In situ sources and cycling of methylmercury in the oxic water column

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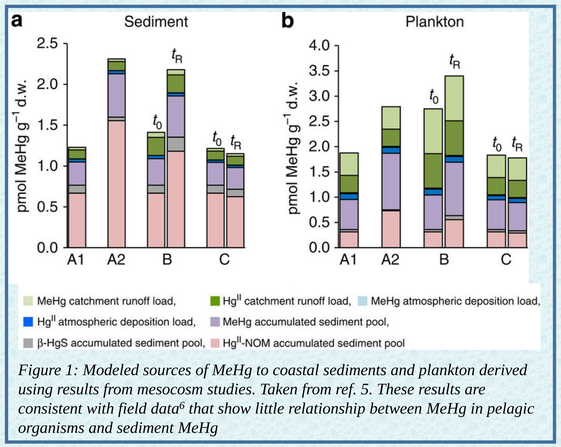

Figure 1: Modeled sources of MeHg to coastal sediments and plankton derived using results from mesocosm studies. Taken from ref. 5. These results are consistent with field data[6] that show little relationship between MeHg in pelagic organisms and sediment MeHg

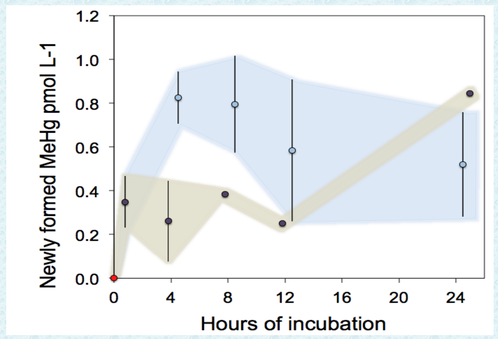

Figure 2: Incubation of seawater from Eastern LIS with $^{199}Hg(II)$ resulted in formation of MeHg. There were differences between dark (brown) and light (blue) incubations. Circles represent means and error bars standard deviations (3 reps). Red point shows no MeHg was formed in acidified seawater upon reagent addition.

Introduction: For humans and wildlife, exposure to methylmercury (MeHg), the most toxic and bioaccumulative form of mercury (Hg), is mostly from seafood consumption[1]. Historically, it has been proposed that MeHg bioaccumulating in marine systems is produced within the sub-thermocline waters of the ocean[2] or in the coastal zone sediments[3], primarily because microbially-mediated production of MeHg occurs in the presence of anaerobic organisms.[4] Mesocosm results point to the significant pool of MeHg formation in sediments, but this is not the dominant source to plankton (Fig. 1)[5], consistent with field data.[6,7] Recent estimates of the photochemical degradation of MeHg suggest that degradation of MeHg in surface waters is substantially higher than previously thought[8], requiring additional MeHg sources to account for the MeHg in open ocean surface waters and food web. While the importance of Hg methylation in ocean surface waters has been proposed, evidence has been lacking. Our results support formation of MeHg in oxic seawater and point to the significance of light and particle aggregates (Figs. 2, 3). Here we discuss our more recent research aimed at examining the importance of methylation in oxic waters as a source to marine food webs. Our current investigations build on these studies and are formulated by overarching hypotheses illustrated in Fig. 4.

Prior Studies have highlighted the potential for oxic waters to be hotspots of Hg methylation. In surface waters, reduced environments can occur in large flocculated material ("marine snow"), where organic matter degradation is high (Figs 2, 3). Our results showed a substantial Hg methylation in the presence of larger particle aggregates (Fig. 3), but not in the smaller particles[9]. Results of the field study in a large estuary in Canada support the significance of particle aggregates in formation of MeHg. Substantial production of MeHg occurred where the river mixed with the estuarine waters, promoting organic matter flocculation and enhanced microbial activity (Fig. 5).[10] Overall, these preliminary results suggest that net methylation within the water column can occur, but that specific conditions are needed for net MeHg formation. Results of the light vs dark incubations with Hg suggest that under light conditions MeHg formation is initially enhanced (Fig. 2).

