

**MERCURY:** Water Quality Enemy Number One

## SUMMARY OF THIS EDITION

The Pulse of the Estuary is the Annual Report of the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP). The RMP is an innovative collaboration of the San Francisco Bay Regional Water Quality Control Board, regulated dischargers, and the scientific community. The RMP endeavors to establish the scientific foundation needed for managing water quality in this treasured aquatic ecosystem. The Pulse is a record of our inquiries and achievements, annually providing essential information on the state of the Estuary to water quality managers, decision-makers, scientists, and the public.

his edition of the Pulse has a special focus on San Francisco Bay's foremost water quality concern: mercury. This pollutant is the primary cause of the fish consumption advisory for the Bay, and concentrations in sport fish show no sign of declining (page 48). Mercury also is a suspected cause of health problems in wildlife. A major study conducted by the US Geological Survey over the last few years has concluded that mercury is causing hatching failure in Forster's terns, and also poses risks to other bird species (page 56). Due to these significant human and wildlife health risks, mercury was the subject of the first TMDL for the Bay, approved by the State Water Resources Control Board in 2007.

Mercury is a challenging adversary, and critical gaps remain in our understanding of this elusive metal's complex cycle of transformation and movement throughout San Francisco Bay. The RMP recently has formulated a Mercury Strategy to remedy these information deficits, providing a foundation for a more timely solution to the mercury problem (page 4).

The first step in implementing the Strategy is understanding where and when methylmercury – the problematic form of mercury – is entering the Bay food web. Measuring mercury concentrations in small fish ("biosentinels") is a powerful means for obtaining this information. The young age and restricted ranges of small fish allow the timing and location of their mercury exposure to be pinpointed with a relatively high degree of precision. Dr. Darell Slotton of UC Davis has performed extensive small fish mercury monitoring in the northern Estuary and the Delta region over the last several years (page 65). An understanding of factors that drive methylmercury production and uptake is beginning to emerge from this work and other biosentinel studies.

Areas with occasional flooding of soils that are usually dry seem to be especially prone to methylmercury production. This principle seems to apply in variety of settings, including river floodplains, managed marshes, and tidal marshes. Other recent studies in Bay marshes (pages 37 and 38) suggest that the elevation of a marsh relative to the tides — which affects the frequency of inundation along with other factors — has an important influence on methylmercury production. A common theme of these studies is that marsh restoration, even in areas where mercury is abundant in water and sediment, will not always lead to increased accumulation in the food web.

The RMP also has performed small fish monitoring on a limited scale for the past three years (page 12). In 2008, in response to the newly developed Mercury Strat-

egy, the RMP began more extensive small fish monitoring in a concerted effort to determine patterns in food web uptake. Other studies initiated in response to the Strategy aim to identify the sources and processes that most contribute to food web uptake in the Bay.

The Mercury Strategy is only one manifestation of the focused RMP planning initiative currently in progress. Another critically important step in this process was the development of an improved statement of the fundamental questions that the RMP aims to address (page 9). An additional facet of the initiative is a strategy for obtaining information on pollutant loads from small tributaries to the Bay, which carry urban and historic mining district runoff from our local watersheds and contribute to mercury contamination of the Bay. RMP studies in the Delta, the Guadalupe River watershed, and a small urban watershed in Hayward have greatly improved our understanding of the pollutant inputs to the Bay that are most important (page 77).

An overview of dredging and sediment management (page 17) is another highlight of this edition. San Francisco Bay is one of the most important maritime thorough-fares in the nation, supporting international trade, commercial and recreational fishing, and aquatic recreation such as boating, swimming, and sailboarding. Each year, an estimated 4,000 commercial ocean-going vessels transit the Bay, carrying more than 75 million tons of cargo worth approximately \$20 billion. Dredging is essential for maintaining access to the Bay's ports and harbors. The regulation and management of dredging and disposal of dredged material in the Bay historically has been a controversial issue. The creation of the Long Term Management Strategy (LTMS) for the Placement of Dredged Material in the San Francisco Bay Region established a multi-agency, stakeholder-driven program to coordinate dredging and disposal activities on a regional scale. Thanks to the LTMS, dredged material that was once dumped at in-Bay disposal sites is now used for wetland restoration, levee rehabilitation, and other projects where sediment is in demand.

As always, the latest information on Bay water quality and long-term trends also is presented. Considerable year-to-year fluctuations in average concentrations of some pollutants have been observed. For example, methylmercury concentrations in sediment in 2007 were well below the long-term average. On the other hand, PCB concentrations in sediment in 2007 were higher than the long-term average. The causes of these fluctuations are not yet understood. Also noteworthy in 2007 was the highest rate of toxicity incidence in sediment samples observed since the RMP began in 1993.

## THE PULSE OF THE ESTUARY

**2008** 

Monitoring and Managing Water Quality in the San Francisco Estuary

**MERCURY:** Water Quality Enemy Number One



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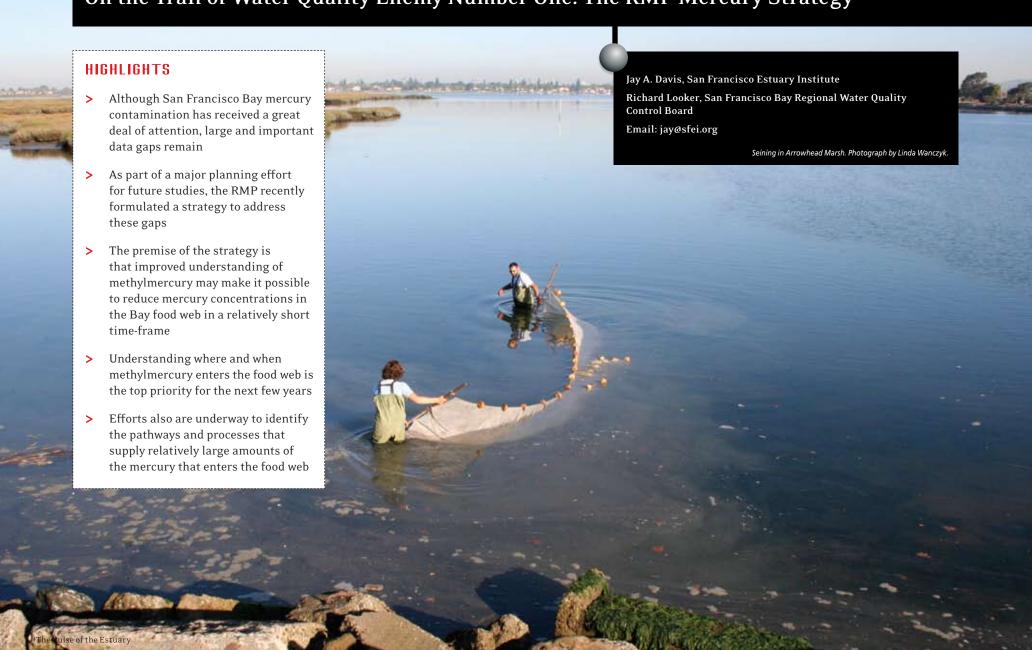
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## MANAGEMENT UPDATE

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## On the Trail of Water Quality Enemy Number One: The RMP Mercury Strategy



## Water Quality Enemy Number One

Mercury is San Francisco Bay's water quality enemy number one. Mercury is a primary driver of the fish consumption advisory for the Bay, and also is a suspected culprit in avian health problems. Consequently, mercury was the subject of the first TMDL for the Bay, approved by the State Water Resources Control Board in 2007. Mercury is a challenging adversary, and large and important gaps remain in our understanding of its complex cycle of transformation and movement throughout San Fran-

Total mercury is the sum of all of the different forms of mercury in the environment. Total mercury is easy to monitor, and its sources, distribution, and trends are relatively well understood. Total mercury is persistent, and is largely bound to sediment particles that are efficiently trapped within the Bay. There are indications that total mercury concentrations in Bay sediment have declined in recent years. Nevertheless, total mercury is so abundant and distributed so widely throughout the Bay-Delta and its watershed that it is expected to take many decades for total mercury concentrations to decline sufficiently to reduce impairment of the Bay.

with total mercury concentrations (Figure 2). The sources of methylmercury in the Bay—particularly the methylmercury that actually gets taken up into the food web—are not well understood. It is not known whether different sources and pathways vary in their contribution to food web uptake.

Methylmercury concentrations in the Estuary have been relatively constant since the early 1970s, but could quite plausibly increase, remain constant, or decrease in the next 20 years. Wetlands are often sites of methylmercury production, and restoration of wetlands in the Bay on a large scale is now beginning, raising concern that

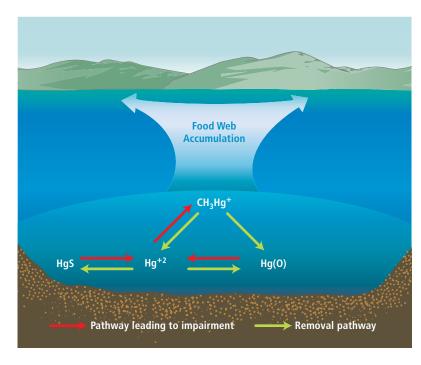
# The premise of the Mercury Strategy is that it may be possible to identify the specific fractions of total mercury entering the Bay and in the Bay that contribute disproportionately to accumulation in species of concern

cisco Bay. The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) recently has formulated a strategy to fill these gaps in understanding and provide a foundation for a more timely solution to the mercury problem.

Mercury is present in the environment in many forms (Figure 1). Two of these forms are commonly studied and considered in a management context: total mercury and methylmercury. These two forms present very different opportunities for management.

Methylmercury is the specific form of mercury that accumulates in the food web and poses health risks to humans and wildlife. Methylmercury is neurotoxic and is particularly hazardous for the developing nervous systems of fetuses, children, and early life-stages of wildlife species. Methylmercury typically comprises only about 1% of total mercury, but these minute amounts are enough to generate potentially toxic concentrations in the food web. In contrast to total mercury, methylmercury is not persistent, and methylmercury concentrations are highly variable over brief periods of time and small intervals of space and do not closely correspond

methylmercury concentrations could increase across major portions of the Bay. However, methylmercury cycling is not yet well understood, and recent findings suggest that some wetlands actually trap methylmercury and remove it from circulation (see "Napa Marsh Story", page 69). Consequently, with improved understanding of methylmercury dynamics in the Bay, approaches might be found that prevent increases in methylmercury concentrations—or possibly even reduce concentrations and associated health risks in the next 20 years.

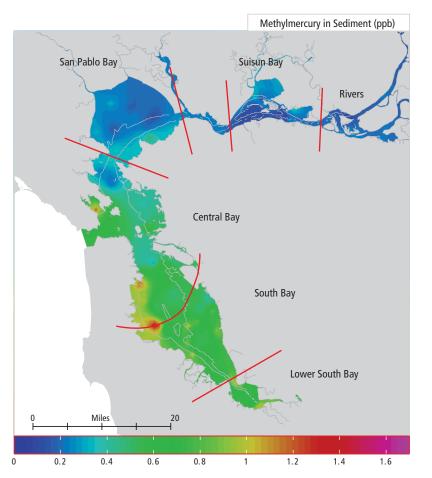


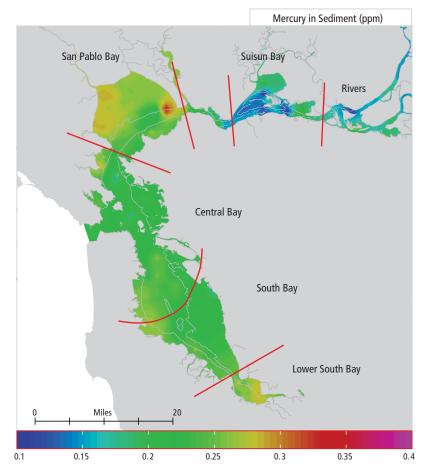
THE PRIMARY FORMS						
BEST KNOWN AS	ALIASES			DESCRIPTION		
Methylmercury	CH3Hg <sup>+</sup> MeHg Mon		Monomethlymercury	The toxic form that accumulates in the food web		
Elemental Mercury	Hg(Ø)		Metallic mercury	Dominant form in gold mining areas and the atmosphere		
Reactive Mercury	Hg <sup>+2</sup>	Hg(ll)	Ionic mercury	The form that can be converted to methylmercury		
Particulate Mercury	HgP	Hg(ll)P		Dominant form in water and sediment		
Cinnabar	HgS	Mercury sulfide	Mineral mercury	Dominant form in mercury ore and mercury mining areas		

COMBINATIONS	
Total Mercury	The sum of all forms of mercury
Inorganic Mercury	Elemental + Reactive + Particulate + Cinnabar

#### FIGURE 1

Mercury exists in many different forms in the aquatic environment, and these forms vary in their potential for food web uptake. To complicate things further, these forms can interact and associate with other substances in ways that also affect their potential for eventual conversion to methylmercury and entry into the food web. This simplified representation shows the major forms and the pathways for conversion from one form to another. Processes that enhance the creation, or prevent the breakdown, of methylmercury lead to increased accumulation in the food web. Some of the important influences on the mercury cycle are bacterial community composition, pH, oxygen availability, and nutrient and sulfate concentrations.





Footnote: Based on RMP data from 2002-2007. Note different units (ppb) from other map.

Footnote: Based on RMP data from 2002-2007. Note different units (ppm) from other map.

Methylmercury concentrations often do not closely correspond with total mercury concentrations. In general, methylmercury concentrations (left) tend to have a loose association with total mercury concentrations (right), but there is a significant amount of variation around this relationship. As one prominent example of this, total mercury concentrations in Bay sediments (right) have been highest over the last few years in San Pablo Bay, while methylmercury concentrations (left) have been highest south of the Bay Bridge. Food web uptake also has generally been highest in the southern reach of the Bay.

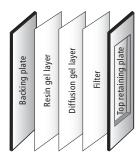
## A Team Effort

In 2007, the RMP began an initiative to make the Program more effective in planning future studies (Sidebar). One component of this new planning initiative was the development of a specific strategy for mercury studies to ensure that the RMP is providing the information most urgently needed to manage this top priority pollutant. The RMP approach to tackling such challenging tasks is to organize a collaborative team effort. Consequently, a Mercury Strategy Team comprised of several RMP stakeholders was formed in the summer of 2007. The Team formulated a series of management questions that, if answered, could lead to actions that would reduce mercury uptake in the Bay food web in a relatively short time-frame.

The focus of the Mercury Strategy is on improving understanding of the production and uptake of *methylmercury*. Concentrations of total mercury in the Bay are expected to slowly decline over coming decades. The premise of this Strategy is that it may be possible to identify the specific fractions of total

mercury entering or already present in the Bay that contribute disproportionately to accumulation in the Bay food web. If this premise is correct and the identified fractions can be controlled, then it may also be possible to reduce mercury accumulation in species of concern in a significantly shorter time-frame than is currently anticipated through management of total mercury. Gathering the information specified by the Mercury Strategy over the next several years will inform the next iteration of the mercury TMDL. If the Mercury Strategy is successful, then a revised version of the mercury TMDL can focus on achieving faster reductions in mercury contamination through controls on methylmercury production and food web accumulation.

The RMP already is conducting a substantial amount of monitoring to understand status, trends, loads, and effects of total mercury and methylmercury; this information collection will continue. The Mercury Strategy Team identified the following high-priority questions that remain to be answered and are considered critical to reducing mercury impairment in the Bay.





DGTs are sampling devices that are being used to investigate methylmercury sources in the Bay and its tributaries. Methylmercury passes through a diffusion gel and is trapped in a resin gel. Concentrations in the resin gel are then measured.

## An Overhaul of RMP Planning

n 2007, the RMP launched an initiative to become more proactive in planning future studies. The Program began developing a Five-Year Master Plan, which identifies high-priority elements, clearly documenting the rationale for each. Each of the RMP Workgroups (Exposure and Effects; Contaminant Fate; Sources, Pathways, and Loadings; and Emerging Contaminants) entered into a deliberate process of identifying the highest-priority management questions and planning a series of studies to answer them. The plans developed by the Workgroups are being incorporated into the Master Plan.

Another step in the overhaul of the RMP planning process was a reevaluation of the objectives framework of the Program. The statement of the fundamental aims of the RMP was changed to include an overarching goal (to collect data and communicate information about water quality in the San Francisco Estuary in support of management decisions), to express general topics of interest in the form of core management questions, and to define two tiers of questions (Level II and Level III) under the core questions that connect specific study elements to the core questions (see Table). Other improvements made to this framework included arranging the questions in a logical sequence and more careful and succinct wording. The RMP Steering Committee approved this set of questions in May 2008.

An additional improvement that accompanied this new planning initiative was the development of a specific strategy for mercury studies to ensure that the RMP is providing the information most urgently needed to manage this top priority pollutant. Developing a specific strategy for one pollutant represented a novel approach for the Program, but one that would help ensure that the most pressing information needs are addressed.

## **LEUEL I (CORE)** Management Questions

- 1. Are chemical concentrations in the Estuary potentially at levels of concern and are associated impacts likely?
- 2. What are the concentrations and masses of contaminants in the Estuary and its segments?
- **3.** What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?
- **4.** Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?
- 5. What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?

## General Goal of the RMP

Collect data and communicate information about water quality in the San Francisco Estuary in support of management decisions

LEUEL I (CORE) QUESTIONS	QUESTION 1 Levels of concern and associated impacts	QUESTION 2  Concentrations and masses (spatial distribution)	QUESTION 3 Sources, pathways, loadings, and processes	QUESTION 4 Increased or decreased (trends)	QUESTION 5 Projected concentrations, masses, and impacts
LEUEL II QUESTIONS	Q1 Which chemicals have potential for impacts?  Q2 What is the potential for impacts due to contamination?	Q1 Are there particular regions of concern?	Q1 Which sources, pathways, etc. contribute most to impacts?  Q2 Opportunities for management intervention for important pathways?	Q1 Effects of management actions on concentrations and mass?  Q2 Effects of management actions on potential for adverse impacts?	Q1 Impacts forecast under various management scenarios?  Q2 Which contaminants predicted to increase?
	<b>Q3</b> What are appropriate guidelines?		Q3 Effects of management actions on loads?		

The RMP Mercury Strategy

## Priority Questions and Plan of Attack

### **QUESTION 1:**

## Where and when does mercury enter the food web?

Only when mercury (in the form of methylmercury) actually enters the food web can we be sure that it is part of the small fraction of total mercury that contributes to impairment. Mercury has a complex cycle in the environment, in which it is converted from one form to another through a number of

higher concentrations with each step up the food web-from water, to phytoplankton, to filter feeders, to small fish, to sport fish and humans or to wildlife-in a process known as "biomagnification." The largest jump in concentration—about 100,000-fold—occurs between water and phytoplankton. Concentrations increase about three-fold with each subsequent step up the food chain. Concentrations in large predatory fish and fish-eating wildlife reach levels that are several million times higher than those in water.

Understanding where and when methylmercury enters the food web is therefore critical in deter-

have had limited spatial and temporal scopes. The most prominent example of a study of fine-scale patterns in food web uptake is the work performed by Dr. Darell Slotton of UC Davis in the CALFED-funded Fish Mercury Project (FMP) (Figure 4 and page 65). His work has used small fish monitoring to identify areas with high and low food web uptake, and is providing information suggesting that certain processes have a large influence on uptake. FMP monitoring will conclude in 2008, and will only have covered limited portions of the Bay (San Pablo Bay and Suisun Bay). The RMP also conducted a small-scale small fish biosentinel pilot study from 2005 - 2007 (Figure 4). This study

## Understanding where and when methylmercury enters the food web is therefore critical in determining how to reduce food web contamination and impairment

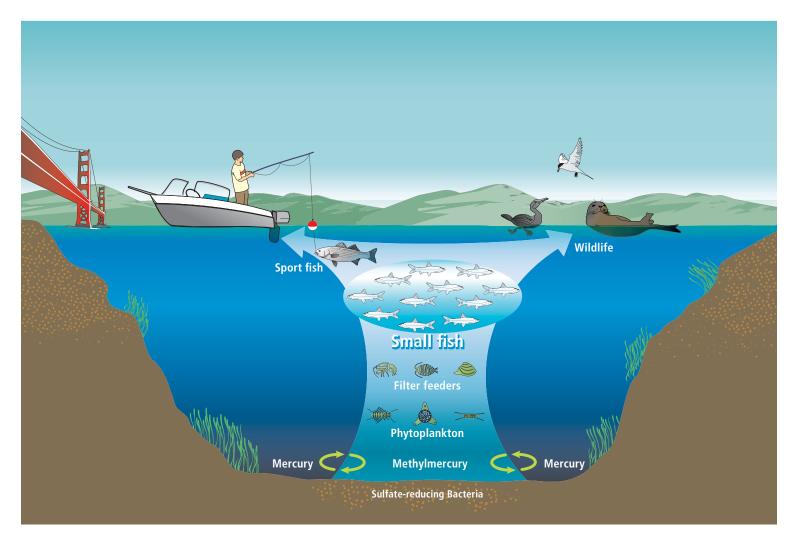
chemical and biochemical processes. Many of the conversions occur through bacterial metabolism, so the conversion processes are heavily influenced by any conditions that affect bacterial activity and the composition of the microbial community. Basic chemical factors such as pH, oxygen content, the presence of organic matter, and nutrient and sulfate concentrations affect bacteria populations and the conversion processes.

The most critical step in the mercury cycle with respect to impairment of Bay water quality occurs when the methylmercury that spins out of the mercury cycle is very efficiently incorporated into organisms at the base of the food web (Figure 3). Methylmercury then reaches

mining how to reduce food-web contamination and impairment. Information is needed at a relatively fine scale. The spatial scale of interest is on the order of one mile or less, so that uptake can be tied to particular pathways or processes occurring in specific habitats. The temporal scales of interest are annual, seasonal, or even shorter, so that the most critical years and seasons for uptake are characterized.

Past RMP monitoring of sport fish and bird eggs has not answered this question with the degree of spatial or temporal resolution needed to allow managers to pin down the origins of the methylmercury entering the food web. Other studies have generated the type of information needed, but they has provided useful information, but the scope has been insufficient to address the Bay as a whole. Past and present efforts therefore have left large gaps in understanding of spatial and temporal patterns in food web uptake.

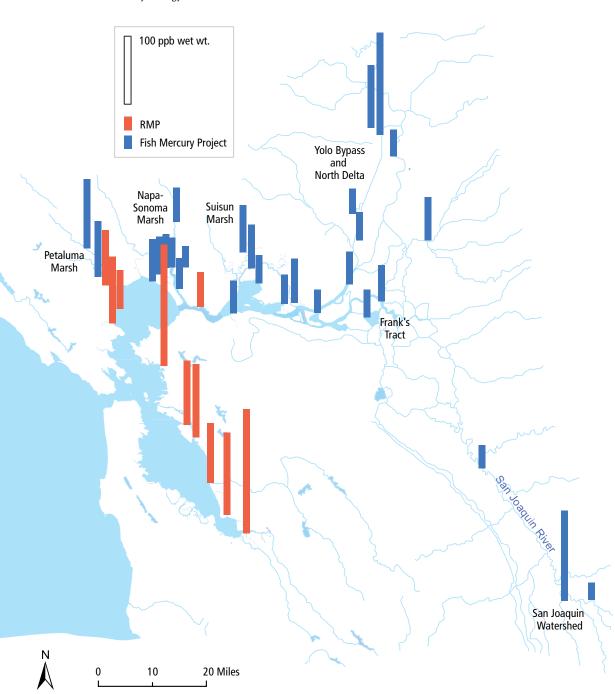
Anwering Question 1 is essential to moving forward with the Mercury Strategy, and this has been identified as the top priority over the next several years. The RMP small fish biosentinel pilot study is being expanded to an annual budget of \$150,000, which will allow for sampling of approximately 50 sites per year (Table 1). The plan is to sample at this level of effort for three years and then to evaluate whether Question 1 has been answered well enough to proceed to a greater emphasis on Question 2.

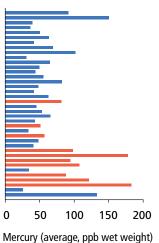


Methylmercury is readily accumulated in the food web and poses a toxicological threat to highly exposed species. Mercury from historic mining districts and other sources is converted to methylmercury principally by bacteria in sediments of aquatic ecosystems. Methylmercury reaches higher concentrations with each step up the food chain—from water, to phytoplankton, to filter feeders, to small fish, to sport fish and humans or to wildlife—in a process known as "biomagnification." Concentrations in large predatory fish and fish-eating wildlife end up being several million times higher than in water. There are complex production and loss cycles for methylmercury in sediments and water. Small fish are an ideal link to monitor, as they provide an integrative measure of methylmercury after it has been incorporated into the food web. Small fish provide sensitive measures of the location and timing of methylmercury exposure in food chains leading to both humans and wildlife.



The RMP Mercury Strategy





mercary (average, pps wer weight,

FIGURE 4

Small fish mercury monitoring is revealing the spatially and temporally dynamic nature of methylmercury concentrations in the Estuary. Two studies in 2007 combined to provide thorough coverage of the Estuary. Darell Slotton and colleagues at UC Davis have sampled large numbers of small fish of several species throughout the North Bay, Delta, and Central Valley in an effort to evaluate the local and regional impacts of habitat restoration on mercury in the food web. One highlight of the UC Davis sampling has been the low concentrations observed in the Napa Marsh complex, site of some of the most extensive wetland restoration activities in the Bay-Delta watershed. This finding was surprising, given the conventional association of wetlands with increased methylmercury production. The RMP also performed a complementary smaller study of mercury in small fish from 2005 - 2007 (pink bars). Concentrations in the South Bay were high compared to the rest of the Estuary. More extensive small fish monitoring throughout the Bay is a key component of the RMP Mercury Strategy.

## RMP STUDIES

ELEMENT		QUESTIONS	2008	2009	2010	2011	2012
Food Web Uptake	Small Fish	Mercury 1	150	150	150	100? <sup>a</sup>	100? <mark>a</mark>
High Leverage Pathways and Processes	DGTs Mercury Isotopes Others?	Mercury 2	100	100		150 <sup>e</sup>	150 <sup>e</sup>
Methylmercury Model Development		Mercury 3, 4	20		25		25
Surface Sediments (THg, MeHg)		Mercury 1	160 <b>b</b>	160 <b>b</b>	160 <b>b</b>	160 <b>b</b>	160 <b>b</b>
Water (THg, MeHg)		Mercury 1	140 <b>b</b>	140 <b>b</b>	140 <b>b</b>	140 <b>b</b>	140 <mark>b</mark>
Sport Fish		Mercury 1		215 <sup>b</sup>	41 <mark>b</mark>		218 <mark>b</mark>
Avian Eggs		Mercury 1		120 <b>b</b>		120 <b>b</b>	
Effects on Birds			70 <sup>c</sup> (34) <sup>d</sup>	50 <sup>b</sup> (20) <sup>d</sup>	50 <sup>b</sup> (20) <sup>d</sup>	50 <sup>b</sup> (20) <sup>d</sup>	50 <sup>b</sup> (20)d
Small Tributary Loading (THg)			100 <b>b</b>	100 <b>b</b>	100 <b>b</b>	100 <b>b</b>	100 <b>b</b>
River Loading (THg)					140 <b>b</b>		
Guadalupe Loading (THg)					65 <mark>b</mark>		
Sediment Cores (THg)					100 <mark>b</mark>		100 <b>b</b>
Guadalupe Model (THg)			75	75			
Watershed Load Model (THg)			40				

THg= Total Mercury MeHg= Methylmercury Numbers indicate dollars in 1000s.

