"Seeing" Mercury Methylation in Progress

Mercury in the environment can easily reach toxic levels. In a process called methylation, Hg is transformed into a form that can be accumulated in the muscle and fatty tissue of fish. Accumulated levels of methylmercury become higher as the fish grow, and levels are magnified up the food web as larger fish eat smaller fish, a process called biomagnification. As a result, mercury concentrations in fish can be millions of times higher than in surrounding waters [1]. Fish advisories have been set to limit consumption of certain fish higher up on the food web, especially for pregnant women and small children (see Figure 1).

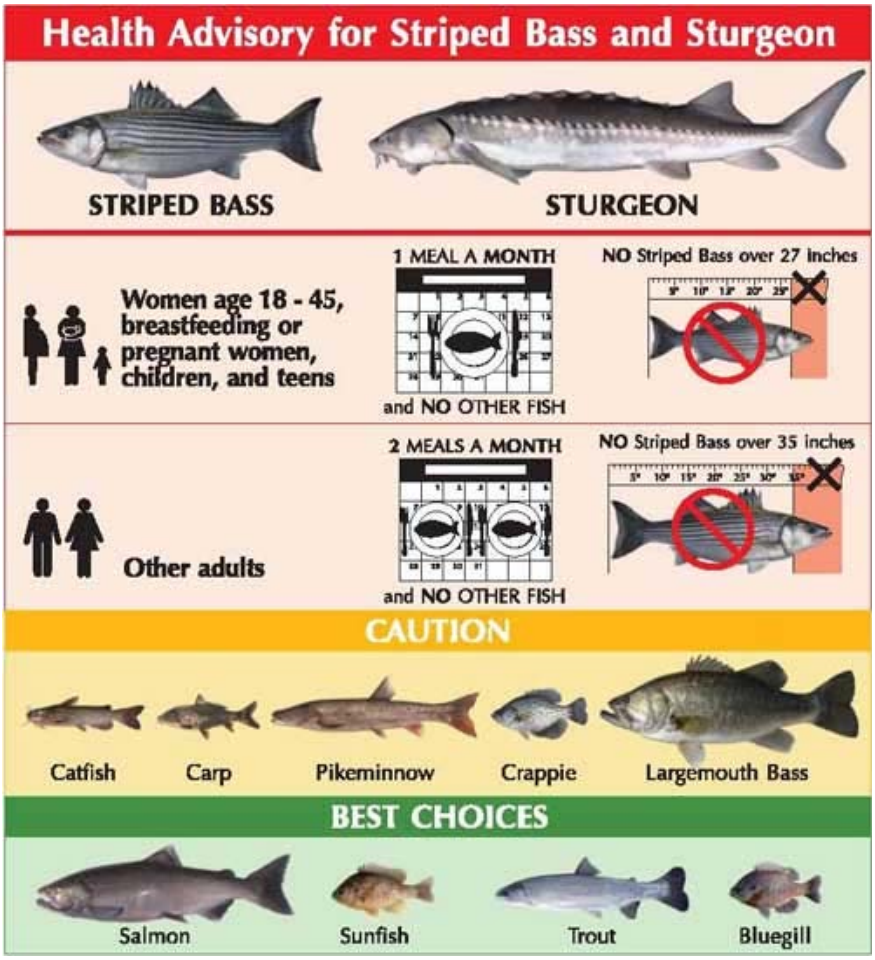

Figure 1: Mercury health risks Health advisory from the CALFED Science Program to limit consumption of fish, in order to avoid excessive accumulation of Hg. Methylated Hg is biomagnified up the food chain, attaining high levels in some types of sportfish. http://science.calwater.ca.gov/images/scinews_hg_da_lg.jpg

Plants and microorganisms in the ecosystem can play an important role in the chemical transformation, including methylation, of mercury. In particular the root zone, or rhizosphere, of plants is an important place where microorganisms such as sulfate reducing bacteria (SRB) can transform Hg [2]. We studied Hg uptake and transformation in the rhizosphere of two species of cordgrass that are prevalent in San Francisco Bay. One is the native species that has an essential role in the ecosystem, including housing nests for endangered species (*Spartina foliosa*), the other a hybrid of this native with an invasive cordgrass species (*Spartina alterniflora* hybrid) [3]. Because these are dominant plants within the SF Bay ecosystem, understanding the chemical transformation of Hg in their root zone can help scientists to characterize their roles in mercury biogeochemical cycling in the estuarine environment, and possibly to determine ways to remediate the problem.