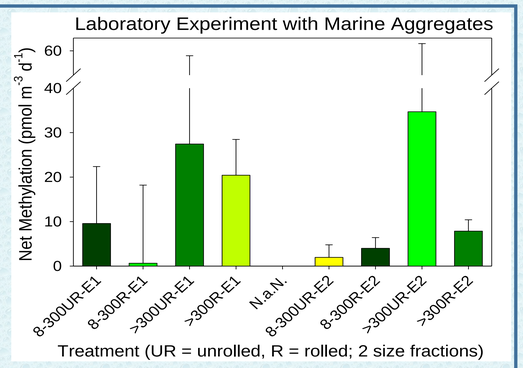

Figure 3: Net methylation rates ($dC/dt = k_m[HgII]-k_{dm}[MeHg]$) for different size fractions collected from 2 experiments and either rolled to enhance floc (R) or not (UR). From ref. 9.

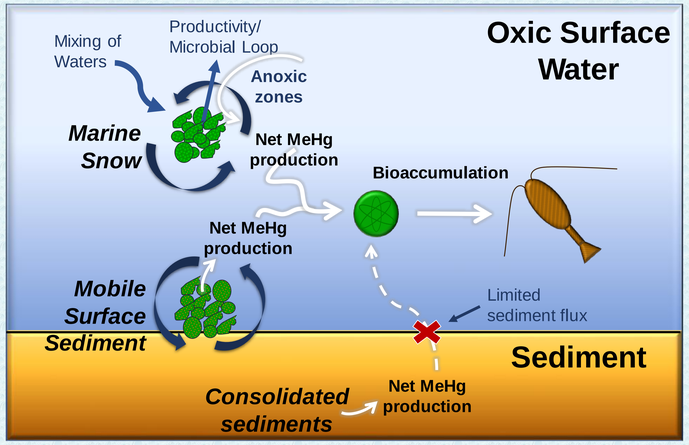

Figure 4: The conceptual model of hypothesized processes important in MeHg formation and pelagic bioaccumulation in coastal waters

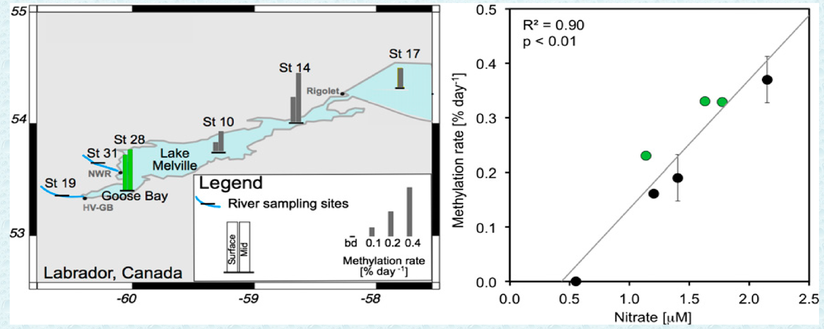

Figure 5: Methylation rates for water from the Churchill River through Goose Bay & Lake Melville into the coastal ocean (Groswater Bay); and methylation rates correlated with nitrate concentrations from these locations. From ref 10.

Recent Results: Mixing of river with seawater has been also found to enhance MeHg formation in Long Island Sound (LIS) supporting the elevated concentrations of MeHg at the mouth of Connecticut River that flows into LIS (Fig. 6). Additionally, marine snow was settled out from water collected from coastal LIS and we found that there were diverse microbial assemblages including anaerobic organisms that were equipped with methylating genes (*HgcA*) (Fig. 7). More research is needed to solidify these initial findings. We therefore suggest that methylation is occurring within the river-estuarine mixing zone, driven by higher Hg(II) concentrations in Connecticut River mixing with freshly produced organic matter, especially at high tide, when we measured the highest net methylation rates in these waters, while in the central basin of LIS there is little net production of MeHg. The river-estuarine interface provides a location of enhanced microbial activity/MeHg formation.

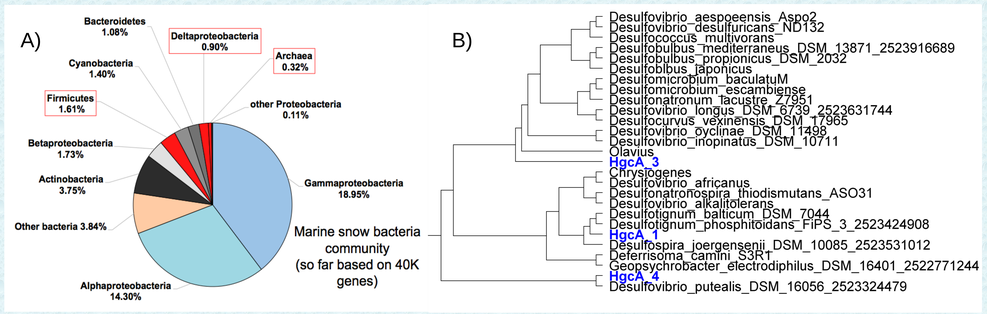

Figure 7: A) Coastal water marine snow bacterial community structure from metagenomic analysis. Known Hg methylators have been identified within groups that are printed in red. B) Phylogenetic tree showing the locations of the identified HgcA genes found for these samples.

