CALFED BAY-DELTA PROGRAM

NEWS FROM THE CALIFORNIA BAY-DELTA AUTHORITY SCIENCE PROGRAM

ScienceAction

BIG PICTURE

Mercury in Every Mix

When Goldilocks was snooping around the three-bear bungalow, she tested each chair (too high, too low), each bed (too soft, too hard), each bowl of porridge (too cold, too hot) until she found those that felt just right. Mercury may be more silver than gold, but it's just as picky as the fairytale heroine. It comes in a lot of chemical shapes and sizes in our watershed, but it only turns from your basic garden-variety to the kind doctors and scientists worry about — the methyl mercury that builds up in fish and threatens the health of the people who eat them — when conditions are just right. When there's just the right mix of bacteria, chemicals, soils, plants, and water at just the right temperature, oxygen levels, and particle sizes to morph the mercury left all over the place by the Gold Rush into methyl mercury.

The places with just that right mix actually have a name down in the Everglades, where scientists and restoration managers have an airborne mercury threat: "Goldilocks areas." Here in Northern California, the threat is even more pervasive and longer-lived, but its source is closer to the ground. More than 150 years ago, gold miners began lining their sluices and chutes with mercury because it drew the gold to its side. The mining and sorting and washing of gold in nearly every river and creek feeding into the Sacramento and San Joaquin rivers spilled up to 13 million pounds of mercury across the landscape, according to state geologists, and runoff from the Coast Range's 239 mercury mines added still more (see Mining Mechanics p. 2).

Inputs from mines far exceed what falls from the skies in California, but almost everywhere else in the world atmospheric fallout is the main source of mercury. This spring, U.S. EPA issued new rules on power plant emissions of mercury nationwide. Fish in Midwestern, Canadian, and European lakes have mercury levels as high as those in California.

"It's everywhere, both from a regional and a global point of view," says the U.S. Geological Survey's (USGS) Charlie Alpers, author of the first definitive fact sheet on mercury contamination from gold mining in California.

The Bay-Delta's mining dose doesn't mean we have a bigger problem than most everyone else — just a more complicated one. After a century of spreading across the landscape, mercury can't just be cleaned up. Luckily, only a small fraction of the mercury in our system is reactive, the kind that forms methyl mercury. But given the way this mercury magnifies as it climbs up the food chain (see p.2), even a small amount is cause for concern. The traces in our drinking water pose little threat, but many large sport fish from the Bay-Delta system carry body burdens near or above U.S. EPA criteria for the protection of human health. And unlike some other contaminants in estuaries — cleaned, filtered, and sequestered by aquatic processes — this one's not going away. Levels in fish have not changed for 30 years.

Mercury has been a perturbing problem for the CALFED Bay-Delta Program (CALFED), one of the many government programs struggling to address this pollutant. Californians created CALFED, a cooperative state and federal program now overseen by the California Bay-Delta Authority, to maximize the state's water supply while minimizing impacts on endangered fish and birds, and restoring the rivers, floodplains, and bays flowing into San Francisco Bay. Right from the CALFED get-go, mercury surfaced at the confluence of almost everything on the table.

"Mercury contamination is a longstanding problem that may or may not be exacerbated by everything from storing and transferring water to strengthening levees, controlling floods, dredging ship channels, removing dams, creating wetlands, and building more cities and towns," says Dan Castleberry, who managed CALFED's Ecosystem Restoration Program until recently. "For our part, we've been carefully scrutinizing our own restoration plans so that we don't increase mercury risks to the ecosystem, and trying to provide coordination and critical data for the myriad other existing efforts to address mercury statewide."

Invaluable to this coordination, everyone agrees, was CALFED's invitation to a group of international experts to develop a mercury strategy for Northern California. The strategy — completed in 2003 with input from diverse stakeholders and more than a dozen state, local, and federal agencies — outlines a framework for scientific study of how mercury moves through the system and the food web, and suggests such actions as cleaning up mines, warning fish consumers, and managing landscapes to reduce methylation.

"The strategy has been more than a book on the shelf," says California Bay-Delta Authority water quality coordinator Donna Podger. "It's been a unifying vision used by the wide group of people and agencies to tie together research and management."

Gold mining dredge, Junction City district, Trinity River, 1935. Note the bucket line behind the gantry at the near end (right side) of the dredge, the stacker conveyor discharging coarse tailings at the far end, and the side sluice discharging fine tailings to the rear. The dredge separated the coarse material inside the housing, and fine material passed through sluices and over tables charged with mercury to capture the gold. Gold dredging occurred on more than a dozen Sacramento and San Joaquin river tributaries between 1898 and 1968, distributing mercury into the river system (see p.2).

Used with permission, California Department of Conservation, California Geological Survey

Even before the strategy, however, half a dozen teams of scientists had begun chasing mercury up and down creeks, in and around mines, under dams, along river beds, through open waters, and among pickleweed and tules — trying to pin down the conditions in all these places that either make them just right or not for mercury methylation. They now know that the wet layer of sediments below wetlands, where plant roots are oxygenating the

METHYL MERCURY BIOMAGNIFICATION (ng/g DRY WEIGHT IN BIOTA)

	Mukooda Lake, MN	Ryan Lake, MN	Almaden Reservoir, CA
Primary Hg Source	Atmospheric	Atmospheric	Mining
Water (wet wt)	0.000018	0.00019	0.00037
Seston (mostly algae)	3.5	8.3	4.1
Zooplankton	17.0	197.0	640.0
Young Fish (age 1) Largemouth bass CA Yellow perch MN	181.0	943.0	4,830.0
Northern pike (55 cm)	1,130.0	9,725.0	

Bioaccumulation factors from water to fish: 1-12 million (based on wet weight concentrations in fish)

Methyl mercury biomagnifies in aquatic food webs. In Voyageurs National Park, Minnesota, concentrations in young yellow perch were more than one million times greater than those in the water, and in adult predatory pike, more than 10 million times greater. In the South Bay's Almaden Reservoir, near an old mercury mine, concentrations were higher in the water than in the Minnesota lakes, which is reflected in the elevated transfer up to the young fish. Concentrations in age 1 largemouth bass were 2.6 million times higher than in the water in which they live.

Source: MN from Wiener et al., Univ. of Wisconsin-La Crosse; CA from Kuwabara et al, USGS, & USEPA

soil and certain kinds of bacteria are churning away, can be as hospitable to mercury methylation as Little Bear's bed was to Goldilocks. "All the things that make wetlands and floodplains good ecosystem components are the same things that make them a juicy environment for mercury methylation. That's the devil's bargain we have to make," says microbial ecologist Mark Marvin-DiPasquale of USGS.

In a 1999 national study, a team of USGS scientists led by Dave Krabbenhoft concluded that wetland density was the single most important watershed factor associated with methyl mercury production. Here in the Bay-Delta region, USGS scientists are moving from the regional watershed to the local site-specific scale, trying to figure out which factors stimulate and which inhibit methylation. "There is no one factor fix. It's all about the interplay," says Marvin-DiPasquale.

The interplay becomes apparent in any reading of the mercury literature, where the word "biogeochemical" clogs every other sentence. But the research of the past six years seems to be producing useful results: We've learned that some fish are high in mercury but others, such as salmon, are less so; that some seasons are worse than others — low summer flows seem to produce the biggest spikes; that plant-rich wetlands may speed methylation while open sunlit waters may actually reverse the process; and that the difference in methyl mercury exported from two side-by-side wetlands can be dramatic — a few among many lessons that may help guide restoration in the future.

Some of these lessons derive from the $31 million in research now underway and presented here that was funded by CALFED's Ecosystem Restoration Program. The mercury challenge is so complex that CALFED's investment in science, as well as in education and remediation actions (see pp. 14-16), is just the tip of the iceberg. Many other agencies have championed and bankrolled essential studies as well, some of which are described here in order to introduce all the basic areas of inquiry, and some of which had to be left out due to space constraints.

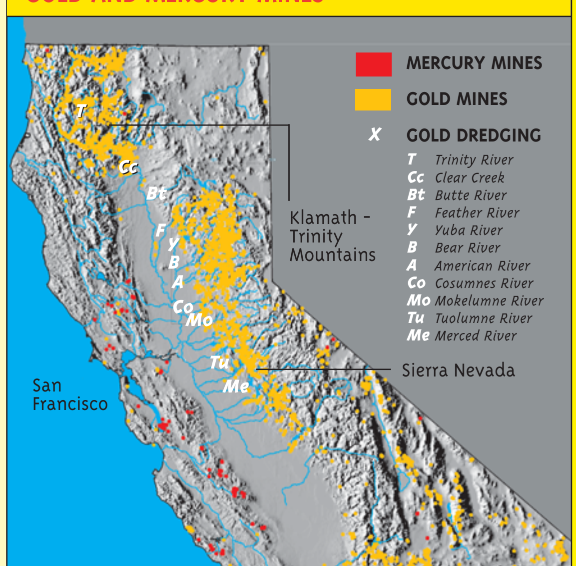
"Time is running short for us on the mercury question worldwide," says Marvin-DiPasquale. "If we really want to do something, we can't fool around in beakers forever. We need to get out on the ground, on an ecosystem scale. If it weren't for CALFED, we wouldn't be able to do this." ARO

MINING MECHANICS

When gold fever struck in the Sierra Nevada, hungry fortune seekers quickly discovered that mercury — as liquid quicksilver — would help them recover the coveted metal. But first the mercury had to be mined from the Coast Ranges, which were rich with red cinnabar, the ore that contains mercury. Miners went to work on the Coast Ranges, including the South Bay's Almaden Hills, with pickaxes and blasting powder, chiseling out the cinnabar. They fed the cinnabar into brick furnaces they built along Coast Range creeks. The freed liquid quicksilver was poured into iron flasks, which were then shipped throughout the Pacific Rim and to other western states. An estimated 26 million pounds were used to mine gold from the Sierra Nevada and the Klamath-Trinity Mountains.

Mercury helped extract gold from two types of deposits: placer (alluvial deposits) and lode (hardrock). Most of the mercury that ended up in the environment was from placer deposits, which were worked using three mining techniques: hydraulic, drift (underground), and dredging. Hydraulic mining probably had the most direct environmental impact: Enormous cannons, called "monitors," shot high-pressure water at the deposits, stripping soil, sand, and gravel from the bedrock. Miners then directed the water and sediment (slurry) into sluices — linear wooden chutes — charged with quicksilver. The quicksilver and gold particles combined in a chemical reaction to form gold-mercury amalgam, which would sink, while the sand and gravel passed over it and through the sluice. Finer-grained particles of gold and

NORTHERN CALIFORNIA GOLD AND MERCURY MINES



Source: Alpers, USGS

mercury often washed through and out of the sluice, but some were trapped in a second set of sluices, called "undercurrents", which were covered in copper plates coated with mercury. Despite efforts to catch the finest particles, an estimated 10% to 30% of the mercury was lost at mine sites and downstream during this process.

