

Importance of photo-demethylation in controlling methylmercury in the Great Salt Lake and surrounding wetlands



Frank Black
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Acknowledgements: Westminster Undergraduates



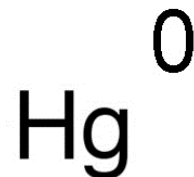
Josh Schmidt



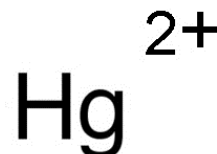
Chris Mansfield

The various forms of Hg differ in their cycling and toxicity

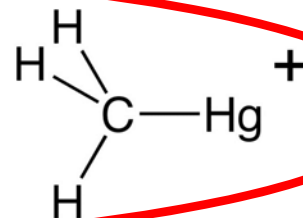
– Elemental mercury - Hg(0)



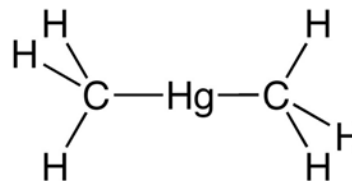
– Inorganic mercury - Hg(II)



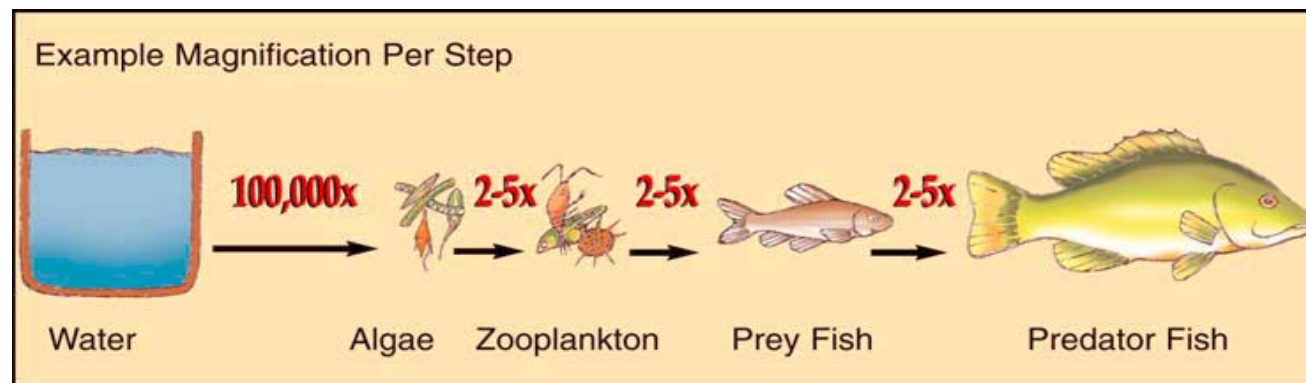
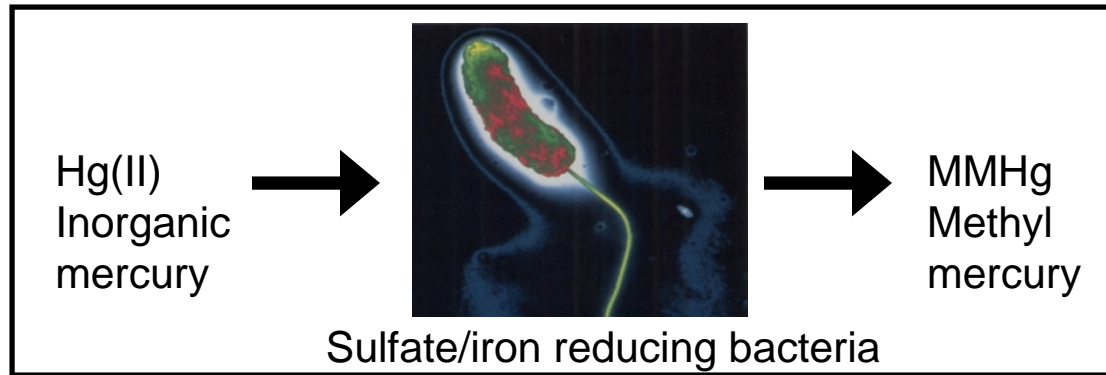
– Monomethylmercury - MMHg