## OTHER STUDIES

ELEMENT		QUESTIONS	2008	2009	2010	2011	2012
Water Environment Research Federation	Literature review	Mercury 2	150	150			
Effluent Monitoring		Mercury 2	30	30	30	30	30
South Baylands Mercury Project	Biosentinels	Mercury 1	225	?	?	?	?
Prop 13 - Mercury Control Options in Tidal Wetlands		Mercury 3	400	400			
Props 40 & 50 - Mercury Control Options in Suisun Marsh		Mercury 3	300	300			

- a The need for continuing this work will be evaluated after three years. This estimate assumes continuation of trend monitoring with small fish.
- b Total mercury and methylmercury are part of a longer list of pollutants covered by this budget.
- C A study by USGS: Mercury-Selenium Effects on Reproductive Success of Terns and Stilts in San Francisco Bay.
- d Matching funds from USGS.
- e Assumes increased emphasis on mercury Question 2 after obtaining answers to Question 1 through small fish work in 2008-2010.

#### TABLE 1

The RMP invests considerable funds in mercury studies, and will be spending approximately \$250,000 annually for the next several years to address needs identified in the Mercury Strategy. This table shows mercury and methylmercury studies and monitoring proposed for the RMP from 2008 to 2012, and planned for other programs. Numbers indicate proposed budget allocations in 1000s. Matching funds from other programs are indicated in parentheses.

### **QUESTION 2:**

Which processes, sources, and pathways contribute disproportionately to food-web accumulation?

Once the critical locations and times for methylmercury uptake are understood, it should be possible to determine where that methylmercury came from. The mercury that fuels uptake may originate from various pathways that carry contaminants into the Bay, or it may originate from mercury pools within the Bay that are mobilized and converted to methylmercury by environmental processes.

With our current state of knowledge, it is not possible to rule out any of these pathways as potentially playing a large role in supplying mercury for food web uptake. In fact, the current mercury TMDL assumes that all mercury in the Bay, regardless of origin or how or when it reached the Bay, is equally likely to enter the food web.

Environmental processes could also lead to increased net production of methylmercury and uptake into the food web. Recent studies suggest that one potentially important example of this is seasonal inundation of soils and sediments in floodplains, wetlands, or ponds. Extensive biosentinel monitoring in the Estuary by UC Davis (page 65)

enough to formulate hypotheses about the specific processes that may be important.

Our present understanding of the relative importance of the different pathways and processes that supply mercury to the food web is very limited. We hypothesize that some processes and pathways are much more important than others, the most important of which are referred to as the "high-leverage" pathways and processes. Prior to 2008, the RMP had not done any significant work to identify high-leverage pathways and processes. A great deal of work, however, has been done with CALFED funding in recent years, leading to the development of the current hypotheses regarding seasonal inun-

## Once the critical locations and times for methylmercury uptake are understood, it should be possible to determine where that methylmercury came from

Contaminants enter the Bay through a variety of pathways:

- > small tributaries that carry urban and nonurban runoff,
- > atmospheric deposition,
- > outflow from the Delta,
- > municipal and industrial wastewater effluent discharges,
- contaminated hotspots in the Bay, and
- > remobilization from sediment within the Bay.

and by the South Bay Salt Pond Restoration Project (page 37) supports this hypothesis. A process that appears to be important in the Delta region is sunlight induced de-methylation of mercury ("photodemethylation"), which converts methylmercury to inorganic mercury. For determining net production, processes that destroy methylmercury are just as important as those that create it. Other processes that affect mercury cycling through altering microbial activity, water chemistry, light penetration into the water column, or other factors could also have a large influence on methylmercury supply to the food web. We have not yet progressed very far in understanding processes affecting mercury uptake into the food web, having just begun to comprehend the intricacies of mercury cycling well

dation and photodemethylation. Other local work found that municipal wastewater effluent from the City of Sacramento was a relatively low-leverage pathway (Larry Walker Associates et al. 2008).

Answering Question 1 will set the stage for addressing Question 2. While we wait for a clear understanding of patterns in uptake to emerge, the RMP is pursuing initial investigations of high-leverage pathways in order to set the stage for expedient management of those inputs. Question 2 is a challenging query, and the best approach is not yet obvious. However, thanks to the clear definition of information needs provided by the Mercury Strategy, the RMP was able to take the proactive approach of issuing a Request

## After the high-leverage pathways and processes are identified, managers can focus on reducing mercury transport into those pathways and the Bay

for Proposals (RFP) on this topic. The response to the RFP was enthusiastic, and proposals were received from many leading mercury scientists. Over the next two years, \$100,000 per year has been allocated to two studies that were selected from the RFP. One study is examining the **isotopic composition** of mercury from different sources and pathways, and in fish from several places in the Bay and its watershed. This work may allow us to determine which mercury inputs are contributing most to accumulation in fish by simply measuring the mercury isotopes in the fish. Another study is using an innovative device that absorbs methylmercury from the water column. These Diffusive Gradient in Thinfilm devices or (DGTs) can be deployed in places where small fish are not available, and may be useful in tracing input pathways leading to food web uptake (page 8).

#### **OUESTION 3:**

What are the best opportunities for management intervention for the most important pollutant sources, pathways, and processes?

The overall goal of the Mercury Strategy is to provide information needed to identify management actions that can reduce mercury impairment and to track the effectiveness of those actions. After the high-leverage pathways and processes are identified, managers can focus on reducing mercury transport into those pathways and the Bay.

Some potential outcomes of RMP mercury studies illustrate this concept. If the current hypothesis that seasonal inundation increases net methylmercury production turns out to be correct, then designing habitat restoration projects that minimize seasonal inundation in areas with a large supply of total mercury may be one example of an opportunity for management intervention. Similarly, if photodemethylation turns out to be an important process in the Bay, habitat restoration designs could emphasize maximizing this process. Aeration of the water column is an example of a management approach that currently is being tested in Almaden Reservoir in the Santa Clara Valley as a means of minimizing methylmercury production by sulfate-reducing bacteria.

Better answers to Questions 1 and 2 are needed to provide a foundation for addressing Question 3 in a cost-effective manner. The RMP has not yet conducted any significant work to answer Question 3, and none is currently planned. Some work is being done through other programs. One example is the aeration study in Almaden Reservoir. Other significant projects funded by Propositions 13 (the Costa-Machado Water Act of 2000), 40, and 50 (Agricultural Water Quality) examine wetland design and management options that would reduce production and uptake of methylmercury in tidal marshes, managed ponds, and associated habitats. Findings from these projects are anticipated in 2009. As understanding grows and we begin to address Question 3, the focus of the RMP likely will be on identifying opportunities for intervention in

pathways and processes within the Bay. Other programs, such as stormwater management programs, will focus on sources, pathways, and processes occurring upstream in Bay Area watersheds.

### **QUESTION 4:**

## What are the effects of management actions?

Water quality managers need to be able to predict and evaluate the effects of their actions. Before the actions are taken, managers need predictions of expected outcomes in order to choose among different possible approaches. Such predictions can be made based on a conceptual understanding, or *model*, of mercury behavior in the ecosystem. After actions are taken, outcomes can be evaluated through *monitoring* of the appropriate water quality indicators.

The knowledge gained from mercury studies in the Bay and elsewhere will make it possible to develop a model of mercury cycling and make predictions of the impact of different management actions on mercury uptake into the food web. Given the complexity of the mercury cycle, these predictions will not always be exactly correct, especially in the initial stages of implementation of the Mercury Strategy. Making predictions requires at least a conceptual model, and ideally a quantitative model, of mercury behavior. Such models also are useful in designing monitoring and in many other ways. They

The RMP Mercury Strategy

should be developed from the beginning and refined continually as knowledge accumulates. A holistic understanding of mercury behavior in the Bay will be needed to predict the effect of any one action on uptake into the food web. The complexity of the mercury cycle and the rapid conversion of methylmercury into other forms make model development unusually challenging.

To date, the RMP has focused on understanding loadings, spatial patterns, and long-term trends in total mercury. The RMP is just beginning to focus on developing a conceptual understanding of methylmercury, beginning with the creation of a simple mass budget (an accounting of all the inputs and losses of methylmercury) in 2008. After this mass budget is completed, the next steps in model development will be determined. The RMP has invested considerable resources into tracking trends in total mercury and methylmercury in the Bay on a broad



Topsmelt. Photograph by Linda Wanczyk.

regional scale, through monitoring of water, sediment, sport fish, and bird eggs. This monitoring is essential in measuring progress toward the goals set forth in the Mercury TMDL, and will continue into the future. More focused monitoring at finer spatial scales likely will be needed to establish a firm link between management actions and water quality improvements.

### **QUESTION 5:**

## Will total mercury reductions result in reduced food web accumulation?

Mercury experts agree that total mercury reductions generally will reduce mercury concentrations in the food web; the mercury TMDL is based on this premise. However, the magnitude of the reduction will be highly dependent on other factors. Very loose correlations exist between total mercury and mercury in the food web, but other factors can superimpose variation of 10-fold or more on top of this relationship.

This question is related to Questions 1 and 2. In relation to Question 1, if we find where food web accumulation is taking place, can we reduce it by reducing the total mercury in that locale? Similarly, in relation to Question 2, if we find that certain pathways or processes are high-leverage, can we reduce food web uptake by reducing related sources of total mercury? Experimental approaches in the laboratory or in the field may be useful in answering this question. The RMP has not yet performed any studies to specifically address this question, and the tentative plan for the next five years currently does not include any.

## Five-Year Plan for RMP Mercury Studies

The culmination of the Mercury Strategy is a plan for mercury studies in the RMP over the next five years (Table 1). The Strategy and five-year plan are living documents that will be evaluated and revised on an annual basis to incorporate new information emanating from the RMP and the mercury research community as a whole.

Development of the Mercury Strategy has proven to be an extremely beneficial exercise. This effort has resulted in a clear direction for obtaining the information managers need to aggressively tackle the mercury problem. Having clear direction enabled the Program to take a more proactive approach, harnessing the creative energy of the research community to identify appropriate studies. This type of planning allows for effective use of RMP funds and provides a framework for evaluating and communicating progress in developing the information needed to reduce the impacts of mercury on the ecosystem. The success of this effort is likely to lead to similar focused planning efforts for other high-priority questions that the RMP is striving to answer.

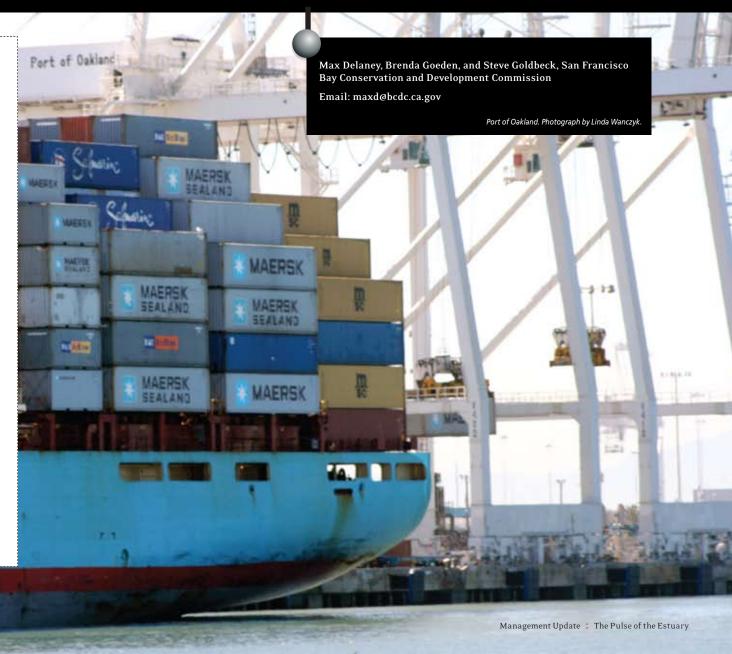
## MANÅGEMENT Update

Technical terms defined in Glossary on page 90

## Dredging and Sediment Management in San Francisco Bay

### HIGHLIGHTS

- Since the mid-1800s, anthropogenic activities have drastically altered sediment movement and supply throughout San Francisco Bay
- The regulation and management of dredging and disposal of dredged material in the Bay historically has been a controversial issue
- > The creation of the Long Term
  Management Strategy (LTMS)
  for the Placement of Dredged
  Material in the San Francisco Bay
  Region established a multi-agency,
  stakeholder-driven program to
  coordinate dredging and disposal
  activities on a regional scale
- The LTMS has resulted in a dramatic reduction in in-Bay disposal of dredged material
- > One of the most important goals of the LTMS is to capture dredged material from ports, marinas, and channels and beneficially re-use the material for wetland restoration projects, levee rehabilitation, and other purposes where sediment is in demand



**Dredging and Sediment Management** 

## A Brief History of "Mud"

Dredging, waterway modification, and myriad other activities altering sediment movement and supply in San Francisco Bay have been occurring since the mid-1800s. For a long time, these activities were conducted with little awareness of the potential impacts on the Bay. The Gold Rush triggered a flurry of hydraulic mining in the Sierra Nevada, producing huge quantities of sediment that eventually blocked waterways, resulting in increased flooding from storms, and gradually washed into the Bay. From the late-1800s to the mid-1900s, most of the Bay's historical tidal marshes were diked and/or filled for agriculture, duck clubs, salt production, and urban development. These actions reduced the tidally-influenced area of the Bay by 60% and also caused most of the remaining slough channels to silt up (CCMP 2007). In recent decades, further changes to both the natural sediment regime and the hydrologic patterns that transport sediment have occurred as a result of channelization, installation of shoreline rip-rap, and the construction of large-scale dams and flood control projects throughout the watershed. Dredging and sand mining projects also have contributed to changes in sediment movement, deposition, and erosion. The net result of all this human activity is that sediment dynamics and processes in the Bay have been drastically altered over the last 150 years.



Each year, an estimated 4,000 commercial ocean-going vessels move through the Bay, carrying over 75 million tons of cargo worth approximately \$20 billion

## The Need for Dredging

San Francisco Bay is one of the critical maritime thoroughfares in the nation, supporting international trade, commercial and recreational fishing, and recreation. Each year, an estimated 4,000 commercial ocean-going vessels move through the Bay (Marine Exchange 2008), carrying over 75 million tons of cargo (USACE 2008) worth approximately \$20 billion (MTC 2004). For over a century navigational channels through the Estuary have been created, deepened, and maintained by dredging (the removal of sediments from the bottom) to enable ships to navigate safely into and out of ports, harbors, and marinas without running aground.

The total volume of material dredged annually from channels, ports, and marinas in the Bay has actually decreased from approximately 8 million

cubic yards (MCY) in the early 1990s to approximately 4.4 MCY in 2007. This decrease is due, in part, to the fact that many large-scale port and federal navigation channel deepening projects have been completed in the last two decades. The Oakland Harbor Navigation Improvement Project ("the 50 Foot Deepening Project"), one of the biggest dredging projects in recent years, is currently slated for completion in 2009. Once this is completed, few large-scale new work dredging projects are anticipated. Further, construction of new marinas and smaller navigation channels has declined in recent decades. As a result, most current dredging is conducted in the Bay to maintain navigability of existing waterways. There is, however, an increasing demand for modest new work dredging projects in smaller marinas and refinery berthing areas around the Bay Area as these facilities strive to accommodate deeper-draft boats.

Cargo ship leaving Port of Oakland, Photograph by Linda Wanczyk.



## Beneficial Uses of the Bay: Navigation

ne of the world's great urban estuaries, San Francisco Bay provides habitat for crabs, fish, marine mammals, and millions of migrating and over-wintering birds. The Bay also is home to a robust shipping industry and many shorefront industries. Commuter ferries, tour boats, fishing boats, Coast Guard and other government vessels, and pleasure craft crisscross the Bay and go in and out through the Golden Gate.

The Water Board adheres to a water quality control plan, known as the Basin Plan, which protects the varied benefits that the Bay offers to our region. The Basin Plan defines these "beneficial uses" of the Bay, specifies the measures (known as water quality objectives) for protecting such uses, and outlines strategies for achieving and continuing to meet these objectives.

Among the beneficial uses of San Francisco Bay listed in the Basin Plan is navigation. Abbreviated as "NAV," navigation is defined as "uses of water for shipping, travel, or other transportation by private, military, or commercial vessels." Listing NAV as a beneficial use means that maintaining open waters is a protected activity, just like protecting the Bay to make sure that there is suitable habitat for wildlife and that it is safe for fishing and swimming.

Protecting the use of the Bay for navigation can be a challenge. San Francisco Bay is a naturally shallow water body. Prior to major impact from human development, sediments draining from its large watershed had formed extensive saltmarshes and mudflats. Hydraulic mining during the Gold Rush added more than a billion tons of sediment to the waterways, and significant quantities of sand and silt reached the Bay. Erosion from agriculture has also added sediments into the waterways.

Dredging to maintain navigability of San Francisco Bay waters has been necessary since the late 1800s. Navigation was recog-



Cargo ship under the Golden Gate bridge. Photograph by Linda Wanczyk.

nized as a major concern in 1893, when the state established the the shipping channels could inadvertently impair navigation in California Debris Commission. This three-member board's mission other areas—specifically, at the disposal sites. The Alcatraz disposal was to restore navigability of the State's rivers in the wake of the site received so much material that what had been a deep pocket impacts from hydraulic mining.

While maintenance dredging is a necessity in the Bay, it is important to make sure that dredging operations and dredged material. In 1991, the agencies responsible for managing dredging in disposal are conducted responsibly. During a 1980s review of the Basin Plan, the Water Board affirmed a commitment to testing dredged material prior to disposal to ensure that protection of one beneficial use would not put other uses at risk.

In 1989, it became evident that dredging to ensure navigation in

became a nuisance mound. Fishermen protested, and the Corps of Engineers dredged and redistributed the sediments within the site.

the Bay came together to develop the Long-Term Management Strategy, or LTMS. The management strategy was published in 1998. Through the LTMS, managers and interested groups continue to work together to balance the needs of navigation with the other beneficial uses of the Bay.

## Beyond Mudlock: The Long Term Management Strategy (LTMS)

Historically, large volumes of dredged material from navigation channels were disposed of at several in-Bay disposal sites (Figure 1); this material was expected to disperse with currents and tidal action. In the 1980s, however, so much material had been placed at the region's primary in-Bay disposal location, the Alcatraz disposal site (SF-11), that significant mounding of dredged material occurred. In addition, many people were increasingly worried about the potential impacts of dredging and dredged material disposal on the Bay's aquatic organisms and other ecological resources. During this time, fishermen and citizens concerned about the impact of dredged material on Bay fisheries even blocked the Alcatraz disposal site with their boats in an event that symbolized Bay "Mudlock." By the early 1990s, the growing controversy and concerns of the previous decade had highlighted the need for improved management of dredging and dredged material disposal in the Bay.

In response to this need, the Long-Term Management Strategy (LTMS) for the Placement of Dredged Material in the San Francisco Bay Region was developed. The LTMS is a collaborative regional management program (Table 1) created by state and federal regulatory and resource agencies and numerous stakeholders to better manage dredging and dredged material disposal in the Bay. The creation of the LTMS involved over thirty participants from government agen-

## The LTMS implemented a new approach to dredging and dredged material management

cies, environmental organizations, the dredging community, development interests, ports, and fishing organizations. The process began in 1993, and by 1998 a final Environmental Impact Report/Environmental Impact Statement (EIR/ EIS) had been completed. Shortly thereafter, a Record of Decision (ROD) was signed by the U.S. Army Corps of Engineers (USACE) and U.S. Environmental Protection Agency (USEPA) (CCMP 2007). The LTMS was subsequently included in amendments to the San Francisco Regional Water Quality Control Board's Water Quality Control Plan (the Basin Plan) and the San Francisco Bay Conservation and Development Commission's (BCDC) San Francisco Bay Plan (the Bay Plan). The LTMS Management Plan was released in 2001.

The LTMS implemented a new approach to dredging and dredged material management for San Francisco Bay by developing program goals and an overall structure to implement them (Table 2). One of the immediate priorities of the LTMS was to reduce the amount of dredged material being disposed of at the in-Bay disposal sites. The plan established a "step-down" process to reduce the total allowable in-Bay disposal volume every three years from an overall volume of 3.0 MCY in 2001 to approximately 1.5 MCY by the year 2012 (Figure 2) (LTMS 2001). At the same time, the LTMS agencies recognized that with less dredged material allowed in the Bay, new disposal alternatives

would be needed. Specifically, the LTMS agencies are promoting beneficial re-use of sediment from dredging projects rather than treating it as a waste product (e.g., for restoration and constructing wetlands, levee rehabilitation projects, or other commercial uses). Therefore, the LTMS management plan also set a goal of achieving at least 40% beneficial re-use and no more than 20% in-Bay disposal, with the remainder of the material being disposed at the San Francisco Deep Ocean Disposal Site (LTMS 2001).

The LTMS agencies carefully track progress of meeting the step-down volume targets each year. If the average annual disposal volume for any three-year period exceeds the prescribed target, the agencies may impose mandatory volume allocations for individual dredging projects to ensure that the annual disposal limits will be met in the future. Naturally, the intent of the LTMS program is to work with the dredging community to develop sufficient beneficial re-use opportunities and disposal alternatives to enable the region to avoid the imposition of allocations.

In order to ensure the effectiveness of the program in meeting its goals, a programmatic review occurs every three years, with each six-year review involving the consideration of policy amendments, if necessary. In addition, the LTMS Management Plan serves as a "living document" which is periodically updated to reflect emerging concerns.

**Dredging and Sediment Management** 



#### FIGURE 1

Prior to the 1970s, dredged material from navigation channels was disposed of at many sites throughout the Bay. Beginning in the early 1970s, disposal was limited to a few designated sites where dispersion and eventual transport to the ocean was expected, with most material taken to the site near Alcatraz Island (SF-11). In 1982, a large mound of undispersed dredged material was discovered at the Alcatraz site. Mounding continued despite attempts to improve site management, thereby posing potential navigation hazards and demonstrating the site's limited capacity. Concurrently, concern grew among the fishing, scientific, and environmental communities regarding dredged material impacts on the Bay's fisheries and other ecological resources. The Long Term Management Strategy (LTMS) for the Placement of Dredged Material in the San Francisco Bay Region was established in response to these concerns. The LTMS has resulted in a dramatic reduction in in-Bay disposal.

#### [ TABLE 1]

#### AGENCIES COLLABORATING ON THE LTMS

THE LTMS AGENCIES ARE:

U.S. Army Corps of Engineers (USACE)

U.S. Environmental Protection Agency (USEPA)

San Francisco Bay Regional Water Quality Control Board (Water Board)

State Water Resources Control Board (State Water Board)

San Francisco Bay Conservation and Development Commission (BCDC)

#### OTHER PARTICIPATING AGENCIES INCLUDE:

The State Lands Commission (SLC)

NOAA National Marine Fisheries Service (NOAA Fisheries)

U.S. Fish and Wildlife Service (USFWS)

California Department of Fish and Game (CDFG)

California Coastal Conservancy (SCC)

#### [ TABLE 2 ]

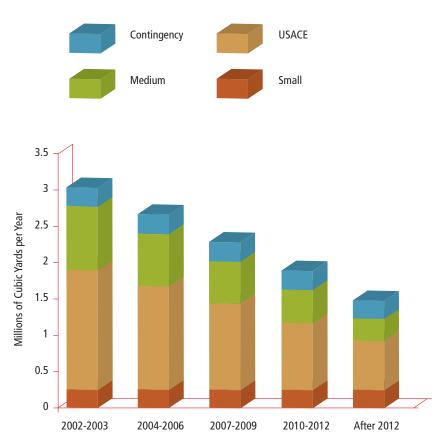
#### LTMS GOALS

Maintain in an economically and environmentally sound manner those channels necessary for navigation in San Francisco Bay and Estuary and eliminate unnecessary dredging activities in the Bay and Estuary

Conduct dredged material disposal in the most environmentally sound manner

Maximize the use of dredged material as a resource

Maintain the cooperative permitting framework for dredging and disposal applications



Footnote: Small = small dredgers, <50,000 CY per year. Medium = medium dredgers, >50,000 CY per year. USACE = US Army Corps of Engineers projects (mainly consisting of maintenance dredging all the major navigation channels throughout the Bay). Contingency = buffer amount of material that the LTMS agencies may allow in case of an unforeseen need in a given year.

**FIGURE 2 LTMS in-Bay disposal volume targets during the 12-year Transition Period.**Every three years, the annual disposal volume limit decreases by approximately 387,500 CY.



Dredging in San Pablo Bay. Photograph by Nicole David.

**Dredging and Sediment Management** 

## Structure of the LTMS

The LTMS is structured so that each agency has an assigned Program Manager to oversee the implementation of decisions at the agency level. Program Managers can elevate larger programmatic issues to the LTMS Management Committee. The Management Committee meets on a regular basis to guide the LTMS program, and maintains strong public involvement through the participation of interested parties and stakeholders. The LTMS is also led by an Executive Committee comprised of the chairpersons of the Water Board, BCDC, and the USEPA, the State Dredging Coordinator from the State Water Board, and the Commander of the South Pacific Division of the USACE. This Committee weighs in on broader policy issues.

In addition, the LTMS program has established several multi-agency work groups that meet on a regular basis and invite stakeholder participation to ensure that the LTMS remains a transparent and collaborative process. These work groups address issues ranging from LTMS-funded research, to assessment of potential environmental impacts of dredging, to the coordination of the timing and logistics of dredging projects.

## Dredged Material Management Office (DMMO)

As part of the LTMS program, the Dredged Material Management Office (DMMO) was created in 1995. The DMMO agencies include BCDC, the Water Board, the State Lands Commission, the USACE, and the USEPA. NOAA Fisheries, USFWS, and CDFG also participate in the review of proposed

dredging and disposal activities. The goals of the DMMO are to:

- streamline the permitting process to allow applicants to fill out one application form which the agencies can review jointly;
- allow for joint agency review of project-specific sampling and analysis plans;
- **3.** review the testing results of the sediment quality sampling; and
- jointly issue suitability determinations for material proposed for disposal (LTMS 2001).

The DMMO was also created to increase efficiency, communication, and coordination between the member agencies and to foster a comprehensive and consolidated approach to handling dredged material management issues. The DMMO also posts permit applications and guidance documents online, is developing a database for tracking project specific data, and produces annual reports evaluating program performance.

The Dredged Material
Management Office (DMMO)
was created in 1995 to review
proposed dredging and
disposal activities

Dredged material delivered to offloader facility in San Pablo Bay.

Photograph courtesy of US Army Corps of Engineers.

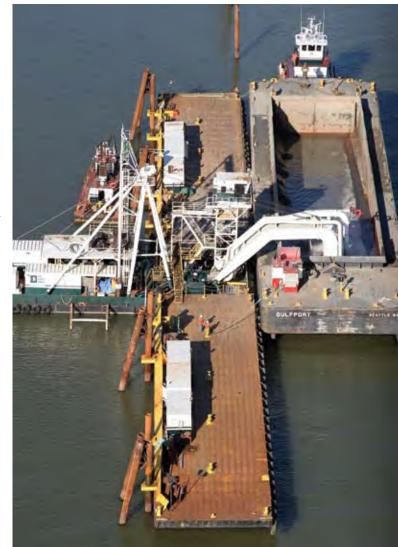
## Relevant Websites for the LTMS Program

### LTMS website:

http://www.spn.usace.army.mil/ltms/

## DMMO website:

http://www.spn.usace.army.mil/conops/dmmo.htm



## The Nuts and Bolts of Dredging Regulation

he passage of the federal Rivers and Harbors Act in 1899 ostensibly marked the beginning of dredging regulation in the United States. This Act made it illegal to make any modifications to the course and capacity of navigable waters, including discharges and dredging, without a permit from the USACE.