The team collected *S. foliosa* and *S. alterniflora* plants from two locations in SF Bay and studied their native Hg levels, as well as their capacity for Hg uptake. Using Hg L_3 XANES collected on Beam Lines 9-3 and 10-2 they determined the overall chemical speciation, or forms, of Hg within the plants and their root zones. Scanning x-ray fluorescence (XRF) and

micro-XANES on Beam Line 2-3 were utilized to map the location, distribution, and speciation of Hg within the plant roots, which appeared in concentrated spots (Figure 2).

Using transmission x-ray microscopy (TXM) on Beam Line 6-2c, it was apparent from 2D images at 40 nm resolution and 3D tomography that the concentrated spots seen with XRF were associated with microorganisms (probably SRB) in which most of the Hg was accumulated within cell walls (Figure 3). Combining data from all techniques used, TXM results indicated that Hg was most likely bound to sulfur in plant roots and microbial walls, presumably transferred to the SRB cytoplasm after methylation. Some Hg also precipitated as metacinnabar (HgS) as part of this process.

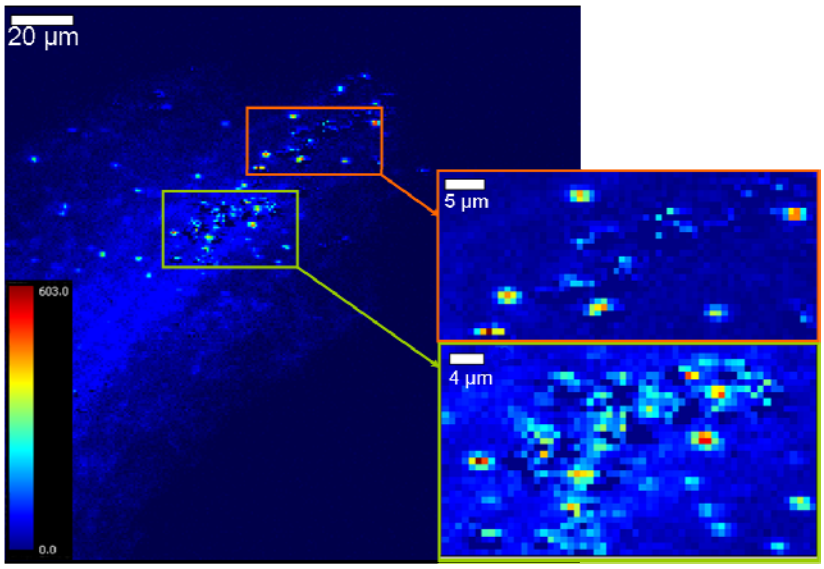

Figure 2. Microprobe map (SSRL BL2-3) of Hg fluorescence on logarithmic scale shows size and distribution of Hg within micron-sized *S. foliosa* roots (A). Micro-XANES points were selected from the highest concentration areas ("hot spots", indicated red). Fluorescent counts (range 0-603) in insets (B and C) were determined as a difference above the Hg edge (12300 eV), minus below (12250 eV). (Figure adapted from Patty et al. 2009)