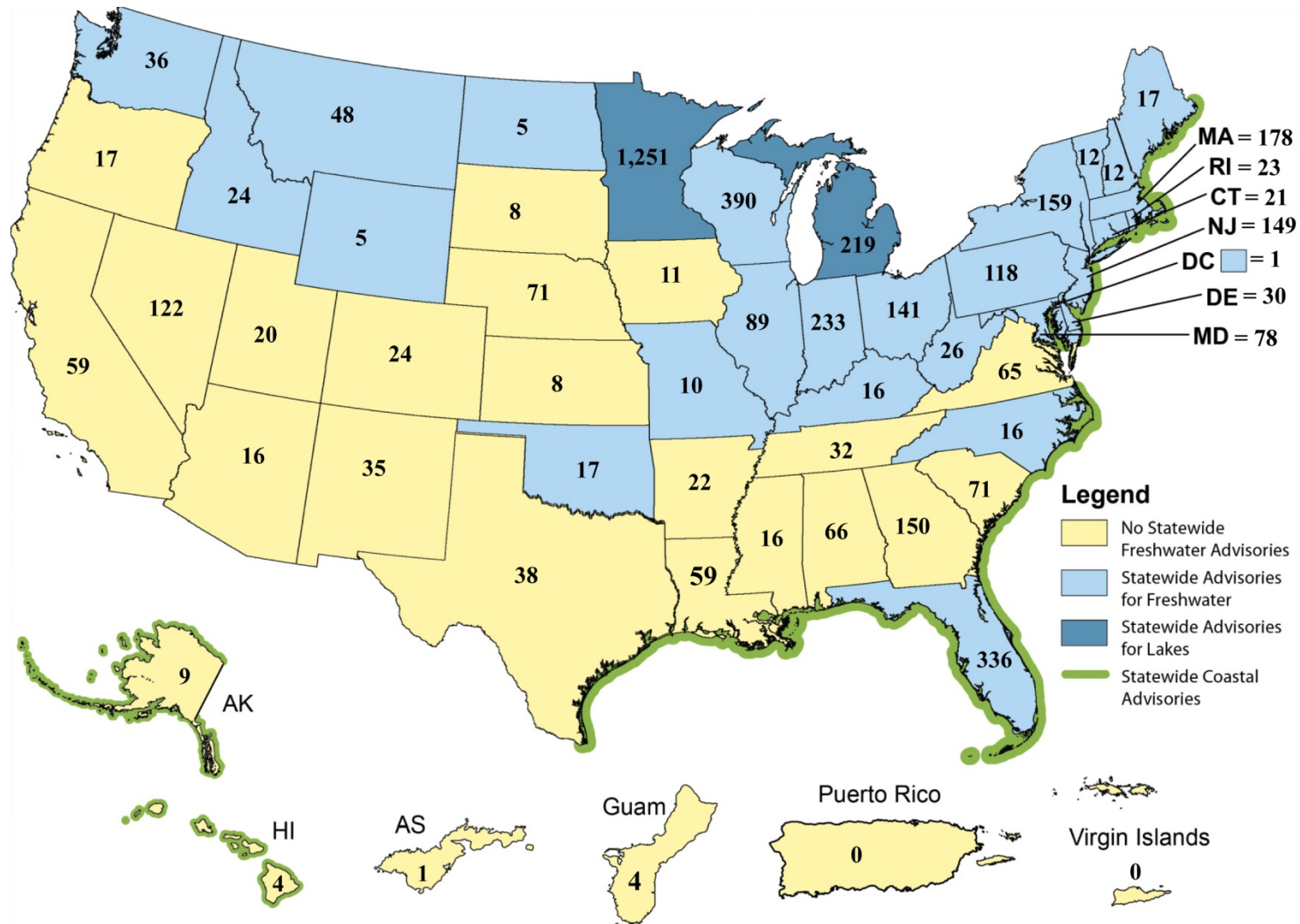
– Dimethylmercury - DMHg



Methylation and biomagnification of mercury

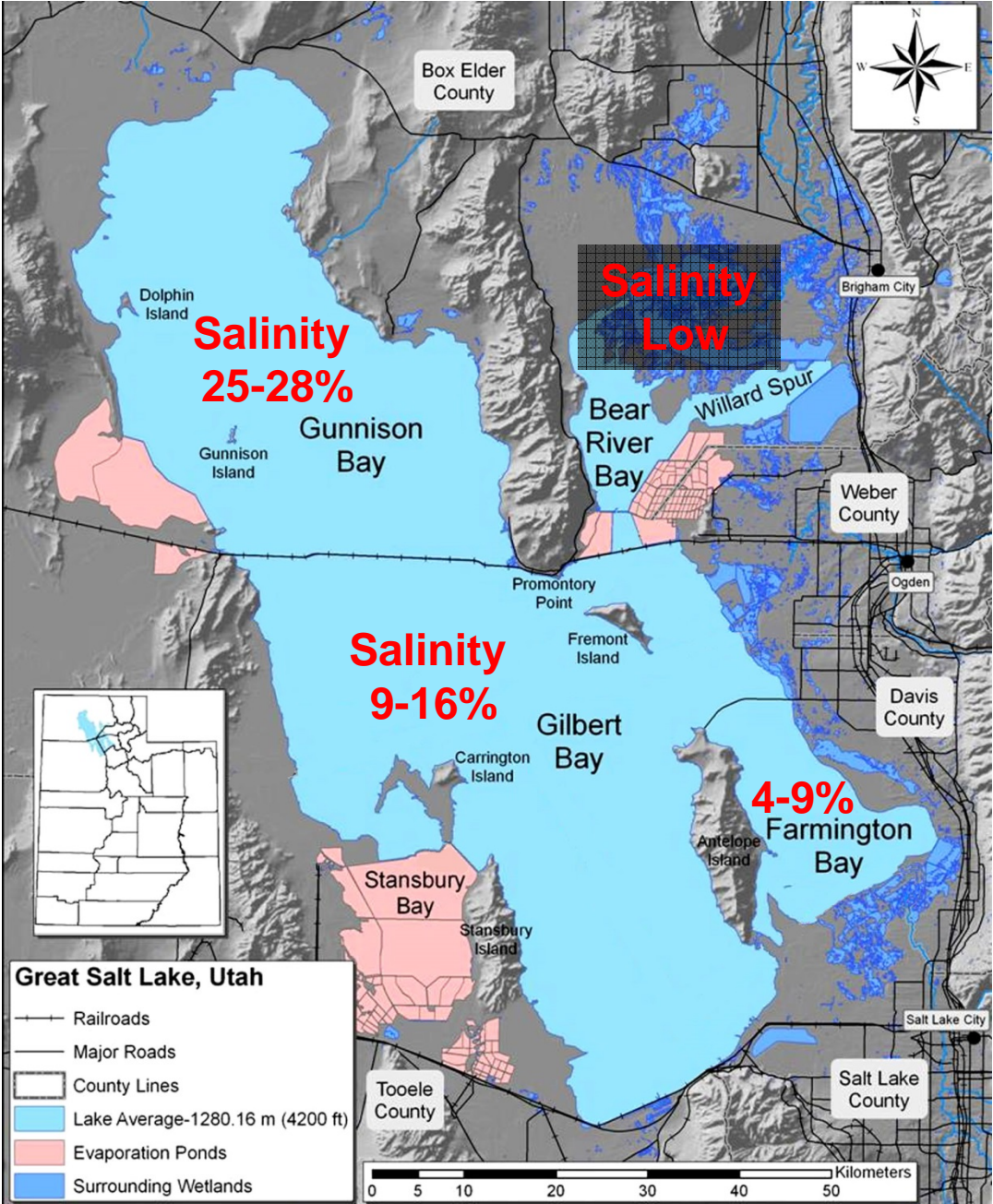


Fish consumptions advisories nationwide



In 2010: 4,598 fish consumption advisories issued, 81% due to Hg. Covers 42% of US lake acreage, 36% of river miles, 42% of coastal waters.

But most of the Great Salt Lake is hypersaline and doesn't have fish



Pathways for Hg exposure from the GSL



Fun facts about mercury at the Great Salt Lake (GSL)

- Highest concentrations of MMHg ever measured in natural waters were in the Deep Brine Layer of the GSL (Naftz et al., 2008; Johnston et al., 2015)
- Highest concentrations of MMHg ever measured in oxic natural waters were in surface waters of the GSL (Black et al., unpublished data; Johnston et al., 2015)
- GLS has the only duck consumption advisory for Hg in the world

