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LEHR Superfund Stormwater Runoff and Putah Creek Mercury Issues

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Stormwater runoff from the University of California, Davis/U.S. Department of Energy Laboratory for Energy-Related Health Research (UCD/US DOE LEHR) Superfund site located on the University of California campus in Davis, California, has been found to contain over 500 ng/L of total recoverable mercury, which is about ten times the California Toxics Rule criterion. This stormwater runoff is discharged to Putah Creek, which is Clean Water Act Section 303(d) listed as impaired for excessive mercury bioaccumulation in edible fish. A discussion is presented on the potential impact of the mercury in stormwater runoff from LEHR leading to excessive bioaccumulation of mercury in Putah Creek fish. The mercury in the stormwater runoff is derived from former flooding of the soils near the creek, which contains mercury derived from abandoned upstream mercury mines located in the Coast Range Vaca Hills to the west of LEHR. The implications of this situation for implementing a Total Maximum Daily Load (TMDL) to control mercury in stormwater runoff to Putah Creek are presented. © *2009 Wiley Periodicals, Inc.*

INTRODUCTION

Studies have been conducted since the mid-1990s on the occurrence of mercury in fish in Putah Creek. The headwaters of Putah Creek are in the Vaca Hills, upstream of Lake Berryessa (Exhibits 1 and 2). Putah Creek is a tributary of the Yolo Bypass, which, in turn, is a tributary of the Sacramento San Joaquin Delta (Delta) in the Central Valley of California. Some of the fish in the Delta, Yolo Bypass, Putah Creek, and many other Delta tributaries contain sufficient concentrations of mercury to pose a health hazard to those who eat the fish. The excessive level of mercury in edible fish is, in fact, one of the most significant public health–related water-quality impairments of the Delta and many of its tributaries, and is also of concern, as it may impact the reproduction of fish-eating birds. Information on the excessive mercury bioaccumulation of mercury in Central Valley fish is available at the Central Valley Regional Water Quality Control Board (CVRWQCB) at http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/index.shtml.

Mercury builds to excessive levels in fish by bioaccumulation of it through the aquatic food web. Mercury in various forms is converted into methyl mercury at the sediment/water interface; that form is taken up by aquatic organisms and is further accumulated in organisms that consume them. In order to control the bioaccumulation of mercury in edible fish, the sources of mercury that bioaccumulate in fish and other aquatic

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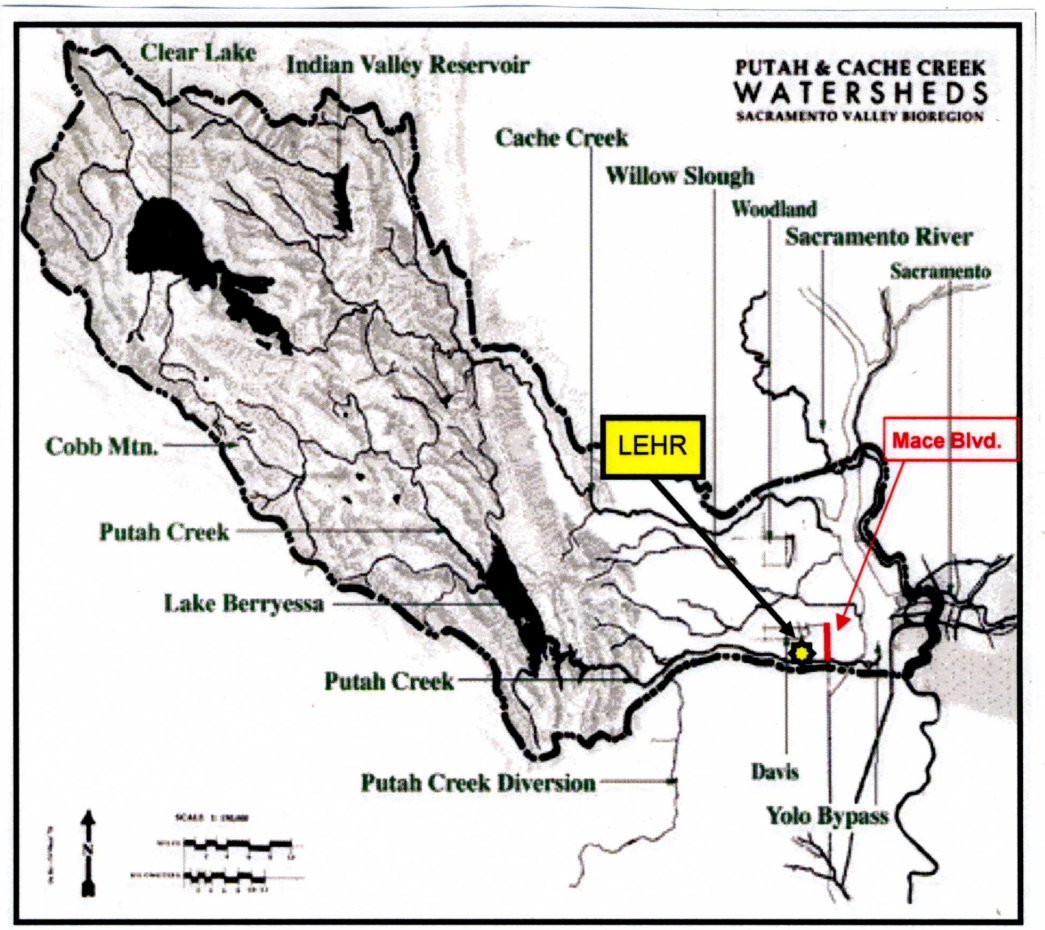