The USACE has primary responsibility for maintaining navigable waters in the United States. Before issuing a permit, USACE staff review all proposed dredging and disposal activities for potential impacts to navigation, biological resources, water and sediment quality, and the general public. The USACE regulates the discharge of dredged material into waters and wetlands of the United States under the Clean Water Act and the transportation and dumping of dredged material into coastal waters and the open ocean under the Marine Protection, Research, and Sanctuaries Act (MPRSA).

The USEPA has the authority to designate ocean disposal sites under the MPRSA. Under the Clean Water Act, they also cooperate with the USACE in the development of criteria for evaluating the potential environmental impacts of proposed disposal activities. While the USEPA does not issue dredging permits directly, it has the responsibility of reviewing permit applications and providing comments to the USACE and other LTMS agencies.

The State Water Board and its nine Regional Water Boards regulate water quality in California. The San Francisco Bay Water Board regulates Bay dredging and disposal activities under the Clean Water Act and the Porter-Cologne Water Quality Control Act. They review dredging and disposal activities in the Bay to ensure that the discharge of dredged material, whether in waters of the U.S. or at upland locations, will not violate state water quality standards.

BCDC, a state agency, regulates dredging and filling activities in the Bay under the McAteer-Petris Act. BCDC reviews dredging and disposal projects to ensure compliance with their Bay Plan before issuing permits. In addition, under the Coastal Zone Management Act, BCDC has the authority to review federal dredging projects to ensure that they are consistent with its Federally-approved Coastal Zone Management Program for the San Francisco Bay segment of the California coastal zone, and issue consistency determinations.

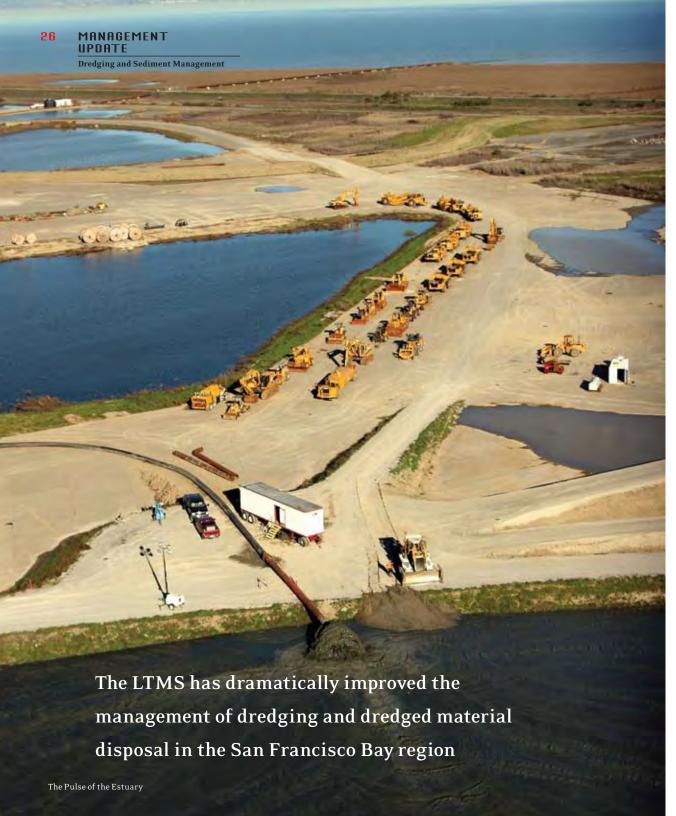
The State Lands Commission (SLC) administers public trust lands in coastal waters (within a three-mile state territorial limit) and other tidal and submerged areas. Written authorization from SLC must be obtained prior to dredging or depositing dredged material on lands under SLC jurisdiction.

In addition, the National Environmental Policy Act (NEPA) and the California Environmental Quality Act (CEQA) require federal and state agencies, respectively, to conduct environmental assessments of each dredging permit application and, if necessary, develop environmental impact reports/statements when an activity may have potential adverse impacts to the environment.

To ensure the protection of wildlife and habitat resources, various resource agencies review dredging activities in the Bay. Under the Federal Endangered Species Act (FESA), federal agencies need to consult with the U.S. Fish and Wildlife Service (USFWS) and NOAA's National Marine Fisheries Service (NOAA Fisheries) on activities that may adversely affect federally-listed species and their habitat before issuing dredging permits. Similarly, the California Endangered Species Act (CESA) requires state agencies to consult with the California Department of Fish and Game (CDFG) to assess potential impacts on state-listed species.

A 1996 amendment to the Magnuson-Stevens Fisheries Conservation and Management Act also requires NOAA Fisheries and regional fishery management councils to minimize, to the extent practicable, adverse effects to Essential Fish Habitat. This Act requires federal agencies to consult with NOAA Fisheries regarding how dredging projects may affect Essential Fish Habitat. Unlike the ESA consultation process, however, these consultations are advisory and conditions can be incorporated into permits based on the discretion of the federal permitting agency.

Some local governments also have jurisdiction over certain types of dredging activities and issue their own permits and approvals. •



## How Is The LTMS Doing?

The LTMS has dramatically improved the management of dredging and dredged material disposal in the San Francisco Bay region and measurable progress has been made toward meeting the program's overall goals. Allowable in-Bay disposal volumes have been reduced by more than 50% compared to pre-LTMS volumes, and actual in-Bay disposal in recent years has been about one-third of historical levels.

## Ocean Disposal and Beneficial Re-use

The LTMS has successfully helped implement and/ or expand new upland and wetland re-use projects. Since the inception of the program, more than 10 MCY of material has been delivered to beneficial re-use sites around the Bay. In the last several years, significant progress has been made on a number of large-scale projects (Figure 3).

- > The Oakland Middle Harbor Enhancement Area in Alameda County has received over 5 MCY of material from various Port of Oakland dredging projects and created 180 acres of shallow water habitat, eelgrass beds, oyster bed shoals, and bird islands.
- > The Hamilton Wetland Restoration Project (HWRP) in Marin County began receiving material in late 2007 and has re-used approximately 1 MCY of material from the Port of Oakland Deepening Project. The project will restore 2600 acres of tidal, seasonal, and transitional wetlands and will capture a total of approximately 24 MCY of dredged material.

Dredged material being pumped onto the Hamilton Wetland Restoration Project. Photograph courtesy of US Army Corps of Engineers.



FIGURE 3

The LTMS has successfully helped implement or expand new upland and wetland dredged material re-use projects.

Since the inception of the program, more than 10 MCY of material has been delivered to beneficial re-use sites around the Bay. In the last several years, significant progress has been made on a number of large-scale projects. The total volume planned for disposal and the total area to be restored for each site is shown.

**Dredging and Sediment Management** 

- The 2007 Water Resources and Development Act officially authorized the expansion of the HWRP to include the adjacent 1576 acre Bel Marin Keys parcel. The Bel Marin Keys parcel will capture approximately 14 MCY of dredged material.
- > The Montezuma Wetlands Restoration Project in Solano County has successfully received 3 MCY of dredged material since 2003, including 300,000 CY of relatively contaminated "non-cover" material. The project will restore approximately 2,000 acres of tidal and non-tidal wetlands.
- > The Bair Island Restoration Project in San Mateo County will receive up to 275,000 CY of dredged material, starting in 2008, and will restore 1400 acres of tidal wetlands.
- > The San Francisco Main Bar or SF-8 Disposal Site outside the Golden Gate, which was historically reserved for USACE dredging projects, became available to other projects in 2003. The USEPA only approves sand to be disposed of at SF-8 and this material feeds the San Francisco Bar nearshore system that nourishes beaches along the west shore of the San Francisco peninsula, including Ocean Beach.
- > The Ocean Beach Demonstration Beach Nourishment Project is a beach restoration project designed to prevent coastal erosion at Ocean Beach in San Francisco. The project was initiated as a pilot project in

- 2005 and to date has re-used almost 800,000 MCY of sand from USACE dredging projects.
- > The USACE and other LTMS agencies are currently proposing to designate the area where sand is being resupplied to Ocean Beach, known as the "Ocean Beach Demonstration Site," as a permanent dredged material disposal site.

the country. After a thorough analysis of location alternatives, the site was chosen at an area outside of the Gulf of the Farallones National Marine Sanctuary, where dredged material would disperse away from the Sanctuary due to prevailing north-northwest currents, and where disposal of dredged material would be least likely to affect hard bottom habitat and spawning, feeding or migration of marine organisms (USEPA 1994).

The LTMS agencies recognized the need to create other disposal options for the dredging community

## San Francisco Deep Ocean Disposal Site

While developing the program, the LTMS agencies recognized the need to create other disposal options for the dredging community. In 1994, the agencies worked with the USEPA to establish the federally-authorized San Francisco Deep Ocean Disposal Site (SF-DODS). The site is at a depth of nearly 10,000 feet deep and 55 miles off the coast of San Francisco, deeper and further offshore than any other designated ocean disposal site in

Disposal rules for SF-DODS include limitations on transit routes and barge loading during inclement weather and monitoring of barge performance (to ensure no spillage or leakage). In addition, biological, chemical, and physical monitoring by the USEPA is conducted on a regular basis at the disposal site and results are available in annual reports. To date, over 10 MCY of material has been successfully diverted to SF-DODS and monitoring results indicate no significant adverse impacts at the site.

## Environmental Work Windows define geographic areas and times of the year when dredging and disposal activities can occur without individual consultations

## Protection of Sensitive Fish Species and Wildlife

When the LTMS was developed, the resource agencies issued a programmatic biological opinion and incidental take authorizations for dredging and disposal activities around the Bay. This programmatic biological opinion was used to create Environmental Work Windows, which define geographic areas and times of the year when dredging and disposal activities can occur without individual consultations. These "Work Windows" are based on the presence and absence of endangered (and some commercially important) fish and wildlife species in the area where a project is planned to occur. Dredging projects that require activity outside of these windows can be authorized through individual consultations.

Prior to 2001, only about 50% of dredging work was performed during Work Windows. But by 2003, 80% of dredging work was performed within the Work Windows (LTMS 2006). In 2007, 82% of projects were dredged within the Environmental Work Windows. In 2005, the USFWS clarified and refined Work Windows for their species. NOAA Fisheries is currently amending their biological opinion to include the green sturgeon as a new federally-listed species.

### LTMS-Funded Scientific Research

The LTMS continues to fund and implement scientific studies on dredging and disposal issues such as data gaps related to Work Windows, mercury methylation potential and management in constructed wetlands, disposal plume tracking and modeling, effects of dredging plumes on herring eggs, and juvenile salmon distribution.

In 2007, the LTMS held its first Science Symposium featuring scientific presentations related to dredging and environmental management of San Francisco Bay. A second Symposium was held in 2008 and drew a larger number of scientists and stakeholders. Based on the success of these two events, the Symposium is slated to occur on an annual basis.

## **Regulatory Improvements**

In the last few years, the LTMS has developed additional tools to help dredgers and contractors fulfill permit requirements while also meeting LTMS disposal targets. As the LTMS program progresses and allowable in-Bay disposal volumes decrease, dredging project sponsors need to place more dredged material at upland, beneficial re-use sites, and/or the Deep Ocean Disposal Site. As required by the

federal and state Clean Water Acts and the Bay Plan, each dredging project must evaluate dredged material disposal options other than in-Bay sites. To assist with this evaluation, the LTMS agencies developed the Integrated Alternatives Analysis, which encourages planning for beneficial re-use of dredged material by evaluating a permittee's overall dredging program for three years and all available disposal and beneficial re-use options. The LTMS agencies also developed the Small Dredger Programmatic Alternatives Analysis that allows small dredging operations (those projects that dredge no deeper than minus 12 feet mean lower low water and remove an average of 50,000 cubic yards of material or less annually) to dispose of dredged material in-Bay without having to prepare an exhaustive list of alternative disposal options. In addition, these agreements reduce paperwork and cost and expedite the processing of permits without compromising environmental protection.

**Dredging and Sediment Management** 

## **Future Challenges**

The LTMS continues to focus on increasing the beneficial re-use of dredged material. Despite the success of recent projects in the Bay, there is a growing need to substantially increase the number of beneficial re-use opportunities, especially in the next several years as the LTMS endeavors to reduce in-Bay disposal to 1 MCY per year. One of the biggest constraints to maximizing beneficial re-use is the need for adequate and reliable funding at the state and federal level. Increasing dredging costs and decreasing budgets and federal policies that favor open-water disposal are continuing problems. Improved state and federal policies and funding mechanisms for beneficial re-use are needed. In addition, finding ways to make the cost of beneficially re-use competitive with in-Bay disposal is increasingly important.

Another emerging issue is the potential for a sediment deficit in the Bay. A variety of factors, such as increasing water diversions upstream of the Delta and morphologic and hydrologic alterations to the major tributaries and rivers, have resulted in the Bay receiving less sediment. Decreasing sediment inputs could impede wetland formation and cause the erosion of existing wetland habitats. The erosion of shorelines, beaches and tidal flats, which has been an issue in many areas around the Bay, could also worsen. Sea level rise is likely to exacerbate erosion issues, cause increased flooding, and cause further changes to sediment supply and dynamics throughout the Bay. Delta islands are especially vulnerable to catastrophic flooding because of land subsidence and the increased risk of levee failure. Adequate

sediment input into the Bay will be increasingly important as the rate of sea level rise accelerates and storms become more intense.

Developing a better understanding of sediment dynamics for the entire Bay-Delta system and how human activities affect it is increasingly important. The sources, sinks, and movement of Bay sediments are still poorly understood. Furthermore, as demonstrated by the LTMS, an adaptive, collaborative sediment management approach that addresses all aspects of Bay sediment dynamics is essential in addressing the impacts of climate change and other natural and human-induced changes on the Bay. LTMS managers continue to work in collaboration with scientists who are mapping and monitoring sediment in the Bay Area and continue to seek opportunities for better understanding sediment dynamics and their broader implications for the Bay-wide system.



The Montezuma Wetlands Restoration Project. Photograph courtesy of the Department of Water Resources.

## MANAGEMENT Update

## The 303(d) List

**Section 303(d) of the 1972 Federal Clean Water Act** requires that states develop a list of water bodies that do not meet water quality standards, establish priority rankings for waters on the list, and develop action plans, called Total Maximum Daily Loads (TMDLs), to improve water quality. The list of impaired water bodies is revised periodically (typically every two years). The RMP is one of several organizations that provide data to the State Water Board to compile the 303(d) List and to develop TMDLs.

The process for developing the 303(d) List for the Bay includes the following steps:

- > development of a draft list by the San Francisco Bay Regional Board;
- > adoption by the State Water Board; and
- > approval by USEPA.

The State Water Board compiled the most recent 303(d) List in 2006 following recommendations from the Regional Boards and information solicited from the public and other interested parties. The draft list was then revised based upon public comments. On October 25, 2006, the State Board adopted the California 2006 Revised 303(d) List. On November 30, 2006 US EPA gave partial approval to California's 2006 Section 303(d) List of Water Quality Limited Segments, with approval only withheld for areas outside of San Francisco Bay. On June 28, 2007, US EPA gave a final approval to the list.

The State Board and the Regional Boards are currently developing an updated 303(d) List for 2008.

The primary pollutants/stressors for the Estuary and its major tributaries on the 2006 303(d) List include:

Trace elements: Mercury and Selenium

Pesticides: Dieldrin, Chlordane, and DDT

Other chlorinated compounds: PCBs, Dioxin and Furan Compounds

Others: Exotic Species and Polycyclic Aromatic Hydrocarbons (PAHs)

More information on the 303(d) List and TMDLs is available from the following web sites.

303(d) List for Region 2 (which includes the Estuary) www.waterboards.ca.gov/sanfranciscobay/TMDL/303dlist.htm

TMDLs: www.waterboards.ca.gov/sanfranciscobay/tmdlmain.htm www.epa.gov/owow/tmdl/

## Regulatory Status of Pollutants of Concern

POLLUTANT	STATUS			
Copper	Site-specific objectives adopted for entire Bay, approved for South Bay			
	San Francisco Bay removed from 303(d) List in 2002			
Cyanide	Site-specific objectives approved in 2008			
Diazinon	Implementation of TMDL approved in 2007			
Dioxins / Furans	TMDL in early development stage			
Legacy Pesticides (Chlordane, Dieldrin, and DDT)	TMDL in early development stage			
Mercury	Implementation of TMDL and site-specific objectives approved in 2008			
Nickel	Site-specific objectives approved for South Bay and South Bay removed from 303(d) List in 2002			
	Delisting of other Bay segments proposed for 2008			
PCBs	TMDL adopted in 2008			
Selenium	TMDL in development - completion projected for 2010			
Pathogens	Richardson Bay TMDL adopted in 2008			
	Bay Beaches (Aquatic Park, Candlestick Point, China Camp, and Crissy Field) added to 303(d) List			

Adopted: San Francisco Bay Water Board adoption Approved: State Board and U.S. EPA approval

## MANAGEMENT Update

## **RMP Committee Members & Participants**

## RMP COMMITTEE MEMBERS

#### **RMP Steering Committee**

Small POTWs, Ken Kaufman, South Bayside System Authority

Medium-sized POTWs, Daniel Tafolla, Vallejo Sanitation and Flood Control District

Large POTWs/BACWA, Dave Tucker, City of San Jose

#### Refineries, Kevin Buchan, Western States Petroleum Association

Industry, Dave Allen, USS-POSCO

Cooling Water, Steve Bauman, Mirant Delta LLC

Stormwater Agencies, Adam Olivieri, EOA,

Dredgers, Ellen Johnck, Bay Planning Coalition

San Francisco Bay Regional Water Quality Control Board, Tom Mumley

RMP Steering Committee Chair in bold print

### RMP Technical Review Committee

POTWs/BACWA, Francois Rodigari, East Bay Municipal Utility District; Rod Miller, San Francisco Public Utilities Commission

South Bay Dischargers, Tom Hall, EOA Inc.

## Refineries, Bridgette DeShields, ARCADIS BBL

Industry, Dave Allen, USS-POSCO

Stormwater Agencies, Chris Sommers, EOA. Inc.

Dredgers, John Prall, Port of Oakland

San Francisco Bay Regional Water Quality Control Board, Karen Taberski

U.S. EPA, Luisa Valiela

City of San Jose, Eric Dunlavey

City/County of San Francisco, Michael Kellogg

U.S. Army Corps of Engineers, Robert

RMP Technical Review Committee Chair in bold print

## RMP PARTICIPANTS

#### **Municipal Dischargers**

Burlingame Waste Water Treatment Plant Central Contra Costa Sanitary District

Central Marin Sanitation Agency

City of Benicia

City of Calistoga

City of Palo Alto

City of Petaluma

City of Pinole/Hercules

City of Saint Helena

City and County of San Francisco

City of San Jose/Santa Clara

City of San Mateo

City of South San Francisco/San Bruno

City of Sunnyvale

Delta Diablo Sanitation District

East Bay Dischargers Authority

East Bay Municipal Utility District

Fairfield-Suisun Sewer District

Las Gallinas Valley Sanitation District

Marin County Sanitary District #5, Tiburon

Millbrae Waste Water Treatment Plant

.....

Mountain View Sanitary District

Napa Sanitation District

Novato Sanitation District

Rodeo Sanitary District

San Francisco International Airport

Sausalito/Marin City Sanitation District

Sewerage Agency of Southern Marin

Sonoma County Water Agency

South Bayside System Authority

Town of Yountville

Union Sanitary District

Valleio Sanitation and Flood Control

District

West County Agency

### **Industrial Dischargers**

C & H Sugar Company

Chevron Products Company

Conoco Phillips (Tosco-Rodeo)

Crockett Cogeneration

Dow Chemical Company

General Chemical Corporation

Rhodia, Inc.

Shell - Martinez Refining Company

Tesoro Golden Eagle Refinery

USS - POSCO Industries

Valero Refining Company

### **Cooling Water**

Mirant Delta LLC

#### Stormwater

Alameda Countywide Clean Water Program

Caltrans

City and County of San Francisco

Contra Costa Clean Water Program

Fairfield-Suisun Urban Runoff Management Program

Marin County Stormwater Pollution Prevention Program

San Mateo Countywide Stormwater

Pollution Prevention Program

Santa Clara Valley Urban Runoff Pollution

Prevention Program

Vallejo Sanitation and Flood Control District

### **Dredgers**

**BAE Systems** 

Chevron Richmond Long Wharf

City of Benicia

Conoco Phillips (Tosco-Rodeo)

Corinthian Yacht Club

Coyote Point Marina

Larkspur Ferry

Marin County - Paradise Cay

Marin Rowing Association

Paradise Cay Yacht Club

Point San Pablo Yacht Harbor

Port of Oakland

Port of San Francisco

Richmond Yacht Club

Strawberry Channel

U.S. Army Corps of Engineers

Valero Refining Co.

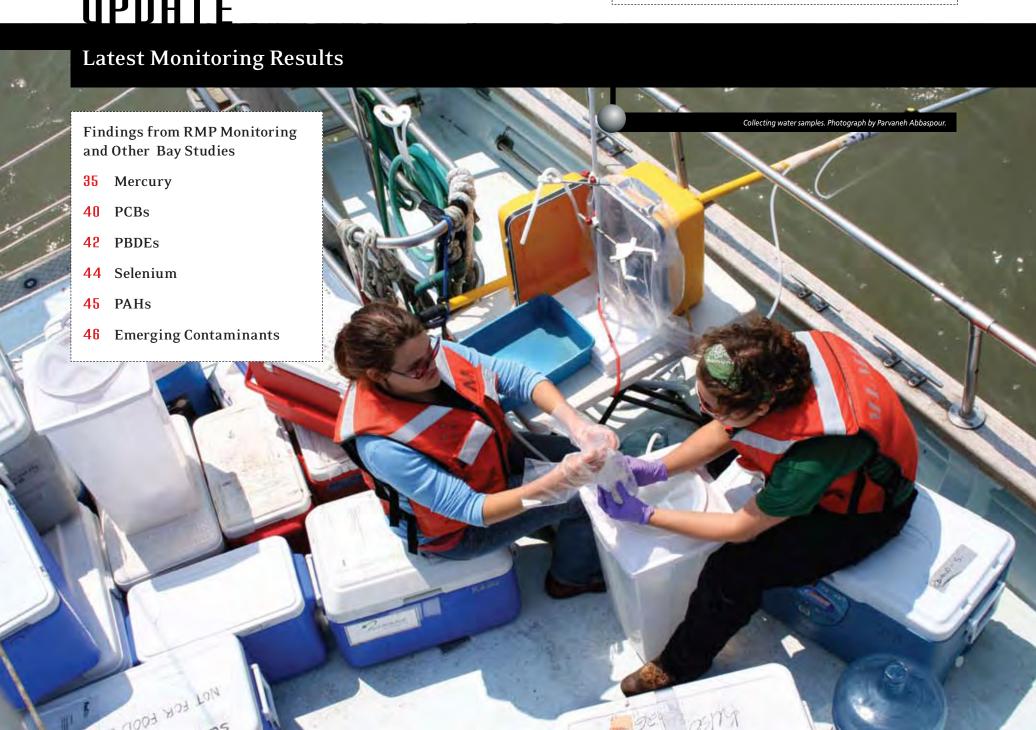
## STATUS AND TRENDS UPDATE

The Latest Findings from Pollutant Monitoring and Research

- 34 The Latest Monitoring Results
- 47 Water Quality Trends at a Glance

# STATUS AND TRENDS UPDATE

> Technical terms defined in Glossary on page 90

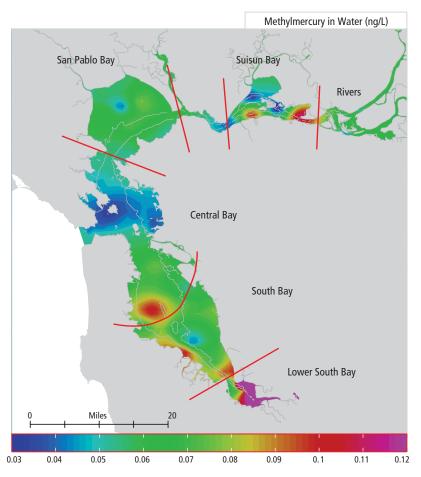


### [ Mercury ]

Mercury contamination is one of the top water quality concerns in the Estuary and mercury clean-up is a high priority of the Water Board. Mercury is a problem because it accumulates to high concentrations in some fish and wildlife species. The greatest health risks from mercury are generally faced by humans and wildlife that consume fish.

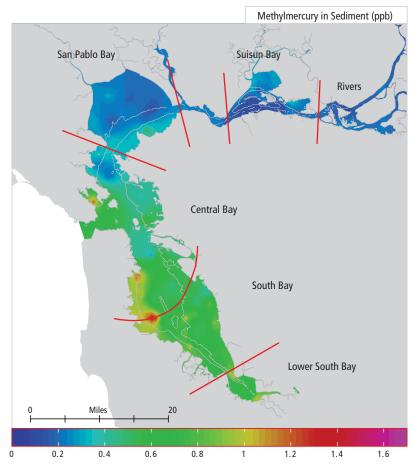


A RMP sampling cuise. Photograph by Nicole David.



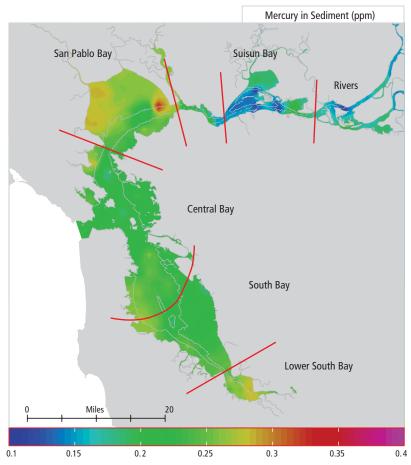
Footnote: Plot based on 53 RMP data points from 2006 and 2007. Earlier years not included because a less sensitive method was employed. The maximum concentration was 0.19 ng/L at a site in Lower South Bay in 2007. Data are for total methylmercury.

Water from Lower South Bay had the highest average concentration of methylmercury (0.11 ng/L) of any segment in 2006 and 2007. Methylmercury typically comprises only about 1% of the total of all forms of mercury in water or sediment, but it is the form that is readily accumulated in the food web and poses a toxicological threat to highly exposed species. Methylmercury has a complex cycle (page 6), influenced by many processes that vary in space and time. The RMP measures methylmercury in Bay water and sediment to better understand the sources of the methylmercury that are accumulated by fish and wildlife. The Bay-wide average for the two-year period was 0.06 ng/L. No regulatory guideline exists for methylmercury in water.