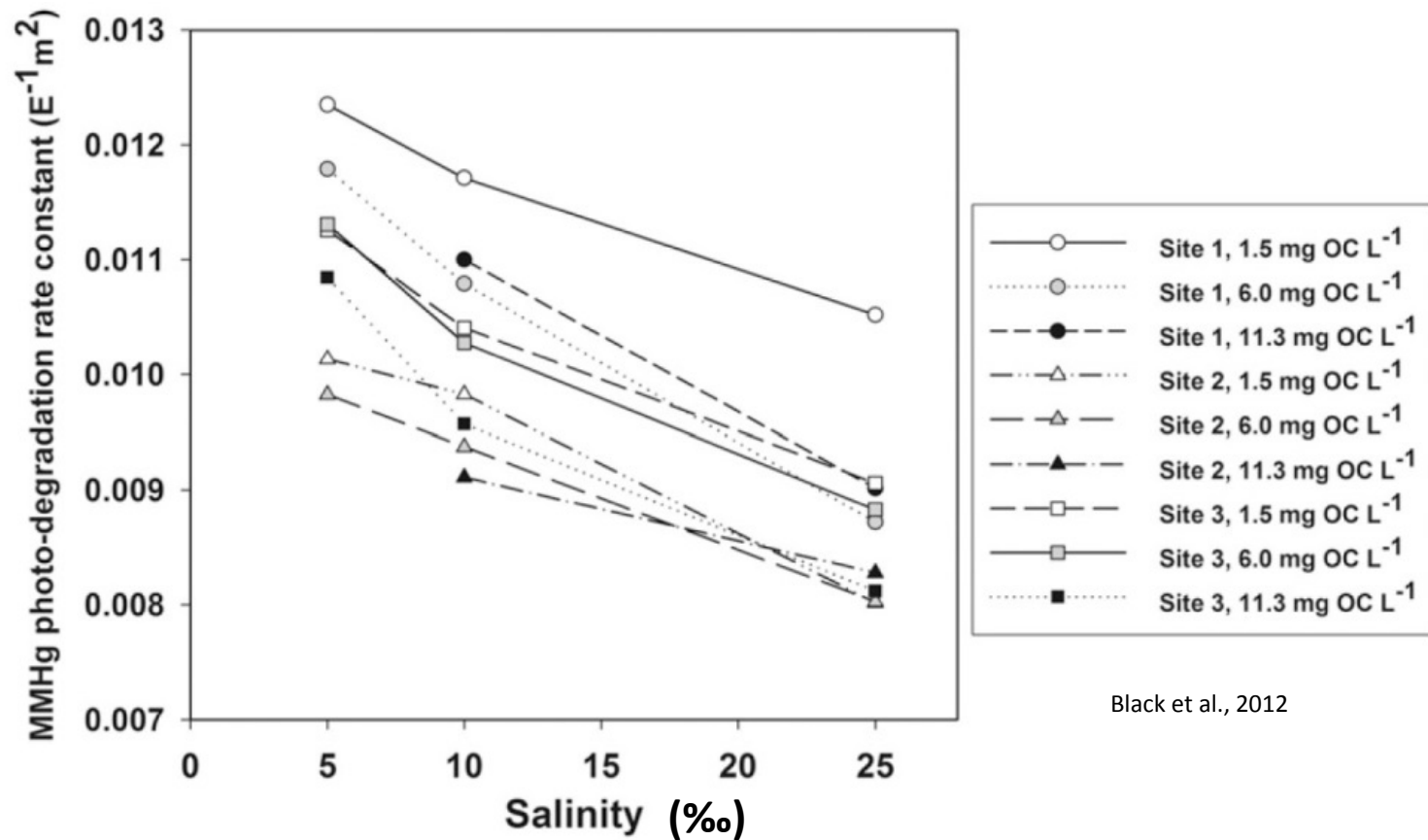


Obvious questions that come to mind

- Why are MMHg concentrations so high in the Great Salt Lake?
- What are some potential ways to reduce environmental exposure to mercury at the Great Salt Lake?

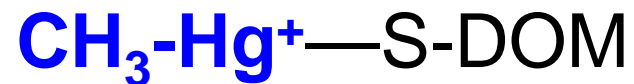


Do slow rates of MMHg photo-degradation at high salinities contribute to elevated MMHg concentrations in the GSL?



Black et al., 2012

Do slow rates of MMHg photo-degradation at high salinities contribute to elevated MMHg concentrations in the GSL?