As the miners dug deeper, they built tunnels to remove debris and drainage from the bottom of the hydraulic mine pits. The tunnels directed the processed sediments — placer tailings — into nearby streams and rivers. Between 1850 and 1884 in the Sierra Nevada, more than 1.5 billion cubic yards of gold-bearing placer gravels were mined; during the processing, an estimated three to eight million pounds of mercury (or more) may have been lost into the environment. An 1884 legal decision prohibited discharge of mining debris in the Sierra Nevada, effectively putting a halt to large-scale hydraulic mining, but the practice continued in the Klamath-Trinity Mountains until the 1950s.

From the mid-1880s to the early 1900s, most of California's gold came from drift mining of placer deposits and underground mining of hardrock gold-quartz vein deposits. The hardrock mines used stamp mills to crush the ore. In these mills, stamps — several-hundred-pound metal pestles — were lifted by a rotating cam and dropped onto the rocks. During this smashing process, mercury was used to recover the gold. The tailings from these stamp mills went downstream.

As recently as the 1960s, mercury was used in dredging floodplain deposits for gold. Adding up mercury inputs to the ecosystem from all types of gold mining over time, USGS scientists estimate that hydraulic mining contributed about 8 million pounds, dredging 2 million pounds, and hardrock mining 3 million pounds. Today, large- and small-scale commercial gold mining operations continue, including solo miners working with small suction dredges and old-fashioned pans. According to the California Department of Conservation's Doug Craig, modern dredgers probably pick up and sort more mercury than they introduce. The recovered mercury can be turned in on mercury "drop-off" days in the Sierra foothills. It is the mercury legacy of the rush for gold over a century ago that remains irrecoverable. LOV

RESEARCH

Doing the Groundwork

Picture two mountain ranges, one full of old gold diggings, the other with abandoned mercury mines. Imagine droplets of mercury and specks of cinnabar hanging on to the finest grains of sand and silt in these watersheds. Rain and runoff wash these grains downstream, leaving them here and there on the sides and bottoms of creeks and rivers or to settle out in the wide-open waters of Delta islands and north S.F. Bay wetlands. Each year adds new layers of the silvery metal and deep red crystals to old layers sent downstream by gold and mercury miners 150 years ago. Along the way, some gets buried, some changes chemical form, and some settles, only to be stirred up again by flows, tides, storms, and humans rearranging the landscape. The question becomes, how much of which kind of mercury is coming from the mountains and rivers, and how much from resuspension of bottom sediments and old deposits, not to mention how much is getting lost along the way, out to sea or up the food chain?

"It's the first time, to my knowledge, that anyone has tried to do a methyl mercury mass balance for the purposes of regulating an estuary," says biologist Chris Foe of the Central Valley Regional Water Quality Control Board. "We knew mercury was moving from sediments to water to fish; what we needed to know was, where was it coming from and going?"

A team of 19 scientists, charged in 1999 with answering this question, measured mercury in the water column and sediments, and in various fish and birds, throughout the watersheds of the Sacramento and San Joaquin rivers and in the Delta. This first major CALFED mercury study, managed by California Department of Fish & Game biologist Mark Stephenson of Moss Landing Marine Labs, revealed a number of things about Cache Creek, the Sacramento River, the Delta, and Suisun Bay — some surprises, some mysteries, some fuzzy edges between inputs and outputs.

"Our expert science advisers told us not to worry about methyl mercury coming from the rivers. They told us to concentrate on the Delta, with all its marshes, where they thought we'd see lots of methylation and associated levels in the biota," says Stephenson. "What we found was a completely different story."

Darell Slotton and Shaun Ayers of U.C. Davis in Sierra waters, collecting aquatic insects to test mercury uptake.

Not surprising was confirmation that the Cache Creek watershed (see map p.5), dotted with eroding old mercury mines, was one of the biggest sources of new mercury inputs to the Delta and S.F. Bay downstream. Scientists confirmed not only that nearly all sediments in historic mining areas had above-background levels of total mercury (a measure of all chemical forms), but also that levels were acutely high below mine sites. But Cache Creek's megadoses to the system only come down after huge storms. "We found very distinct seasonal ups and downs in exposure," says U.C. Davis biologist Darell Slotton, who tracked bioaccumulation in creek fish.

Comparing Coast Range creeks such as Cache with Sierra creeks, researchers found that while the methylation potential starts out very different in the two mountain ranges due to the different types and amounts of mercury found there, by the time it's transported to valley streams and the Delta, it evens out.

More revolutionary, says Stephenson, was the discovery that in a normal year, Sacramento River inputs of total mercury far outweigh those of Cache Creek. The river loads go up in the winter and down in the summer, he says. But because the Sacramento supplies most of the Estuary's water, it also supplies a big slug of mercury (60% to 85% of the total load).

Doing the Groundwork

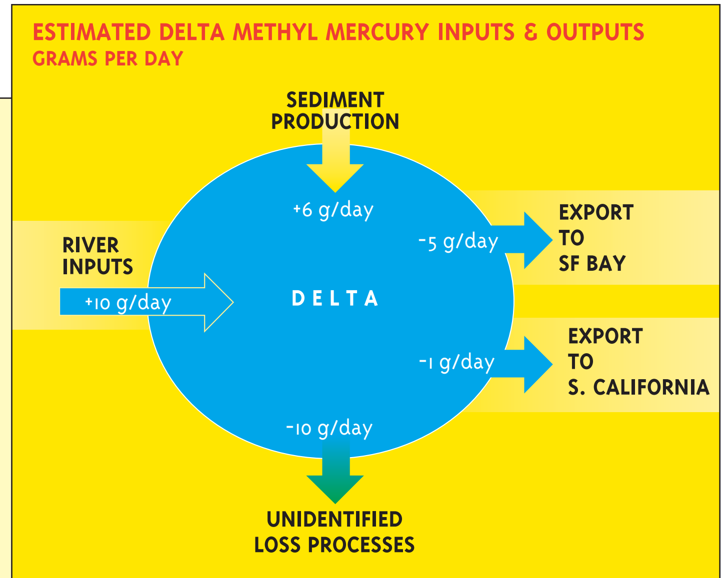
Big hits of total mercury from these two heavyweights — Cache Creek and the Sacramento River — are joined by some lesser but still notable hits from the San Joaquin system to all flow through the Delta. Chris Foe found, for example, that methyl mercury concentrations and loads increase threefold to fivefold in the 300-mile transit of water down the Sacramento River from Shasta Reservoir to the state capital. Right below Rio Vista, however, methyl mercury mysteriously diminishes by about 50%, and stays that way as waters migrate south and west down to the export pumps and Suisun Bay.

"All our results suggest the loss of methyl mercury in transit from the tributaries through the Estuary. Mercury's getting dropped off in certain regions of the Delta," says Texas A&M University geochemist Gary Gill, part of the team.

Dropped off or not, methyl mercury can also re-emerge in "flux" — to use the science term for exchange between sediments and water. To measure this, Gill used a device called a benthic flux chamber. "We capture a piece of the bottom water in contact with sediment, then leave the device there, sample periodically, and watch for the buildup or loss of components like methyl mercury inside the chamber," he says. Gill found that flux becomes the dominant source of methyl mercury in the Delta during summer low-flow conditions, when river inputs drop to a mere quarter of benthic (bottom) inputs. Summer peaks were confirmed in sediments across the Delta by other investigators.

Chris Foe added this research to his own two-year sampling at all major input and output sites in the Delta to come up with an estimated methyl mercury mass balance for the region. The result is a balance sheet suggesting that the Delta gets about 16 grams a day in inputs and loses about six grams in outputs, leaving 10 grams unaccounted for. "The Delta turns out to be a net methyl mercury sink," says Foe.

This inputs and outputs balance sheet is a useful starting point in our big picture understanding of mercury in the system. Much more remains to be learned on a finer scale about the Delta's internal methyl mercury production and loss processes, and how the region's complex hydrodynamics affect mercury movements and transformations. A lot has been learned, however, about another whole side of the ecosystem balance sheet: exposure. The results of CALFED studies on where and how bottom-dwelling organisms, and the fish and birds that eat them, are picking up mercury can be found in detail in later pages (see Bioaccumulation pp. 9-11). But as Foe sums up, just as in sediments and water, fish exhibited high concentrations at the mouths of tributaries; these decreased across the Delta and then rose again around Suisun.

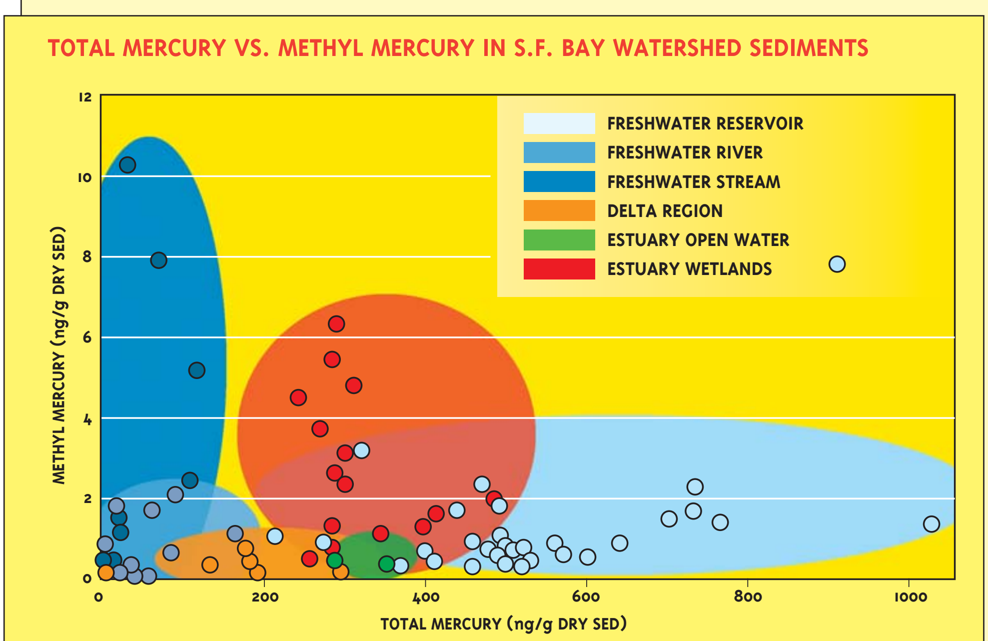


Source: Foe, CVRWQCB

While it may be clear from the big picture side that the Delta is not presently a methyl mercury hotspot, going down to ground level in its marshes, the action heats up. The science team conducted a number of wetland studies. Some did wetland transects — measuring methyl mercury production in the inner, middle, and outer marsh areas of places like Weber Tract, Mandeville Cut, and 14-Mile Slough. Methyl mercury always proved higher in the inner marshes than in the outer channels, and higher overall in the marshes than in open water areas.

Another study comparing non-vegetated deep water with tule marsh and *Egeria* habitats along the Cosumnes River and Franks Tract (a large flooded island) found that areas congested with submerged invasive plants produced the most methyl mercury. "*Egeria* sites are hotspots relative to others because the plant traps the fine-grained material and creates a nice warm canopy over juicy organic matter for the microbes to do their methylation work," says U.S. Geological Survey researcher Mark Marvin-DiPasquale.

