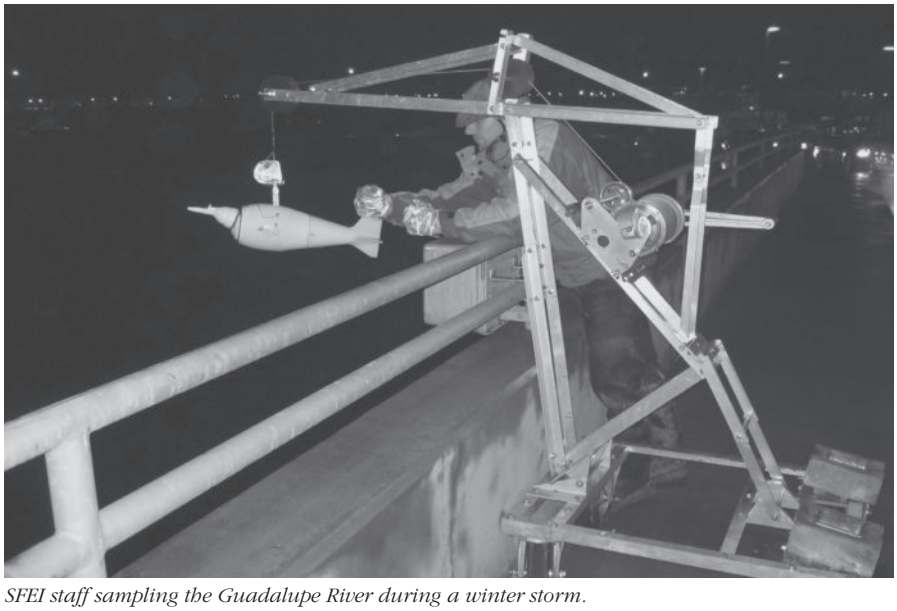
RMP Update

Winter 2004/2005

NEWS FROM THE REGIONAL MONITORING PROGRAM FOR TRACE SUBSTANCES

Mining Legacy in the Guadalupe Watershed:

Reducing Mercury Entering San Francisco Bay



SFEI staff sampling the Guadalupe River during a winter storm.

by Jennifer Hunt, Lester McKee, and Jon Leatherbarrow

Historic mercury (Hg) inputs to San Francisco Bay have resulted in contaminated sediments and potentially harmful mercury levels in wildlife. Most of the mercury in the Bay entered many decades ago and thus mercury is often described as a legacy pollutant. However, mercury is still entering the Bay today, mainly through stormwater runoff. In addition, there are ongoing small inputs of mercury from the atmosphere and from industrial and municipal wastewater. The majority of the legacy mercury as well as the ongoing annual input comes from the mining of naturally occurring mercury deposits in the Coast Range of California. These deposits were mined, beginning in the 19th century, for use in gold mining and other industrial applications.

The South Bay hills are the home of the former New Almaden mining district which lies within the Guadalupe River watershed. This mine operated from 1845-1975 and was the largest mercury producing mine in North America. The mine is closed and is currently a tourist attraction. Mercury is still leaching from the mine and contaminated sediment in adjacent creeks is moving down into the Guadalupe River and eventually into the Bay **(see Figure 1).** The Guadalupe River is one of the largest inputs of mercury to the Bay, but also considered one with good potential for reduction. The Regional Monitoring Program for Trace

Continued on page 2

Emerging Contaminants:

Perfluorinated Chemicals

Daniel R. Oros

Perfluorinated chemicals (PFCs) are a class of synthetic compounds that have recently been discovered to be widespread in human blood and wildlife tissue at concentrations that are generating concern from scientists and the US Environmental Protection Agency (EPA) (Hansen et al., 2001, Giesy et al., 2001; Kannan et al., 2002a,b; Martin et al., 2004, U.S. EPA, 2003). PFCs have been manufactured for over 50 years and have been widely used as refrigerants, surfactants, and polymers, and as components of pharmaceuticals, fire retardants, lubricants, adhesives, cosmetics, paper coatings, and insecticides. Common products that contain PFCs include Teflon®, Gore-Tex®, and Scotchguard®. Perfluorooctanoic acid (PFOA) is one of the PFCs that has been found in human blood and also in drinking water supplies near a PFOA manufacturing plant in West Virginia (Hogue, 2004). PFOA and perfluorooctane sulfonate (PFOS) both have received considerable attention due to their widespread occurrence as global environmental contaminants and

Continued on page 4

For more information

about the RMP, or to receive the RMP newsletter, contact the San Francisco Estuary Institute (SFEI) at 510-746-7334 or visit the RMP Web site at <http://www.sfei.org/rmp>.