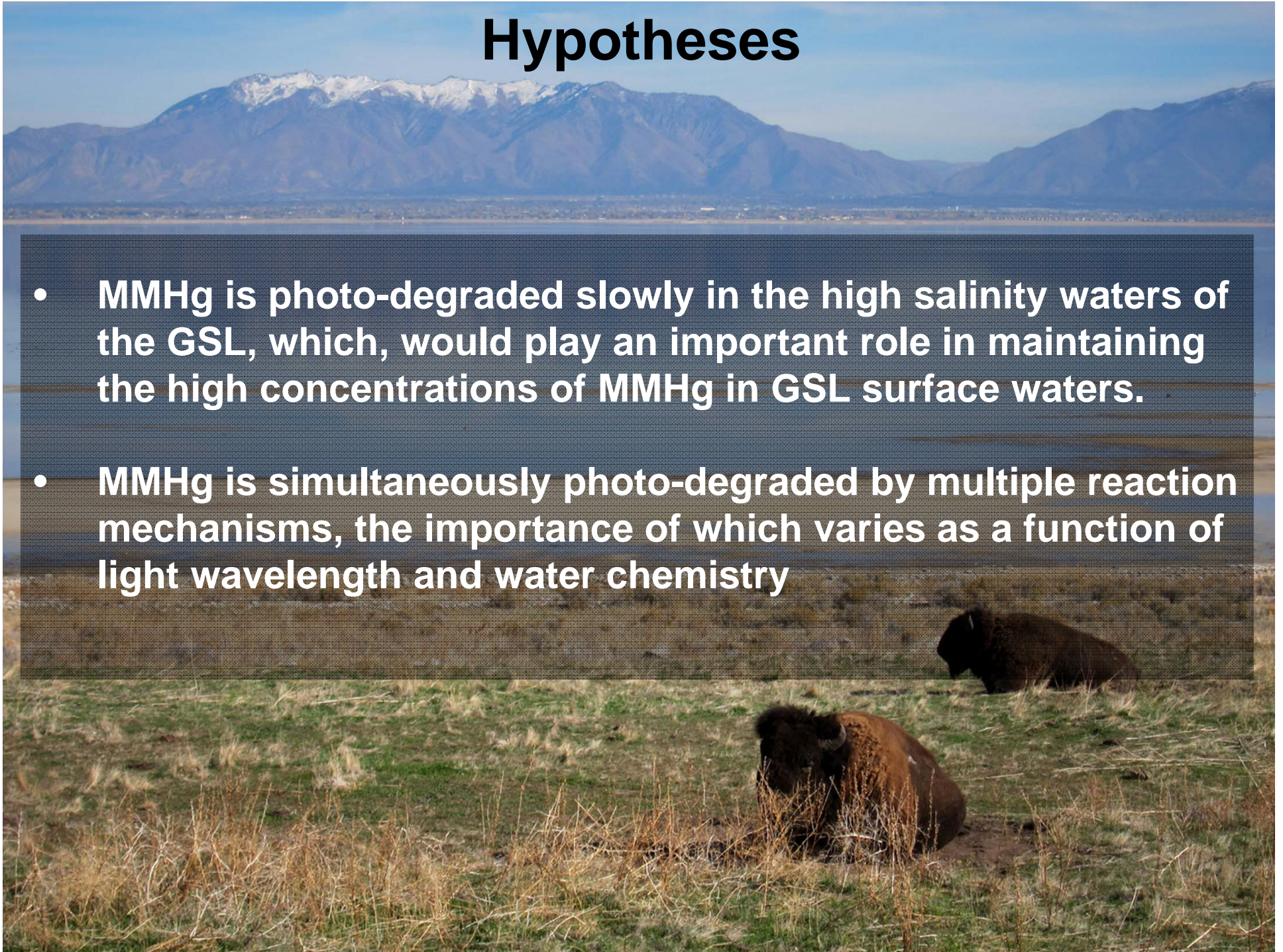
**Fast photo-degradation of
MMHg-thiol complexes**