Once the wetlands and the water get saltier in Suisun Bay, mercury methylation mounts again. In Suisun



This data, collected from surface sediments in multiple research projects throughout the S.F. Bay watershed between 1999 and 2004, suggests that habitat type may have more of an influence on methyl mercury production and concentration than the amount of total mercury.

Source: Marvin-DiPasquale, USGS

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and the North Bay, USGS scientists have long documented the erosion of the bayfloor, and the likely liberation of legacy mercury deposits. Some suspect as much inorganic mercury is eroding off the floors of Suisun and Grizzly bays as is coming in from the Central Valley.

Last year, Stephenson got more into the nitty-gritty of the Suisun situation. In summer 2004, he monitored mercury coming and going in water and suspended solids at seven stations in Suisun Marsh and Grizzly Bay and found methyl mercury concentrations in the marsh five to 10 times higher than those down near Grizzly Bay in open water.

The twist this time, however, is the massive tidal to-and-fro. "The amount traveling back and forth overwhelms the amount traveling down from Suisun Marsh. So instead of the marsh polluting the Estuary, it looks like the reverse," he says.

These new findings come from a major CALFED follow-up study on mercury, involving 17 scientists and started in 2003. The aim is to answer questions raised by the first round of research. Why, for example, do we lose methyl mercury in the Delta? Some speculate that tides and salinity play a role; some that the rivers widen and deepen just above Rio Vista, promoting more particle settling and demethylation; some that there's something else going on that we've yet to fathom.

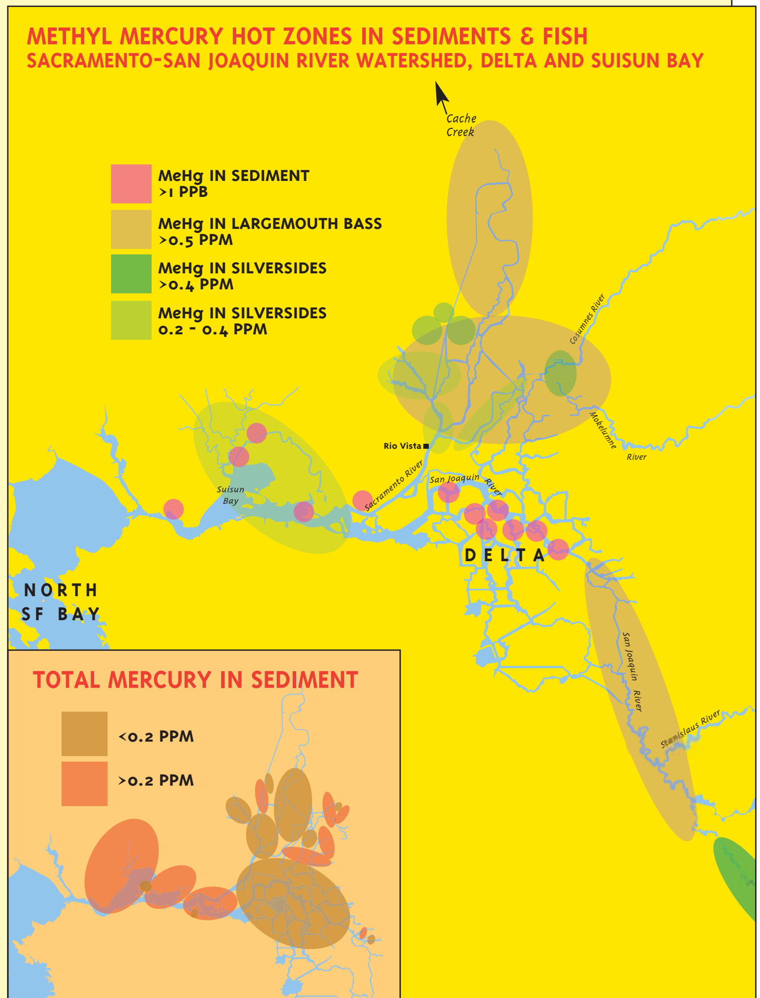
Amy Byington, a Moss Landing grad student, has begun gathering clues by chasing water masses down the river with drogues (a drifting device she crafted out of a trash can); tracking salinity, temperature, and turbidity using a flow-through sensor; and floating light and dark Teflon bottles filled with mercury-spiked surface water for hours at a time. All these methods are designed to see whether mercury is being lost by dilution, settling, long residence time, food web uptake, or photo demethylation — hence the bottles. Methyl mercury can break down in sunlight.

Moss Landing's Kenneth Coale collecting a sediment sample for mercury.

Though results are highly preliminary, Byington found that particle settling and photo demethylation due to longer residence time offered the most promising explanations for mercury loss, while water dilution alone could not explain it. "I was surprised to see such a high rate of photo demethlyation in this first stab," she says. "Now I know it's worth looking into." The results from her light and dark bottle float experiments suggest a summer loss of up to 22% of the methyl mercury in the water during daylight hours.

Another looming question is the contribution of wetlands to the mercury balance sheet. Are they hoarding methyl mercury or exporting it to the larger Estuary? To answer this question, the science team is scrutinizing a mix of natural and constructed marshes. These include the managed duck clubs of Suisun, the older tule marshes with established root systems of Browns Island and Mandeville Cut, and two side-by-side human-engineered wetlands built on Twitchell Island originally for subsidence studies. "All these sites have one big channel coming out, which gives us a good clear mercury signal," says Stephenson.

Small changes in wetland configurations and management may make big changes in mercury exports. On the side-by-side Twitchell wetlands, Stephenson found that one exported nine times more methyl mercury than the other. The reason? Something to do



Inflowing tributaries consistently show the highest biotic signals, with a secondary rise in the west Delta and a notable low area in the Delta proper.

Source: Stephenson et al., MLML (Sediments: Heim, MLML; Silversides: Slotton, U.C. Davis; Bass: Davis, SFEI)

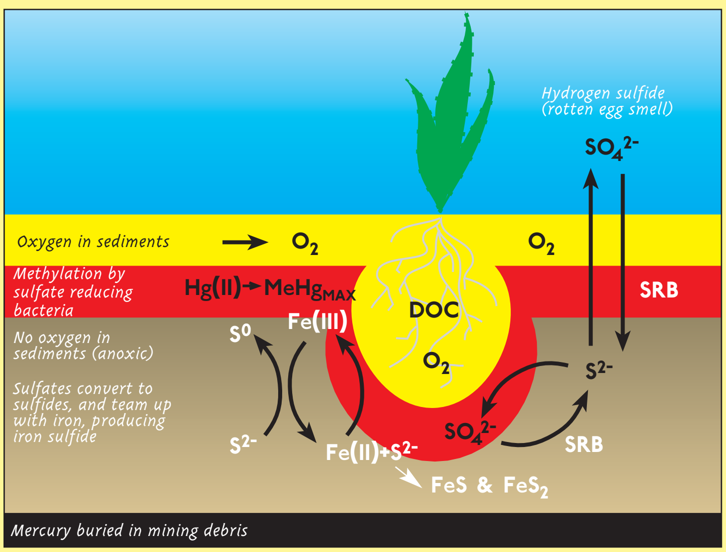
with the thickness of the tules and the water movement through the channels, Stephenson speculates. On the side with 100% tule and cattail cover — the bigger exporter — water is forced through the root zones where methylation conditions are good. On the side with only 70% cover, water has the option of flowing through channels. The different sizes and depths of these ponds may also play a role in terms of dilution and photo demethylation.

"Wetlands may produce a lot of methyl mercury but they also catch and trap a lot of particles. Twitchell tells me that a blend of engineering and science might someday design a wetland that minimizes the export of mercury," says Stephenson.

So looking at the whole landscape, what have we found? In a nutshell, the concentration of methyl mercury in water diminishes as the Sacramento River flows to the pumps, and the biotic data show the same pattern, so the Delta situation is what scientists call "tributary dominated." In other words, the methyl mercury is coming from the tributaries, rather than being produced in the Delta itself. Beyond the Delta, sediment and water concentrations start to rise again around the big North Bay marshes and over the eroding bayfloors.

On the horizon are studies that will look more closely at where the region's two main rivers are making their methyl mercury and whether marshes merely have localized effects on methyl mercury loads, or whether they actually pollute the larger system. Stephenson hopes to tackle the import-export question via a multidisciplinary study coordinating monitoring of flows, tides, suspended solids, and methyl mercury concentrations. "It's the way the whole future of mercury research has to go," he says. ARO

METHYLATION ZONE IN A VEGETATED SALT MARSH



Chemical terms

O_2	oxygen
HgS	cinnabar
Hg(II)	inorganic divalent (oxidized) mercury
MeHg	methyl mercury
S^0	elemental sulfur
S^{2-}	sulfide
SO_4^{2-}	sulfate
Fe(II)	reduced iron
Fe(III)	oxidized iron
FeS & FeS_2	solid phase iron-sulfur minerals, iron monosulfide and pyrite
DOC	dissolved organic carbon
SRB	sulfate-reducing bacteria

Source: Marvin-DiPasquale, USGS

Biogeochemical Basics

Chemistry, the blackboard kind scratched with equations and transformations, has never entered into CALFED restoration questions as much as it has with mercury. Researchers have been tracing the myriad conversions and combinations by which garden-variety mercury becomes methyl mercury. The biogeochemical "axis of evil" in these conversions, according to one scientist, is carbon, sulfur, and mercury. The evil occurs only when these elements interact, and only in just the right way. "They all fit together; you pull on one and the other two get stretched," says chemist George Aiken of the U.S. Geological Survey. Add water, and the mercury goes mobile.

The biogeochemical basics are these: Mercury comes in many forms, called "species." Whatever the species, they all derive from the earthy red cinnabar mined in the Coast Range (mercuric sulfide) or from elemental mercury made by roasting cinnabar. The roasting produces the liquid "quicksilver" used in everyday thermometers and in the Sierra to amalgamate gold.

The transformation of these species into methyl mercury is a complicated multi-step, multi-factor process that defies simplification (see links for more technical papers p. 16). But at a basic level the steps involve first oxidation (in the case of elemental mercury only) and then methylation. Once in an oxidized form, Hg(II), the mercury can more easily react with things dissolved in water (sulfur, carbon, chloride, etc.) and create other gaseous, aqueous, and solid species of mercury.

The next transformation moves from the chemical to the biological, as the microbes that engineer and catalyze the methylation reaction with the Hg(II) come into play. These "sulfate-reducing bacteria" thrive in the low oxygen zone down at the bottom of our rivers, marshes, and bays. The bacteria convert sulfate into sulfide to "make their living," just as humans convert oxygen to CO_2, says microbial ecologist Mark Marvin-DiPasquale. In the process, they can also take oxidized dissolved mercury species and convert them to methyl mercury. If no sulfate is present in their environment, the microbes may switch to other ways of making their living (via the fermentation of organic matter) and still create methyl mercury. Other strains and kinds of bacteria, meanwhile, make their living in ways that actually degrade methyl mercury.