Regional Monitoring Program
San Francisco Estuary Institute
7770 Pardee Lane, 2nd floor
Oakland, CA 94621
510-746-7334
http://www.sfei.org

Guadalupe

Continued from page 1

Substances (RMP) is collaborating with the Clean Estuary Partnership and other local partners in quantifying the mercury input to the Bay from this watershed.

Mercury and Biological Effects

Mercury, in the form of methylmercury, bioaccumulates in living organisms and is associated with a variety of adverse effects. In humans high levels of mercury have been linked to birth defects and learning disorders (Clarkson, 1992). Methylmercury in Bay sport fish is a primary reason for the development of a consumption advisory issued by the Office of Environmental Health Hazard Assessment (OEHHA) (http://www.oehha.ca.gov/fish.html). In birds, mercury has been associated with reproductive effects such as low hatchability rates (Schwarzbach and Adelsbach, 2003). Reproductive effects may have consequences for the population of a species and are especially a concern for threatened and endangered species. Several species of Bay birds have concentrations of mercury in their eggs that may be problematic. Mercury has been found in California clapper rails, an endangered wetland bird, at concentrations above effects thresholds established for other bird species (Schwarzbach et al., 2003). Wildlife higher in the food web such as fish-eating birds and mammals have the potential to accumulate high concentrations of mercury because of their diet.

Regulators Response to High Mercury in the Bay

Due to the concerns for human and wildlife health, mercury in the Bay is now seen as a high priority issue and is being addressed by regulators. The San Francisco Bay Regional Water Quality Control Board (Regional Board) is charged with maintaining the water quality of the Bay and implementing the provisions of the federal Clean Water Act. The Bay is on a federal list of impaired water bodies due to mercury contamination. In order to meet water quality standards, the Regional Board is developing a mercury Total Maximum Daily Load (TMDL) to regulate the discharge of mercury into the Bay.

The mercury TMDL calls for a 60% overall reduction in mercury loadings to the Bay. The Regional Board is projecting that it will take approximately 120 years, after implementation of the plan, to reduce the levels of mercury in Bay sediments to safe levels (Looker and Johnson, 2004). The sediments of the Bay are the target for the TMDL, but ultimately the goal is to reduce the mercury levels in fish so that they are safe for consumption by wildlife and humans **(see Figure 2).** Implementation of the mercury TMDL is an example of adaptive management. Actions to reduce mercury loading to the Bay are being taken based on the current state of scientific knowledge. Researchers will continue to gather scientific information that will be evaluated and potentially utilized to modify future actions to further reduce the amount of mercury entering the Bay. The RMP is supporting this process by providing the monitoring needed to track progress.

The Guadalupe River: A Source of Mercury

The RMP and Clean Estuary Partnership (CEP) are conducting a study to quantify inputs of mercury and other contaminants from the Guadalupe River watershed. San Francisco Estuary Institute (SFEI) staff are collaborating with the US Geological Survey (USGS) and the US Department of Agriculture's Redwood Sciences Laboratory to collect data on stream flow, suspended sediment and turbidity in order to get a better understanding of the mechanisms of mercury transport in