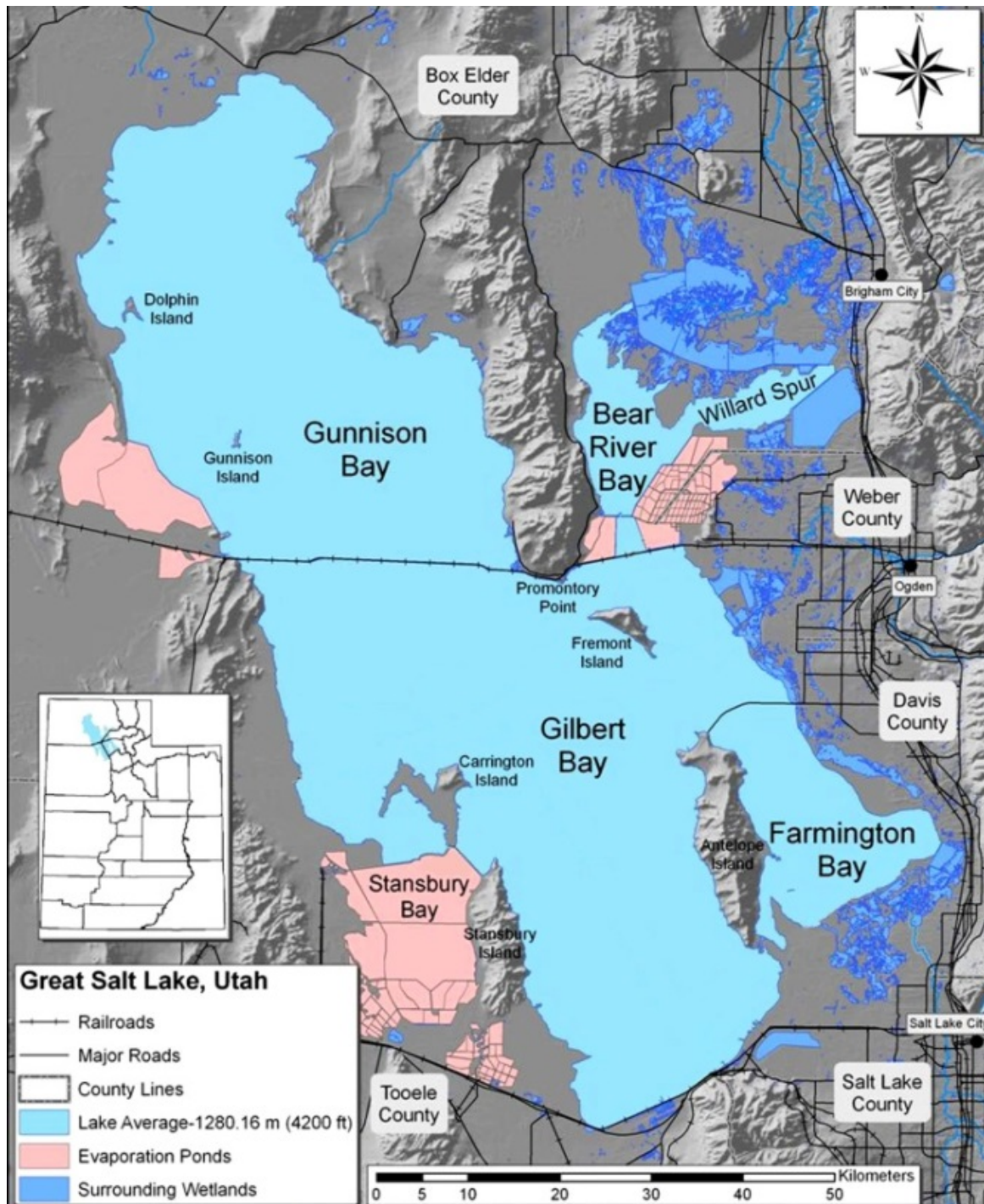


**Slow photo-degradation of
MMHg-chloride complex**

Hypotheses

- **MMHg is photo-degraded slowly in the high salinity waters of the GSL, which, would play an important role in maintaining the high concentrations of MMHg in GSL surface waters.**
- **MMHg is simultaneously photo-degraded by multiple reaction mechanisms, the importance of which varies as a function of light wavelength and water chemistry**





**GSL surrounded by
~400,000 acres of
wetlands**

(U.S. EPA. 2010)

**Wetlands are
hotspots of mercury
methylation**

(Babiarz et al., 1998; Hurley et al., 1998; St. Louis et al., 1996; Marvin-DiPasquale et al., 2003)

Additional Project Goal

- Use understanding of controls on MMHg photo-degradation to identify strategies to maximize this process in managed wetland surface waters to reduce export of MMHg to adjacent aquatic ecosystems



MMHg photo-degradation experiments



- 250 mL of 0.45 μm filtered surface water spiked with 2 ng/L MMHg.
- 250 mL Teflon bottles in water baths exposed to sunlight for 10 hours ($101.4 \text{ mol/m}^2 \text{ PAR}$) during clear summer day.
- Salinity and chloride concentrations varied by addition of NaCl and sea salts.
- Light treatments and dark controls (Al foil wrapped) performed in triplicate.