USGS's Jennifer Agee sampling sediment in an anoxic glove bag.
Photo: Mark Marvin-DiPasquale

The rate of methylation or demethylation is influenced by a wide variety of things in the aquatic environment: carbon (organic compounds from plants, algae, peat, etc.); sulfur and salinity levels (associated with marine influences, geothermal springs, or agricultural runoff); the amount of oxygen in the soil; iron (which in combination with other elements can either stimulate or inhibit methylation); the depth of old mining debris (buried under cleaner sediments or eroding off the bay floor); the depth of the water and amount of sunlight (see p. 5); aquatic plants (the more roots, the more mercury methylation in many cases); and the temperature.

Taken as a group, these biogeochemical twists and turns become a mind-bending puzzle not only for scientists, but also for restoration managers. But scientists are hopeful. "We're just beginning to understand the interplay between microbial activity, sediment chemistry, and plant physiology that controls methylation," says Marvin-DiPasquale. "What's complicated is that controlling chemistries differ from place to place, and season to season, within our Estuary."

Over the past 10 years, within and outside CALFED work, Marvin-DiPasquale has been analyzing bottom sediments from various ecosystems in terms of factors that control methylation and demethylation with the help of radioactively tagged mercury compounds. These compounds simulate natural mercury compounds in the system, allowing him to more easily track the many microbial and chemical transformations mercury can undergo as a result of changing environmental conditions.

Based on this research, Marvin-DiPasquale estimates that less than 5% of legacy mercury in the Bay-Delta's backyard is "reactive," meaning available for microbial methylation. It is this small fraction, and its pathways for interaction with carbon and sulfur, that hold the key to future management. "Lots of things control reactivity across the ecosystem. The trick is to find those places along the way, those critical points in the process, that control the larger story," he says.

One critical point is the intersection between the mining debris layer and water. In a 2000 study of San Pablo Bay, where the debris is actually on or very near the surface, Marvin-DiPasquale examined its depth relative to the zone of maximum microbial activity at three open water sites and one marsh site. Though total mercury concentrations derived from the debris were similar at all sites, Marvin-DiPasquale saw a big difference in methyl mercury production. "The take-home message is that sediment geochemistry is a much more important control than the amount of total mercury present," he says. The marsh site on the periphery of the bay, where microbes were more active and plants were taking oxygen down to the debris level (see chart p. 6), produced 10 times more methyl mercury than the other three sites.

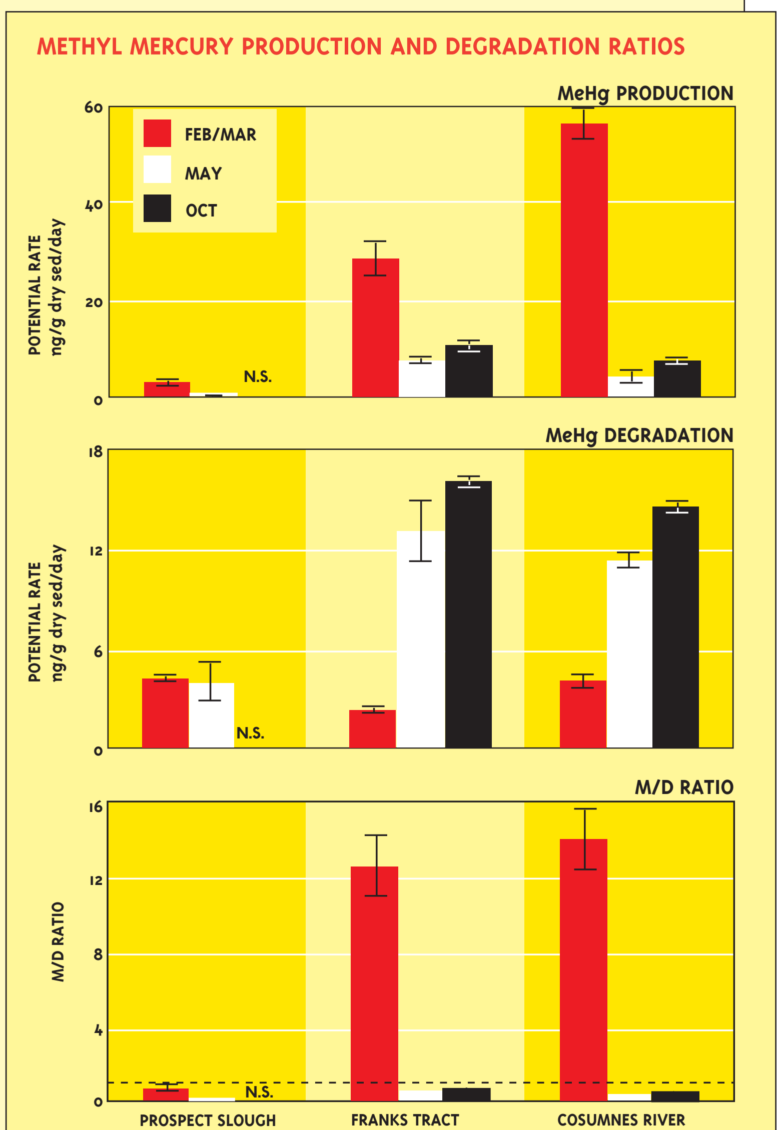
On the sulfur corner of the blackboard, Marvin-DiPasquale found some interesting things in a 2001 study of Franks Tract (a Delta island), the Cosumnes River (last undammed river in the system), and Prospect Slough (downsteam of Cache Creek and the Yolo Bypass). He found that the SRB microbes that stimulate methylation only do so when sulfide levels are low to moderate. As the bacteria themselves produce more and more sulfide end products, methylation decreases. "It's a dynamic cycle," says Marvin-DiPasquale, explaining how scientists must balance processes controlling gross methyl mercury production and those controlling gross degradation to estimate net production in the environment (see chart).

On the carbon side of the blackboard, even more potential controlling factors on methylation are emerging. Dissolved organic carbon (DOC) — derived from the breakdown of plankton, peat soils, crops, and other vegetative matter — actually has the power to increase the amount of mercury dissolved in the water column, according to studies done by George Aiken. DOC can accomplish this sinister task without any help from microbes or minerals by dissolving cinnabar or mercury associated with soils or sediments.

The dissolution has to do with certain key components in the DOC called "aromatic humic acids," thinks Aiken. By measuring these and other key components, he hopes to find a way to predict the reactivity of different kinds of DOC with mercury and sulfur.

Part of the problem is how much mercury likes to cozy up to passersby. "Mercury really likes particles. If it binds onto a soil grain, it won't methylate; but if it binds to DOC, it can become available for methylation by microbes," says Aiken.

The quality or chemical nature of the DOC is much more important in the mercury mix than the quantity. Alluding to our coffee culture, Aiken says, "You can either have double caf, like you get in the Delta, or single caf, like you get in the Sacramento River." The more "caffeine," namely reactive organic molecules, in the presence of mercury and sulfate-reducing bacteria, the bigger the bioreactive buzz.



MeHg production, degradation, and methylation-demethylation ratios at three 2001 sampling sites in 0-2 cm of surface sediment. The dashed line indicates where the ratio = 1 (theoretical net production and degradation are in balance).

Source: Marvin-DiPasquale, USGS

Aiken sees more promise in managing the DOC and sulfur in his axis than the mercury. In the Everglades, the Goldilocks areas identified as hot for methylation (see cover) are missing one critical point in the axis — sulfur. But restoration plans to move a lot of water around this Florida wetland could import the sulfur in runoff from nearby sugarcane farms (an important local source of sulfur in this freshwater landscape). By being aware of the sensitivity of some areas, and managing adaptively, resource managers may be able to control some of the ecological backwash, Aiken says.

Plants, as a controlling factor, star in the next wave of research being undertaken by various mercury sleuths, including Marvin-DiPasquale. Comparing methylation levels in pickleweed, bulrush, and non-vegetated mudflats at the South Bay's Steven's Creek Marsh, for example, he found that in the summer, methylation can be four to six times higher in the root zone of the pickleweed vs. the mudflat just two meters away. In the winter, however, when migratory birds arrive to poke for worms in the oozes, the mudflats were more active methylators. "There's a seasonal flip-flop," he says. "Birds may be getting their mercury fill in S.F. Bay during their overwintering period."

Terns Photo: Rob E. Holt/MMS

The plants themselves affect the sediment chemistry by pumping oxygen from the air down into the root zone, which lowers sulfides and primes the pump for methylation (see diagram p. 6). In an Army Corps study done at the Hamilton Air Force Base wetland restoration site in Marin County, pickleweed outpaced cordgrass as a zone for mercury methylation.

Scientists hasten to say that all the information on the impact of different wetland plant species on methylation rates is in its infancy. Questions remain to be explored about the influence of different plant types, not to mention what goes on above ground in the leaves. Do plants pull mercury up from down deep and then excrete it into the air, or re-enrich the soil surface as they die back each year, for example?

Back to the basics, more about the carbon side of the axis of evil may be learned soon. CALFED recently provided $2 million to Aiken and Roger Fujii, also of USGS, to delve deeper into organic carbon interactions with mercury in different tidal wetland environments.

So how will all this effort to follow the path of mercury through sediments, water, plants, and air help? Scientists hope to know enough in the next five years to help Bay-Delta managers work on promoting one biogeochemical process over another as they design wetlands, move water, staunch mine erosion, and treat wastewater.

On the distant horizon glimmer new computer models combining certain parameters of reactivity (among the DOC, mercury, and sulfur) with data on methylation pathways and processes.

"Somewhere down the road, we should be able to write a biogeochemical model that can predict the effect of tweaking a condition in the Delta or the Everglades or San Diego," says Aiken. "If we can get a reasonable number at the end, we'll be able to do the smart things in terms of adaptive management and restoration, rather than just proceeding blind." ARO

FOLLOWING THE FOOD

Scientists have been scratching their heads over why biota at the bottom of Delta tributaries, on some islands, and in reservoirs in the South Bay's Guadalupe River watershed carry high methyl mercury levels relative to aquatic critters hanging out elsewhere in the system. One hypothesis is that there's something different about the food chain in these areas — more trophic levels, different species, or interference from invaders.

In a CALFED-funded study now in its third year, Robin Stewart and Mark Marvin-DiPasquale of the USGS are scrutinizing two distinct habitats — riparian river plain (Cosumnes) and flooded island (Franks Tract) — trying to tease out not only how mercury cycles through them, but also where and how organisms feed within each habitat. Stewart has been using stable isotopic fingerprints and ecological methods to construct food webs. "I can get a measure of how long they are, who's eating whom and where, and what is at the bottom of the food chain," she says.

Based on the data gathered to date from this and past CALFED-funded studies, Stewart suspects that epiphytic algae (algae attached to the surfaces of aquatic plants like the invasive *Egeria densa*) may play a critical role in the first transfer steps, particularly in the central Delta food webs. In other food webs, organisms eat phytoplankton instead of the algae, a variation in the mercury transfer pathway. To find out its significance, Stewart is testing a new technique that deploys Teflon sheets shaped like *Egeria* leaves to collect the algae so they can be tested for mercury.