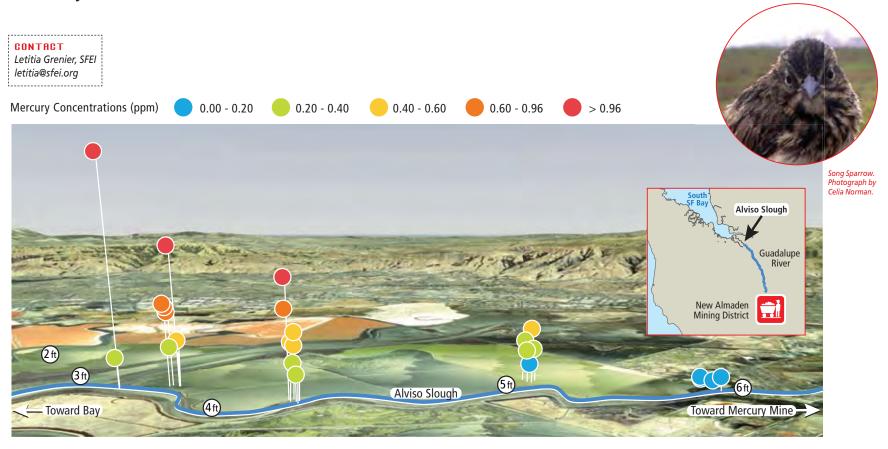
Footnote: Plot based on 280 RMP data points over a six-year period from 2002 – 2007. The maximum concentration was 2.4 ppb at a site in Central Bay in 2002.

Concentrations of methylmercury in sediment south of the Bay Bridge have been consistently higher than those in the northern Estuary. Mercury is converted to methylmercury mainly by bacteria in sediment. Methylmercury production can vary tremendously over small distances and over short time periods, so the figure shown should be viewed as the result of several "snapshots" of Bay conditions at the time of the surveys in the summers of 2002 - 2007. The Bay-wide average concentration in 2007 (0.39 ppb) was well below the overall average for the six-year period (0.55 ppb). However, the general spatial pattern still held with Suisun and San Pablo bays below the Bay-wide average for 2007, and Central, South, and Lower South bays above the Bay-wide average for 2007. No regulatory guideline exists for methylmercury in sediment.



Footnote: Plot based on 279 RMP data points over a six-year period from 2002 – 2007. The maximum concentration was 0.78 ppm near Mare Island in 2004

In contrast to methylmercury, long-term average total mercury concentrations in sediment generally have been highest in San Pablo Bay (0.27 ppm), slightly lower in the Central Bay (0.24 ppm), South Bay (0.22 ppm), and Lower South Bay (0.26 ppm), and lowest in Suisun Bay (0.14 ppm). Total mercury is the summation of all forms of mercury in a sample (page 6), and is a rough index of the amount of mercury available for conversion into methylmercury. The Baywide average for the six-year period was 0.23 ppm. A site near Mare Island in San Pablo Bay sampled in 2004 had the highest concentration by far (0.78 ppm).

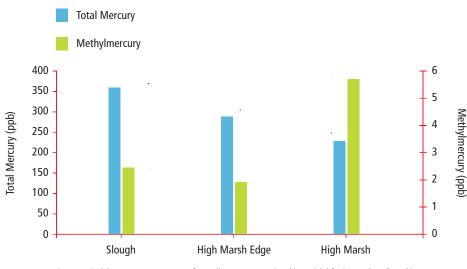


Extent that land subsided in feet #ft

Footnote: Concentrations in ppm wet weight. Subsidence data are from Poland, J.F., and Ireland, R.L., 1988, Land Subsidence in the Santa Clara Valley, California, as of 1982, U.S. Geological Survey Professional Paper 497-F: US Government Printing Office.

Subsided tidal marshes in the South Bay may have lower methylmercury production. Tidal marsh song sparrows sampled in 2007 showed a gradient in mercury concentrations along Alviso Slough in the Lower South Bay. Mercury concentrations in the blood of these year-round marsh residents decreased with distance from the Bay and proximity to the New Almaden historic mercury mining district. Alviso Slough carries runoff from New Almaden (inset). This decrease in sparrow mercury concentrations parallels a gradient in subsidence of the land caused by groundwater pumping several decades ago. These parallel gradients have led to the hypothesis that lowered elevation and increased inorganic sediment content of the marsh plain due to subsidence are related to reduced net methylmercury production. This research was completed for the South Baylands Mercury Project, a collaboration between the San Francisco Estuary Institute, the U.S. Geological Survey, and the Santa Clara Valley Water District. The study aims to provide information to the South Bay Salt Pond Restoration Project about mercury issues related to restoring the Alviso Pond Complex.







Footnote: Each bar represents average surface sediment concentrations (dry-weight) for 24 samples collected in spring and summer of 2005 and 2006.

Higher-elevation portions of tidal marsh in the North Bay also generate more methylmercury, even though total mercury in these areas is lower. In a recently completed study of marshes along the Petaluma River, total mercury concentrations in sediment were higher in marsh channels and lower in the edge and interior locations in the high marsh. Total mercury and methylmercury concentrations in slough sediments were similar to those seen in Bay surface sediments. In contrast, methylmercury concentrations were greatest in the high marsh, where drainage is slow and plants supply abundant organic matter, allowing sediment bacteria to generate anoxic conditions, enhancing methylmercury production. Potential rates of methylmercury production in these marsh sediments were quite rapid, capable of generating all of the methylmercury present in the marsh sediments in one or two weeks. Most of the methylmercury found in these marshes therefore probably originates from production within the wetland. Higher concentrations of methylmercury observed in the high marsh sediments and measured in the slough channel during ebb tide suggest that the net transport of methylmercury is from the high marsh to the sloughs.

### [Mercury] continued CONTACT Don Yee, SFEI Atmospheric deposition sampler. donald@sfei.org Photograph by Sarah Rothenberg. A 2005 California Estimated Mercury Emissions Mercury in Rainwater 25 Cement Plant Reference Site 20.0 14.9 20 16.0 Mercury Emissions (µg/m²) Mercury (pptr) 15 12.0 6.6 10 8.0 4.1 3.6 4.0 2.5 5 1.9 0.0 0 Bay Area San South Mojave Imperial San Jan - Dec Feb Diego Joaquin Coast

Footnote: Data from California Air Resources Board (www.arb.ca.gov/applemsinv/facinfo/facinfo.php).

Atmospheric emissions in the Bay Area may be an important source of mercury. Atmospheric deposition of mercury may be a "high leverage pathway," potentially leading more directly than other pathways to mercury accumulation in the Bay food web. Figure A: Estimates by the California Air Resources Board indicate that the Bay Area has a higher rate of mercury emissions than other areas in California. A study led by SFEI in 2007 and 2008 investigated the impact of emissions from a large cement plant in Cupertino that burned petroleum coke as a fuel source. Figure B: Rainwater was collected weekly between November 29, 2007 and March 20, 2008; this included a period in February when cement production was minimized due to annual plant maintenance. During January, when rainwater was collected simultaneously at the cement plant and a nearby control site, average total mercury concentrations were 7.4 times higher and total mercury deposition was 5.8 times higher at the cement plant; both parameters were roughly equal at the two sites in February.

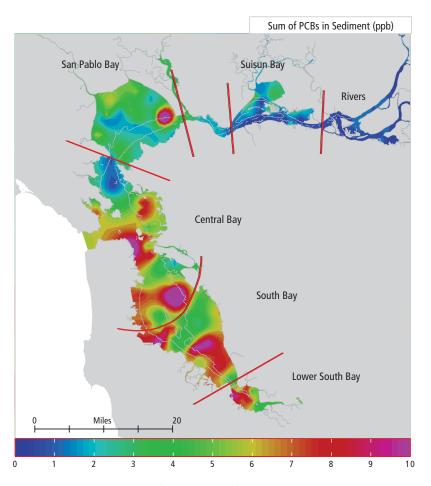
**Latest Monitoring Results** 

### [PCBs]

PCB contamination remains one of the greatest water quality concerns in the Estuary, and PCB clean-up is a primary focus of the Water Board. PCBs are a problem because they accumulate to high concentrations in some Bay fish and pose health risks to consumers of those fish.

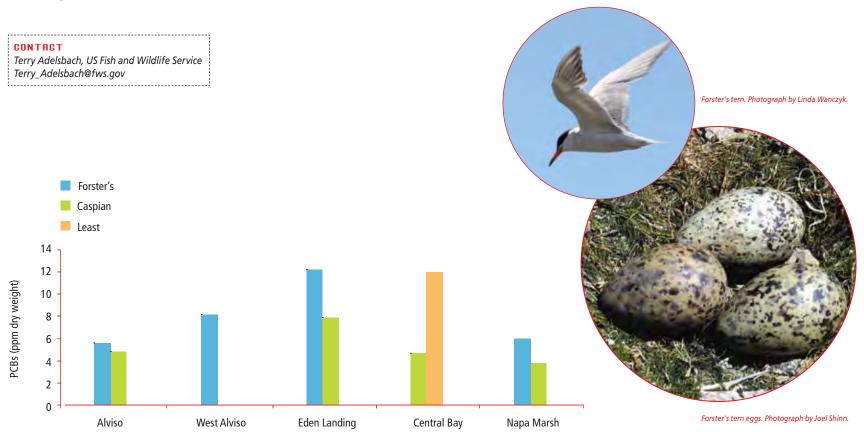


Collecting a sediment sample. Photograph by Nicole David.



Footnote: Plot based on 188 RMP data points from 2004 – 2007. Data from 2002 and 2003 are not available. The maximum concentration was 27 ppb in Central Bay in 2007.

Average PCB concentrations in Bay sediment measured from 2004 - 2007 were highest in the southern reach of the Estuary: Lower South Bay (7.5 ppb), South Bay (6.5 ppb), and Central Bay (6.9 ppb). Average concentrations were lower in San Pablo Bay (4.2 ppb) and Suisun Bay (2.0 ppb). Concentrations in 2007 were higher in all Bay segments than in previous years. The Bay-wide average for 2007 was 8.7 ppb, well above the overall long-term average of 5.7 ppb. The cause of this fluctuation is not known. Models suggest that sediment PCB concentrations must decline to about 1 ppb for concentrations in sport fish to fall below the threshold of concern for human health.



Footnote: Bars indicate average concentrations. California least tern eggs were all failed-to-hatch eggs and thus represent a potentially biased and worst case sample with regards to contaminant accumulation. Data from Adelsbach, T.L. and T. Maurer. 2007. Dioxin Toxic Equivalents, PCBs, and PBDEs in Eggs of Avian Wildlife of San Francisco Bay. U.S. Fish and Wildlife Service, Sacramento, CA.

PCB concentrations in the eggs of some San Francisco Bay terns appear to be high enough to pose health risks to these species. In sampling conducted from 2000 - 2003, the U.S. Fish and Wildlife Service found that approximately 17% of 149 tern eggs were above an effects threshold for terns of approximately 16 ppm dry weight. Maximum concentrations observed in both Forster's terns and Caspian terns were similar and nearly five times greater than the lowest observed adverse effect level. Maximum concentrations of PCBs and other contaminants (dioxins, PBDEs, and mercury) were observed in Forster's terns, suggesting that this is a valuable indicator species for multiple contaminants of concern. The Eden Landing area in South Bay had the highest concentrations of PCBs (and dioxins and PBDEs as well). Comparison of the results of this study to concentrations measured in Bay tern eggs in the 1980s indicates that little decline has occurred in the last 20 years.

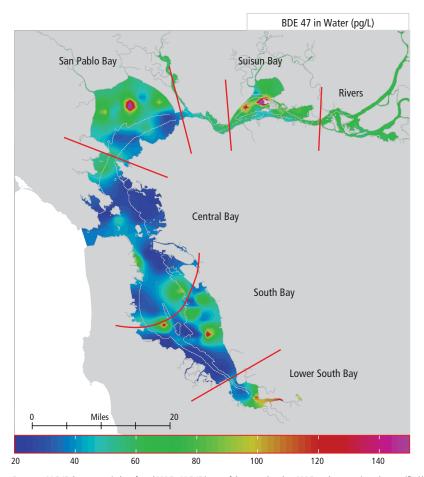
**Latest Monitoring Results** 

### [PBDEs]

PBDEs, a class of bromine-containing flame retardants that was practically unheard of in the early 1990s, increased rapidly through the 1990s and are now a pollutant of concern in the Estuary. The California Legislature has banned the use of two types of PBDE mixtures. Tracking the trends in these chemicals will be extremely important to determine what effect the ban will have and if further management actions are necessary. No regulatory guidelines exist yet for PBDEs.

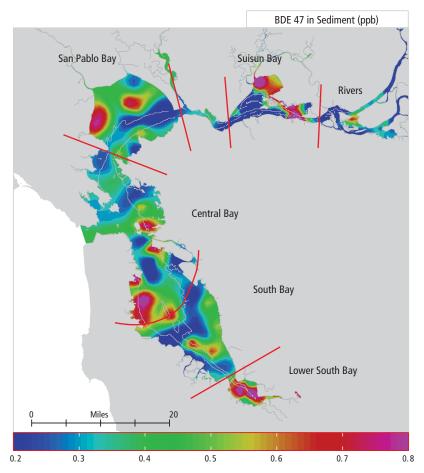


Sediment sampling. Photograph by Nicole David



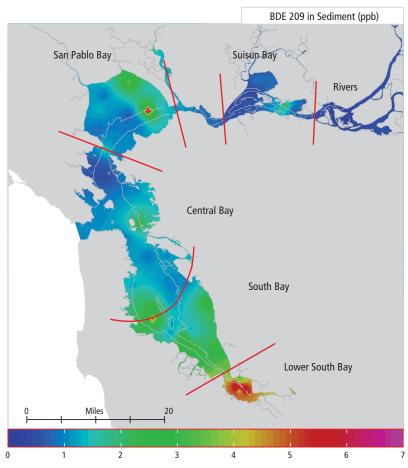
Footnote: BDE 47 shown as an index of total PBDEs. BDE 47 is one of the most abundant PBDEs and was consistently quantified by the lab. Plot based on 168 RMP data points from 2002 – 2007. The maximum concentration was 337 pg/L observed in Suisun Bay in 2004. Data are for total BDE 47 in water.

The highest average concentrations of PBDEs in water from 2002 - 2007 were found in Suisun Bay. The highest concentrations of BDE 47 (one of the most abundant PBDEs and an index of PBDEs as a whole), two samples greater than 300 pg/L, were observed at locations in Suisun Bay and San Pablo Bay, both in 2004. Suisun Bay had the highest average concentrations over the six-year period (81 pg/L), suggesting the presence of PBDE inputs into the northern Estuary.



Footnote: BDE 47 is one of the most abundant PBDEs and was consistently quantified by the lab. Plot based on 187 RMP data points from 2004 – 2007. Data from 2002 are available but were inconsistent with data for the other three years. The maximum concentration, by far, was 3.8 ppb in Lower South Bay in 2005.

In contrast to the results obtained from water monitoring, average concentrations of BDE 47 in sediment from 2004 - 2007 were highest in Lower South Bay (0.81 ppb) and lowest in Suisun Bay (0.38 ppb). The cause of this disparity between the water and sediment data for BDE 47 is not understood. Average concentrations in the other segments were all between 0.39 ppb (South Bay) and 0.46 ppb (Central Bay). In 2007, average concentrations within each segment and in the Bay as a whole were similar to previous years.



Footnote: BDE 209 shown as an index of the "deca" PBDE mixture. Plot based on 135 RMP data points from 2004, 2006, and 2007. The maximum concentration was 52 ppb in San Pablo Bay in 2007.

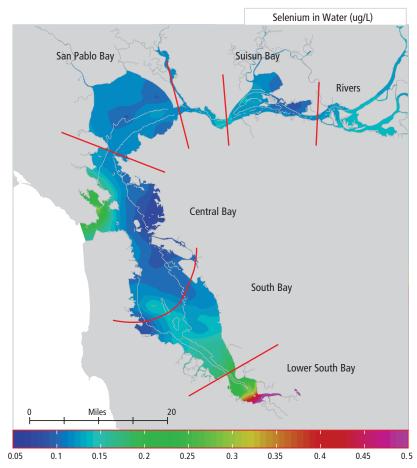
The Bay-wide average concentration of BDE 209 in sediment in 2007 was higher than in previous years (2004 and 2006), but that result was driven by one sample from San Pablo Bay with a very high concentration. BDE 209 (also known as "decabromodiphenyl ether") is important because it represents the one remaining class of PBDEs that can still be used in California. Data from only three years are available because BDE 209 is challenging to measure. Similar to BDE 47, average concentrations of BDE 209 in the three years were highest in Lower South Bay (5.7 ppb). Average concentrations in the other segments ranged from 3.5 ppb in San Pablo Bay to 1.0 ppb in Suisun Bay. The average concentration for San Pablo Bay in 2007 (7.4 ppb) was higher than in previous years, driven by the one sample with an extremely high concentration (52 ppb). Average concentrations in Lower South Bay, South Bay, and Central Bay were lower in 2007 than in 2006.

### [Selenium]

Selenium contamination is a continuing concern in the Estuary. Selenium accumulates in diving ducks in the Bay to concentrations that pose a potential health risk to human consumers. Selenium concentrations also pose a threat to wildlife in the Estuary. Recent studies suggest that selenium concentrations may be high enough to cause deformities, growth impairment, and mortality in early life-stages of Sacramento splittail and white sturgeon.



Surf scoter in San Pablo Bay. Photograph by Susan Wainwright.



Footnote: Plot based on 167 RMP data points from 2002 – 2007. The maximum concentration was 1.2 µg/L at a historical station in the Southern Sloughs in 2002. Data are for total selenium.

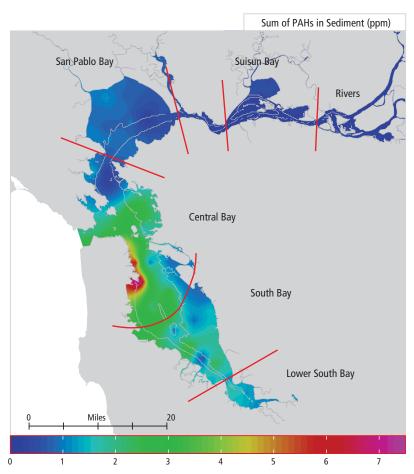
Selenium concentrations in water are well below the water quality objective established by the California Toxics Rule. However, concerns still exist for human exposure as indicated by a duck consumption advisory and for wildlife exposure as indicated by studies on early life-stages of fish. The highest concentration observed in water from 2002 to 2007 was 1.15  $\mu$ g/L, much lower than the CTR objective (5  $\mu$ g/L). The Lower South Bay had a higher average concentration over this period (0.25  $\mu$ g/L) than the other Bay segments, which had strikingly consistent average concentrations (all other averages were between 0.12 and 0.13  $\mu$ g/L). The Bay-wide average concentration in 2007 (0.10  $\mu$ g/L) was slightly below the long-term average (0.12  $\mu$ g/L).

### [PAHs]

PAHs (polycyclic aromatic hydrocarbons) are included on the 303(d) List for several Bay locations. Concentrations tend to be higher near the Bay margins, due to proximity to anthropogenic sources. In addition to historic industrial sources along the Bay margins, increasing population and motor vehicle use in the Bay Area are cause for concern that PAH concentrations could increase over the next 20 years, due to deposition of combustion products from the air directly into the Bay and from the air to roadway runoff and into the Bay via stormwater. On the other hand, PAH concentrations in Bay Area air have declined over the past ten years, and if PAH inputs to the Bay can be decreased, concentrations are expected to drop quickly.



Old pilings and oil refineries are associated with PAH contamination. Photograph by Nicole David.



Footnote: Plot based on 283 RMP data points from 2002 – 2007. The 1 ppm threshold is based on Johnson, L.L., Collier, T.K., Stein, J.E. 2002. An analysis in support of sediment quality thresholds for polycyclic aromatic hydrocarbons (PAHs) to protect estuarine fish. Aquatic Conservation: Marine and Freshwater Ecosystems 12, 517-538. The maximum concentration was 12 ppm in Central Bay in 2005. The seven highest concentrations in the six-year period were all measured in Central Bay.

PAH concentrations in sediment have been highest along the southwestern shoreline of Central Bay. Central Bay had the highest average concentration (3.3 ppm) of any Bay segment from 2002 to 2007. South Bay had the next highest average concentration (1.9 ppm), followed by Lower South Bay (1.6 ppm), San Pablo Bay (0.9 ppm), and Suisun Bay (0.4 ppm). The Bay-wide average in 2007 was 1.8 ppm, slightly lower than the Bay-wide average for the six-year period (2.0 ppm).

**Latest Monitoring Results** 

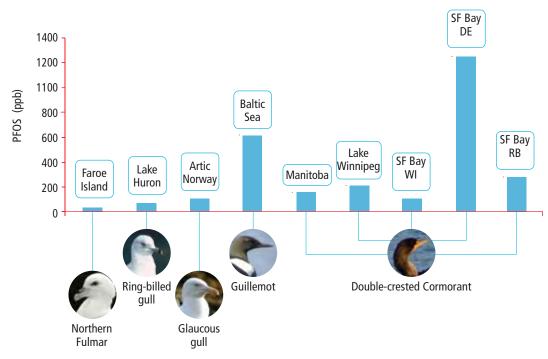
### [Emerging Contaminants]

CONTACT

Meg Sedlak, SFEI, meg@sfei.org



Double-crested cormorants. Photograph by Linda Wanczyk.



WI-Wheeler Island

DE-Don Edwards NWR

RB-Richmond Bridge

Footnote: San Francisco Bay data from eggs collected in 2006. Each bar represents one composite sample comprised of 10 randomly selected eggs.

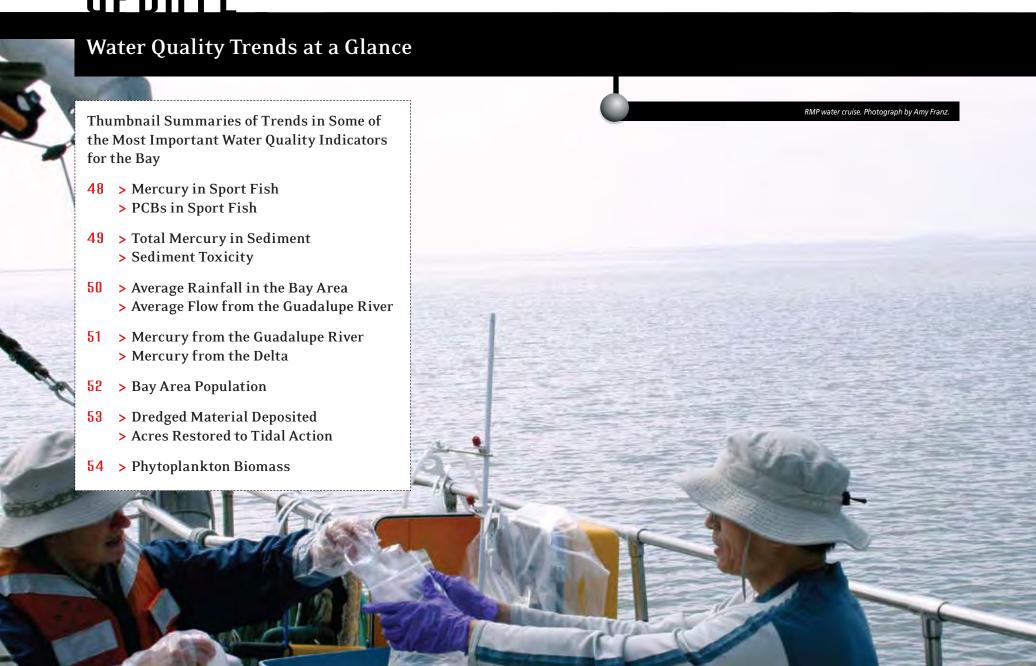
Fluorinated stain-repellents appear to be reaching concentrations of concern in the Bay food web. Perfluorinated chemicals (PFCs) have been used extensively over the last 50 years in a variety of products including textiles treated with stain-repellents, fire-fighting foams, refrigerants, and coatings for paper used in contact with food products. As a result of their chemical stability and widespread use, PFCs such as perfluorooctane sulfonate (PFOS) have been detected in the environment. PFOS and related PFCs have been associated with a variety of toxic effects including mortality, carcinogenity, and abnormal development.

In 2006, the RMP began analyzing bird eggs for PFCs. As apex predators that primarily eat fish, cormorants are good indicators of the presence of emerging contaminants in the aquatic food web. Consistent with other published studies, PFOS was the dominant PFC detected in cormorant eggs. Concentrations of PFOS were highest in the South Bay, and higher than concentrations reported in other regions (Houde et al., 2006).

## STATUS AND TRENDS UPDATE

Technical terms defined in Glossary on page 90

Status and Trends Update-Water Quality Trends at a Glance : The Pulse of the Estuar

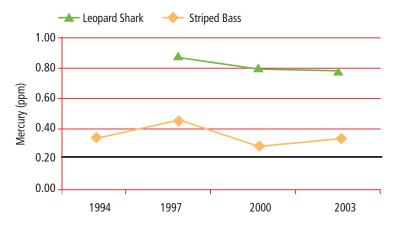


### [ Mercury in Sport Fish ]

#### CONTACT

Jennifer Hunt, SFEI jhunt@sfei.org





Footnote: Baywide medians. Striped bass: 45-59 cm. Black line indicates TMDL target for sport fish tissue (0.2 ppm). Data from the RMP and Fairey et al. (1997).

Mercury in Sport Fish. Striped bass accumulate relatively high concentrations of mercury and are popular with Bay anglers, making them important indicators of mercury impairment. Mercury concentrations have shown no clear long-term trend but have consistently been higher than the o.2 ppm TMDL target for sport fish tissue. A more detailed study of contaminants in striped bass is in progress; data for 2006 will be available in late 2008.

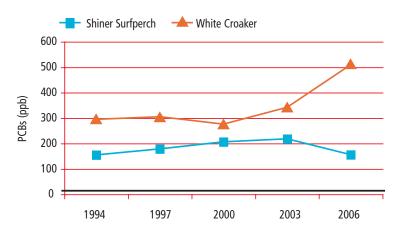
### [ PCBs in Sport Fish ]

### CONTACT

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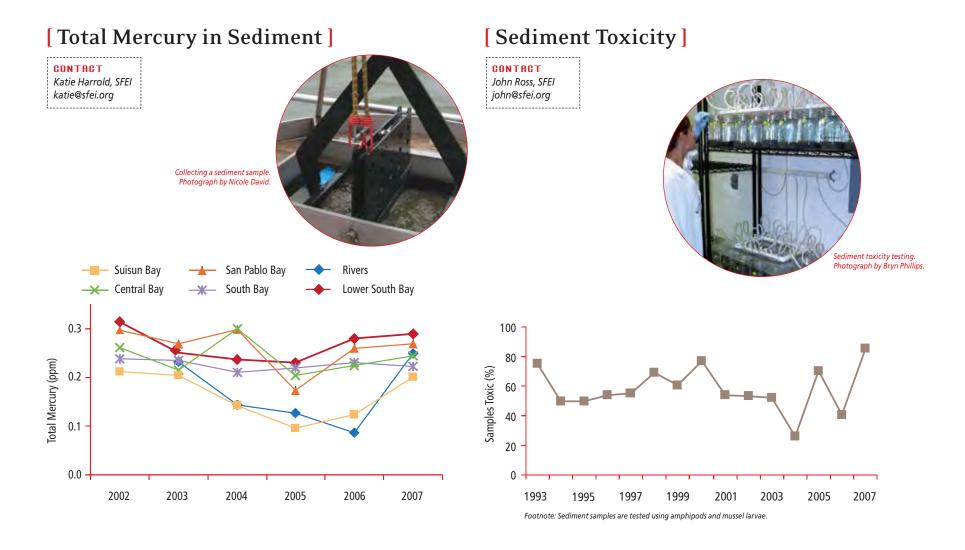


Fishing at San Francisco Municipal Pier. Photograph by Jay Davis.