Measuring MMHg at < 1 part per trillion (< 5 pM) concentrations is laborious

**LIMNOLOGY
and
OCEANOGRAPHY: METHODS**

ASLO

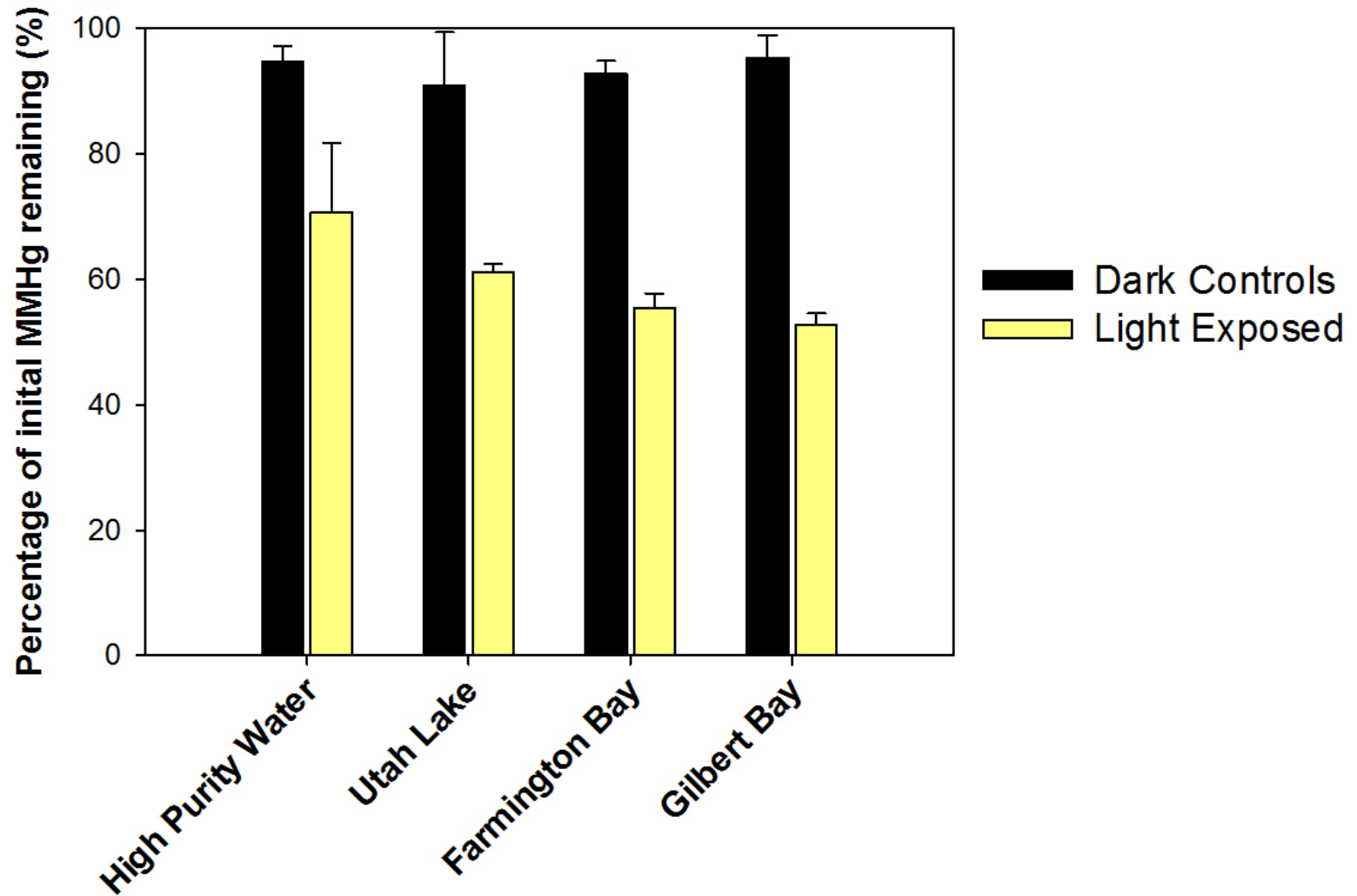
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doi: 10.1002/lom3.10009