USGS's Mark Marvin DiPasquale extracting sediment from the root zone of tules growing in the Delta's Franks Tract. *Photo: Jennifer Agee*

In another USGS study independent of CALFED, researchers explored methyl mercury bioaccumulation in the food webs of four reservoirs and a flooded quarry pit in the Guadalupe River watershed, an area with some of the highest mercury contamination in the Bay-Delta system due to the presence of the New Almaden Mine. Sampling occurred in 2004 during the fall, a season when low reservoir water levels produce a combination of conditions scientists suspect promote methylation and food web uptake (see p. 13). Snapshot measurements found that methyl mercury consistently represented less than 11% of the total mercury in phytoplankton, then leaped to 40%-85% in zooplankton. The relative methyl mercury concentrations started out low down at the bottom of the food web but then rose rapidly. "The critical transition step appears to be from the phytoplankton to the zooplankton, and it's much more complicated than has been reported in other aquatic systems where atmospheric mercury sources dominate," says USGS's Jim Kuwabara. ARO

Keeping Tabs on Bioaccumulation

There's a perfect machine for measuring mercury buildup in the aquatic food web, but it wasn't assembled in any high-tech instruments lab in Texas. The caddisfly, whose green caterpillar-like larvae never move far from under the river rock where they were born, is one of the chosen. Other perfect machines are a slim silver fingerling called the inland silverside, and a number of equally diminutive crayfish, gobies, and shiners. These small fry carry a big weight on their backs: standing sentinel in our creeks, rivers, and bays to warn us of mercury's spread.

"A large fish tells you the bottom line, if mercury levels are bad or good, better or worse, but not necessarily where it came from and when," says Darell Slotton, explaining that big fish like striped bass build up their mercury across several years and from diverse locations. "It's the short-lived, localized organisms that can help us answer the tricky questions of time and place."

Slotton, a U.C. Davis aquatic biologist, has been putting these organisms to work as "biosentinels"—jumping or wading into the water to catch fish and insects, then cleaning, freezing, drying, and grinding them up into powder to measure their body burden of methyl mercury. These organisms not only have to be small, young, and not long for this world to make the biosentinel team, but also be abundant, popular as lunch for larger fish, unimaginative in their own diets, and stay-at-home types. "They allow us to pinpoint mercury problems to place and time of year, which is something we might be able to do something about in terms of management," he says.

Everywhere he's been in the past 10 years—polishing his biosentinel techniques in CALFED and other studies across the Sierra, the Coast Range, and the Delta—Slotton's been chasing the links between mercury in the environment, biosentinels, and big fish. "We're starting to get a handle on how they all relate to each other," he says. In a major Cache Creek study, his research group did some of the most comprehensive sampling of mercury in water, biosentinel organisms, and fish ever done. What they found, among many other things, was that methyl mercury in the water correlated directly with mercury in fish, whereas total mercury in water did not correlate well with either. Their results have led to some innovations in the state's regulatory approach to mercury.

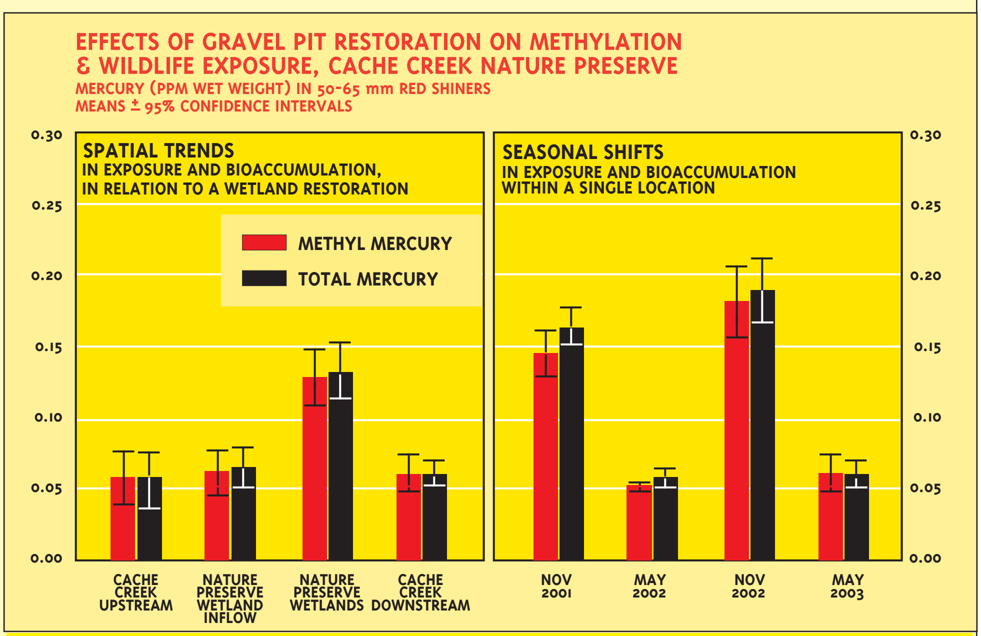
Slotton's biosentinel results also suggest, in a general way, just how much the warm season correlates with increased mercury uptake by insects, fish, and other aquatic animals. "Spring comes, bacterial activity heats up, methylation increases, plants and fish grow, put on weight, pick up mercury," he says.

Isolating just how much of measured changes in mercury bioaccumulation are due to natural variability—the wildcard common to California's flashy climate—vs. local methylation processes and hotspots is also important. In an older, bigger fish, mercury changes are very muted year to year. But in silversides in the Delta, for example, Slotton saw changes of up to 30% in the amount of exposure depending on the wetness of the year and the associated ups and downs in new annual inputs from tributaries.

Red Shiner

"We all went into this whole mercury project thinking that it might be hopeless, with this backlog of legacy mercury everywhere," he says. "But now that we see these seasonal and spatial spikes, we're thinking it's the new inorganic mercury brought down from mining areas with winter storms, not the old stuff lying around, that may be more bioavailable for methylation."

The stuff may certainly be more bioavailable in wetlands. In research comparing gravel pits used to construct wetlands along Cache Creek with the sloughs flowing in and out of them, Slotton found that another biosentinel fish, red shiners, picked up more than double the amount of methyl mercury in the restored wetlands than in the inflowing sloughs. Warm season uptake was typically three times higher than in the cool season.



Yolo County hopes to eventually convert a string of 17 major gravel pits along lower Cache Creek into a healthy riparian corridor. In this pilot project, researchers found that restoring one pit to a wetland almost doubled mercury exposure and bioaccumulation compared to inflowing water levels. The data and actual uptake patterns in red shiners show, however, that seasonal management of water releases from the wetland (limiting fall releases, for example) can dramatically reduce downstream exposure and discharges of mercury. Though funded by Yolo County, this research builds significantly on prior CALFED studies.

Source: Slotton, U.C. Davis

Keeping Tabs on Bioaccumulation

On the western slope of the Sierra, Slotton and colleagues have identified numerous mercury hot zones, including the Middle and South Yuba rivers, locations of some of the largest Gold Rush-era hydraulic mines. These river reaches are also candidates for the re-introduction of endangered native steelhead and spring-run chinook salmon, and resource managers eager to improve fish passage upstream and over dams asked the U.S. Geological Survey's Charlie Alpers and Slotton to assess mercury risks. The two scientists narrowed the danger zone for migrating fish to a 25-mile reach between 3,000 feet in elevation and Englebright Dam. In this reach, mercury levels in biosentinel young trout were five times higher than in upstream reaches. As a next step, Alpers hopes to take a closer look at methyl mercury in spawning redds (the gravel nests in which anadromous fish lay their eggs).

On a parallel track, other mercury researchers have been keeping tabs on the bigger sport fish that anglers catch and eat. According to the S.F. Estuary Institute's Jay Davis, who conducted the first major CALFED sport fish study on mercury, the oceangoing salmon that so many people like to eat aren't even on the health warning radar screen. It's the bass, catfish, and pike minnow — big predator fish that hang out in deep spots, reservoirs, and flooded islands waiting to lunch on littler guys — that are of greatest concern for pregnant women and children.

AVIAN TROPHICS

A Caspian tern skimming the Bay for fish might actually be healthier if it were a dumpster-diving gull. Recent CALFED-funded studies of more than 300 bird eggs revealed that birds that eat only fish (like terns), use specialized habitats, or nest and forage in Bay "hotspots" are ingesting more methyl mercury than birds that feed part-time in parking lots or dumps.

"We thought gulls, being fish eaters, would have high mercury, but they don't," says U.S. Fish & Wildlife's Tom Maurer, although their cholesterol may be bad from all those french fries, he adds. "In general, the higher up the food chain, the more mercury you're ingesting."

Exposure to mercury is not only related to what birds eat, but also to where they eat. Levels of mercury in eggs from great blue herons at five locations in the Delta correlated directly with mercury in silversides (their prey fish). Eggs from birds like black-necked stilts and snowy plovers that feed in potential methylation zones — around the Bay's perimeter, at the interface of land and water, or near the South Bay salt ponds — also had elevated mercury concentrations.

Mercury can affect a bird's behavior, hearing, the growth of its nestlings, and the hatchability of its eggs. Some of those things are so subtle they are difficult to measure — especially when birds are migrating and nesting elsewhere, and also being exposed to many other contaminants. "Trying to tease all these things out can be tricky, and there is no easy way to generalize," says Maurer.

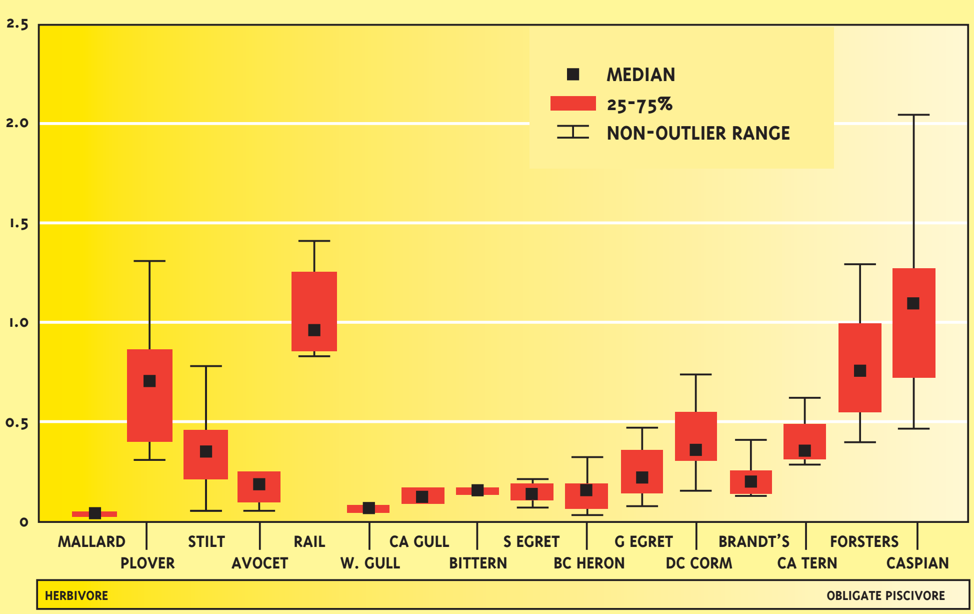
Birds can shunt contaminants such as mercury into their eggs. As a result, hatchlings may get a double dose — one inherited from their mothers via the egg, the second from the fish their parents bring to feed them.