Footnote: Baywide medians. Black line indicates the TMDL target for white croaker (10 ng/g). Data from the RMP and Fairey et al. (1997).

PCBs in Sport Fish. White croaker and shiner surfperch are sport fish species that accumulate high concentrations of PCBs and are consequently important indicators of PCB impairment. Concentrations in white croaker in 2006 were the highest observed since monitoring began in 1994. In contrast, concentrations in shiner surfperch were among the lowest observed. The causes of these patterns are unknown. PCB concentrations in white croaker have consistently been much higher than the 10 ppb TMDL target for this species.

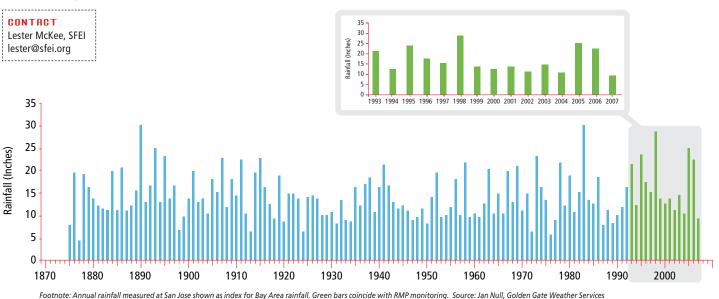


Annual Average Total Mercury in Sediment by Bay Segment. Concentrations of total mercury in sediments from each segment of the Bay were higher in 2007 than average concentrations measured since the RMP began to sample in a manner that yields representative average concentrations for each Bay segment in 2002. In contrast, methylmercury concentrations were relatively low in 2007 (page 36). The causes of these fluctuations are not understood.

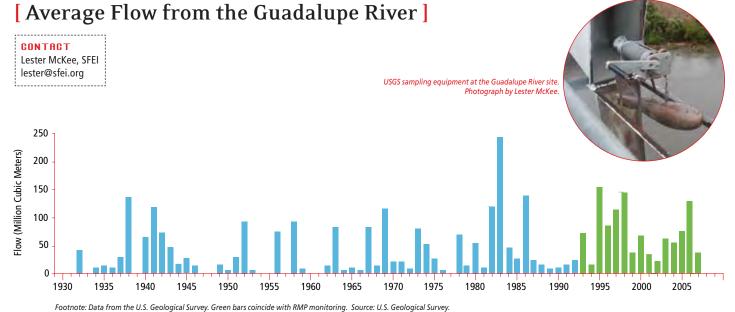
Percent of RMP Sediment Samples Causing Toxicity in Lab Tests. The frequent occurrence of toxicity in sediment samples from the Estuary is a major concern. In every year since sampling began in 1993, 26% or more of sediment samples have been determined to be toxic to one or more test species. In 2007, the highest percentage of toxic samples (85%) for the 15-year period of record was observed. No long-term trend is apparent in this time series.

Water Quality Trends at a Glance

### [ Average Rainfall in the Bay Area ]

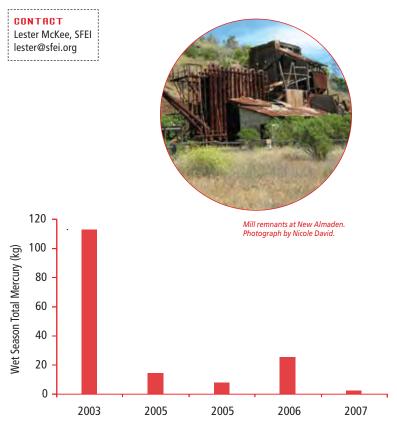


Annual Rainfall in the Bay Area. Freshwater flow, as indicated by rainfall, fluctuates widely from year to year, making it more challenging to measure the trends in pollutant inputs and water quality, which are heavily influenced by flow. Records for San Jose date back to 1875. Rainfall at this location in 2007 (9.3 inches) was the lowest recorded during the 15 years of RMP monitoring.



**Annual Average Flow from** the Guadalupe River. Stormwater flows are a primary influence on pollutant loads from local Bay Area watersheds. Flows from the Guadalupe River, a major contributor of mercury to the Bay, were relatively high from 1995 through 1998, and at or below the long-term average from 1999 through 2004. The average flow for 2007 (36 million cubic meters) was lower than the long-term average (43 million cubic meters). Year to year variation in flow from the Guadalupe watershed is a rough index of variation in flows from other local watersheds.

### [ Mercury from the Guadalupe River ]



Footnote: Total loads for each water year (Oct 1 – Sep 30). Additional matching funds for this RMP study were provided by the CEP, USACE, SCVWD, and SCVURPPP.

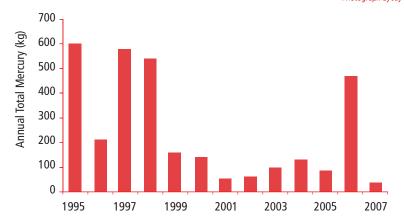
Annual Loads of Mercury from the Guadalupe River. The Guadalupe River is a significant pathway for transport of mercury and other pollutants into the Bay, and the first small tributary to the Bay selected for a rigorous evaluation of loads. Loads fluctuate from year to year due to variation in rainfall intensity, water flow, and other factors. For example, even though flow during 2006 was relatively high, it was a year of relatively low rainfall intensity; consequently there were many small-magnitude floods that did not transport a large amount of mercury. The load estimated for 2007 was the lowest recorded since monitoring began in 2003 (2.3 kg). The year-to-year fluctuations are thought to be driven by climatic variation, and not indicative of a long-term trend.

### [ Mercury from the Delta ]

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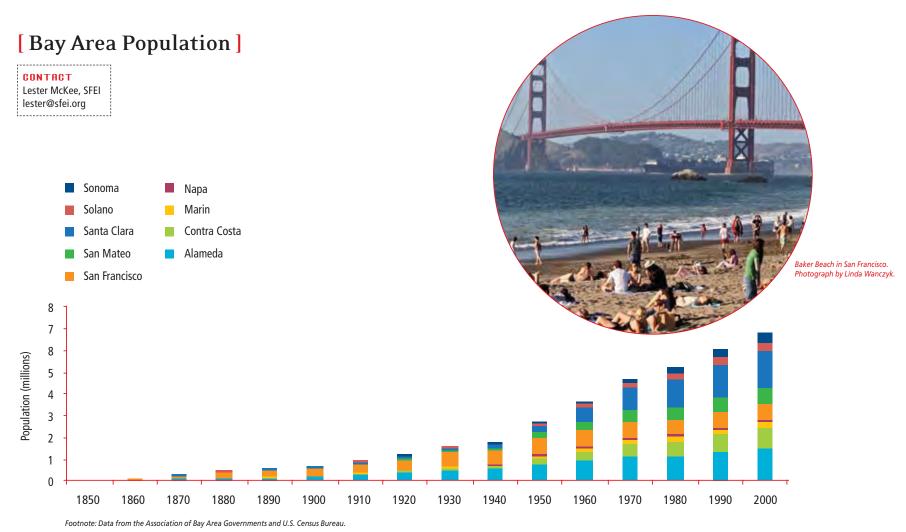
Sample collection at Mallard Island.
Photograph by Jay Davis.



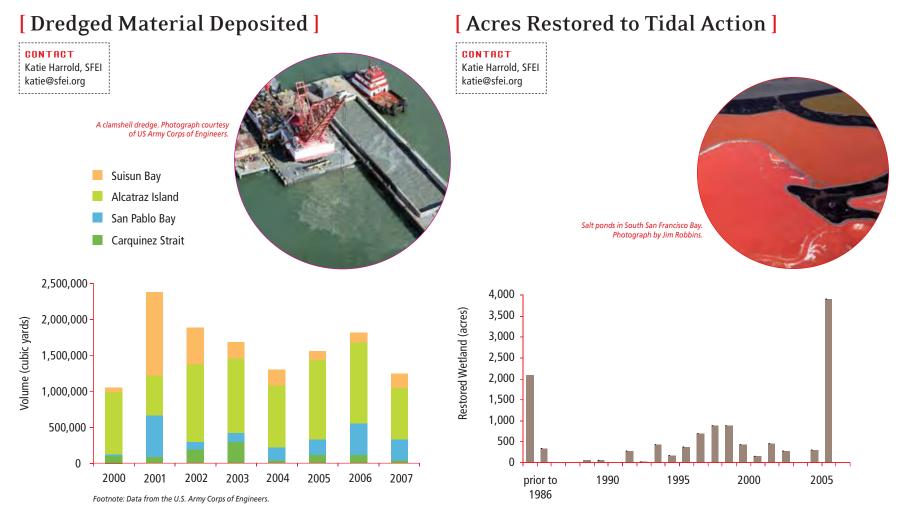
Footnote: Total loads for each water year (Oct 1 – Sep 30). Loads from 2002 – 2007 are based on field data. Loads for earlier years are estimated from relationships observed between suspended sediment and mercury in 2002 -2007.

Annual Loads of Mercury from the Delta. Delta outflow carries significant loads of mercury and other pollutants from the vast Central Valley watershed into the Bay. RMP studies have allowed estimation of loads from 1995 to the present. Loads of many pollutants are especially large in years with high flows. Sampling conducted during the high flows of January 2006 helped to refine the annual estimates, which had been significantly underestimated for large flood events previously due to a lack of information on concentrations during high-flow events. The annual load in 2007 was the lowest estimated for the 13-year period. Average flow and sediment load were also lowest in 2007.

Water Quality Trends at a Glance



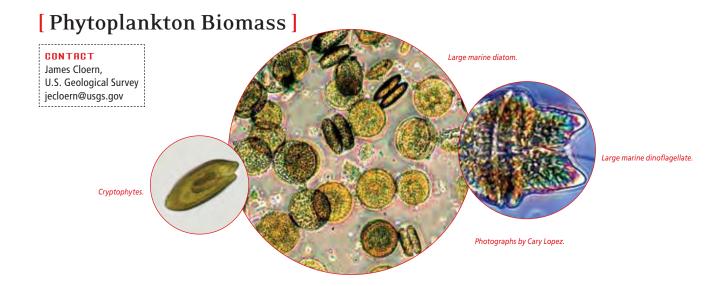
Bay Area Population. The large and growing human population of the Bay Area places increasing pressure on Bay water quality through expanding urbanization, vehicle usage, and other mechanisms. The population of the Bay Area reached 6.8 million in 2000 and is predicted to grow by another million by 2020.

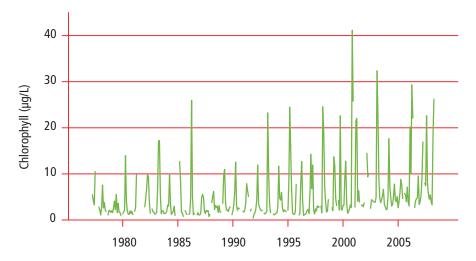


Annual Volume of Dredged Material Disposed of in the Bay. Dredged material disposal is one of the pathways for pollutant redistribution within the Bay. In 2007, 1.2 million cubic yards of dredged material were deposited at the four disposal sites in the Bay (page 22). Other dredged material was disposed of in the ocean and used in upland restoration projects. Dredged material management agencies plan to reduce in-Bay disposal to 1.5 million cubic yards per year by 2012.

Acres of Salt Pond or Other Habitat Opened to Tidal Action. San Francisco Bay is home to the most ambitious tidal wetland restoration project ever attempted on the west coast of North America, the South Bay Salt Pond Restoration Project, which plans to restore 16,500 acres of San Francisco Bay salt ponds to tidal marsh. Several other major tidal wetland restoration projects are also underway (some are shown on page 27). These projects could have a significant influence on Bay water quality, with the potential for increased mercury in the food web a particular concern. SFEI and others continue to conduct studies to assist restoration managers to develop methods to limit the production of methylmercury. In 2007 there were no significant areas opened to tidal action.

Water Quality Trends at a Glance





Footnote: Chlorophyll concentrations are an index of the abundance of phytoplankton in the Bay. Data for USGS Station 27. Median of all measurements shallower than 3 meters depth. Data from the U.S. Geological Survey (http://sfbay.wr.usgs.gov/access/wadata/).

Graph prepared by Alan Jassby, U.C. Davis (adjassby@ucdavis.edu)

Reference: Cloern, J.E., A.D. Jassby, J.K. Thompson, and K.A. Hieb. 2007. A cold phase of the East Pacific triggers new phytoplankton blooms in San Francisco Bay. Proceedings of the National Academy of Sciences (104): 18561–18565.

Annual and Seasonal Trends in Phytoplankton Biomass. Since the late 1990s, significant changes in phytoplankton population dynamics in San Pablo, Central, and South bays have occurred; these include larger spring blooms, blooms during other seasons, and a progressive increase in the "baseline" or annual minimum chlorophyll. As an example, this series of monthly chlorophyll concentrations from one monitoring location shows the increase in baseline chlorophyll (the minimum value each year), and occurrences of autumn/winter blooms in the past decade. According to an article published in 2007 (Cloern et al. 2007), the increase in phytoplankton biomass and new blooms are thought to be caused by a cascade of effects driven by increased upwelling in the coastal ocean, leading to strong recruitment of flatfish and crustaceans into the Bay. These species are bivalve predators that appear to have reduced the populations of bivalves that consume phytoplankton.

# FEATURE ARTICLES

The Big Picture of Water Quality in the Estuary

- 56 Mercury Bioaccumulation and Effects on Birds in San Francisco Bay
- New Evidence of Factors Driving Methylmercury Uptake
- 77 Advances in Understanding Pollutant Mass Loadings from Rivers and Local Tributaries

## FEATURE ARTICLES

> Technical terms defined in Glossary on page 90

### Mercury Bioaccumulation and Effects on Birds in San Francisco Bay

### HIGHLIGHTS

- San Francisco Bay is an important wintering and breeding ground for more than 1 million waterbirds annually
- Mercury concentrations are highest in birds that eat fish and that reside in the Lower South Bay
- When Forster's terns arrive in the Bay in spring to breed, mercury concentrations in their blood increase by four-fold in a six week period
- > Based on mercury concentrations in blood, nearly 60% of all breeding Forster's terns sampled in the Bay are at high risk of toxic effects
- One important piece of evidence of impairment of reproduction in Forster's terns is that average mercury concentrations in failedto-hatch eggs were statistically significantly higher than in randomly selected eggs
- Avian eggs represent an ideal matrix for assessing bioaccumulation because they are indicative of short-term, localized exposure and are central to predicting risk in multiple lifestages

Collin Eagles-Smith and Josh Ackerman, U.S. Geological Survey, Western Ecological Research Center Davis Field Station, Davis, CA Email: ceagles-smith@usgs.gov

Black-necked stilts. Photograph by Josh Ackerman.



### San Francisco Bay: An Avian Haven

San Francisco Bay is the largest estuary on the West Coast and serves as an important wintering and breeding ground for more than 1 million waterbirds annually. Although the Bay has lost approximately 80% of its tidal wetland habitat, the remaining habitat mosaic, including open bay, tidal mudflats, tidal marsh, diked marsh, and salt ponds, supports a diverse and abundant community of waterbirds. Currently, the Bay is undergoing large-scale wetland restoration and enhancements, including the South Bay Salt Pond Restoration Project, as well as smaller wetland enhancements throughout the Bay.

Unfortunately, the Bay is also highly contaminated with mercury, due primarily to a legacy of gold mining in the Sierra Nevada and mercury mining in the Coast Range. There is concern that wetland restoration may enhance conditions that stimulate the bacterial conversion of legacy mercury to the toxic and bioaccumulative form, methylmercury. Mercury accumulates to high concentrations at the top of the food web, and avian reproduction is particularly sensitive to the toxic effects of mercury. Consequently, several waterbird species are suspected to be experiencing deleterious effects due to mercury exposure, and this situation may worsen as wetland restoration moves forward.

Recent extensive research by the US Geological Survey (USGS) has examined mercury exposure and bioaccumulation in waterbirds, as well as mercury effects on avian reproduction. This work has been funded by CALFED, the Regional Monitor-

### Blood mercury concentrations were generally highest in lower South Bay, intermediate in Napa Marsh, and lowest in upper South Bay

ing Program, and USGS. These results are important not only for elucidating the overall risk of mercury to waterbird populations within the Bay, but also for facilitating management actions and development of restoration targets by establishing mercury toxicity thresholds for birds breeding in San Francisco Bay.

### Patterns of Mercury Exposure in Waterbirds

Mercury concentrations differ among waterbird species, reflecting variation in diet and foraging habitats among species. Mercury concentrations in birds that eat fish are substantially higher than those in shorebirds which primarily consume aquatic invertebrates (insects and crustaceans). For example, average mercury levels in the blood of fish-eating Forster's terns and Caspian terns from locations throughout San Francisco Bay were 1.41 and 1.37 ppm, respectively, whereas black-necked stilts and American avocets (two invertebrate-eating species) had average concentrations of 0.99 ppm and 0.30 ppm, respectively (Ackerman et al. 2007a).

Sampling location and date are also important factors influencing mercury concentrations in waterbirds (Ackerman et al 2007b; Ackerman et al. 2008b). In fact, location was the single most important factor in determining blood mercury concentrations in pre-breeding adult stilts and avocets (Ackerman et al. 2007b), and among the most important factors in pre-breeding Forster's

terns (Ackerman et al. 2008b). Waterbird exposure to mercury appears to follow different spatial patterns in different regions of the Bay: lower South Bay (south of the Dumbarton Bridge), upper South Bay (Dumbarton Bridge to San Mateo Bridge), and Napa Marsh. For each species, blood mercury concentrations were generally highest in lower South Bay, intermediate in Napa Marsh, and lowest in upper South Bay (Figure 1).

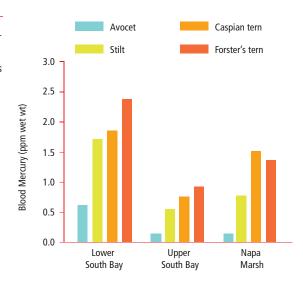
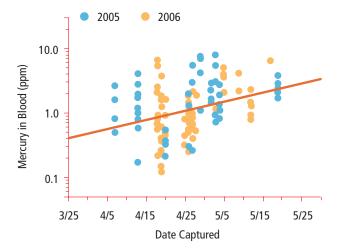


FIGURE 1
Mercury concentrations were highest in blood of Forster's terns and Caspian terns across all study regions, whereas concentrations in stilts were moderate, and those in avocets were generally lowest. Concentrations were substantially higher in all birds from the lower South Bay than in those from upper South Bay or Napa Marsh.

Mercury Bioaccumulation and Effects on Birds

Although birds are highly mobile, following bird movements with tiny radio transmitters (radiotelemetry) coupled with measurements of site-specific mercury concentrations suggest that waterbirds have relatively high site fidelity, making them excellent indicators of mercury exposure in specific locations. In fact, radiotelemetry data showed that avocets, stilts, and Forster's terns generally remained within the wetland where the birds were captured.

Date of sampling also can be an important factor influencing mercury concentrations in waterbirds in San Francisco Bay, particularly for migratory species that spend a portion of the year outside of the Bay. Forster's terns overwinter mainly outside of the Bay (though exact wintering locations are currently unknown) and arrive in early March, prior to breeding, with relatively low mercury concentrations (approximately 0.5 ppm) in their blood. Yet, by mid-May when nest initiation begins, blood mercury concentrations increase by over four-fold to 2.0 ppm (Figure 2).



Footnote: Note log scale of graph. Total mercury reported on a wet weight basis. Linear regression line shown. From Ackerman et al. 2008b. This dramatic increase in mercury concentrations after arrival in the Bay, over a period of about six weeks, coincides with nest initiation. Thus, mercury concentrations in Forster's terns become particularly elevated during the egg-formation stage when mercury circulating in the bloodstream is often deposited into eggs. Moreover, mercury concentrations in breeding Forster's terns were observed to increase even more during and after nesting, indicating that terns continued to accumulate mercury in the Bay at a very fast rate during a sensitive time-frame in the breeding cycle (Figure 3).

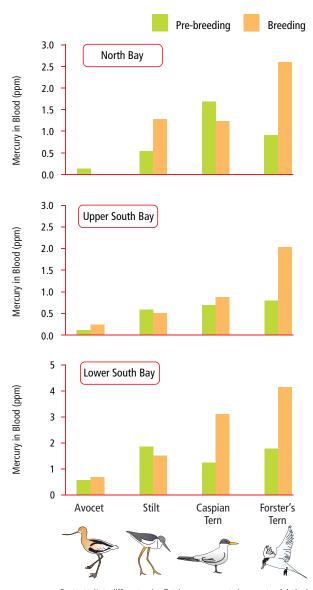
In contrast to terns, sampling date was of little importance in determining mercury levels in adult pre-breeding stilts and avocets, nor were there any clear temporal trends between pre-breeding adults and breeding adults across regions (Figure 3). This finding is likely because stilts and avocets overwinter in the Bay where they are exposed to elevated mercury concentrations year-round. These results suggest that resident shorebirds such as avocets and stilts may be effective indicators of year-round mercury accumulation in the Bay.

# FIGURE 2 Mercury concentrations in blood of pre-breeding Forster's terns increase at later dates of capture, indicating that concentrations increase with time spent in the Bay. Concentrations increase by about 4-fold over a 6-week time period from when they arrive in the Bay to when they begin breeding.

## The Influence of Diet and Foraging Habitat

Although some locations clearly have higher mercury exposure than others, the foraging ecology of each species also has an important influence on mercury bioaccumulation. Two important factors include trophic level (position in the food web) and foraging habitat. Both Forster's terns and Caspian terns primarily forage on fish (higher in the food web), whereas the prey of stilts and avocets is dominated by insects and crustaceans (lower in the food web). Because mercury biomagnifies, increasing in concentration with each successive step up the food chain, it is not surprising that terns also have higher mercury concentrations than avocets and stilts.

Tern mercury concentrations also are highly dependent on their diet at each colony. For example, we have used fish delivered to colonies by mates and parents to quantify colony-specific tern diets at several sites in the Bay. The results indicate that tern diet varies considerably among colonies, and predominant prey fish include both water column (e.g., Mississippi silverside, three-spine stickleback) and bottom-dwelling (e.g., long-jawed mudsucker, yellowfin goby) fish (Figure 4). Thus, tern mercury concentrations depend not only on spatial variation in mercury contamination but also on prey preferences and foraging range. As a result, individual fish species can be poor indicators of mercury concentrations in the eggs of fish-eating birds (Ackerman et al. 2007a).



Footnote: Note different scales. Total mercury reported on a wet weight basis.

FIGURE 3
Mercury concentrations in blood of pre-breeding and breeding American avocets, black-necked stilts, Caspian terns, and Forster's terns in three regions of San Francisco Bay. Forster's terns show dramatic increases between pre-breeding and breeding time periods in all three regions, suggesting that they forage in sites of particularly high exposure in the Bay.

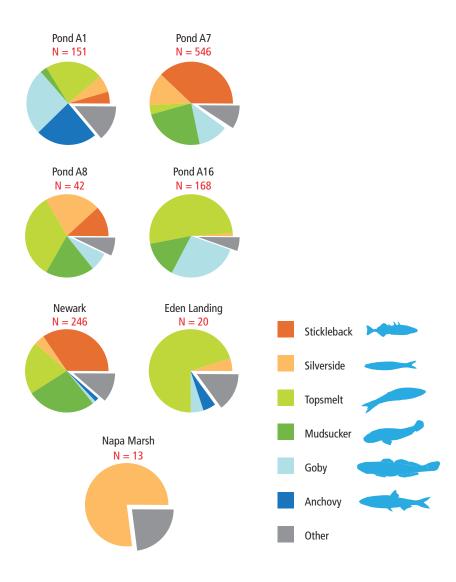


FIGURE 4
Diet composition of Forster's terns varies substantially among several colonies in San Francisco Bay. These results indicate that terns are likely very opportunistic foragers, and that no single fish species serves as a good indicator of tern diet in the Bay.

### FEATURE ARTICLES

Mercury Bioaccumulation and Effects on Birds

Interestingly, stilts have substantially higher mercury concentrations than avocets, even though they are often co-located and forage in similar areas on similar species (invertebrates). These results suggest that in some circumstances trophic level may have less of an influence on mercury bioaccumulation than other factors. In fact, chemical tracers (carbon isotopes) indicate that stilts and avocets forage in substantially different micro-habitats. Our radiotelemetry data support this interpretation, and indicate that stilts feed in salt marsh habitat more than avocets, whereas avocets feed more in tidal flats and tidal marsh than stilts (Ackerman et al. 2007b). These results suggest that foraging

San Francisco Bay were at high to extra-high risk of toxic effects (Ackerman et al. 2007a), and the entire remaining population was considered to still be at moderate risk. Interestingly, a much smaller proportion of the Caspian tern population (10%) is considered to be at high to extra-high risk, despite also being fish-eaters. Although 5% of stilts sampled were at high to extra-high risk, most breeding stilts were at moderate and low risk to mercury, and all avocets were at low to moderate risk.

Although these results indicate substantial risk to waterbirds such as terns in San Francisco Bay, it is important to evaluate this interpretation cautiously.

studies is thought to be substantially more toxic than mercury naturally deposited into an egg by a mother bird. It is therefore difficult to base management decisions on these laboratory studies. Thus, there is a need to evaluate the actual toxicity of mercury to species breeding in the Bay to determine whether mercury is having an impact on bird populations, as well as to enhance the utility of monitoring results. Currently, USGS scientists are working on establishing better toxicity thresholds for birds breeding in San Francisco Bay. These thresholds will be established for egg hatchability, but other toxicity endpoints such as chick growth and survival may also be evaluated.



# Although these results indicate substantial risk to waterbirds such as terns in San Francisco Bay, it is important to evaluate this interpretation cautiously

Forster's Tern. Photograph by Josh Ackerman.

habitat is an important consideration when evaluating potential risk of mercury to waterbirds

### **Evidence for Significant Risks**

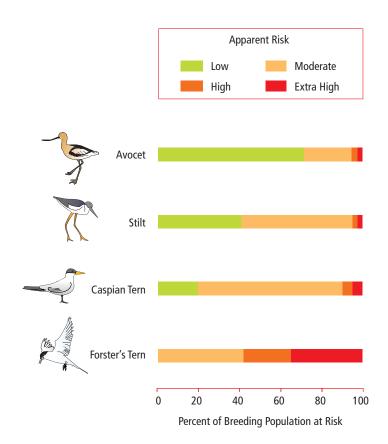
As discussed above, risk of mercury to birds in San Francisco Bay varies with trophic level, foraging habitat, and location. Another important factor is species-specific sensitivity to mercury. Based on risk thresholds developed for other bird species (Evers et al. 2004, Heinz 1974), Forster's terns appear to be at highest risk in the Bay to the deleterious effects of mercury on avian reproduction (Figure 5).