Adapted from UCD Putah-Cache Bioregion Project: UCD Davis, http://bioregion.ucdavis.edu/where/featrmap.html

Exhibit 1. Map of Putah Creek Watershed

life must be defined. As discussed further below, abandoned mercury mines in the headwater area of Putah Creek contribute mercury to Putah Creek and its upstream tributaries.

PREVIOUS STUDIES

The authors' interest in the bioaccumulation of mercury in Putah Creek fish began in the mid-1990s when Dr. Lee became U.S. Environmental Protection Agency Superfund Technical Assistant Grant (TAG) technical advisors to the Davis South Campus Superfund Oversight Committee (DSCSOC) on the adequacy of the investigation/remediation of the University of California, Davis/U.S. Department of Energy Laboratory for Energy-Related Health Research (UCD/US DOE LEHR) national Superfund site on the UCD campus in Davis, California. Information on the LEHR Superfund site and the DSCSOC is available at http://www.gfredlee.com/DSCSOC/DSCSOC.htm.

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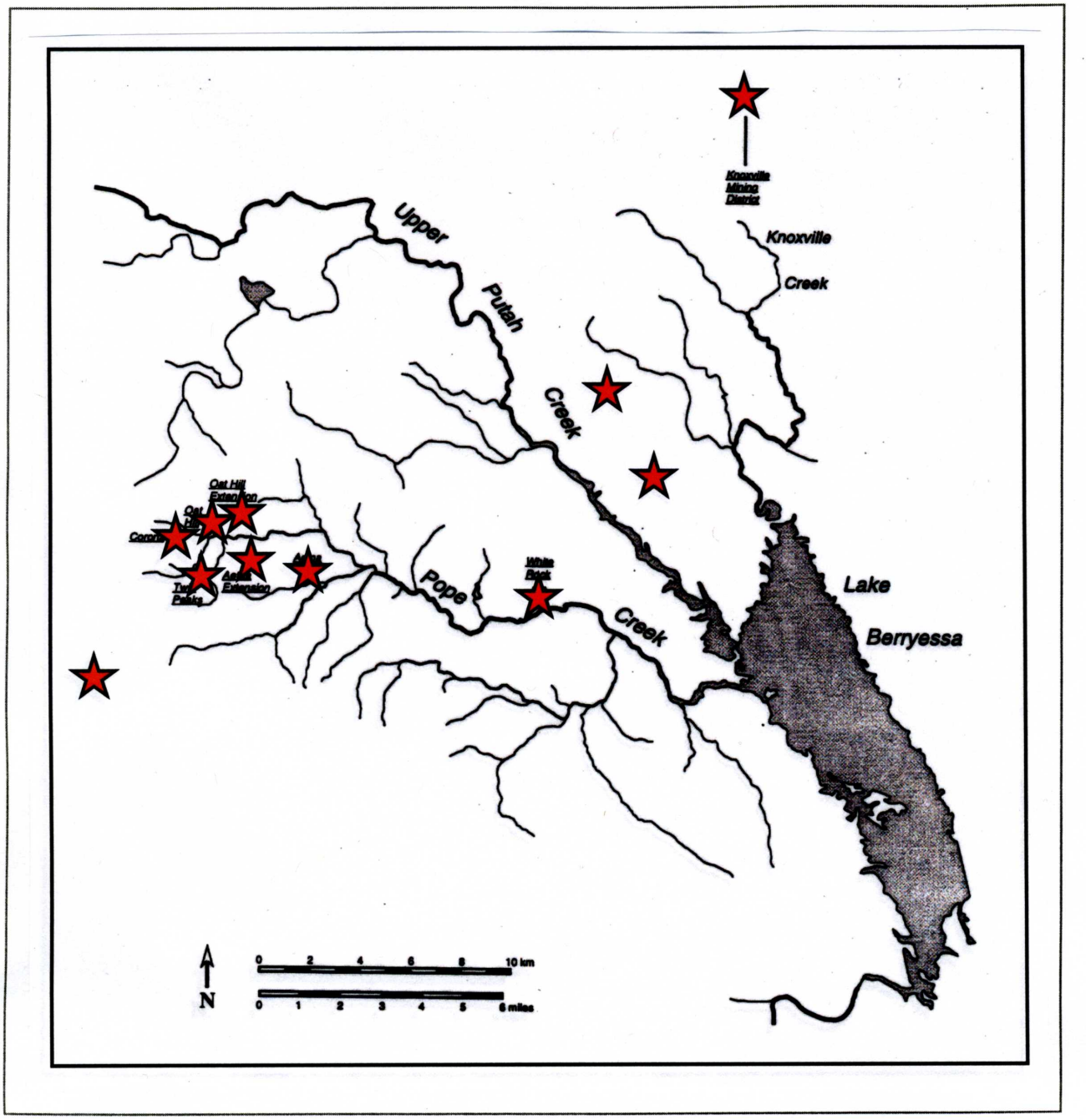