Further enlightenment should come from a new study in which USGS and U.S. Fish & Wildlife will track mercury through the entire lifecycle of some birds, from egg to adulthood to nesting and reproduction. In the study, biologists will attach radiotransmitters to bird legs to confirm that they are breeding locally and pinpoint where they feed in the Bay. They can then test the food organisms in those areas, as well as the eggs, feathers, and blood of the locally nesting birds.

Bird biologists are also paying close attention to the endangered clapper rail. In a recent study, U.S. Fish & Wildlife researchers concluded that mercury concentrations in Wildcat Marsh clapper rail eggs that had failed to hatch were likely embryotoxic. Diminished reproductive success, they say, could mean trouble for future Bay clapper rail populations and for those trying to restore their habitats. How much trouble mercury will cause no one quite knows.

Whatever the trouble, the $5 million that CALFED's Ecosystem Restoration Program recently approved for further bird studies will help restoration managers address it head on. "We know enough to know that we need to know more," says Maurer. LOV

MERCURY CONCENTRATIONS IN BIRD EGGS
PARTS PER MILLION, WET WEIGHT



Source: Maurer, USFWS

Silversides *Photo: Slotton*

Davis compared mercury levels in 10 species of sport fish with U.S. EPA screening values for human health risk, and largemouth bass were among the most contaminated (see map p. 5). In the Delta, 80% of these bass had over 0.3 ppm of methyl mercury (EPA screening level) and 17% had over 1 ppm (FDA action level). As a result of studies by teams working with Slotton, Davis, and Alpers, the state has issued new consumption advisories for Bear Creek (Cache watershed), several northern Sierra lakes, the Lower American River, and Lake Natoma.

One place the health risk for fish consumers seems lower is the very heart of the Delta. A number of sport fish species in this labyrinth of favorite fishing coves and river bends frequently had levels below U.S. EPA health-risk criteria. "It's a ray of hope," says Davis. "It means that mercury is not necessarily high everywhere in the food web. It means there may be other places we can tell anglers it's safe to go fish."

More rays of hope, or at least light, are in the pipeline. This spring, scientists began hammering out the details of an amibitious new CALFED fish-monitoring program with input from diverse advisers. The group is choosing 12 long-term biosentinel index sites for annual monitoring, paired with more intermittent sport fish monitoring, as well as surveys in mystery zones where there are no fish data and spot checking as needed at large restoration and research sites. "We're going out of our way to get biosentinel data from right in the middle of other mercury research projects," says Slotton. Indeed, the entire fish-monitoring program should also benefit from tighter, stricter protocols so that multi-species, multi-site data can be better correlated.

"The bottom line in dealing with our mercury problem is always the fish. If it's not in the fish, it's not in the fish," says Slotton. ARO

Tricky Tailings

Once upon a time, gold was our region's most coveted resource, but these days gravel seems equally precious. Those trying to recreate floodplains and salmon spawning beds — in rivers where most of the natural gravel supply lies stuck behind dams, and where holes dug by gravel-mining operations gape to be filled — have been eyeing the big piles left by gold dredges. Gold dredges moved along rivers, digging up the floodplain and channel gravels, separating out the gold (with the help of mercury), and stacking tailings (cobbles, pebbles, and other coarse materials) on the banks. And while this form of mining may have left behind a cheap local gravel resource, it also ruined habitat and disrupted river processes along 11 rivers and creeks in the Bay-Delta watershed. In these areas, river restorers must not only find materials to rebuild spawning grounds and river beds, but also shift the oft-mined landscape around to widen channels and recreate floodplains. Managers are worried that the disruption, and the reuse of tailings, may mobilize mercury.

In 2003, researchers, restoration managers, and regulators joined together to form a special work group on tailings. In a major collaborative effort, this Dredge Tailings Work Group (including California Bay-Delta Authority staff) is now drafting an issue paper that lays out considerations for restoration managers.

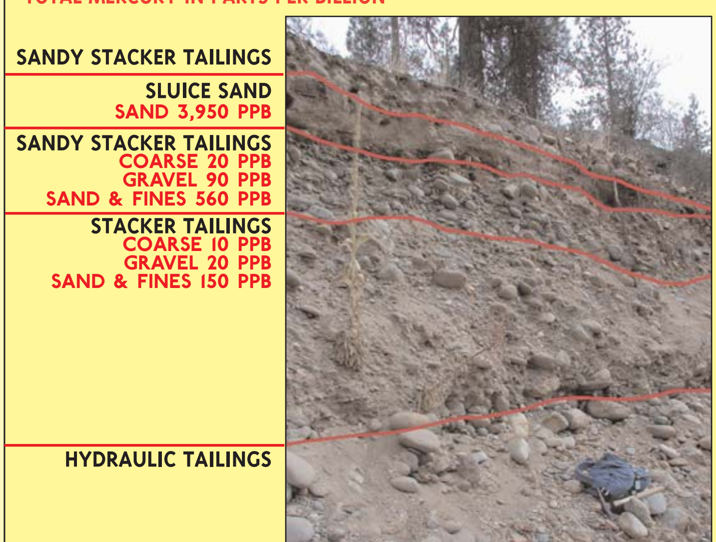
Scientists, meanwhile, are learning more every day about how mercury in tailings might behave as a result of various restoration uses. The CALFED program, USGS, and other agencies have launched diverse research projects in recent years. The projects cover Clear Creek and the American, Merced, and Trinity (non-CALFED studies) rivers — comparing mercury levels in tailings piles and surrounding waters to background levels, tracking mercury's chemical transformations as tailings are disturbed or exposed to different ecological processes, and experimenting with sorting and washing to eliminate the most contaminated material, among other topics.

"The coarse material is always very low in mercury, but the fine material can be very high," says Roger Ashley of the USGS. "What's interesting is that we're not really finding much of the elemental mercury used for gold amalgamation anymore. In the course of a half century, it's been transformed into other species of mercury, some of which are more of a worry."

Ashley and James Rytuba, among others at USGS, have been scrutinizing the Clear Creek and Trinity River situations. They have been using a "sequential extraction" method to identify different species of mercury in tailings samples — enhancing understanding of how and when mercury transforms into more soluble, mobile, and bioavailable forms. (Rytuba and other researchers have also been simulating how natural waters containing salts and organic acids may remove mercury from tailings.)

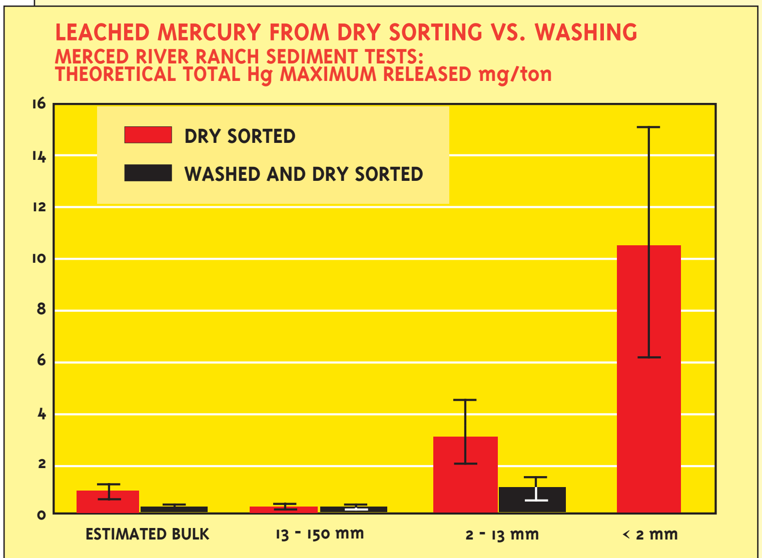
Ashley, meanwhile, can look at a riverbank where dredge tailings were left behind and identify which deposits and layers came from the sluice and which from the stacker (see left and cover photo). Some of the sluice tailings may contain more than 100 times background levels of mercury, Ashley found, whereas the coarser stacker tailings have close to background levels

TAILINGS SECTION, BUCKTAIL BRIDGE, TRINITY RIVER
TOTAL MERCURY IN PARTS PER BILLION



Source: Ashley, USGS

Tricky Tailings



Source: Fleming-Singer, Stillwater Sciences

(see chart below). Results confirm that the mercury associates with the silt and clay fractions (less than 63 micrometers in diameter).

Despite the mercury levels, restoration using these materials will not necessarily have obvious effects on biota because most projects are recreating floodplains or active stream channels — environments where methylation is low, says Ashley. Ponds in tailings piles, however, can be methylators, especially if the water chemistry is favorable.

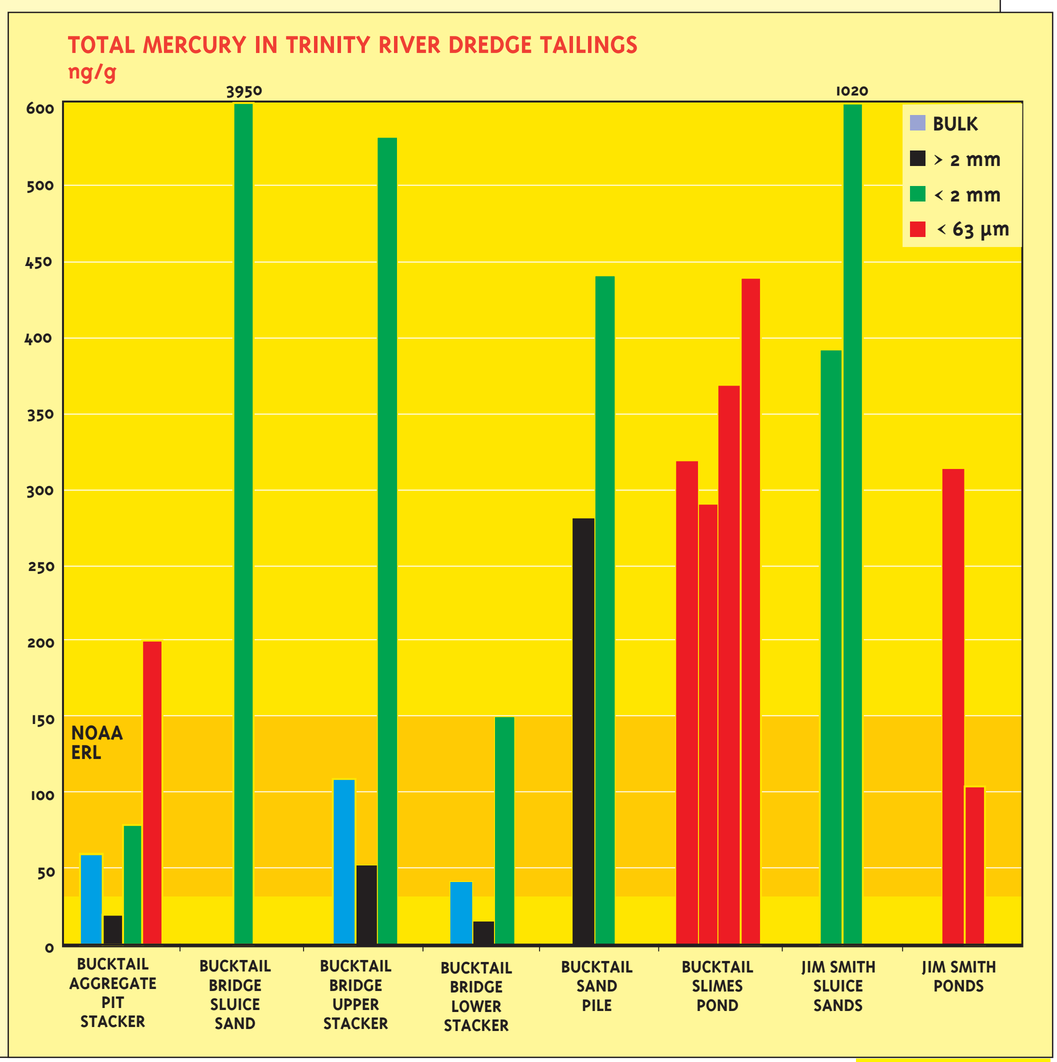
Not all rivers tell the same mercury story. Along the Merced River, tailings tested by Maia Fleming-Singer of Stillwater Sciences turned out to be close to natural background levels, even within the sands and fines (less than 2 millimeters).

