### DELTA SCIENCE PROGRAM



Factors Affecting Methylmercury Accumulation in the Food Chain

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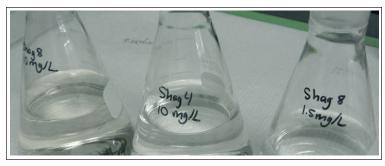
## SUMMARY

The common scientific wisdom is that dissolved organic debris (from rotting dead plant material, for example) reduces the biological activity, and hence toxicity, of heavy metals such as mercury. Prior to the start of this project, however, a study showed that organic debris could also sometimes enhance build up of the toxic form of mercury in phytoplankton. This toxic form is called methylmercury (MeHg). It is produced in the aquatic environment by sulfur-reducing bacteria and biomagnifies through aquatic food chains.

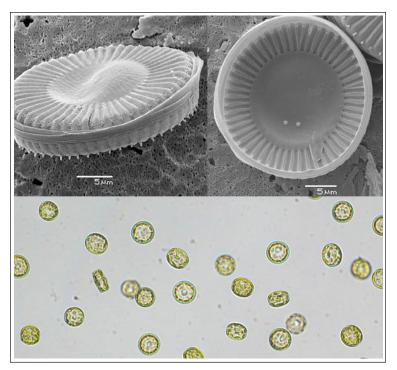
This project sought to establish whether different types (and amounts) of organic debris collected from the San Francisco Bay-Delta might enhance or suppress MeHg accumulation in a resident species of phytoplankton. Based on radiotracer experiments, scientists report that small amounts of dissolved organic matter (DOM) – regardless of the type – caused a sharp initial decline in algal MeHg concentrations. This effect slowed dramatically and eventually plateaued at higher concentrations. Notably, living algae accumulated two to four times more MeHg than dead cells, implying that algae are not passively absorbing the metal but actively bringing it into cells (for reasons that are unknown). Feeding trials with amphipods – tiny bug-like crustaceans – confirmed that the mercury in algae was transferred up the food chain to these algae-grazers.

### BACKGROUND

In most parts of the world, coal-fired power plants are the main source of mercury pollution. The San Francisco Bay-Delta is unique, as its source of the heavy metal dates back to the Gold Rush, when miners used "quicksilver" to bind to gold in slurries. By some estimates, as much as 10,000 tons of mercury was released into the Sierra Nevada during this era. To this day, heavy rains or snowmelt will send mercury-contaminated flows into rivers and creeks emptying into the Bay-Delta. There are various fish advisories in place throughout the region to reduce human exposure to MeHg. A main motivation for this project was to explore processes controlling amounts of MeHg entering the food chain.



Flasks containing varying concentrations of organic matter from Shag Slough. Credit: A. Luengen



Micrographs of the diatom *Cyclotella meneghiniana* studied in this project. Credit: Ghent University, Belguim

### PROJECT

More specifically, the goal of this project was to investigate effects of dissolved organic matter on MeHg accumulation in the diatom Cyclotella meneghiniana. To increase the project's relevance to the San Francisco Bay area, DOM isolates were collected from four sites in the Bay-Delta. The general design of the experiment was to add phytoplankton cells to flasks with different DOM treatments, including treatments with no DOM and controls with no added algae cells. The controls allowed scientists to quantify the amounts of MeHg stuck to the filters and walls of the flasks. Radiolabelled MeHg was added to each flask, and its concentrations were measured in the water and cells over time. To determine whether mercury accumulation was an active or passive cellular process, MeHg accumulation rates were compared for living and dead cells. There were also experiments with different factions of field-collected DOM (transphillic and hydrophobic) to investigate whether certain DOM components might account for most of the observed variations in mercury uptake rates. Feeding experiments were also conducted with amphipods and the diatom, to study the sequential accumulation of MeHg from water to algae to algae-grazers.

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## RESULTS

All types of DOM suppressed MeHg accumulation, and the scientists attributed this suppression to the formation of DOM and MeHg complexes. The organic matter, in a sense, outcompetes algae for MeHg.

The greatest reduction in MeHg accumulation rates occurred at low DOM concentrations. Higher amounts of DOM further reduced MeHg accumulation rates only marginally. It is theorized that, under low-DOM conditions, free MeHg binds to both weak and strong binding sites on the organic material. At higher DOM concentrations, MeHg may preferentially select the strongest binding sites, likely thiols (sulfur-containing compounds with, often, garlic-like aromas). When all of the MeHg is bound to the strongest binding sites, the addition of more DOM will cease to affect algal uptake rates.

While total DOM concentrations were the most important factor controlling MeHg uptake, the hydrophobic fraction was observed to be more aromatic (and thus better at sopping up MeHg) than the transphilic fraction. Transphillic compounds are neither hydrophobic (water repelling) nor hydrophilic (water loving) and attract compounds with intermediate polarity.

Research conducted by other scientists has shown that neutrally charged mercury compounds can passively diffuse through cell walls. While some passive diffusion cannot be ruled out, in the experiments conducted for this project, living algae were observed to contain two to four times more MeHg than dead cells. This suggests that most MeHg uptake is an active and energy-dependent process.

Feeding studies verified that this mercury could also accumulate in algae-eating amphipods. Notably, however, the most significant point of entry for MeHg into the food chain occurred in the transfer of mercury from the environment into algae. Algae typically had 100,000 times more mercury inside them (more or less, depending on DOM concentrations) than the ambient water. Amphipods in contrast concentrated MeHg by a factor of 2-3 (relative to algae). A similar rate of biomagnification is believed to occur at subsequent higher trophic levels.

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#### PUBLICATION

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# MANAGEMENT

The bacteria that methylate (chemically change) inorganic mercury into toxic MeHg thrive in low-oxygen, high-sulfur marsh sediments. All else being equal, wetland restoration and recreation would thus be expected to increase MeHg production by expanding these microorganisms' habitat. Wetlands also, though, produce plant detritus, which, as this project shows, can suppress the MeHg bioactivity.

Yet another topic relevant to managers is whether algal blooms might also intensify MeHg production. The line of logic supporting this concern: the bacteria that decompose dead algal cells following a bloom can create hypoxic (low-oxygen) conditions, the same conditions that favor methylating bacteria. But, as this project shows, the added algal carbon can also create a biofeedback that inhibits MeHg sequestration. In addition, some researchers have speculated that higher algal counts during a bloom could have a dilution effect, reducing the amount of mercury in individual cells.

Human health risks from MeHg exposure are significant. A National Academy of Sciences report estimates that more than 60,000 children are born each year in the United States at risk of "adverse neurological development" due to in utero exposure to MeHg. These children may have trouble learning in school or have compromised verbal skills, among other things. While mercury cannot be removed from fish, this project highlights the importance of processes at the base of the food chain (and within the surrounding environment) in ultimately determining toxin exposure from eating fish.



Allison Luengen, a Delta Science Fellow from 2007 to 2011, holds a Geiger counter (and wears a lead vest) to check for the presence of radiolabelled methylmercury.

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