Based on mercury concentrations in blood, nearly 60% of all breeding Forster's terns sampled in the

The risk categories were derived from toxicity endpoints from other species (common loons and mallards), as well as from studies done in the lab (Heinz et al. 2008). Sensitivity to mercury is known to differ among species, and results from lab studies are often difficult to apply in the field. Recent work comparing the effects of mercury on hatchability in 26 species has shown that sensitivities can vary by up to 10-fold. For example, the LC50 (concentration at which 50% of the eggs exposed died) for common terns, a species closely related to Forster's terns, was 4.35 ppm dry weight (Heinz et al. 2008). Unfortunately, 82% of all Forster's tern eggs sampled in San Francisco Bay exceeded this level, suggesting that mercury levels in this San Francisco Bay biosentinel species may exceed levels of concern. However, the methylmercury injected into eggs for the lab

## Is Mercury Impairing Waterbird Reproduction?

Mercury can impair waterbird reproduction in several ways, including altering adult nesting behavior, reducing egg hatchability, and reducing chick growth, health, and survival. Egg hatchability is generally thought to be the most sensitive stage, and may have the largest impact on reproduction. There is evidence that hatchability in Forster's terns may be impaired by mercury in the Bay. One compelling piece of evidence is that average mercury concentrations in failed-to-hatch eggs were significantly higher than those in random eggs sampled from successful nests, and in abandoned eggs (Figure 6).



Percent of population of breeding birds at risk from mercury exposure in San Francisco Bay. These risk evaluations indicate Forster's terns are at substantially higher risk from mercury than other waterbird species. In fact, nearly 60% of Forster's terns breeding in the Bay have mercury concentrations in their blood that are at or above high risk thresholds developed for other bird species. In contrast, Caspian terns and stilts are at moderate risk, and avocets are generally at low risk.

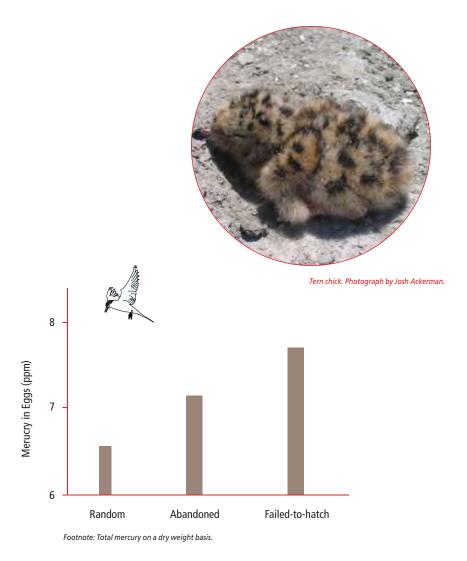


FIGURE 6
Mercury concentrations in failed-to-hatch egg of Forster's terns were statistically significantly higher than those in abandoned eggs and random eggs sampled from successful nests. This suggests that mercury is impairing hatchability of Forster's tern eggs in San Francisco Bay.

### FEATURE ARTICLES

Mercury Bioaccumulation and Effects on Birds

However, defining a threshold for mercury impairment of egg hatchability is confounded by many factors that make interpreting egg mercury concentrations difficult. Both predation and prey availability are important variables influencing natural hatchability and nest success in waterbirds in the Bay, and the relative impact of each factor can vary considerably among sites and years. Moreover, these factors may also interact with mercury

multiple sites. The Regional Monitoring Program is currently funding a USGS study to further define hatchability thresholds and interactions with **selenium** for Forster's terns in the Bay.

After an egg hatches, mercury may still influence subsequent chick growth and survival. Blood mercury concentrations are highest in chicks just after hatching, when they are still influenced by merchicks are at elevated risk from mercury. These critical time periods are important developmentally, as chicks avoid predators, acquire the necessary nutrients for rapid growth, and learn to forage and fly independently. As a neurotoxin, methylmercury may have important impacts on chick behavior that can influence the likelihood of mortality. Mercury concentrations in down feathers sampled from black-necked stilt chicks



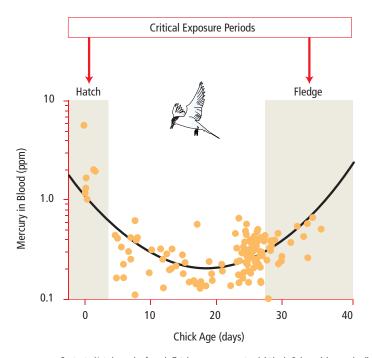
After an egg hatches, mercury may still influence subsequent chick growth and survival. The timeframes just after hatching and at fledging are especially sensitive periods when chicks are at elevated risk from mercury.

Stilt chick. Photograph by Josh Ackerman.

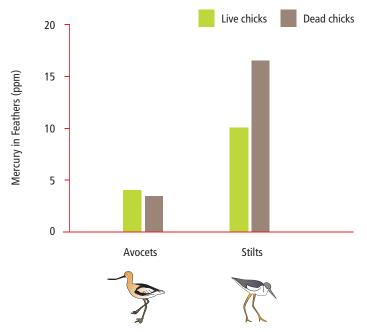
in subtle ways to further complicate threshold development. For example, sites with heavy predator impacts and low mercury would bias threshold estimates low, whereas sites with high rates of depredation and elevated mercury may bias estimates high. To account for the effects of these factors in relation to hatchability and mercury concentrations, thresholds must be developed using information gathered over several years and across

cury exposure from the egg. Concentrations then decline rapidly with age as the mercury is shunted into growing feathers and diluted by body growth. When feather growth and body growth slow just before and after fledging, mercury concentrations begin to increase again (Figure 7).

Thus, the timeframes just after hatching and at fledging are especially sensitive periods when found dead within a colony in San Francisco Bay were significantly higher than those from similarly-aged, apparently healthy, live chicks (Figure 8). Avocet chicks on the other hand, which have substantially lower mercury concentrations overall, showed no differences in mercury concentrations in down feathers of dead and live chicks (Figure 8).



 $Footnote: Note \ log \ scale \ of \ graph. \ Total \ mercury \ on \ a \ wet \ weight \ basis. \ Polynomial \ regression \ line \ shown.$ 



Footnote: Total mercury reported on a fresh weight basis. From Ackerman et al. 2008a.

FIGURE 7
Mercury concentrations in blood of Forster's tern chicks are highest immediately after hatching and just before fledging. These critical exposure periods are also critical stages of development.

### FIGURE 8

Mercury concentrations in down feathers of recently-hatched stilt chicks that were found dead were significantly higher than in randomly-sampled live chicks, suggesting that mercury may reduce stilt hatchling survival. In avocet chicks, mercury concentrations were substantially lower overall, and there were no differences between alive and dead chicks.

Mercury Bioaccumulation and Effects on Birds

## Future Directions and Management Implications

Recent research has shown that waterbirds in San Francisco Bay appear to be at elevated risk of reproductive impairment from mercury. Important regions (e.g., lower South Bay and Napa Marsh) and habitats (e.g., diked salt marshes, tidal marshes) for enhanced mercury accumulation also have been identified, helping to assess likely impacts to waterbirds and other sensitive wildlife. Additionally, steps have been taken to quantify actual risks to waterbird reproduction in the Bay.

Future efforts in evaluating deleterious effects of mercury to waterbirds should include:

- > continued development of appropriate egg hatchability thresholds for the highest risk species;
- > evaluation of toxicity thresholds for growth and survival of chicks; and
- evaluation of the cumulative effects of mercury and other contaminants, such as selenium, PCBs, and PBDEs, on waterbird reproduction.

These steps will provide critical information to managers that will serve as a scientifically defensible foundation for thresholds that can be applied to minimize risk to waterbirds. Additionally, the results from this research will be essential for guiding site selection for waterbird habitat enhancement relative to mercury risk, as well as for evaluating the effects of restoration activities on methylmercury production and subsequent bioaccumulation in waterbirds.

Waterbirds are ideal Bay biosentinels for measuring the actual bioaccumulation of mercury into sensitive species, and for interpreting observed concentrations relative to likelihood of effects. Eggs in particular represent an ideal matrix for assessing toxicologically relevant bioaccumulation because they are indicative of short-term, localized exposure, and are central to predicting risk in multiple lifestages (Figure 9).

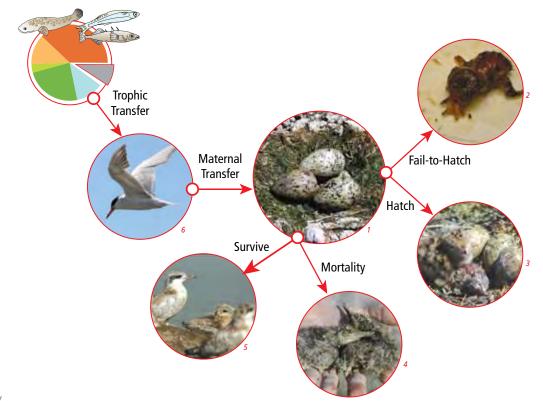


FIGURE 9
Conceptual model illustrating the utility of eggs as a monitoring tool for multiple lifestages, providing a measure of exposure and effects in adults, chicks, and eggs in a single tissue monitoring matrix.

Photographs 1, 2, 3, 4, and 5 by Josh Ackerman Photograph 6 by Linda Wanczyk.

## FEATURE <u>ARTICLES</u>

> Technical terms defined in Glossary on page 90

### New Evidence of Factors Driving Methylmercury Uptake

### HIGHLIGHTS

- > Small, young-of-the-year fish, or "biosentinels", are sensitive, finescale indicators of methylmercury uptake in aquatic food webs
- > The UC Davis Biosentinel Program has been monitoring dozens of sites across the Delta region and North Bay, particularly in and around wetland restoration areas
- Tidal wetlands that remain inundated, without periodic drying cycles, were found to have relatively low methylmercury uptake, including the Napa Marsh and parts of the North Delta
- Significant seasonal and year-toyear trends were found in some areas downstream of Central Valley floodplains, with particularly dramatic increases linked to episodic flooding of normally dry soils
- Managed seasonal flooding in Suisun Marsh also appeared to increase uptake
- Biosentinels are useful for identifying and ranking methylmercury sources in contaminated watersheds and tracking the effectiveness of cleanup at remediation sites



Factors Driving Methylmercury Uptake

### Why Biosentinels?

Small, young-of-the-year fish are an extremely valuable mercury monitoring tool. These localized and short-lived little fish are referred to as mercury "biosentinels." Small biosentinels complement sport fish and human health monitoring by providing a sensitive measure of methylmercury uptake into the aquatic food web. "Methylmercury uptake" refers to that key fraction of mercury that has been converted to toxic methylmercury, made its way through complex production and loss cycles in the sediments and water, and made its way into the aquatic food web. In particular, biosentinels can provide detailed information about varying levels of methylmercury uptake for fish, both geographically and over time. In other words, they help to answer the "where" and "when" questions of how methylmercury is getting into the food web.

The amount of mercury in adult sport fish (those caught for recreation or subsistence) is a result of the methylmercury taken up throughout their multi-year lives and throughout the varied locations where they have lived. By virtue of the young age and restricted home ranges of small biosentinel species, the timing and location of their mercury exposure can be pinpointed with greater precision. Their absolute mercury concentrations typically are considerably lower than those of larger, older sport fish, but well above analytical detection limits, and it is the relative differences between similar samples from different sites and times that are key to characterizing patterns of food web uptake.

# Biosentinels help to answer the "where" and "when" questions of how methylmercury is getting into the food web

Analyses of methylmercury in sediments and water are important components of mercury research, but can present a range of difficulties for routine monitoring. Complex and variable cycling of methylmercury in both sediments and water can make it difficult and costly to quantify the average levels that biota are exposed to. Small fish biosentinels are a central component of state and national strategies for methylmercury exposure monitoring because they provide a sensitive measure of methylmercury after it has been clearly and unambiguously incorporated into the food web.

The UC Davis Biosentinel Mercury Program has established a network of long-term index sites across the inland watershed, Delta, and North Bay, together with an extensive series of sites in and around major wetland restoration areas (Figure 1).

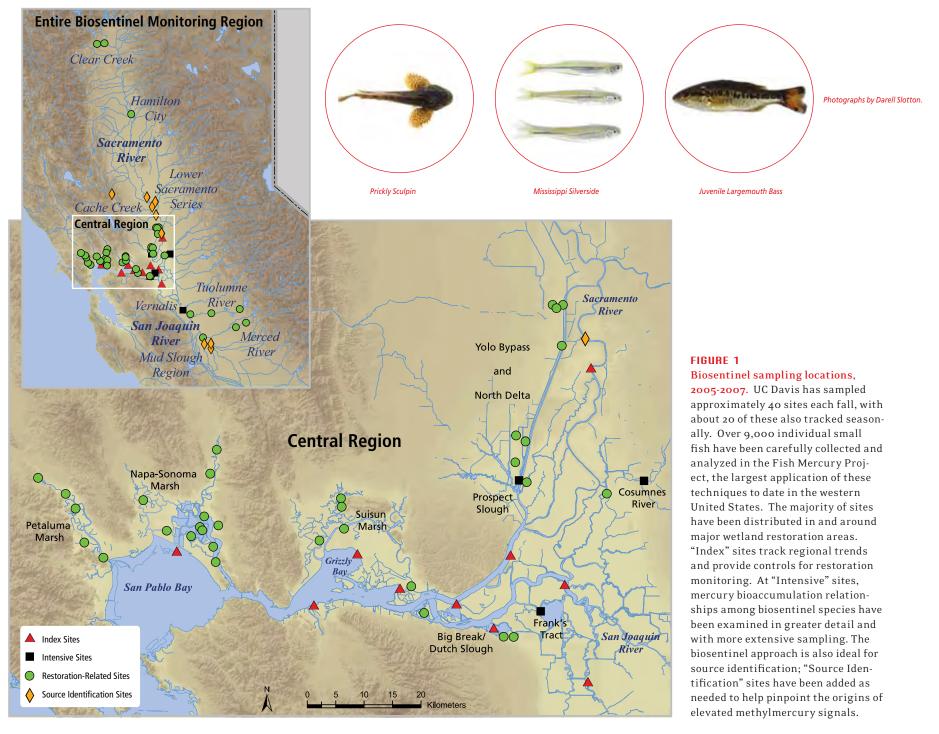
## An Ideal Feedback Tool for Managers

A major focus of UC Davis biosentinel monitoring is tracking and providing feedback on the potential effects that various wetland restoration projects may have on local and regional methylmercury uptake. Certain wetland environments have been shown to provide ideal conditions for the production of methylmercury, often resulting in increased concentrations in fish. As large new wetland restoration projects are implemented in the Bay-Delta region, there is concern that they may result

in elevated exposure, both locally and regionally. Biosentinel monitoring provides quick and detailed feedback on how exposure may change in relation to these developments. Biosentinel monitoring is a powerful tool for identifying the management practices and natural processes that result in higher or lower levels of methylmercury uptake by fish.

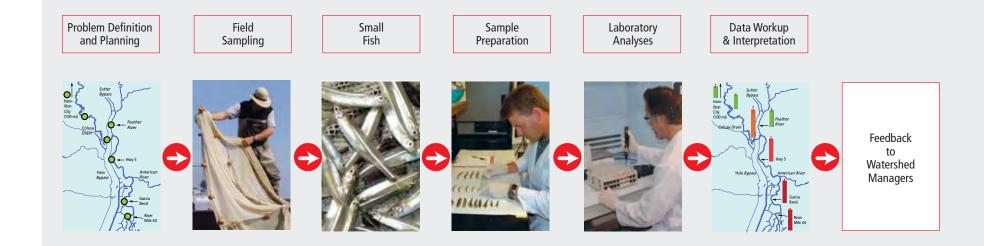
Biosentinel fish can be used to differentiate methylmercury uptake between adjacent wetland tracts or neighboring tributaries. Other important uses of biosentinel monitoring are the identification and ranking of mercury sources in contaminated watersheds and the tracking of cleanup effectiveness at remediation sites such as abandoned mercury mines.

Current approaches to biosentinel monitoring are based on 20 years of method development and refinement by our laboratory, in dozens of projects conducted throughout the state and beyond. We employ an integrative approach, from sampling design through field collections, sample processing, in-house laboratory analyses, data work up, and interpretation (Sidebar). Previous regional studies by our group have demonstrated that mercury levels in biosentinel organisms are closely linked to average, integrated methylmercury concentrations in water, as well as to mercury concentrations in sport fish. They provide a dynamic and direct measure of uptake into the food web. They also provide an index of mercury levels in the prey items of both sport fish and fish-eating wildlife.



### From Planning to Monitoring to Management

he Biosentinel Mercury Program designs sampling in conjunction with specific management questions as well as for broader, regional coverage. Targeted small fish species are collected using a wide array of techniques and are carefully preserved in the field. Samples are weighed, measured, dried, and powdered prior to analysis. Laboratory analyses for mercury and related parameters are conducted, followed by data analysis and interpretation. Information generated by the Program is then provided to environmental managers to help them track conditions and refine management strategies for mercury.



## Accurate Measure of Change Over Time

Because the biosentinels used are typically young-of-the-year fish, samples from one year to the next are, by definition, entirely different crops of fish, each exposed solely to the conditions of the year sampled. They thus provide quick and significant feedback to watershed managers if food web uptake changes from year to year. At index sites across the watershed, this annual information contributes to an invaluable longterm record of fluctuating methylmercury uptake that can be linked to both natural and managed processes. In addition to assessing long-term trends, annual data can also provide a measure of natural, year-to-year variability at index sites, which should be taken into account when assessing trends at restoration and remediation sites. Finally, the short life spans of these little fish cause them to register changes in uptake on a seasonal basis. Seasonal fluctuations in uptake by fish were in fact found, in the most recent work. to be far more important than anticipated. This finding, and several other fundamental advances in understanding emanating from recent biosentinel monitoring, are described below.

The fall data were surprising.

Fish samples from the central marsh region did not exhibit elevated mercury concentrations relative to surrounding areas. Instead, they had statistically lower concentrations than matching fish from upstream on the Napa River or outside the marsh in San Pablo Bay

### Not All Wetlands are Mercury Hot Spots: The Napa Marsh Story

The former salt ponds of the Napa Marsh are undergoing some of the most extensive wetland restoration activities in the watershed. CALFED recently constructed a 623 acre project at the base of the American Canyon on the east side of the Napa River. The California Department of Fish and Game (CDFG) manages the large former salt ponds on the west side of the River. In spring 2006, CDFG reconfigured the formerly isolated Ponds 4 and 5 of the complex (1,731 acres), opening them to tidal flows. CDFG also added new tidal openings and reconfigured the large Pond 3 (1,314 acres), which had been illegally breached several years earlier (2002) and is currently without vegetation. Another pond (2A, 561 acres) was opened to tidal flows 13 years ago and has evolved into a fully vegetated wetland, providing a local example of the conditions likely to develop over time in the new restoration projects.

Additional restoration projects are planned. This region has received the most intensive biosentinel monitoring coverage to date.

The fall 2005 Mississippi silverside (*Menidia audens*) data, which were collected prior to the 2006 DFG salt pond projects, were somewhat surprising (Figure 2). Fish samples from the central marsh region did not exhibit elevated mercury concentrations relative to surrounding areas. Instead, they had statistically lower concentrations than matching fish from upstream on the Napa River or outside the marsh in San Pablo Bay. Furthermore, silversides in the fully vegetated Pond 2A had the lowest concentrations of mercury of all the Napa Marsh sites.

At sites outside of the Napa Marsh, mercury concentrations in corresponding samples of near-identical silversides taken a year later in the fall of 2006 remained the same as those of 2005, including the Napa River upstream in Napa and downstream at Highway 37; San Pablo Bay; and

Factors Driving Methylmercury Uptake

Black John Slough off the Petaluma River. Within the Napa Marsh itself, however, concentrations dropped relative to 2005. Silversides collected within the recently breached Pond 4/5 complex not only contained dramatically lower mercury levels than all other samples in the local region, they had the lowest levels we have ever recorded for this species across the entire watershed, averaging 14 ppb. Statistically significant declines from 2005 levels were also seen at adjacent sites (China Slough, American Canyon wetlands, and Pond 2A), though at a more moderate concentration range of 28 - 38 ppb. These data indicate that the newly breached

older, vegetated Pond 2A indicate that this large restoration zone may represent an important case where vegetated wetland environments do not result in a local or regional increase in methylmercury uptake in the aquatic food web.

Additional encouraging results were found in parts of the North Delta, where biosentinel fish from vegetated marsh habitat at Liberty Island and Little Holland Tract showed statistically lower mercury levels than fish from adjacent non-vegetated sites, despite being closer to upstream sources of inorganic mercury from Cache Creek. Also, recent

plex. This was consistent with findings of elevated uptake in higher elevation marsh habitats of the Petaluma watershed by a research team including the San Francisco Estuary Institute, the US Geological Survey, the US Fish and Wildlife Service, and others. There are a number of hypotheses as to why the high marsh habitat appears to lead to elevated methylmercury uptake. Periodic drying and subsequent episodic flooding of this habitat on extreme high tides may be a critical factor. Episodic flooding of vegetated sediments was found to be a primary cause of elevated small fish mercury at diverse sites across the entire watershed.

# One important factor that these and many other relatively low uptake regions had in common was that they are tidal sites that generally remain inundated or wet at all times

ponds are creating a net decline in methylmercury uptake into the food web. This decline may be related to the sulfide-rich chemistry of the former salt pond sediments inhibiting the production of methylmercury and/or its subsequent bioaccumulation by aquatic organisms. Small fish mercury bioaccumulation in 2007 remained lower in this region than elsewhere in the marsh, though the difference was not as extreme. It is unclear whether this fascinating pattern will persist over the long-term. However, the continued lower fish mercury levels throughout the Napa Marsh, as compared to surrounding control sites, and low levels in the

Sonoma Creek data indicate a low uptake environment in that part of the Napa-Sonoma Marsh. One important factor that these and many other relatively low uptake regions had in common was that they are tidal sites that generally remain inundated or wet at all times.

In contrast, 2006 and 2007 sampling of the upper Petaluma River region indicated a high uptake environment, with biosentinel fish containing more than double the concentrations seen in the Napa-Sonoma Marsh and ten times higher than levels in the recently breached Napa Pond 4/5 com-

The large differences in methylmercury uptake between and across these nearby North Bay systems are remarkable. The biosentinel approach provides a valuable tool in monitoring trends and provides important feedback to wetland managers as they try to develop critical wildlife habitat without adding to the mercury problem. The North Bay data demonstrate how well these young fish can be used to differentiate uptake at nearby locations and habitats, as well as between years.

## Major New Finding: The Importance of Episodic Flooding

Extensive seasonal sampling was conducted in conjunction with the large flooding that occurred in the watershed in 2006. Some areas received flooding that came in the form of winter rain-runoff. Others experienced flooding later in the spring and early summer that was linked to snowmelt. Still others underwent man-made seasonal flooding due to management practices, notably in the Suisun Marsh (Figure 3) and Yolo Bypass. All of these conditions were found to lead to significant increases in food web uptake of methylmercury.

The San Joaquin and Cosumnes rivers experienced heavy flooding in 2006 in conjunction with spring snowmelt. Extreme (400-500%) increases in small fish mercury concentrations were found downstream of these two sites by July (Figure 4). Concentrations in 2 to 3 inch fish reached levels averaging 243 ppb at Vernalis and an astounding 869 ppb in the Cosumnes River, with individual fish as high as 2,000 ppb. These were concentrations of serious concern, particularly in relation to wildlife exposure, occurring at a time of year when many species were raising their sensitive young. Quickly growing, rapidly regenerating small fish species subsequently returned to lower levels, while other fish remained highly elevated for up to a year following the flooding events.

The flooding-related increases in food web uptake measured with the biosentinels in several diverse habitats closely corresponded to results from



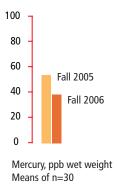
Mississippi silversides. Photograph by Darell Slotton.

water studies by other researchers that found elevated concentrations of methylmercury in water at some of the same locations and dates. What these sites had in common was *episodic flooding* of normally dry valley soils. Subsequent monitoring in 2007, which was a relatively dry year with little or no natural flooding, supported this relationship: small fish biosentinels exhibited no increases during the same times of year that had shown the dramatic increases in conjunction with flooding (Figure 4). Year-on-year July sampling of identical small fish found approximately ten-fold lower mercury concentrations in the subsequent year without major flooding.

Effects linked to the extensive flooding in 2006 included significantly elevated small fish mercury concentrations virtually across the Bay-Delta, particularly from the main tributaries westward to Carquinez Strait. Elevated average concentra-

tions were accompanied by greatly increased individual variability in some regions, notably downstream of the North Delta on the Sacramento River through Suisun Marsh. Increased variability, with groups of highly elevated individuals, indicated the presence of localized hot spots of methylmercury uptake.

The following year (2007) also provided dramatic data. With the low level of watershed flooding occurring that year, not only did mercury bioaccumulate to much lower concentrations at the sites of prior dramatic spike increases, but a general return to lower concentrations and lower individual variability was seen throughout the watershed east of Carquinez Strait. However, at sites experiencing managed seasonal flooding, such as Suisun Marsh and the Yolo Bypass, small fish mercury levels continued to rise in conjunction with seasonal flooding cycles.



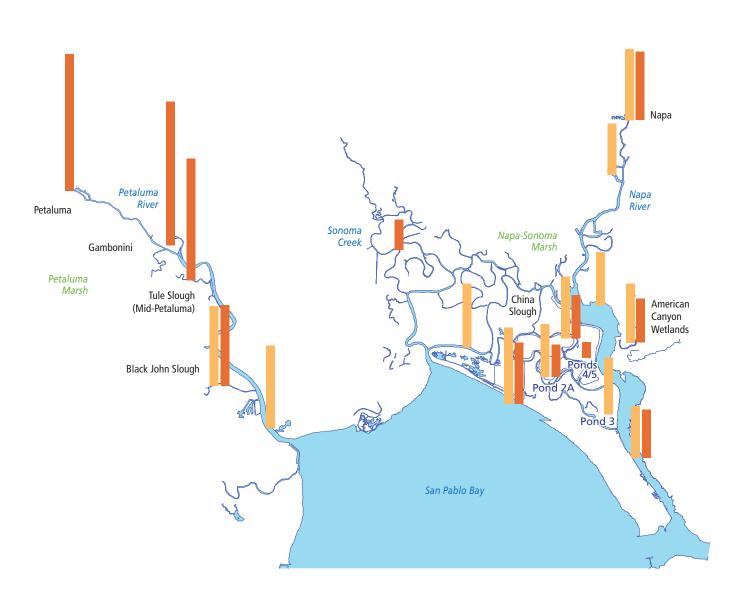
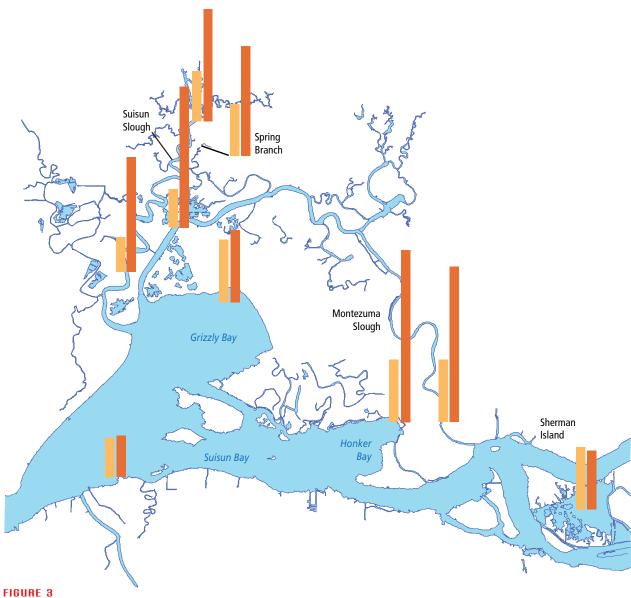


FIGURE 2

North Bay 2005 and 2006 biosentinel mercury trends. Biosentinel monitoring found fish from the Napa-Sonoma Marsh to contain lower mercury concentrations than those from adjacent aquatic habitats. This is notable, as the Napa-Sonoma Marsh is the site of some of the most extensive new wetland restoration work in the watershed, but is not resulting in elevated concentrations of mercury in fish at this time. The Petaluma River, in contrast, was identified as a zone of clearly elevated uptake, possibly linked to episodic tidal flooding of the extensive high marsh that is characteristic of this area.