On the state's Merced River Ranch, Fleming-Singer examined tailings piles 6 to 15 feet high from base to crest, and 20 to 30 feet deep in some places. A look at prickly sculpin and caddisfly larvae found that these biosentinels picked up more mercury upstream of the ranch than below. "Finding a site where there actually wasn't a huge mercury signal was great news," says Fleming-Singer. Compared to levels in fish and insects in other rivers, the Merced tests came up relatively clean.

Just because levels proved low in ranch site samples doesn't mean there aren't mercury hotspots elsewhere along the river, or that disturbing the ranch's finer materials isn't a problem. Sorting and washing candidate materials for restoration can help, but to different degrees, according to tests done by Fleming-Singer. For the larger-size fractions, washing made little difference to the total mercury leached from gravel surfaces, whereas in the smaller size it did (see chart). "Dry sorting removed 72% of the total mercury, so size separation appears to be really worth it if you're just going after bigger spawning gravels," she says.

As for why the Merced had relatively low mercury in tested tailings, Fleming-Singer admits it's something of a mystery. But the take-home message is clear. "You can't assume one way or another that mercury will be a problem at your site. It can go both ways," she says, suggesting that careful management, as well as batch testing and sorting, should be done at every site, regardless. "The good news is that at the Merced River Ranch, our coarser material may be usable as spawning gravel resource, and we're not necessarily stuck with a toxic pile of rocks." ARO

Joshua Weinstein separates the largest dredger material at the Merced River Ranch.



Source: Ashley, USGS

Mine Sites, Reservoirs, and Dams

Reservoirs have something in common with old mercury mine sites: They're potential methylation factories. But while abandoned mine sites tend to export mercury through erosion, reservoirs keep most of it all bottled up. And while the downstream threat from mine sites comes largely with big winter storms, it is the lack of water in summer and fall that can bring on mercury and methyl mercury spikes in some reservoirs.

At mine sites, it's the old tunnels, canals, pits, and ponds — where water interacts with mercury in the presence of sufficient sulfate and organic carbon — that seem to load resident bugs up with methyl mercury. Non-CALFED studies at Sierra Nevada gold mines (by Charlie Alpers and his USGS colleagues) found consistently high levels in water striders — those long-legged bugs that seem to scissor across the water's surface, and that eat other bugs that interact with contaminated sediments.

Waters immediately downstream of some abandoned gold and mercury mines are acutely high in methyl mercury. The presence of nearby geothermal springs, as in areas of Sulphur and Bear creeks in the Cache Creek watershed, or of acid mine drainage, as in some parts of the Sierra Nevada, can exacerbate methlyation by introducing more sulfate (see p. 6).

Downstream of mines, putting a dam across the river may not have been an entirely disastrous thing from the mercury perspective. The dams trap and sequester the eroded mining sediments in their reservoirs. While this may keep the harm in check, it can also concentrate the mercury problem. "The reservoir itself is like a landfill; you wouldn't want to live there," says Alpers. Tests above and below dams confirm lower total mercury and methyl mercury levels on the downstream end.

Tests also confirm that as much, or more, total mercury can flux out of the reservoir sediments into the water as comes down the river into the reservoir. At Camp Far West Reservoir on the Bear River, one watershed south of the Yuba, a 2002 non-CALFED study by the USGS's Jim Kuwabara found that in an unusually dry year at least, the reservoir bed was the dominant source of dissolved mercury to the water column. "You can't just use riverine discharge from station x, at flow y, and concentration z to determine your mercury loads and risks," he says.

Within reservoirs, mercury methylation and uptake into the food web may have a lot to do with the development of different water layers in the reservoir (stratification) and the duration of low oxygen (anoxic) conditions conducive to methlyation in the summer and fall, when water levels get low. While methyl mercury may largely be produced at the anoxic sediment-water interface down at the bottom, when there's a turnover between upper layers and lower layers the methyl mercury gets mixed into the entire water column. In reservoirs that stratify, upper and lower layers commonly turn over at least once each year, typically in the fall, as the upper layer cools down, changing the water's density.

The fall timing of these kinds of methyl mercury releases to the full water column can be bad timing for the aquatic food web. Phytoplankton (tiny plants) tend to bloom in the fall and winter, followed by blooms of zooplankton (tiny animals) in the spring. "The critical seasonal sequence seems to be first reservoir stratification, then methyl mercury production, then the lakes turn over, phytoplankton bloom, zooplankton bloom, and you've got methyl mercury headed onward and upward into the food web," says Alpers, citing trophic transfers monitored by his USGS colleague Robin Stewart in non-CALFED studies at Camp Far West Reservoir.

As methyl mercury magnifies up the reservoir food chain, the fish that live in the reservoirs may become better candidates for catch and release than Sunday dinner. But when all that's on the dinner table is a glass of water from a reservoir, the mercury levels scientists are measuring aren't enough to raise eyebrows.

Some dams and reservoirs don't provide drinking water but do offer significant impediments to fish migrating upstream. Daguerre Point Dam (1910) and Englebright Dam (1940) were built on the Yuba River to stem the tide of hydraulic mining debris. Now that restoration managers are considering taking them down, or modifying them in ways that would release sediment, Alpers and his colleagues have been examining mercury in trapped sediment. As part of a CALFED study at Englebright Lake, Alpers drilled through the pile of post-reservoir sediments in six locations, including one site more than 100 feet thick. Alpers found detectable amounts of methyl mercury way down deep. Concentrations of total mercury tended to increase with depth, as did other trace metals. "Lead, arsenic and other trace metals from hardrock mining sources are much more abundant in reservoir sediments older than 1964, when there was one of the largest floods on record. We think this means that the flood wiped the watershed clean of hardrock mining wastes. Mercury, on the other hand, continues to escape from hydraulic mining sites, and concentrations have not declined as much as the other trace metals," says Alpers.

Those wishing to remove or modify these or other dams should be prepared for a slug of fine material that, at least in the case of the Yuba River dams, contains about 300-1,000 parts per billion (ppb) total mercury and up to about 1-3 ppb methyl mercury. Scientists say such releases will probably have more of an impact downstream, especially in areas already suffering from high mercury bioaccumulation levels, rather than immediately below dams. ARO

CAMP FAR WEST RESERVOIR IN THE SIERRA


APRIL


NOVEMBER

Source: Kuwabara, USGS

MANAGEMENT

People First, Landscape ASAP

The wait for more science hasn't kept CALFED and other programs wrestling with mercury from getting busy. In the three years since the CALFED Mercury Strategy became a unifying vision for mercury research and management throughout the watershed, many of the actions at its heart have gotten underway, with a priority on tracking mercury levels in the fish that people eat most, and beefing up outreach to at-risk Delta communities. In its work to implement the Strategy, CALFED has also helped identify the truly bad actors among mercury mines for priority cleanup, investigated management options that might control the exposure of endangered and other wildlife to methyl mercury, and supplied solid science to back up the region's water boards in their efforts to regulate mercury discharges into streams, rivers, and the Bay.

"We need to make sure we're not doing something in one place that will cause problems in another," says Johnnie Moore, CALFED's chief scientist. "In the long term, it's really about education, well-planned restoration, and balancing risks."

Most at risk are the wives and children, both the unborn and the very young, of those casting lines out into Bay-Delta waters and bringing home fresh fish for dinner, some of which may contain mercury. For the developing fetus, mercury can cause measurable decreases in learning, attention, and memory. Other more serious problems associated with mercury range from tremors and slurred speech to kidney and neurological disorders. These days, most of the mercury anyone accumulates comes from eating large, long-lived fish of both commercial and sport derivation. So it's no wonder fish consumption advisories for women of childbearing age and children are the backbone of any education effort on mercury.

The feds began to warn pregnant women about mercury in shark and swordfish in the early 1990s, but expanded national advisories for all fish, commercial and sport, didn't come out till March 2004. Also last year, the state released 10 local advisories for Bay-Delta counties.

Whether state, regional, or local, the job of creating these warnings isn't easy. Bob Brodberg, a senior toxicologist with the state's health hazard office, must patch together fish tissue information gathered by dozens of different agencies to create uniform, defensible advisories.

With CALFED and state funding, Brodberg will be laying the groundwork for a Cosumnes and Mokelumne river advisory in 2005, and analyzing existing Delta data for a San Joaquin River advisory. Next year, he'll work on the area north of the San Joaquin up into the Sacramento. River advisories are much more challenging than reservoir advisories for the obvious geographical reasons. "It's harder to communicate risk when you have to say that if you're fishing in the San Joaquin at Landers Ave., only eat one meal a week of this species, but if you're at Laird Park, you can eat more," he says. "The ultimate goal is to point people to fish they can eat more, not less, of."

Reaching the right people with the right information is the job of Alyce Ujihara of the Department of Health Services. "These communities are challenging to reach because of language and cultural barriers. If you put up a sign, they may not read it," she says.

Ujihara's agency began conducting outreach to these communities in five counties of the Delta watershed with support from CALFED, the Delta Tributaries Mercury Council, and the Central Valley Regional Water Quality Control Board. She started by creating local advisory groups within the Bay-Delta and Sacramento River watershed, striving to enlist the assistance of people within targeted communities. These groups help to develop, translate, and distribute educational material, and liaison with other more technical advisory groups. Materials produced include a colorful warning postcard picturing both "safer" and "less safe" fish types, and detailing how many meals of what size fish are safe to eat per month (see above). A Delta poster has also been created in eight languages.