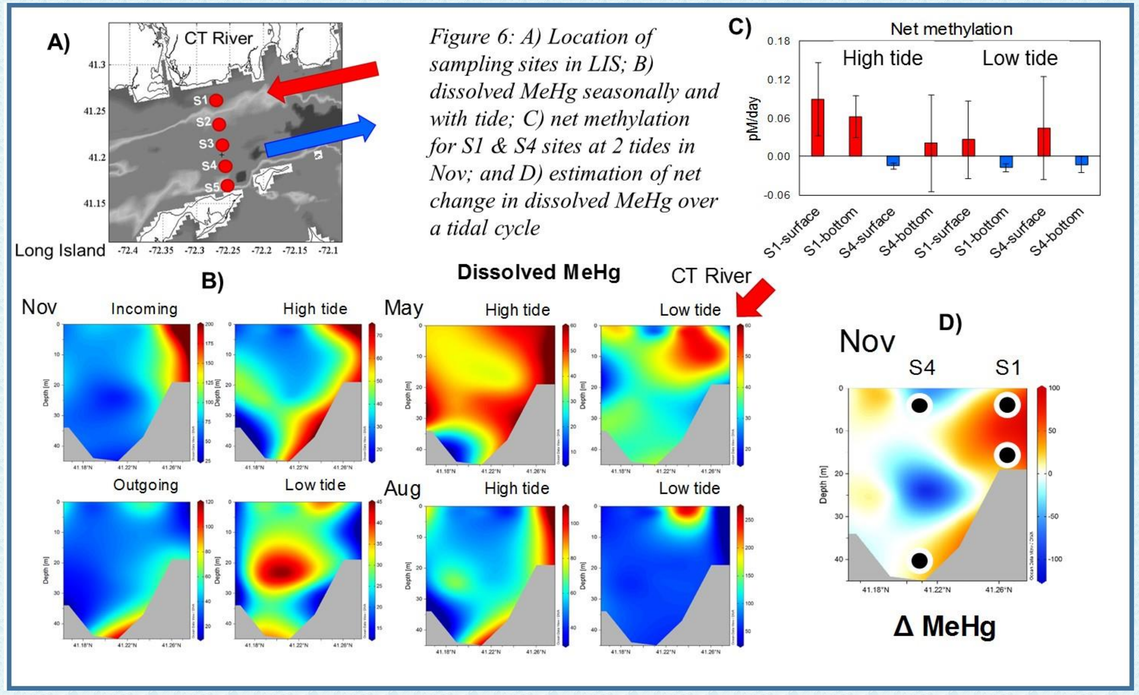

Figure 6: A) Location of sampling sites in LIS; B) dissolved MeHg seasonally and with tide; C) net methylation for S1 & S4 sites at 2 tides in Nov; and D) estimation of net change in dissolved MeHg over a tidal cycle

Conclusion: Water column methylation is enhanced in regions where conditions promote the formation of large particulate flocs, and where redox gradients are strong and anaerobic bacteria that methylate inorganic Hg persist. We propose that water column methylation is an important process delivering MeHg for food webs in coastal and open ocean surface waters.

References: 1: Sunderland, E. M. (2007). *Environ. Health Persp. 115*(2), 235-242; **2:** Mason et al. (2012). *Environ. Res. 119*, 101–117; **3:** Hollweg et al. (2009). *Mar. Chem. 114*, 86-101; **4:** Podar et al. , (2015). *Science Advances, 1*; **5:** Jonsson et al. (2014) *Nature Comm*.5, Art # 4624; **6:** Chen et al. (2014). *Plos One, 9*(2); **7:** Balcom et al. (2015). *Mar. Chem. 177*, 721-730; **8:** DiMento & Mason *Mar. Chem.* 196, 116-125; **9:** Ortiz et al. (2015). *Mar. Chem. 177*, 753-762; **10:** Schartup et al. (2015). *PNAS, 112*(38), 11789-11794.

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