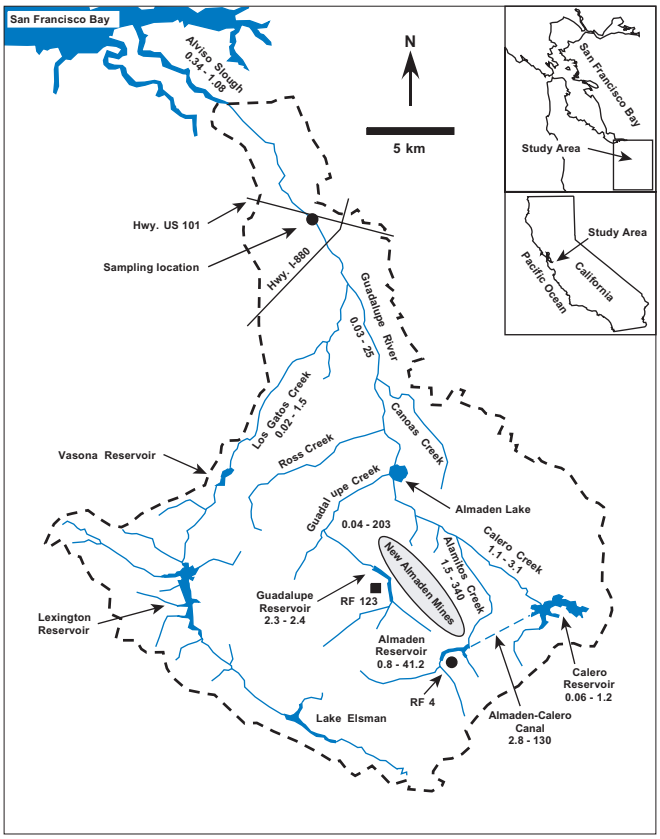


Figure 1: Map of the Guadalupe River watershed and creeks. Numbers represent measured mercury concentrations in the creek sediments (µg/g). The data were compiled from various authors.

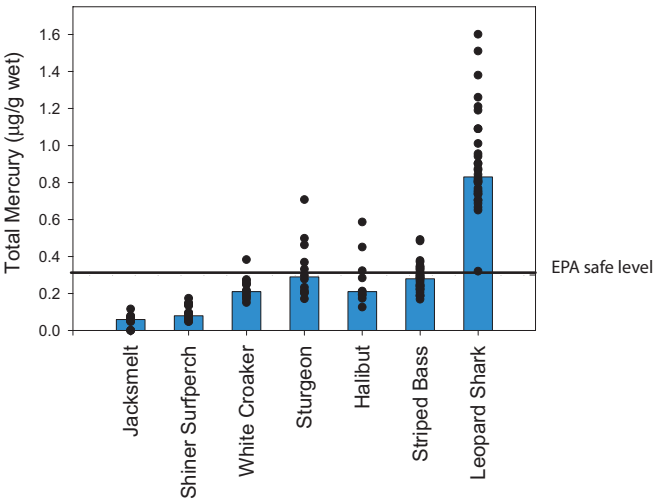


Figure 2: Mercury concentrations in various sport fish species caught from San Francisco Bay. Bars represent the average and dots represent individual sample mercury concentrations.

stormwater runoff. Contaminant sampling occurs during major storms since runoff from these events is responsible for large inputs of contaminants to the Bay. Samples are being collected from a site in the lower reach of the River in order to quantify mercury input from the entire watershed.

The results of the first year of this study (water year 2003) have led to some new theories about how mercury is transported from the watershed. Mercury concentrations generally increased over the course of a storm event **(see Figure 3).** One hypothesis for this is that the rising stage of a flood contains water primarily originating from the lower watershed since the runoff from this area will reach the sampling site first. As a flood peaks and starts to fall, water from the upper watershed dominates flow past the site. The waters from the upper watershed may contain higher concentrations of mercury, as some of the flow is runoff from the old mining area. It is also suspected that there is a rainfall threshold, both for a storm's duration and for a season, over which we start to see increasing mercury concentrations. The threshold is crossed when the soils in the watershed become saturated and can no longer absorb the rainfall. This saturation point can be the result of intense rainfall over a short period of time (6-24 hours) or the result of longer-term build-up to saturation (seasonal). Once this point has been reached, it is thought that excess water runs off and transports mercury into the tributaries and down into the Guadalupe River. Further sampling over the next two years will help to refine the understanding of the transport of mercury in the Guadalupe River.

Many sport fish, caught from San Francisco Bay, are unsafe to eat because of mercury (Hg) contamination in both water and sediments.

The sediments of the Bay are the target for the TMDL, but ultimately the goal is to reduce the mercury levels in fish so that they are safe for consumption by wildlife and humans.

Mercury Input Estimates and the TMDL

Preliminary estimates of annual mercury input to the Bay from the Guadalupe River watershed have been calculated from the first year of data. Mercury input from the Guadalupe River was estimated at 116 kg for the year. This estimate includes mercury input from all parts of the watershed, not just the mining area. This number is our best present estimate of how much mercury is transported in a year of average rainfall and streamflow. Inputs could increase or decrease in future years depending on the amount and timing of rainfall. Further study will help refine our current estimate and factor out inputs from different sources in the watershed to better assist the development of management strategies related to the TMDL. The TMDL calls for a reduction in mercury input from the mining area to just 2 kg/year within 20 years.