Ujihara's agency isn't just trying to get the warnings to anglers. As she points out, those most at risk are the wives and children of anglers, not the anglers themselves. To this end, she began a survey in 2004 of 500 low-income women at a "WIC" (Women, Infants & Children) clinic in Stockton.

Delta fish consumption advisory postcard. DHS

In addition to the WIC survey, Ujihara will survey boaters and anglers, conduct training sessions for county staff and community organizers, and collaborate on the Food Stamp Nutrition Education Program in the Delta watershed.

CALFED has also helped her provide mini-grants of $10 thousand to groups from Cambodian, Russian, Latino, and African-American communities to help them educate their own. "For the most part, when we went to these groups, they knew very little about the risks," she says. "We think awareness is higher now, but we aren't sure if we've changed behavior. It's hard to measure concrete results unless you go into kitchens and monitor what people cook and eat."

Beyond the human health question lies the question of how to gain control of the places and processes that expose fish to mercury in the first place. As it moves from sediments to water to fish, mercury poses an unusual challenge to state water quality managers used to setting concentration limits for much less changeable pollutants. But set limits they must. Both the Delta and the Bay are on the federal "303(d)" list of waterways whose beneficial uses are impaired by mercury, requiring the state to come up with total maximum daily loads (TMDLs) allocated among all sources.

At press time, there were four mercury TMDLs in various stages of approval: two for watersheds believed to be the biggest polluters in terms of mines, Cache Creek high in the Coast Range northwest of Sacramento and the Guadalupe River (home of the New Almaden Mine) down in the South Bay. Two regional TMDLs, one for the Delta and one for the Bay, are also in progress. This March, the State Board asked the two regional water quality boards to integrate the TMDLs.

This integration shouldn't be too difficult, according to the S.F. Bay Board's Dyan Whyte. Sediment level targets, source control actions, and the emphasis on commonly caught and consumed sport fish as indicators all have "the same endpoints" in the various TMDLs, she says. The main difference between the two regions is that the Central Valley Board's proposed regulations are based on methyl, as opposed to total, mercury. For the S.F. Board, the total mercury approach seemed more appropriate. "When you discharge mercury into an estuary vs. a freshwater river, the geochemistry is different. In a river system, where you're only looking at what's going past a specific point, you have a different mercury uptake and degradation dynamic," she says. "But other than that, we're pretty much in sync in terms of where we need to go with the TMDLs."

One place everyone wants to go is the settling basin at the base of Cache Creek, which traps 50% of the mercury (total) headed downstream from this mine-dotted watershed, according to a 1998 Central Valley Board study. Options for increasing the basin's capacity to stem the spread of mercury downstream are now being researched (see photo p. 16). Studies have identified a number of other high-priority source control projects: dredging and disposal of mine tailings in the bed of Sulfur Creek; and rerouting water around mine waste piles, as well as curbing and containing erosion, at the Abbott and Turkey Run mines near Harley Gulch. "The most difficult question is how to pay for mine site cleanup and long-term maintenance," says Central Valley Board senior engineer Patrick Morris. Private landowners are fearful of such liabilities, which can overwhelm individual pocketbooks. With Prop. 13 funds, CALFED will be able to provide $15 million in financial support. TetraTech, which conducted a review of mine sites and their remediation potential for CALFED, estimates the Abbott and Turkey Run projects alone could cost between $2.6 and $5.9 million.

Upstream cleanup could prove more cost-effective than more wastewater treatment downstream. "It would take a great deal of money to get another gram or two of methyl mercury out of our discharges," says Vicki Fry of the Sacramento Regional County Sanitation District. The Sanitation District sees merit in "offsetting" any load reductions the TMDL places on dischargers by contributing to Cache Creek settling basin improvements or supporting a mine cleanup. But such offset programs, also known as pollutant trading, have never been tried for mercury in water.

An offset program feasibility study submitted by the Sacramento County discharger to the Central Valley Board this March suggests load reduction upstream (through trading), support of more science on methylation processes, and outreach and education. "One of the biggest science questions for us in terms of future trading is, how do we equate one methylation site with another? Can we combine bioavailability, location, and uncertainty factors in one equation?" Fry says. However it's done, any trading proposal faces an uphill battle with the U.S. EPA, which has a policy against trading programs for any persistent bioaccumulative substance other than on a small pilot scale.

Sampling for mercury in zooplankton at Camp Far West Reservoir

"In the end, what we really need to clean up mercury sources are resources (money) and some federal legislation to address liability problems — these are really the two impediments to major progress in the mercury arena," says CALFED's Donna Podger.

MARSH DESIGN WITH MERCURY IN MIND

Though reducing mercury methylation in their marshes may be a new priority for restoration managers, scientists are still busy researching how different conditions and habitats measure up in the mercury mix.

"The water depth at which you build a wetland may turn out to be critical. Likewise, certain elevation changes, certain flow characteristics, and certain vegetation types may decrease methylation," says geochemist Gary Gill of Texas A&M University.

These are the types of restoration details that a new CALFED study launched this spring hopes to uncover. Over the next three years, the eight-member multi-agency study team, led by Donald Yee of the S.F. Estuary Institute, will be comparing marsh habitats along the Petaluma River. Variations in environmental characteristics — marsh age, salinity and tidal regime, channel size, geomorphic features, vegetation, food web, total mercury in sediments — will all be examined in terms of their influence on the rate of methyl mercury production and bioaccumulation.

Prior studies have revealed noticeable differences between sediment concentrations of methyl mercury in large and small channels, and scientists have linked channel size with reproductive failures in clapper rails. "In smaller channels, the boundary of the anoxic environment is nearer the surface of the marsh. The physical closeness of all parameters here — the anoxic boundary, the feeding wildlife, the methyl mercury in the anoxic zone — may increase the chance of this toxin entering the food web," says Institute wetland ecologist Josh Collins.

With the results of the study, CALFED hopes to give more detailed advice about how and where to proceed with tidal wetland restoration projects. For example, if methyl mercury production is elevated within a particular range of sulfate concentrations (Goldilocks areas), restoration projects might better be pursued in areas outside this range. Similarly, if wet-season flows deposit the most sediment-bound mercury, decisions about the timing of dike breaching could be adjusted accordingly. And if methyl mercury is associated with certain landscape features within wetlands, like small channels or shallow pools, projects may be designed to minimize these features.

The link between habitat design and methyl mercury creation and uptake is not only being researched through CALFED. A Prop. 13-funded project, managed by the Association of Bay Area Governments and Levine-Fricke, will spend more than $1 million conducting a series of pilot projects exploring the relationship between wetland design, methylation, and food web uptake in the Bay region. In addition, wetland restoration projects at Marin's Hamilton Air Force Base and on 16,500 acres of North and South bay salt ponds are actively collecting and analyzing more site-specific information on mercury as they begin reintroducing tides, plants, and landscape diversity to former baylands.

Just because such projects are big doesn't mean they will produce more methyl mercury than smaller ones, says Collins. Clearly the variables, and their effects on methylation, are myriad in the restoration game. In the meantime, "start slow, monitor, learn, correct" seems to be the mantra. ARO

People First, Landscape ASAP

Raising the height of this outlet weir is one of a number of possible improvements to a 1930s-era settling basin where Cache Creek empties into the Yolo Bypass near the city of Woodland. The basin traps an estimated half of the mercury coming downstream in wet years.

CALFED is only one of many programs, organizations, agencies, and individuals working on the mercury problem. Recycling efforts have been gathering steam up and downstream, as dental fillings, old thermometers, and mercury from current gold mining activities are collected and processed, rather than entering the waste stream. Millions have been spent cleaning up the New Almaden Mine state Superfund site in the Guadalupe River watershed. And in one reservoir in that watershed, the Santa Clara Valley Water District will soon be experimenting with aerating the lower layers of water during high methylation seasons.

Despite all the action and research, scientists are quick to say they are still about five years away from knowing enough to give restoration managers any guidelines for minimizing mercury risks. "Mercury has dealt us a lot of surprises, so those of us who work in the field are a little gun-shy of making specific recommendations," says Mark Marvin-DiPasquale of USGS. In the meantime, the CALFED Mercury Strategy details a sound framework for organizing adaptive management and monitoring of restoration projects.

Beyond the printed word, there are other opportunities for researchers and the public to learn about and share progress on mercury projects. About six years ago, three separate mercury stakeholder efforts came together and reformed to create the Delta Tributaries Mercury Council. As a sub-committee of the Sacramento River Watershed Program, this council provides a forum for outreach, education, and exchange of scientific data; identifies opportunities to improve public policy on mercury management; and acts as a sounding board for ideas. Projects like those highlighted in these pages are often presented and discussed at the bimonthly meetings of the council. CALFED program staff actively participate in this forum, and the two organizations have worked collaboratively on various mercury advisory groups. Other active working groups include the Sierra-Trinity Abandoned Mine Lands Agency Group, which consists of agency staff collaborating on abandoned mine restoration efforts, and the Dredge Tailings Workgroup, which is developing an issue paper on the technical, regulatory, and management challenges of using dredge tailings for restoration.

"In the last five years, our dialogues have grown from the local to the regional scale," says Carol Atkins, who organizes communication and meeting activities for all three groups. "Now we want to bring the discussions up a notch, to a larger dialogue with more cross-talk among different disciplines and projects. We need to network the mercury issues with the organic carbon and environmental restoration issues."

Networking requires information sharing not only among landscape and water quality managers, but also among various research efforts. To make sure all its own programs generate compatible data, CALFED is now putting a comprehensive quality assurance program in place. Data is also being fed into the California Environmental Data Exchange Network — a collaborative project on the part of state and regional water quality boards, the California Department of Fish & Game, and the Department of Water Resources, among others — to make data more accessible, via the download button, to all.

"It's easy to get hung up on how complicated the behavior of mercury in the environment can be, especially in view of the extraordinary variation within the Bay-Delta ecosystem over space and time, but communication is the primary key to success," says Jim Wiener, a professor at the University of Wisconsin-La Crosse, who led the development of the Mercury Strategy and regards the Bay-Delta's ongoing investigations as one of the most advanced efforts of its kind. "The bottom line is that the scientists and managers involved with this contaminated ecosystem must find the time to sit down and communicate; otherwise, they won't succeed in applying this very technical information to management issues on the ground. The greatest strength of the Mercury Strategy is that everyone involved in its development has a sense of ownership about it, and is working together to address a problem that promises to challenge us for a very long time."

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RESOURCES & REPORTS

CALFED Mercury Strategy & Research http://calwater.ca.gov/Programs/Ecosystemrestoration/ecosystem mercuryproject.shtml
http://loer.tamug.tamu.edu/calfed/
FAQ About Mercury in Fish (510)622-4500
Guadalupe Watershed Mercury TMDL www.valleywater.org
S.F. Estuary Mercury News www.sfei.org
TMDLs www.waterboards.ca.gov
USGS Mercury & Mining Fact Sheet http://pubs.usgs.gov/fs/fs2005-3014.html
8th International Mercury Conference www.mercury2006.org

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