Quantification of monomethylmercury in natural waters by direct ethylation: Interference characterization and method optimization

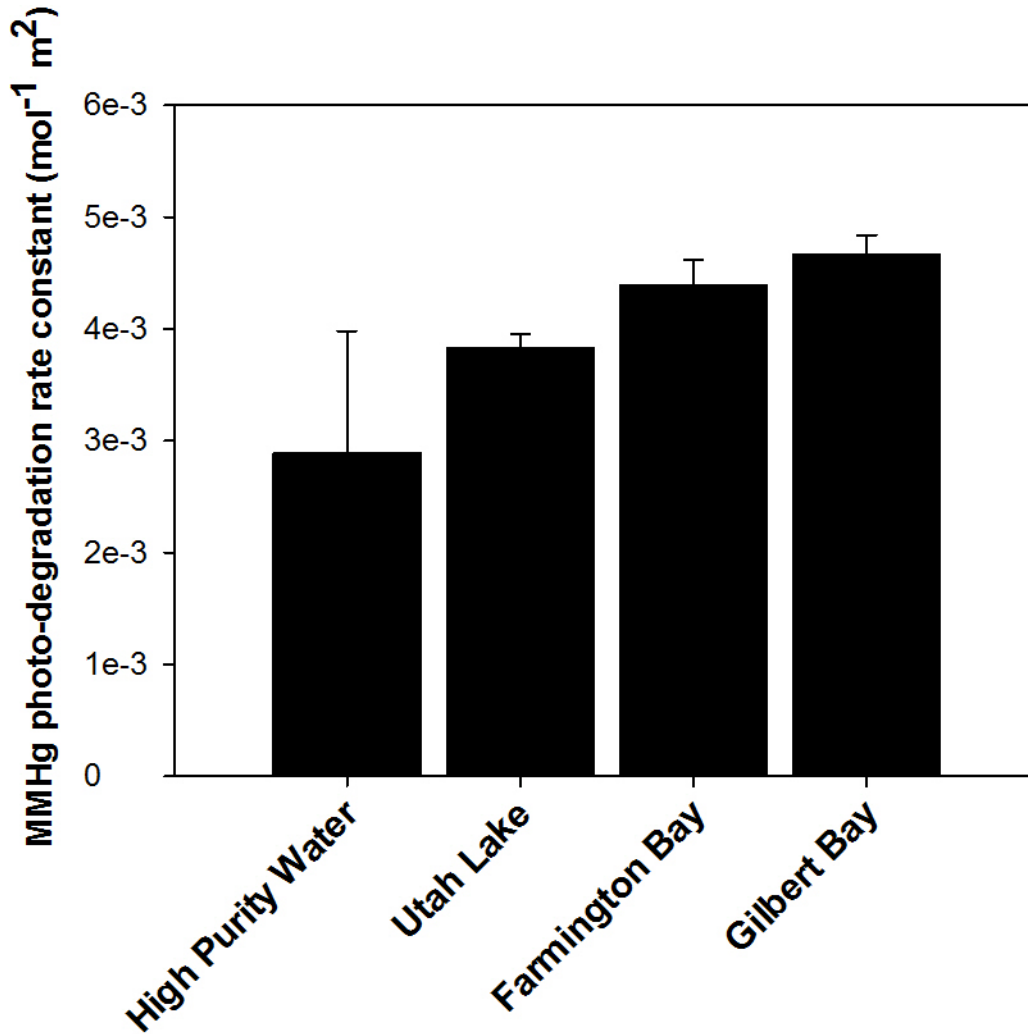
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Degradation of MMHg was photo-chemical



Rates of MMHg photo-degradation are not low in GSL surface waters



Rate constants from previous studies (mol⁻¹ m²):

Seawater = 3 × 10⁻³

Coastal wetlands: 9 × 10⁻³

Freshwater lakes = 3–10 × 10⁻³

(Lehnherr and St. Louis, 2009; Hammerschmidt and Fitzgerald, 2009; Black et al., 2012)

Ongoing work

- Test if MMHg is simultaneously photo-degraded by multiple reaction mechanisms, which vary as a function of light wavelength.
 - Direct vs. Indirect mechanisms (singlet oxygen, hydroxyl radicals, photo-Fenton reaction, triplet state DOM)
- Reevaluate effect of chloride and other water chemistry parameters on MMHg photo-degradation.