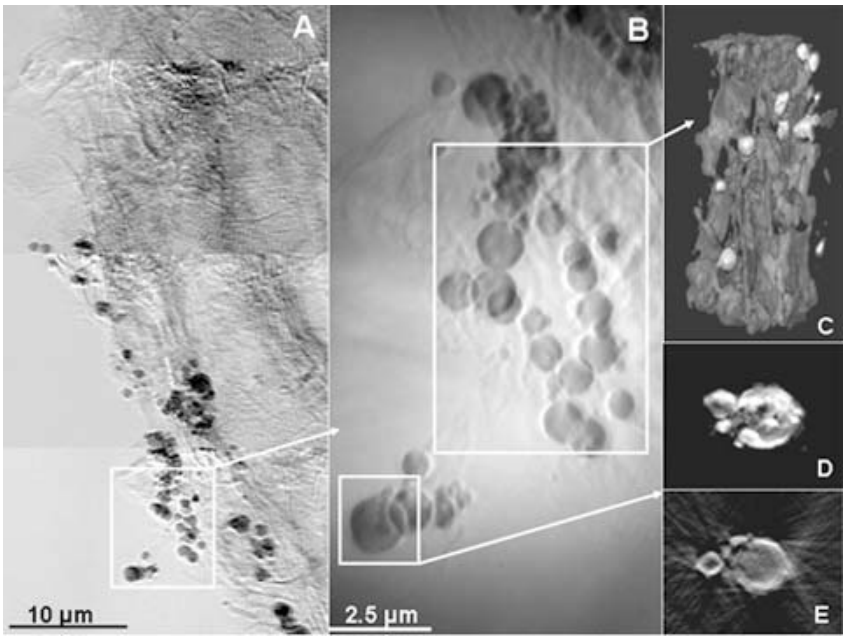

Figure 3. Transmission X-ray Microscope (SSRL BL6-2) mosaic image of *S. foliosa* roots taken at 9 keV in absorption contrast at 40 nm resolution shows dark particles and dark channels due to absorption by Hg (A). Blowup (B) shows greater detail. 2D stills from tomography of particles from (B) show particles with greatest absorption (lightest), possibly surrounded by biofilms (C). (See movie) 2D tomographic still (D) and slice (E) of large particle indicate that highest Hg concentrations (lightest intensity) are on the outside of the fairly hollow particles. (Figure adapted from Patty et al. 2009)

In summary, the use of X-ray microscopy combined with Hg L_3 XANES has permitted us to obtain a "snapshot" of mercury methylation and metacinnabar precipitation in *S. foliosa* and

S. alterniflora. This "snapshot" of Hg methylation in progress provides insight into the spatial and biochemical relationships between SRB and *Spartina* roots, revealing areas of Hg concentration within both. Although we found that the native *S. foliosa* has the capability for greater Hg uptake, perhaps due to its longer adaptation to the Hg-contaminated area; total Hg concentrations are the same in both species in the field, indicating that there is no significant difference in the amount of methylmercury that would be produced by each species. Although concentrations in the field average 0.1 ppm for both Spartina species, these are dominant florae within SF Bay and other locations. If an average of 10% of this Hg is methylated, *Spartina* must be carefully considered for its role in mercury methylation in the SF Bay estuarine ecosystem. This work has been published in Environmental Science and Technology.

Primary Citation

Patty C, Barnett B, Mooney B, Kahn A, Levy S, Liu Y, Pianetta P, Andrews JC (2009) Using X-ray Microscopy and Hg L_3 XANES to study Hg Binding in the Rhizosphere of *Spartina* Cordgrass. Environ Sci Technol 43: 7397-7402.

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Acknowledgments

We thank Susan Opp for her help in statistical treatment of the Hg uptake data; and Sam Webb, Sean Brennan, Jennifer Cassano, and Sarah Hayes for their help with data collection. A. Kahn and B. Mooney were supported by awards from the CSU East Bay Associated Students, and CSU East Bay provided support to J. C. Andrews. SSRL is supported by the Department of Energy, Office of Basic Energy Sciences. The transmission x-ray microscope is supported by NIH/NIBIB grant number 5R01EB004321.

The SSRL Structural Molecular Biology Program is supported by the Department of Energy, Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and the National Institute of General Medical Sciences.

SSRL is primarily supported by the DOE Offices of Basic Energy Sciences and Biological and Environmental Research, with additional support from the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and the National Institute of General Medical Sciences.