The RMP will continue to monitor the Guadalupe in water year 2005 with additional funding provided by the US Army Corps of Engineers and the Santa Clara Valley Water District. With three years of data, mercury inputs from the Guadalupe can be determined with more accuracy and we can better refine our understanding of the extent of remediation needed to meet the goals of the TMDL. The Guadalupe River study is a good example of how improved knowledge can aid regulators in zeroing in on the biggest and most manageable sources of contaminants to the Bay.

Continued on page 4

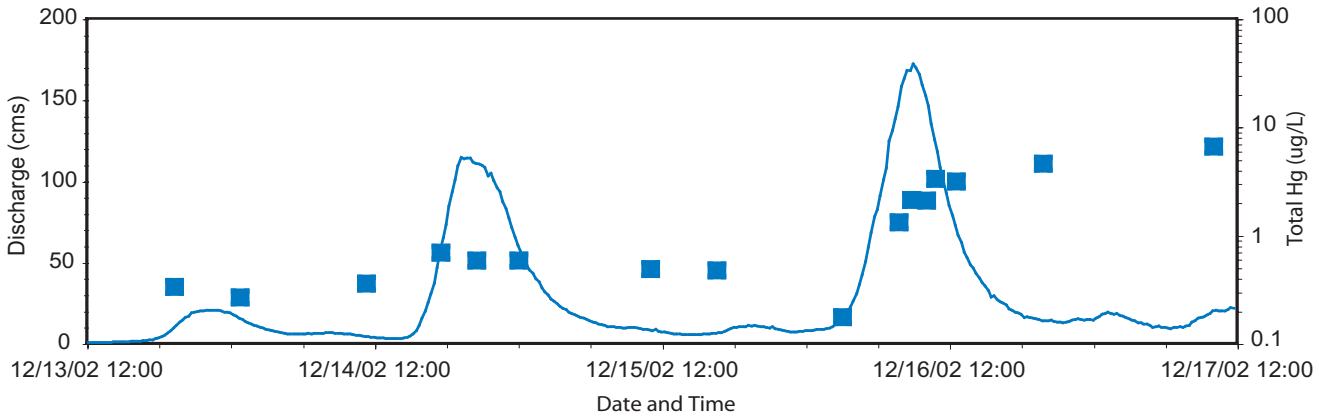


Figure 3: Mercury concentrations (squares) in Guadalupe River water (µg/L) during a winter storm. The line graph represents water discharge of the Guadalupe River in centimeters/seconds.

Guadalupe

Continued from page 3

References

Clarkson, T.W. 1992. Mercury: major issue in environmental health. *Environmental Health Perspective*. 100:31-38.

Looker, R. and B. Johnson. 2004. Mercury in San Francisco Bay: total maximum daily load (TMDL) proposed basin plan amendment and staff report. San Francisco Bay Regional Water Quality Control Board.

Schwarzbach, S., and T. Adelsbach. 2003. Assessment of Ecological and Human Health impacts of Mercury in the Bay-Delta Watershed: Draft Final Report. CALFED Bay-Delta Mercury Project.

Schwarzbach, S.E., Albertson, J.D. and C. M. Thomas. 2003. Impacts of predation, flooding and contamination on the reproductive success of the California clapper rail (*Rallus longirostris obsoletus*) in San Francisco Bay. Submitted.

Leatherbarrow, J.E., Hoenicke, R. and L.J. McKee. 2002. Results of the Estuary interface Pilot Study, 1996-1999. Final Report. San Francisco Estuary Institute. Oakland, CA.

Thomas, M.A., Conaway, C.H., Steding, D.J., Marvin-DiPasquale, M., Abu-Saba, K.E. and A.R. Flegal. 2002. Mercury contamination from historic mining in water and sediment, Guadalupe River and San Francisco Bay, California. *Geochemistry: Exploration, Environment, Analysis*. 2:1-7.

Tetra Tech. 2003. Guadalupe River Watershed Mercury TMDL Project: Draft Conceptual Model Report, Technical Memorandum 4.1. Prepared for Santa Clara Valley Water District by Tetra Tech inc. Lafayette, CA.

PFCs

Continued from page 1

their bioaccumulation in humans and wildlife. PFOA has been found in human blood and wildlife tissue at distances thousands of miles from their manufacturing site.