100 | 80 | 60 | Fall 2005 | Fall 2006 | 20 | 0

Mercury, ppb wet weight Means of n=30

Suisun Marsh identified as a 2006 watershed "hot spot." Annual sampling found large increases in concentrations of mercury in biosentinel fish in Suisun Marsh in 2006, while control sites outside the Marsh remained unchanged from 2005. Possible causes are under investigation. These data demonstrate the utility of the small fish biosentinel approach in clearly differentiating methylmercury uptake among nearby locations and between years.

February/March September November 300 275 869 250 225 200 Mercury (ppb) 175 150 125 100 75 50 25 San Joaquin San Joaquin Cosumnes Cosumnes at Vernalis at Vernalis River River (2006)(2007)(2006)(2007)

Footnote: Mercury in small fish on a wet weight basis.

Strong seasonal trends identified, linked to flooding events. Historically high spring snowmelt runoff and flooding in 2006 was followed by large summer increases in small fish mercury downstream on the San Joaquin and Cosumnes rivers. In contrast, 2007 was a non-flooding year and biosentinel fish responded with dramatic reductions in mercury bioaccumulation. Episodic flooding of usually dry soils has been implicated, through the biosentinel work, to be a primary factor leading to elevated methylmercury in the food web. This effect has been found in the summer at sites flooded by snowmelt runoff, in the winter and spring at sites flooded by rain runoff, and throughout the year in relation to man-made seasonal flooding conducted for management practices.

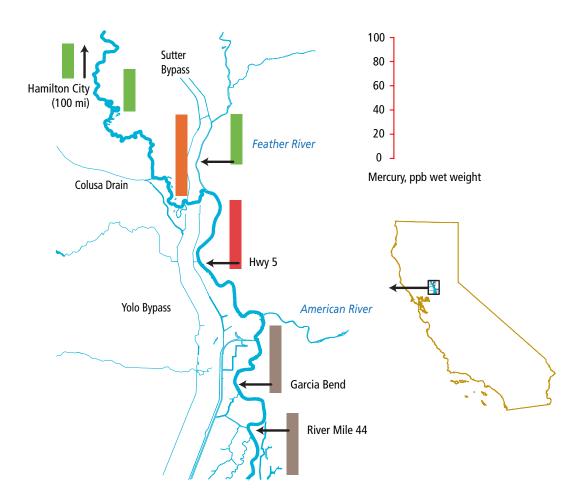
### Tracking Down Methylmercury Sources: The Sacramento River Series

Biosentinel monitoring has also been used to assess potential sources of mercury. A study conducted along the Sacramento River identified a significant increase in small fish mercury between two widely spaced sites along the river. A series of strategic collections were made within that stretch in 2006, in conjunction with the Sacramento Regional County Sanitation District's Localized Mercury Bioaccumulation Study, with the goal of ranking and identifying potential sources of the increased uptake (Figure 5). Sacramento's municipal wastewater discharge was found to not be the principle source of the elevated uptake.

Prickly sculpin (Cottus asper) was the primary biosentinel species available across much of the Sacramento River's length. Prickly sculpin are slowgrowing, longer-lived small fish, and their mercury levels integrate longer exposure periods, on the order of a year, as compared to young-of-the-year silversides which typically integrate periods of 1 to 3 months. Sculpin data from 2005 were notable in that fish from River Mile 44, near the entrance to the Delta, at 51 ppb, averaged more than double the mercury concentration found in near-identical fish 150 river miles upstream at Hamilton City (23 ppb). The difference was strongly significant statistically and suggested a substantial mercury source between these two points. In the corresponding 2006 sampling, the trend was very similar and statistically unchanged, with sculpin mercury averaging 30 ppb at Hamilton City and 53 ppb at River Mile 44. Similarly, in 2007, the sculpin from the two regions averaged 23 and 58 ppb.

While the downstream concentrations were not highly elevated relative to all the fish data from across the watershed, the Sacramento River is the primary source of water to the entire Bay-Delta. In 2006, using five additional biosampling sites, we further investigated potential sources of the approximate doubling in methylmercury uptake across this 150 mile stretch of river. A portion of this additional sampling was funded by the Sacramento Regional County Sanitation District, in conjunction with their 2006 Mercury Bioaccumulation Study.

As the River Mile 44 site is located downstream of the City of Sacramento's treated wastewater discharge point, that discharge was one potential source of the observed increase. Sampling was conducted at a site upstream of the Sacramento wastewater discharge but downstream of the American River (Garcia Bend). In extensive work with other biosentinel species that integrate over shorter time spans, including silversides, juvenile largemouth bass (Micropterus salmoides), and caged and local clams, the Mercury Bioaccumulation Study found an approximate 10% increase in concentrations downstream of the municipal discharge relative to the site immediately upstream. These test organisms integrated uptake conditions during the summer through fall period of lowest base River flows and associated dilution. In contrast, extensive sculpin sampling from the two sites, integrating uptake throughout the year, showed no increase (58 ppb above versus 53 ppb below the wastewater discharge).



Sacramento River series: biosentinel small fish as a source identification tool. Prickly sculpin were used to investigate the potential source of an observed doubling in food web uptake of mercury on the Sacramento River between Hamilton City and River Mile 44. The increase was not found to be primarily linked to the Sacramento municipal wastewater discharge or any of the major gold mining tributaries. Instead, the data suggest that the Colusa Drain (an agricultural drain) may be an important methylmercury source to the lower Sacramento River. This Canal drains fields that are seasonally flooded for rice farming and wildlife management.

# The Colusa Drain may be an important source of the methylmercury in the food web of the lower Sacramento River

Other potential sources of the increased mercury uptake across the 150 mile stretch of river below Hamilton City included inflows from the historic Sierra Nevada gold mining rivers: the Feather, Yuba, Bear, and American. First, we sampled the Sacramento River just above all these potential sources, above Knight's Landing and 100 river miles downstream of the Hamilton City location. Sculpin mercury concentrations averaged 36 ppb, a 20% increase from Hamilton City. These data suggested that the primary source of the observed doubling downstream was located within the 50 river miles between this point and Sacramento. To test the American River as a possible source, sampling was conducted at a site upstream of the American River but downstream of the Feather River (Highway 5). Mercury levels in sculpin samples from this site were found to be very similar to levels below the American River. Average concentrations ranged from 59 ppb at Highway 5 below the Feather River, to 58 ppb at Garcia Bend below the American River and 53 ppb at River Mile 44 below the Sacramento wastewater discharge.

These results suggested a mercury source somewhere in the approximately 24 river miles between Highway 5 and the site above Knight's Landing. The Feather River is the dominant water inflow

along this stretch. We sampled the Feather River upstream of its confluence with the Sacramento. In the course of sampling this area and repeatedly launching near the Colusa Canal's confluence with the river, we noted extensive, turbid agricultural drainage from it and decided to also sample this potential source. We were not able to sample the Canal directly, but were able to obtain a sample of sculpin from the several mile stretch of the Sacramento River located downstream of the Colusa Drain but upstream of the Feather River and Sutter Bypass. Mercury levels in the Feather River samples were somewhat elevated compared to those from the Sacramento River site above Knight's Landing (43 versus 36 ppb), but not enough to account for the significantly higher concentrations downstream. In contrast, mercury in sculpin from the site above the Feather River and downstream of the Colusa Drain were significantly higher (70 ppb), suggesting that the Colusa Drain may be an important source of the methylmercury in the food web of the lower Sacramento River. We note that this Canal drains an extensive area of rice farming and managed waterfowl units, both of which receive managed, seasonal flooding. Again, episodic flooding was implicated as an important driver of elevated methylmercury uptake and incorporation into the food web.

## Valuable Information for Managers

The UC Davis Biosentinel Program has developed an effective monitoring network across the watershed and has identified:

- > broad and fine-scale geographic trends in food web uptake of methylmercury;
- > significant changes between years;
- > seasonal increases in uptake; and
- > links to natural and managed processes that alter uptake.

The Program has demonstrated that biosentinel monitoring provides targeted, fish-based feedback that is essential to managing wetlands and other aquatic habitats more effectively for mercury. Extensive biosentinel monitoring in the Delta and North Bay over the last few years has greatly advanced our understanding of patterns in food web uptake of mercury and has led to the formation of credible hypotheses regarding processes that could be driving these patterns. Additional broad-scale biosentinel monitoring by the Regional Monitoring Program to be conducted in the next few years should bring us much closer to identifying the origins of the mercury that contaminates the aguatic food web of San Francisco Bay, and may set the stage for actions to achieve a timely reduction of mercury exposure in this ecosystem.

## FEATURE <u>ARTICLES</u>

Technical terms defined in Glossary on page 90

## Advances in Understanding Pollutant Mass Loadings from Rivers and Local Tributaries

#### HIGHLIGHTS

- Understanding the mass loading of pollutants from various sources and pathways is an essential step in controlling contamination and cleaning up the Bay
- > TMDL cleanup plans for the Bay and the Guadalupe River emphasize the reduction of mercury and PCB loads associated with urban runoff and mercury-tainted soils from the New Almaden historic mining district
- Field studies in the Delta, the Guadalupe River watershed, and a small urban watershed in Hayward are rapidly improving our understanding of the sources and pathways that are most important
- Compared to estimates made just a few years ago, urban runoff and the Guadalupe River are now thought to contribute a larger proportion of the total load of mercury to the Bay
- The RMP is developing a Small Tributaries Loading Strategy that will identify priority information needs to support future decisions on managing loads from this important pathway



### Why Measure Mass Loadings?

A fish consumption advisory for San Francisco Bay has been in place for 15 years due to contamination by mercury, polychlorinated biphenyls (PCBs), and other pollutants. Over that time there has been considerable debate about the amount of pollutants entering the Bay from various sources and pathways. This article summarizes the information that has been developed on the mass loadings from one group of pathways (rivers, creeks, and

Substances such as mercury and PCBs were once used in great quantities and in many applications (some uses remain). Both are harmful and persistent when released into the environment. Mercury, PCBs, and many other pollutants of concern strongly attach to soils and aquatic sediments where they may persist for decades. They also accumulate in aquatic wildlife, increasing in concentration as they migrate upwards through the food chain. Wildlife and humans at the top of the food chain are most at risk through consump-

sediment quality problems and contamination in fish, and explain how controlling mass loadings will lead to less risk to wildlife and humans. The need for better estimates of mass loadings led the RMP to form the Sources, Pathways, and Loadings Workgroup in 1999 and to fund a continuing series of studies on this topic. The Bay TMDLs incorporate the results of these studies and also recognize a need to periodically refine and update loading estimates to measure progress and guide adaptive management of Bay contaminants.

# The need for better estimates of mass loadings led the RMP to form the Sources, Pathways, and Loadings Workgroup in 1999 and to fund a continuing series of studies on this topic

storm drains) and describes how the accuracy of loading estimates has changed through time. This article also discusses the important questions that remain to be answered. Continued development of a sound understanding of mass loading will be essential in controlling contamination and ultimately reaching the goal of eliminating the Bay's fish consumption advisory.

Mass loading is the term used to describe the rate at which a pollutant enters the Bay from a source (e.g., motor vehicle exhaust) or via a pathway (e.g., rivers); it is specified as a mass per period of time. For example, scientists typically express PCB and mercury loadings in kilograms per year (kg/yr) and sediment loadings in metric tons per year (t/yr).

tion of contaminated fish. Health risks due to these substances still exist long after their use has largely diminished.

The San Francisco Bay Regional Water Quality
Control Board (Water Board) has placed a high
priority on addressing PCB and mercury contamination. Mass loading information from the various
sources and pathways is needed for these and
many other pollutants (Table 1). The Water Board
has initiated Total Maximum Daily Load (TMDL)
projects to address mercury in the Guadalupe
River and mercury and PCBs in San Francisco
Bay. These TMDLs estimate mercury and PCB
mass loadings from known sources and pathways,
describe the ways these loadings link to water and

SUBSTANCE	PRIORITY
Mercury and PCBs	Тор
Polybrominated diphenyl ethers (PBDEs)	High
Current use pyrethroid pesticides	Medium
Dioxins	Medium
Selenium	Medium
Legacy pesticides (DDT, chlordane, dieldrin)	Medium
Copper and nickel	Medium
Polycyclic aromatic hydrocarbons (PAHs)	Medium
Silver, arsenic, cadmium, chromium, lead, and zinc	Low
Organophosphate pesticides (OPs)	Low
Nutrients (nitrogen, phosphorus)	Low

#### TABLE 1

The Water Board has place a high priority on addressing PCB and mercury contamination. Mass loading information from the various sources and pathways is needed for these and many other pollutants

## What Are the Main Sources and Pathways of Pollutants?

Many pollutants were widely used in a great variety of applications, often before their harmful properties were recognized. Consequently, they are now found in a variety of lcoations throughout the landscape. These locations are called "sources" or "source areas." The term "pathway" is used to describe the conveyance or process that delivers water, sediment, and pollutants from a source or source area to receiving waters such as the Bay. For example, the main pathways described in the mercury and PCB TMDLs are atmospheric deposition, municipal and industrial wastewater, flow from the mining impacted Guadalupe River, urban stormwater, non-urban stormwater, and flow from the Central Valley via the Sacramento and San Joaquin rivers (Figure 1).

The TMDLs call for reductions in loadings from the pathways with the largest mass loadings. Urban stormwater is deemed a large and to some extent controllable pathway for mercury and PCBs. The TMDLs call for a greater than 50% reduction in mercury loadings and a 95% reduction in PCB loadings from this pathway in the next 20 years. A 95% reduction in mercury loadings from the Guadalupe River watershed also is specified. In contrast, loadings from other pathways are mostly smaller, and some are considered less controllable.

During larger storms, when mercury may have been coming from upstream areas located closer to historic mining sources, particle concentrations averaged 220 ppb

### What Stormwater Loadings Studies Have Been Completed?

### The Sacramento and San Joaquin Rivers

In December 2002, following a literature review, the RMP began its first loadings study. RMP scientists gathered water samples annually for five years during wet season storm flows at Mallard Island located at the eastern end of the Bay near Pittsburg. The samples were analyzed for total mercury, PCBs, and other pollutants. The goal was to estimate pollutant loadings entering the Bay from the Central Valley via the Sacramento and San Joaquin rivers. The study benefited from a long-term dataset on suspended sediment concentrations in water that David Schoellhamer of the USGS began collecting in 1994 and from a long-term dataset on outflow from the Sacramento - San Joaquin River Delta (dating back to 1956) provided by the California Department of Water Resources (DWR).

Total mercury concentrations in water ranged between 3 and 75 parts per trillion (pptr) and were

closely related to flow and suspended sediment concentrations. Three distinct patterns were observed relating mercury and suspended sediment concentrations. During dry conditions, mercury concentrations on sediment particles in the water column reflected those in bottom sediments of Suisun Bay (about 290 ppb) (Figure 2a). During small storms when mercury was flushed mainly from the Delta, particle concentrations averaged 110 parts per billion (ppb) (Figure 2a). In contrast, during larger storms, when mercury may have been coming from upstream areas located closer to historic mining sources, particle concentrations averaged 220 ppb (Figure 2b). In the case of PCBs, concentrations in water ranged between not detected and 6,700 parts per quadrillion (ppq) and particle concentrations were highly variable and less predictable (2.2 - 226 ppb).

The data on pollutant and suspended sediment concentrations and Delta outflow allowed us to calculate loadings on a daily basis; these were added to form annual totals (Table 2). In the case of mercury, we were able to use the long-term measurements of suspended sediment concentrations to estimate mass loadings over the longer term.

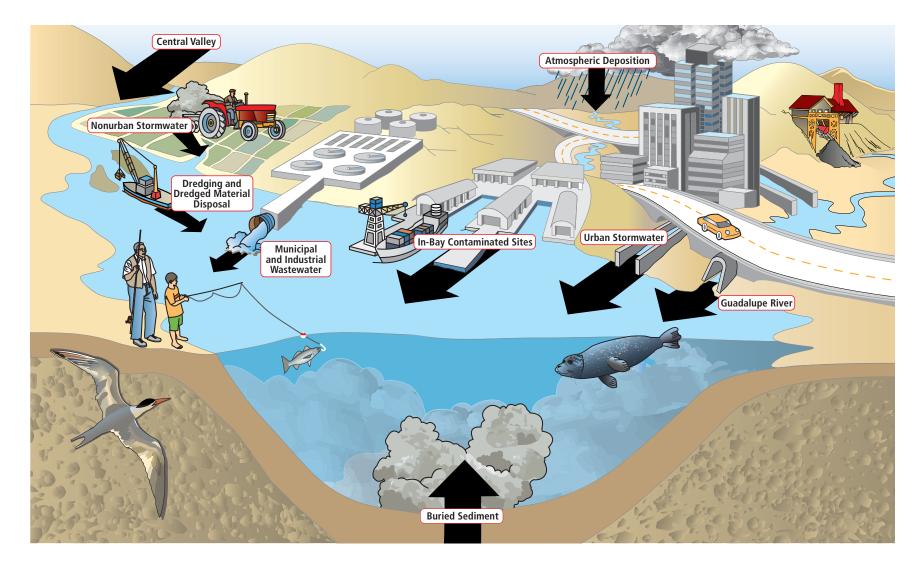
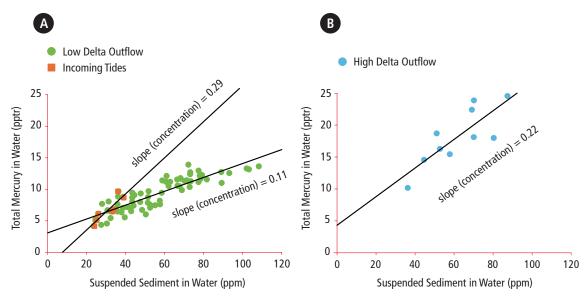


FIGURE 1

The main pathways for pollutant transport into the Bay are atmospheric deposition, municipal and industrial wastewater, flow from the mining impacted Guadalupe River, urban stormwater, non-urban stormwater, and Central Valley flows via the Sacramento and San Joaquin rivers. Urban stormwater is deemed a large and to some extent controllable pathway for mercury and PCBs. Loadings from other pathways are mostly smaller, and some are considered less controllable.



High flows resulting from large storms mobilize sediment with relatively high mercury concentrations in the watershed and carry substantial loadings to Bay. In order to estimate loadings from the Central Valley, the RMP analyzed how concentrations of pollutants

FIGURE 2

related to flow and suspended sediment concentrations. These graphs show mercury data as an example. The slopes of the lines indicate the average concentration of mercury on suspended sediment particles. The steeper line in (A) is associated with incoming tides and suggests that suspended sediment originating downstream in Suisun Bay had a relatively high mercury concentration (0.29 ppm). The flatter line is associated with small storms carrying less contaminated sediment (0.11 ppm) from the Delta. During a very large storm (B), concentrations on suspended sediment were also relatively high (0.22 ppm), suggesting mobilization of contaminated sediment in the Central Valley watershed.

YEAR	DELTA OUTFLOW (Million cubic meters per year)	SUSPENDED SEDIMENT LOAD (Million metric tons per year)	TOTAL MERCURY LOAD (kg per year)	PGB LOAD (kg per year)
1995	51,559	2.58	599	
1996	31,436	1.01	211	
1997	42,307	2.24	579	
1998	53,639	2.42	538	
1999	27,805	0.84	163	
2000	22,394	0.66	142	
2001	8,565	0.26	53	
2002	11,303	0.31	61	3.3
2003	17,330	0.55	101	19.6
2004	18,577	0.64	131	4.1
2005	18,588	0.42	86	8.0
2006	50,020	1.99	466	17.5
2007	7,700	0.1	38	
Average of years of observation	27,786	1.08	244	10.5
Estimated long term average (1973 - 2002)	24,278	0.95	211	9.6

TABLE 2 Current estimates of mercury and PCB loads from the Central Valley are lower than the estimates available eight years ago when the RMP began investigating mass loadings. Annual flows from the Central Valley via the Delta vary mainly in response to rainfall and snow accumulation in the Sierra Nevada. Factors associated with the variation in annual loadings of mercury and PCBs to the Bay include the flow energy in the river system and where precipitation occurred. Our current best estimates of the long-term average loadings are 0.95 million metric tons per year for suspended sediment and 211 kg and 9.6 kg per year for mercury and PCBs, respectively.

**Pollutant Mass Loadings** 

### The Guadalupe River

With funding from the RMP and a variety of other sources, annual monitoring for mercury, PCBs and other pollutants began in the Guadalupe River watershed in November 2003 and continued for four years. Water samples were collected during wet season flows at a station in San Jose located where Highway 101 crosses the river near the bottom of the watershed. The Guadalupe River watershed is the fourth largest in the Bay Area, with an area of about 400 square kilometers. This study benefited from USGS flow gauging beginning in 1930 and a partnership with Redwood Sciences Laboratory and USGS to carry out sediment gauging. An important component of the study was a probe that measured turbidity, an index of suspended sediment concentrations that can be used as a surrogate for pollutant concentration. Readings were recorded every 15 minutes during the wet season. RMP scientists collected water samples during storm flows each winter and were able to review flow and turbidity data to make real-time decisions on the timing of water sample collection.

Very high and variable concentrations of total mercury (not detected to 18,700 pptr) and PCBs (700 to 123,000 ppq) were observed. The highest total mercury concentrations were observed after intense rainfall in the New Almaden historic mining district and on the falling stage of the hydrograph after the peak of the storm had passed (Figure 3). In contrast, the highest concentrations of PCBs were observed when rainfall was heavy in the urban areas. This usually occurred during the rising stage (before the peak in river flow), when

flow from urban areas was not diluted with cleaner runoff from the upper, non-urban watershed (Figure 4). Loadings of each pollutant were determined for the study years by combining complex and varying relationships between suspended sediment concentrations and pollutant concentrations with USGS flow data (Table 3). Longer-term estimates of annual average loading were made using rainfall and flow data for 1973 to present.

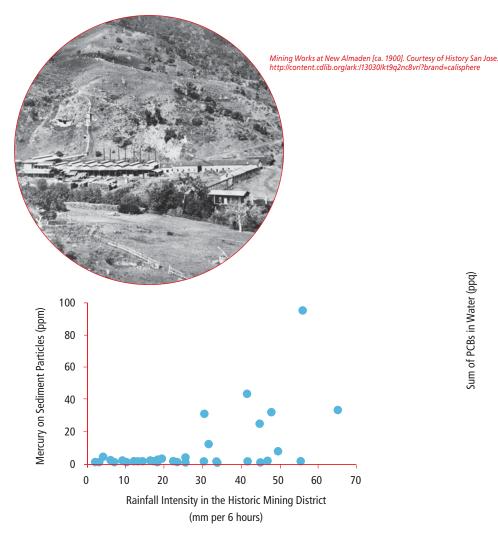
## A Small, Highly Urbanized Watershed in Hayward

Using methods similar to the Guadalupe River study, the RMP began monitoring a small, highly urbanized watershed on the Bay margin in Hayward in November 2006. This watershed was chosen because we want to estimate loadings from a variety of watershed types. The Hayward watershed contrasts markedly with the Guadalupe River watershed: it is small (4.5 km²), has lower rainfall, and completely lacks any natural channels. There is no historic flow gauging record for this site. RMP staff worked with RiverMetrics to install equipment to allow for continuous monitoring of turbidity, water flow, rainfall, and collection of water samples for laboratory analysis.

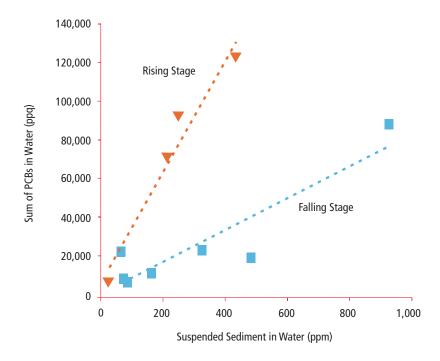
Despite water year 2007 recording only 70% of the mean annual rainfall, flow was very quick to respond when rainfall did occur. As little as one millimeter of rain produced a flow that usually peaked within an hour of maximum rainfall. Concentrations of mercury and PCBs varied in response to flow, generally showing elevated concentrations during peak flow. Total mercury concentrations

ranged between 1.9 and 55 pptr, and concentrations of mercury on particles ranged between 0.08 and 1.3 ppm, averaging 0.23 ppm, about one-tenth of the concentrations measured in the Guadalupe River. These low levels were an encouraging observation given the Water Board TMDL sediment target of o.2 ppm mercury. PCB concentrations ranged between 400 and 46,000 ppg, about 40% of the concentrations observed in the Guadalupe River. Table 4 shows estimated pollutant loadings to the Bay from the Hayward watershed during water year 2007, including 0.025 kg of mercury and 0.014 kg of PCBs. These loads are likely deceptively small given that water year 2007 was very dry and that this watershed represents only about 0.6% of the urban area in the Bay Area.

To compare pollutant loadings between the Hayward and Guadalupe River watersheds, the load estimates were scaled to the areas of each watershed for two years of similar rainfall and runoff (Table 4). In the case of the Guadalupe River, the loads were scaled to the area downstream of the reservoirs. Keeping in mind that the uncertainty associated with our loadings estimates are about plus or minus 35%, this comparison shows some very interesting results. The Guadalupe River has greater area-scaled loadings of suspended sediment, mercury, and nickel, likely due to mining and natural sources in this watershed's rocks and soils and the steep erosive peaks of Loma Prieta and Mt. Umunhum in the Santa Cruz Mountains. Silver, cadmium, copper, lead, PCBs, PBDEs, and **DDT** and dieldrin (organochlorine pesticides that are no longer in use) loads were similar in the two watersheds. For zinc and perhaps methylmercury,



More intense rainfall in the New Almaden historic mining district mobilizes sediment particles with high mercury concentrations. Concentrations of mercury on suspended sediment particles in the Guadalupe River are highly variable. When rainfall occurred in urban areas or when a winter storm was short-lived or rainfall had a relatively low intensity, typical concentrations of mercury on particles were approximately 1.5 ppm. When rainfall was more intense, especially in and around the New Almaden historic mining district, mercury concentrations on particles were as high as 95 ppm, and median concentrations were about six times higher than during other storms. These observations helped improve the accuracy of loadings estimates and provided evidence of mercury loadings from the historic mining district.



PCBs in the Guadalupe River watershed predominantly originate from urbanized areas in the lower watershed. This graph shows an example from water year 2005 of the relationship between PCB and suspended sediment concentrations in the Guadalupe River. PCB concentrations on particles were greater (steeper regression line) in samples collected during rising-stage flows from urban areas compared to falling-stage flows (flatter regression line) from the upper non-urbanized watershed.

