioaccumulation into higher trophic levels in aquatic food webs, from bacteria to plankton, micro- and macro-invertebrates, and ultimately to herbivorous and piscivorous fish. The dominant form of mercury in the fatty tissue of fish is MeHg, a potent mammalian neurotoxin even at very low concentrations. MeHg is formed mainly in suboxic and anoxic sediments by the interaction of inorganic Hg with organic matter and microorganisms. The conversion of Hg to MeHg is widely accepted to be governed by the action of sulfate reducing bacteria (SRB), which enzymatically catalyze the methylation of inorganic Hg. The exact mechanism of methylation is not known, but it is believed that during heterotrophic organic carbon metabolism, passive uptake of inorganic Hg occurs through the cell membrane of methylating bacteria. Due to the lack of information regarding the sedimentary biogeochemical conditions which promote mercury methylation, microcosm incubation studies were conducted to investigate the transformation of Hg to MeHg and the factors that affect MeHg production.

Microcosm incubations using lake-sediments were designed to examine the influence of (1) an organic carbon amendment (as lactate) and (2) sulfate on the observed ORP and MeHg production. Sediments used in this study were obtained from a site known to be impacted by mercury contamination. Incubations were analyzed for both the rate and extent of MeHg production. Methylation rates were estimated by analyzing MeHg and Hg after 48 hrs, 7 d, 10 d,14 d, 28 d, and 42 d. The production of dissolved gases as a proxy for metabolic utilization of carbon substrate was also monitored. In all treatments amended with sulfate and SRB, MeHg (97 ng/g-sediment dry weight (DW)) was produced after only 48 hrs of incubation. MeHg concentrations then increased to122 ng/g-sediment DW at day 28 of the incubation. The concentration of sedimentary MeHg however declined after 28 d to 110 ng/g-sediment DW.

Experimental Approach

Methyl mercury production was monitored under controlled incubations

- Variable sulfate concentrations
- Variable lactate concentrations
- With and without mercury spike
- With and without addition of SRB
- Incubations for a 42 day period
- Time points Day 0, 2, 7, 10, 14, 28, 42

Incubations were prepared as:

- 10 g dry weight sediment
- 100 mL final volume of solution
- Mercury spike 15 mg/L final concentration
- SRB (*Desulfovibrio desulfuricans*)
- Lactate Addition (0, 250 mg/L, 1000 mg/L)
- Sulfate Addition (0, 50 mg/L, 192 mg/L)

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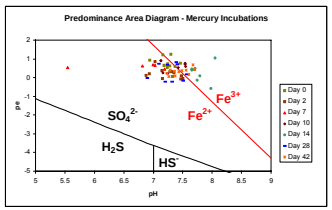
Sediment and Incubation Geochemical Characteristics

Contaminated Sediments: Initial Conditions

Metals (Total)	(mg/kg – dry weight)
Mercury	39.9
Arsenic	7.46
Barium	147
Cadmium	0.571
Chromium	41.4
Lead	21.1
Selenium	9.05
Silver	Below Detection
Methyl Mercury	5.22 µg/kg

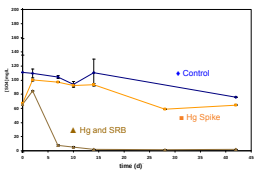
Anions (Dissolved)	(mg/L)
Chloride	105
Sulfate	202

Sediments contain elevated sulfate, relative to typical unaffected freshwater sediments.

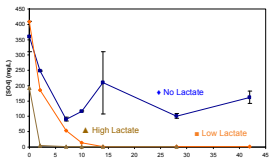


Although sulfate reducing conditions are expected, Fe(II)/Fe(III) is the apparent dominant redox couple

Microbial Sulfate Reduction



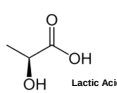
- Controls without added mercury or SRB exhibit relatively slow sulfate reduction kinetics
- Sulfate is reduced to negligible levels after 1 week in presence of SRB



- Even high concentrations of sulfate are rapidly reduced in lactate amended microcosms
- Sulfate reduction is promoted by available carbon substrate

Organic Acids – Metabolic Fuel for SRB and Methanogens

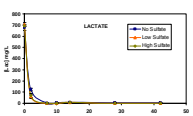
- SRB use lactate, transforming it first to acetate and eventually to CO_2
- With excess lactate, other fermenters (methanogens) can compete, producing propionate
- SRB, which produce MeHg, can use propionate, but not as efficiently as lactate or acetate

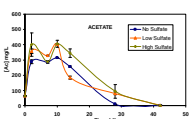


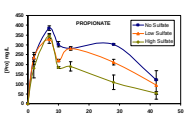
Lactic Acid

Acetic Acid

Propionic Acid



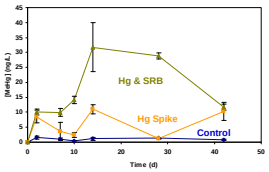




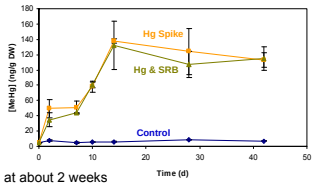
- Even with high lactate addition, all lactate is consumed within 5 days
- Acetate is produced initially, and consumed by day 42
- Propionate persists throughout incubation, evidence for competition by methanogens

Microcosm Methyl Mercury Production

Aqueous Methyl Mercury

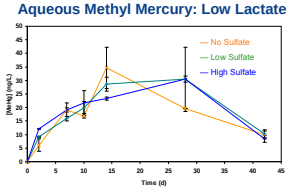


Sediment Methyl Mercury

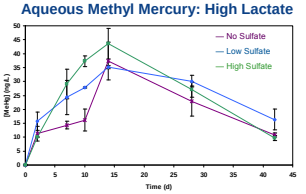


- MeHg production reaches a maximum concentration at about 2 weeks
- Depletion of sulfate and competition by methanogens most likely limit overall Hg methylation by SRBs

Aqueous Methyl Mercury: Low Lactate

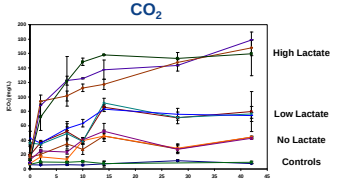


Aqueous Methyl Mercury: High Lactate

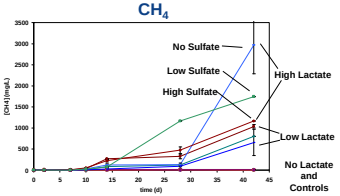


Production of Dissolved Gasses – Carbon Dioxide and Methane

CO_2



CH_4



- Carbon dioxide is produced proportionate to lactate addition as SRB convert it to acetate and CO_2
- Maximum methane concentrations were observed in incubations with high lactate and no sulfate; competition from methanogens for available metabolic resources

Summary and Conclusions

- The results of this study demonstrate that in the presence of an organic carbon substrate, sulfate and the appropriate consortia of microorganisms, sedimentary mercury will be transformed into MeHg.
- SRB methylation is limited by depletion of sulfate and carbon, and appear to be sensitive to competition by methanogens for carbon substrate
- These studies offer valuable insight into potential remediation strategies to specifically limit MeHg production, and also the ability to make predictive estimates for the production of MeHg from areas of mercury contamination depending upon the biogeochemical condition of the sediments and sediment pore-waters.