Two common PFCs:

- PFOA: Perfluorooctanoic acid. Used in the manufacture of fluoropolymers including DuPont's Teflon®, and in breathable, waterproof fabrics.
- PFOS: Perfluorooctane sulfonate. Used in the Scotchguard® brand of stain-resistant coatings.

Manufacturing phase-out

In May 2000, the sole manufacturer of PFCs at that time, 3M Corp., began a voluntary manufacturing phase out of these chemicals due to building evidence of their bioaccumulation in humans and wildlife. However, Dupont Corporation began production of PFOA in 2001 (Hogue, 2004). The EPA has recently announced possible human health concerns (i.e., developmental toxicity) that may be linked to low-level PFOA exposure (U.S. EPA, 2003) and is negotiating with Dupont on an investigation to identify possible sources and the extent of potential contamination (Hogue, 2004).

PFCs in wildlife

In contrast to the behavior of other halogenated organic contaminants such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), which both bioaccumulate, PFCs distribute primarily to the liver and blood and do not accumulate in fat tissue. PFOS has been found in aquatic mammals in locations around the world including the Arctic, Baltic Sea, Mediterranean Sea and the Pacific Northwest. Canadian scientists have found a fairly wide range of PFC concentrations in the livers of Arctic animals (Martin et al., 2004). Animals lower in the food web such as lake and brook trout had concentrations in the low part per billion (ppb) range (31 ppb and 39 ppb PFOS, respectively). Animals higher in the food web had higher PFC concentrations with polar bear livers having mean concentrations of 3.1 parts per million (ppm). Another study of PFOS worldwide concentrations showed that Alaskan polar bear livers had concentrations an order of magnitude lower (mean=0.35 ppm) than the Canadian study (Giesy and Kannan, 2001). In the 2001 study, PFOS was detected but not quantifiable in the livers of sea lions, seals and sea otters along the California coast.

PFCs in the environment

In water, PFCs tend to remain in solution and do not escape into the atmosphere. This property enhances their entry into the aquatic food web where they have the potential to become highly concentrated in predatory species. It is now possible to measure perfluorinated chemicals at the very low pg/L level (parts per quadrillion) in seawater or other liquid samples (e.g., blood) using very sensitive laboratory instrumentation (liquid chromatography/mass spectrometry or LC/MS). This sensitivity of detection will be important for tracking temporal trends of these contaminants in the environment.

PFCs in San Francisco Bay

PFCs are now on the radar screen of scientists and regulators. The next stage of research will involve identifying the sources of these contaminants, the transport pathway from their sources into aquatic systems and into organisms and the concentrations at which there could be potential health effects. The results from the various global studies lead us to pose the following questions concerning the San Francisco Bay: Are perfluorinated chemicals present in the Bay? And if so, are they found at concentrations of concern? As a first glimpse, the Exposure and Effects Pilot Study (EEPS) will be analyzing for PFCs in double crested cormorant eggs that were recently collected from the Bay. The RMP will consider screening for PFCs in Bay water, sediments, and other aquatic biota to determine if they are emerging contaminants of concern in the San Francisco Bay.

References Cited

Giesy, J.P., Kannan, K., Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science and Technology*, 2001, 35:1339-1342.

Hansen, K.J., Clemen, L.A., Ellefson, M.E., Johnson, H.O., Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environmental Science and Technology*, 2001, 35, 766-770.

Hogue, C. Perfluorinated pollutant puzzle: PFOA is found in human blood but sources of this persistent compound remain elusive. *Chemical and Engineering News*. August, 2004.

Kannan, K., Corsolini, S., Falandysz, J., Oehme, G., Focardi, S., Giesy, J.P., Perfluorooctanesulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from Coasts of the Baltic and the Mediterranean Seas. *Environmental Science and Technology*, 2002a, 36, 3210-3216.

Kannan, K., Newsted, J., Halbrook, R.S., Giesy, J.P., Pefluorooctanesulfonate and related fluorinated hydrocarbons in mink and river otters from the United States. *Environmental Science and Technology*, 2002b, 36, 2566-2571.

Martin, J.W., Smithwick, M.M., Braune, B.M., Hoekstra, P.F., Muir, D.C.G., Mabury, S.A., identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environmental Science and Technology*, 2004, 38, 373-380.

U.S. EPA. Preliminary risk assessment of the developmental toxicity associated with exposure to perfluorooctanoic acid and its salts. Office of Pollution Prevention and Toxics, Risk Assessment Division, 2003.