**Pollutant Mass Loadings** 



Cinnabar from the New Almaden district, Santa Clara County, California. Cinnabar is a mercury sulfide with the chemical formula HgS. It was the main ore of mercury at many California mercury mines. It is characterized by its bright red color. Mercury was recovered by heating the cinnabar and collecting and cooling the mercury vapors that were produced.

 $Image\ courtesy\ of\ California\ Geological\ Survey.\ http://www.conservation.ca.gov/cgs/minerals/hazardous\_minerals/mercury/Pages/index.aspx$ 

Water Year	River flow (Million cubic meters per year)	Suspended sediment (Metric tons per year)	Total Mercury	Methylmercury	Total Silver	Total Arsenic	Total Cadmium	Total Chromium	Total Copper	Total Nickel	Total Lead	Total Zinc	Sum of PCBs	Sum of PBDEs	DDT	Chlordane	Dieldrin
2003	61	10,600	110		3.1	100	11	760	790	1,500	610	3,300	1.2		1.1	0.8	0.08
2004	53	8,490	15		2.5	85	8.7	620	650	1,200	480	2,700	0.7		0.7	0.6	0.05
2005	73	4,920	8.0	0.03	2.8	88	5.8	310	470	660	370	1,800	0.7	2.3			
2006	130	11,800	26	0.06									1.5	4.8			
Average of years of observation	78	8,940	40	0.05	2.8	92	8.4	560	640	1,100	480	2,600	1.0	3.6	0.9	0.7	0.07
Estimated long term average (1973 -2002)	58	14,000	130	0.03	3.5	110	12	1,700	890	3,235	1,000	3,700	0.9	2.3	1.7	1.6	0.12

Loads in kg/yr, except as noted. The estimated long-term average loads are based on extrapolation using the recent contaminant measurements and long-term data on flow. The averages based on the four years of observation are different from the long-term (30 year) averages due to differences in average flow in these two periods.

Footnote: The list of pollutants varied slightly from year to year due to varying RMP priorities. In particular, methylmercury and PBDEs were added during the 3rd and 4th year of the study and historic use pesticides (DDT, chlordane and dieldrin) were removed.

#### TABLE 3

Distinct differences in wet and dry years lead to high variability in mercury loadings to the Bay. Loadings in the Guadalupe River were measured for four years. Mercury loadings were more variable from year to year than the other pollutants studied. Most of the mercury loading was associated with release from the New Almaden historic mining district during intense rainfall. During dry years, this source of mercury was diminished. In contrast, pollutants such as copper and lead originate mostly from urban areas and were released more continuously due to wash off from impervious surfaces. Methylmercury was only a small fraction of the total mercury loading to the Bay, but during dry years the fraction was greater.

MASS LOADINGS																
	Area (km²)	Suspended Sediment (t)	Mercury	Methylmercury	Silver	Cadmium	Chromium	Copper	Nickel	Lead	Zinc	Sum of PCBs	Sum of PBDEs	DDT	Chlordane	Dieldrin
Hayward Urban Watershed (2007)	4.5	110	0.025	0.00072	0.036	0.19	6.4	11	8.0	7.9	92	0.014	0.041	0.017	0.0060	0.0013
Guadalupe River (2004)	414	8,500	15	0.021	3.0	10	640	710	1,200	520	3,000	0.77	1.6	0.77	0.59	0.060

Loads in kg/yr, except as noted.

AREA SCALED LOADINGS															
	Suspended Sediment (t/km²)	Mercury	Methylmercury	Silver	Cadmium	Chromium	Copper	Nickel	Lead	Zinc	Sum of PCBs	Sum of PBDEs	DDT	Chlordane	Dieldrin
Hayward Urban Watershed (2007)	24	5.6	0.16	8.0	43	1,400	2,500	1,800	1,800	21,000	3.2	9.0	3.7	1.3	0.30
Guadalupe River (2004)	21	36	0.050	7.2	23	1,500	1,700	2,900	1,300	7,200	1.9	3.8	1.9	1.4	0.15

Footnote: For the purposes of the comparison, the load estimates were scaled to the areas of each watershed for two years of similar rainfall and runoff. The shaded cells in the table indicate when an area-normalized loading is statistically greater in one watershed relative to the other. All data in µg/m² except as noted.

#### TABLE 4

Loadings of pollutants entering the Bay from a small urban watershed in Hayward during water year 2007 and a comparison to loadings entering the Bay from the Guadalupe River watershed in San Jose. The Guadalupe River has greater area-scaled loadings of suspended sediment, mercury, chromium, and nickel, likely due to mining and natural sources in this watershed's rocks and soils. Silver, cadmium, copper, lead, PCBs, PBDEs, DDT, and dieldrin loads were similar in the two watersheds. For zinc and perhaps methylmercury, data to date indicate that the Hayward watershed has greater area-scaled loadings to the Bay. In contrast, it appears that Guadalupe may have greater area-scaled loadings of chlordane.

**Pollutant Mass Loadings** 

these data indicate that the Hayward watershed has greater area-scaled loadings to the Bay. Zinc has a variety of urban uses including galvanizing and plating, tires, and batteries but we are not aware why Hayward would differ so greatly from San Jose in the use of zinc. It is perhaps surprising that methylmercury loading per unit area may be greater in Hayward compared to Guadalupe, given the abundance of inorganic mercury load from the historic mining areas in the upper Guadalupe River. In contrast, it appears that Guadalupe may have greater area-scaled loadings of chlordane (another legacy organochlorine pesticide).

For example, in 2000, the long-term average mercury loading to the Bay from the Central Valley was estimated to be between 560 and 1,150 kg per year, with a best estimate of 607 kg per year. In 2008, based on measurements at Mallard Island, we are now more confident in our estimate that the long-term average mercury loading is between 140 and 290 kg with a best estimate of 211 kg per year. We also understand that loadings can vary from less than 38 kg during a very dry year (e.g., 2007) to greater than 580 kg during a very wet year (e.g., 1997). Similarly, in 2000, the long-term average mercury loading to the Bay from the Guadalupe

estimate of 42 kg per year. In 2008, based on our measurements during storm flows, we can now more confidently say that the long-term average loadings are between 6 and 13 kg, with a best estimate of 9.6 kg per year.

Estimates of loadings to the Bay from municipal and industrial wastewater, atmospheric deposition, and erosion of Bay sediments have also changed through time. The combination of all these changes has led to a much different picture of the mass loading to the Bay for total mercury (Figure 5) and PCBs (Figure 6). In particular, urban

### Understanding of loading of pollutants to the Bay has advanced considerably in the past eight years

### What Have We Learned?

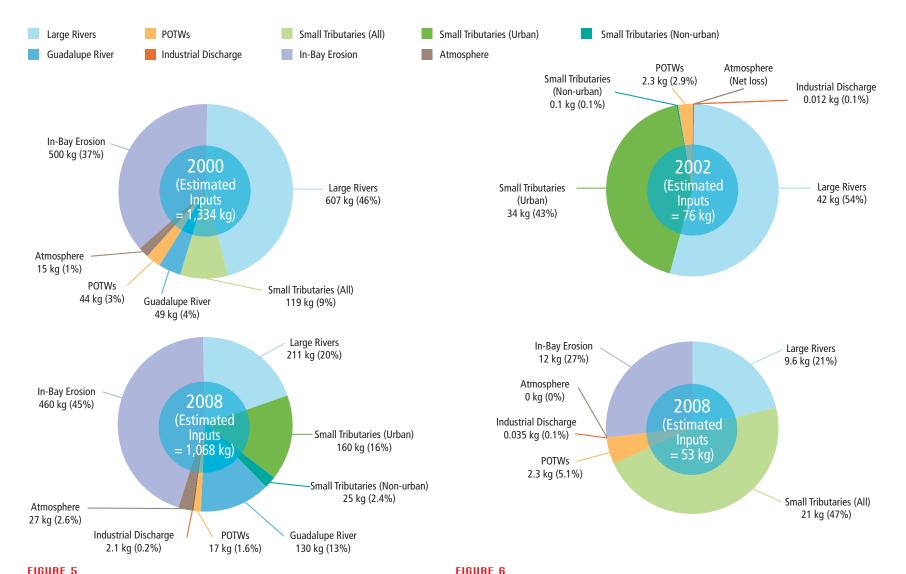
Understanding of loading of pollutants to the Bay has advanced considerably in the past eight years. In 2000, our estimates were based on literature reviews and a simple model that converted rainfall to flow based on land use. Estimates of mercury loading from the Central Valley via the Sacramento and San Joaquin rivers and from the New Almaden historic mining district via the Guadalupe River were based on estimates of suspended sediment loadings and mercury concentrations on particles. These first estimates were very uncertain, leaving managers with little information on the pathways that provide the best opportunities for reduction of pollutant loads.

River was estimated at between 7 and 70 kg per year, with a best estimate of 49 kg per year. After four years of data collection from the Guadalupe River, we now estimate that long-term average mercury loading is between 90 and 170 kg, with a best estimate of 130 kg per year.

A different story can be told for PCBs. In 2000, the only available estimate of PCB loadings from the Central Valley to the Bay was 11 kg per year, but there was very low confidence in this estimate because it was based merely on combining the average concentrations from two RMP sampling stations with Delta outflow. In 2002, during the development of the first draft of the PCB TMDL project report, this same method was used again but with additional years of data to derive a higher

runoff is now thought to contribute a larger proportion of the total load of mercury and has remained a large contributor of PCBs. The mercury contribution from the Guadalupe River also is larger than estimated previously. Accordingly, the TMDLs emphasize the reduction of mercury and PCBs loads associated with urban runoff and mercury loads from the New Almaden historic mining district. Other pathways are smaller contributors, deemed uncontrollable, or less likely to impact the Bay.

These changes in estimated loads have been driven by improved estimates of sediment loads and contaminant concentrations on sediment particles. In the case of Central Valley mercury loadings, our best estimate was reduced by more than 50%, primarily because estimated loadings of suspended



Estimates of annual average total mercury loadings entering San Francisco Bay from the main pathways have changed significantly over the past eight years. In terms of magnitude, the largest change was for the large rivers pathway; current estimated loadings are about one-third of the estimates made in the year 2000. Current estimated loads from the Guadalupe River are about 2.5 times greater than the estimates made in 2000.

Over the past six years we have learned much about the relative contributions to PCB loadings from the major pathways. One of the most important changes is in our estimated by the property of the most important changes is in our estimated by the property of the most important changes is in our estimated by the property of the proper

loadings from the major pathways. One of the most important changes is in our estimate of the relative proportions of PCB loadings between the large rivers pathway and the small tributaries. In 2002, the estimates indicated similar loadings from small tributaries and large rivers. In contrast, we currently estimate that the small tributaries loading is about double that from the large rivers. Another major change is the addition of an estimated load from erosion of legacy contaminated sediment in the bed of the Bay. In 2002, there were no estimates available for in-Bay bed sediment erosion; recent estimates have been made possible through the multi-box model for PCB fate in San Francisco Bay developed by the RMP.

**Pollutant Mass Loadings** 

sediment were reduced by more than 50% from 2000, while the particle concentrations remained roughly the same. In contrast, our measurements of concentrations of PCBs during floods are about twice as high as the RMP data available in 2000, causing the current PCB loadings estimate to remain similar to our estimate in 2000 despite dramatic changes in the estimated suspended sediment load. In the case of Guadalupe River mercury loadings, the measured suspended sediment load is 35% of the estimate that was available in 2000, but our measured concentrations of mercury are much larger, leading to an increase in the estimate of long-term average loadings. In this case, our current best estimate of particle concentrations is much greater than it was eight years ago.

## What Are the Remaining Questions?

A number of significant data gaps remain. At this time, the estimate of loadings from urban stormwater in the mercury TMDL is based on bed sediment data collected by the stormwater agencies and an estimate of regional-scale sediment loads. Before our Hayward study, we had no reliable data on mercury concentrations during storms in any urban tributary and we still are not certain if the Hayward watershed is typical of other Bay Area urban watersheds. In addition, we have very little information on mercury speciation - in particular, what proportion of the mercury loadings are methylmercury (the form of mercury of greatest toxicological concern in the environment), or forms readily converted to methylmercury (reactive mercury). The Guadalupe River watershed is not typical of urban areas for mercury loadings or speciation because of the mining influence.

The Small Tributaries Loading Strategy will specifically address information needs relating to TMDL load-reduction requirements and provide a vision for the kind of observations, modeling, and statistical methods that can be used to answer key questions

In the case of PCBs, the Guadalupe River watershed may be typical of other large urbanized watersheds with a mix of residential, commercial and old industrial areas, but we still have a limited understanding of PCB loading from smaller, highly urbanized watersheds. The Hayward study will provide a valuable data set, but additional watersheds need to be evaluated to improve regional loading estimates.

Many questions remain regarding the reduction of pollutant loadings from Bay watersheds, a necessary action for meeting TMDL goals. As we begin to tackle this challenging task, it will be important to track progress, but discussions are only beginning on how best to accomplish and monitor the reductions.

The RMP is engaged in a concerted planning effort to prioritize the largest data gaps and decide how to best address them with the limited resources available (page 8). Particular attention is being given to developing monitoring and management strategies related to selected high priority topics. One example is the Mercury Strategy (page 4). A strategy also is being developed for small tributary loadings. The Small Tributaries Loading Strategy will specifically address information needs relating to TMDL load-reduction requirements and provide a vision for the kind of observations,

modeling, and statistical methods that can be used to answer key questions over the next 5, 10, and 20 years. Future steps may include additional field studies to estimate loadings from representative watersheds, extrapolating to other watersheds that lack field data, modeling regional-scale loadings, and determining long-term trends in pollutant loadings in relation to management efforts to track progress at local and regional scales. We may also use modeling approaches at the watershed scale to refine loading estimates and inform the selection of watersheds where management actions will receive high priority.

Thus, the Small Tributaries Loading Strategy will build upon our accomplishments to date in estimating pollutant loadings. The Strategy will guide ongoing efforts to refine these estimates, and new studies such as a recently initiated RMP investigation to model the Guadalupe River watershed. It will also be important to dovetail small tributaries studies with other elements of the RMP and with work being conducted through other programs. We are optimistic that the lessons learned will help us implement and refine the TMDLs, clean up the Bay, and eventually eliminate the need for fish consumption advice for pollutants such as mercury and PCBs.

## <u>REFERENCES</u>

### MANAGEMENT UPDATE

#### Davis

Larry Walker Associates. 2008. Final Report: Localized Mercury Bioaccumulation Study. Prepared for: Sacramento Regional County Sanitation District, Sacramento, CA. http://www.bemercuryfree.net/offsets.html

#### **Delaney**

- (CCMP) Comprehensive Conservation and Management Plan. 2007. San Francisco Estuary Project, Oakland, CA. 243 pp.
- LTMS. 2001. Long-term management strategy for the placement of dredged material in the San Francisco Bay Region. viii+ES-1 to 15-2pp.+app.

  A-S. July. Prepared by the U.S. Army Corps of Engineers (USACE), USEPA, BCDC. SFBRWOCB. and SWRCB.
- LTMS. 2006. Long Term Management Strategy (LTMS): Six Year Program Review.
- The Marine Exchange of the San Francisco Bay Region website. 2008. http://www.sfmx.org.
- MTC (Metropolitan Transportation Committee). 2004. Goods Movement Study for the San Francisco Bay Area: Final Summary Report, December 2004 (http://www.mtc.ca.gov/planning/rgm/).
- USACE. 2008. U.S. Army Corps of Engineers' Navigation Data Center
  -Waterborne Commerce Statistics Center. U.S. Waterborne Container
  Traffic by Port/Waterway in 2005 (http://www.iwr.usace.army.mil/ndc/ wcsc/wcsc.htm).
- (USEPA) U.S. Environmental Protection Agency. 1994. Ocean Dumping; Designation of Site: Final Rule. Federal Register: 40 CFR Part 228, August 11, 1994.

## STATUS AND TRENDS UPDATE

#### The Latest Monitoring Results

Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. 2006. Biological Monitoring of Polyfluoroalkyl Substances: A Review Environ. Sci. Technol.; (Critical Review); 40(11); 3463-3473.

#### Water Quality Trends at a Glance

Fairey, R., K. Taberski, S. Lamerdin, E. Johnson, R.P. Clark, J.W. Downing, J. Newman and M. Petreas. 1997. Organochlorines and other environmental contaminants in muscle tissues of sportfish collected from San Francisco Bay. Marine Pollution Bulletin 34(12): 1058–1071.

### FEATURE ARTICLES

#### **Eagles-Smith**

- Ackerman JT, Eagles-Smith CA, Heinz GH, Wainwright-De La Cruz SE, Takekawa JY, Adelsbach TL, Miles AK, Hoffman DJ, Schwarzbach SE, Suchanek TH, Maurer TC. 2007a. Mercury in birds of the San Francisco Bay-Delta: trophic pathways, bioaccumulation and ecotoxicological risk to avian reproduction. 2006 Annual Administrative Report to CALFED, U. S. Geological Survey, Western Ecological Research Center, and U. S. Fish and Wildlife Service, Environmental Contaminants Division, 41 pp.
- Ackerman JT, Eagles-Smith CA, Takekawa JY, Demers SA, Adelsbach TL, Bluso JD, Miles AK, Warnock N, Suchanek TH, Schwarzbach SE. 2007b. Mercury concentrations and space use of pre-breeding American avocets and black-necked stilts in San Francisco Bay. Sci Tot Environ 384:452-466.
- Ackerman JT, Takekawa JY, Eagles-Smith CA, Iverson SA. 2008a. Mercury contamination and effects on survival of American avocet and blacknecked stilt chicks in San Francisco Bay. Ecotoxicology 17:103-116.
- Ackerman JT, Eagles-Smith CA, Takekawa JY, Bluso JD, Adelsbach TL. 2008b. Mercury concentrations in blood and feathers of pre-breeding Forster's terns in relation to space use of San Francisco Bay habitats. Environ Toxicol Chem 27:897-908.
- Evers DC, Lane OP, Savoy L, Goodale W. 2004. Assessing the impacts of methylmercury on piscivorous wildlife using a wildlife criterion value based on the common loon, 1998-2003. Unpublished Report BRI 2004-2005 submitted to the Maine Department of Environmental Protection. BioDiversity Research Institute, Gorham, Maine, U.S.A., 2004.
- Heinz G. 1974. Effects of low dietary levels of methyl mercury on mallard reproduction. Bull Environ Contam Toxicol 11:386-392.
- Heinz GH, Hoffman DJ, Klimstra JD, Stebbins KR, Konrad SL, Erwin CA. 2008. Species differences in the sensitivity of avian embryos to methylmercury. Arch Environ Contam Toxicol, in press.

## <u>GLÓSSARY</u>

#### Adaptive management

Taking actions of limited scope commensurate with available information to make progress toward attaining water quality standards while continuously improving understanding of the problem and its solutions.

#### Atmospheric deposition

The transfer of pollutants from the atmosphere to the water or land surface.

#### Basin Plan

Water Quality Control Plan for the San Francisco Bay Basin The Water Board's master water quality control planning document for the Bay. It designates beneficial uses and water quality objectives, and includes programs of implementation to achieve water quality objectives.

#### Beneficial uses

Specific benefits derived from a water body that water quality managers strive to protect. Some important uses of the Bay are fishing, habitat for aquatic life, contact and non-contact water recreation, and shellfish harvesting.

#### Bioaccumulation

The accumulation of pollutants by living organisms.

#### **Bioaccumulative**

Describes pollutants with a tendency to accumulate in living organisms.

#### Biomagnification

The progressive increase of concentrations as a pollutant moves up the food chain.

#### Biosentinel

A species used as an indicator of water pollution.

#### Cadmium

A heavy metal used in batteries, pigments, and other products, that is known to cause cancer and occurs with zinc ores.

#### Carbon isotopes

Carbon atoms with different numbers of neutrons and therefore different atomic masses; since different isotopes behave differently in the environment they can be used as tracers of different food webs.

#### Chlordane

A persistent, chlorine-based organic chemical widely used as an insecticide until it was banned in 1988.

#### Copper

A heavy metal used in many products, including brake pads and pesticides, that is highly toxic to aquatic life, especially bivalves and algae.

#### Cyanide

General term for a group of compounds containing carbon and nitrogen, some of which are toxic. Small amounts of cyanide are formed in municipal wastewater treatment plants as a by-product of disinfection processes, such as chlorination.

#### **DDT**

A ubiquitous, persistent, chlorine-based organic chemical widely used as an insecticide until it was banned in 1972.

#### Delta outflow

Water and associated sediment and pollutants that flow from the Sacramento-San Joaquin Delta into the Bay.

#### Diazinon

An organophosphate insecticide commonly used in agriculture and residential pest control through the 1990s. Residential use was banned in 2004.

#### Dieldrin

A persistent, chlorine-based organic chemical widely used as an insecticide until it was banned in 1988.

#### **Dioxins**

Highly toxic, persistent organic chemicals that are primarily by-products of combustion and accumulate in food chains.

#### **Estuary**

A semi-enclosed coastal body of water with one or more rivers or streams flowing into it, and with a free connection to the open sea.

#### **Exotic species**

Non-native aquatic species introduced to the Bay.

#### Filter-feeders

Species that feed by filtering food particles from its surrounding aqueous environment.

#### Furan compounds

Highly toxic, persistent organic chemicals that are primarily by-products of combustion and accumulate in food chains.

#### Hydraulic mining

The largest-scale, and most devastating, form of placer gold mining in the Sierra Nevada in which high pressure streams of water were used to wash entire hillsides through enormous sluices. Debris from hydraulic mining clogged downstream waterways, including San Francisco Bay.

#### Hydrograph

Graph of the flow of a river as a function of time.

#### **Impairment**

Interference with a beneficial use.

#### Industrial wastewater

Wastewater generated from an industrial process that is treated and discharged from industrial facilities into the Bay.

#### Isotopic composition

The mixture of atoms of an element with different numbers of neutrons and therefore different atomic masses.

#### Lead

A heavy metal used in building construction, batteries, and other applications that is a potent neurotoxin but does not biomagnify.

#### Legacy pesticides

Includes DDT, Dieldrin, and Chlordane. Persistent insecticides widely used in the 1950s and 1960s, banned in the 1970s and 1980s, but still accumulate in the food chain.

#### Maintenance dredging

Dredging to maintain existing channels at their present depths.

#### Mass loadings

The rate at which a pollutant enters the Bay from a source (e.g., motor vehicle exhaust) or via a pathway (e.g., rivers); it is specified as a mass per period of time.

#### Mean lower low water

A tidal datum. The average of the lower low water height of each tidal cycle.

#### Mercury

A heavy metal that accumulates in the food chain and is highly toxic.

#### **Mercury speciation**

Characterization of the different forms of mercury (see page 6) present in an environmental sample.

#### Methylation

The conversion of reactive (or ionic) mercury to methylmercury through the addition of a methyl group.

#### Methylmercury

The problematic form of mercury that comprises only about 1% of total mercury in aquatic ecosystems, but accumulates in the food chain and is highly toxic.

#### Municipal wastewater

Wastewater generated from homes and businesses that is collected by cities, treated, and discharged into the Bay.

#### New work dredging

Dredging projects that create new channels or deepen existing channels.

#### Nickel

A heavy metal used in many products that is moderately toxic to aquatic life.

#### Nonurban runoff

Runoff from nonurban lands, such as agricultural lands, pastures, and open space.

#### Nonurban stormwater

Stormwater flows from nonurban lands, such as agricultural lands, pastures, and open space.

#### **Nutrients**

Nitrogen, phosphorus, and other elements that stimulate growth of algae.

#### Pathogen

Bacteria or viruses that can cause illness.

#### **Pathways**

The routes through which contaminants enter the Bay, such as urban runoff, streams and rivers, deposition from the atmosphere, or wastewater discharge. Pathways are sometimes misconstrued as sources.

#### **PBDEs**

Polybrominated diphenyl ethers A class of flame retardant chemicals that contain bromine and accumulate in aquatic food chains.

#### **PCBs**

Polychlorinated biphenyls Persistent, toxic organic chemicals that were widely used by electrical utilities and industry, banned in 1979, but still accumulate in the food chain today.

#### pН

The measure of the acidity or alkalinity of a water sample.

#### Photodemethylation

Sunlight-induced conversion of methylmercury to reactive (ionic) or elemental mercury (see page 8).

#### Phytoplankton

Organisms that drift in the water column and obtain energy through photosynthesis.

#### Polycyclic aromatic hydrocarbons (PAHs)

A group of more than 100 organic chemicals that are formed during the incomplete burning of coal, oil, gas, wood, or other organic substances. PAHs bioaccumulate and some are carcinogenic.

#### **Processes**

Environmental reactions that can produce or degrade methylmercury, such as methylmercury production by sulfate-reducing bacteria, or methylmercury degradation by photodemethylation.

#### Radiotelemetry

Using radio transmitters on free-ranging wild animals to track their position and acquire detailed data on habitat use, home range size, mortality and survivorship, and migration timing and routes.

#### Selenium

An element that enters the Bay from agricultural runoff and wastewater effluent, accumulates in the food chain, and is toxic to aquatic life.

#### Silver

A heavy metal formerly used in photo processing that is highly toxic to aquatic life.

#### **Small tributaries**

Rivers, creeks, and storm drains that drain to the Bay from local watershed (distinguished from the large rivers that drain the Central Valley).

#### Sources

Activities leading to the release of pollutants into the environment, such as combustion of gasoline in a car engine or application of a pesticide to an agricultural crop.

#### Sport fish

Wild fish that are caught and consumed by anglers.

#### **Sulfate**

A form of sulfur that is common in aquatic ecosystems and has an important influence on methylmercury cycling.

#### Sulfate-reducing bacteria

Bacteria that require sulfate for their metabolism and generate methylmercury as a by-product of their metabolism.

#### Suspended sediment concentrations

Concentrations of particles of solid material suspended in the water column; often used as an index of concentrations of pollutants that associate with particles.

#### TMDL

Total maximum daily load A cleanup plan called for by the Clean Water Act, based on determining the maximum load that an aquatic ecosystem can receive without adverse impacts.

#### Total mercury

The overall sum of all forms of mercury.

#### Toxicity endpoints

Responses to pollutant exposure that are measured in toxicity assays.

#### Trophic level

Position in the food chain, ranging from low (phytoplankton and other organisms that obtain energy from photosynthesis primary producers) to species that graze on the photosynthesizers (primary consumers), to species that prey on primary consumers (secondary consumers or carnivores), to the highest level carnivores that prey on other carnivores.

#### Urban runoff

Runoff from urban areas driven primarily by rainstorms but also by irrigation.

#### Urban stormwater

Runoff from urban areas driven by rainstorms.

#### Water column

The volume of water between the surface of the Bay and the bottom sediment of the Bay.

#### Water quality objectives

Legally enforceable numerical or narrative guidelines, usually based on federal water quality criteria, established to protect beneficial uses of a water body.

#### Water year

The 12-month period from October 1 through September 30.

#### Young-of-the-year fish

Fish that are less than one year old.

#### Zinc

A heavy metal used in galvanizing steel, metal alloys, batteries and other applications that can be toxic to plants, invertebrates, and fish.

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The following reviewers greatly improved this document by providing comments on draft versions:

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Front Cover





Photographs by Linda Wanczyk.

Back Cover



(1) Susan Klosterhaus; (2, 3, 6) Linda Wanczyk; (4) Jon Leatherbarrow; (5) Nicole David; and (7) Mary Beth Spaeth.

## **Regional Monitoring Program** for Water Quality in the San Francisco Estuary

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