Exhibit 2. Portions of Upper Putah Creek Watershed showing primary abandoned mercury mines (Slotton et al., 1999)

In his early work as the TAG advisor to the DSCSOC, Dr. Lee found that inadequate attention had been given to the bioaccumulation of waste chemicals in runoff from the LEHR site in Putah Creek fish, which are used by some people as food (Lee & Jones-Lee, 1998).

In 1995, the DSCSOC requested that the Agency for Toxic Substances and Disease Registry (ATSDR) determine, as part of its Public Health Assessment of the LEHR Superfund site, whether Putah Creek fish near LEHR contained concentrations of

Exhibit 3. Mercury concentration in largemouth bass from Putah Creek—October/November 1997 (from ATSDR, 1997)

Fish Size	Mean ± SD (mg of Hg/kg)
Small (<415 g)	0.17 ± 0.06
Medium (540–730 g)	0.32 ± 0.14

Exhibit 4. Mercury concentrations in Putah Creek fish 1998–1999 (Slotton & Ayers, 1999)

Fish Type and Location	Mean ± SD (mg of Hg/kg) [no. fish]
Trout—Near Lake Berryessa	0.85 ± 0.03 [11]
Bluegill—Upstream of UCD	0.21 ± 0.06 [7]
Bluegill—Downstream of UCD	0.2 ± 0.08 [5]
Largemouth Bass—Downstream of UCD	0.46 ± 0.23 [6]
Roach—Upstream of Lake Berryessa (only small fish)	Range: 0.08–0.17

hazardous chemicals that could pose a public health threat to those who consume those fish. The initial 1996 ATSDR/US EPA fish sampling of Putah Creek fish found that largemouth bass taken from Putah Creek near the LEHR site contained 0.11 to 0.81 mg/kg of Hg (wet weight; ATSDR, 1997). That level was of sufficient concern that the ATSDR recommended that the area of Putah Creek be posted as having unsafe fish, but no action was taken. The ATSDR/US EPA data for mercury in Putah Creek fish collected in the fall of 1997, summarized in Exhibit 3, further established that some fish in Putah Creek near Davis, California, contained mercury at levels that pose a threat to human health (ATSDR, 1998). Lee (1998a, 1998b, 1999) discussed those findings and issues for the DSCSOC.

Slotton and Ayers (1999) subsequently found that some types of fish throughout Putah Creek below Lake Berryessa contained excessive levels of mercury. Slotton et al. (1999) also found elevated concentrations of mercury in small fish taken from tributaries of Lake Berryessa in the mercury mine area. A summary of the Slotton data on fish mercury concentrations in Putah Creek fish in the late 1990s is presented in Exhibit 4.

The findings of excessive bioaccumulation of mercury in fish from Putah Creek caused the DSCSOC to request that the Central Valley Regional Water Quality Control Board list Putah Creek as a Clean Water Act Section 303(d) water-quality-limited waterbody. The listing of this waterbody in 2003 by the CVRWQCB/State Water Resources Control Board (SWRCB)/US EPA requires that all National Pollutant Discharge Elimination System (NPDES)-permitted discharges of wastewaters and some stormwaters not exceed the water standard/objective for mercury.

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REGULATORY STANDARD FOR MERCURY

The current water-quality standard for mercury is the California Toxics Rule (CTR) criterion of 50 ng/L (nanograms/liter) of total recoverable mercury. As discussed by the US EPA, at the time of promulgation of that CTR criterion, the 50 ng/L value was established for regulatory expedience; it was recognized that achieving that level in receiving water would not prevent the excessive bioaccumulation of mercury in fish. It is believed that excessive bioaccumulation will be minimized if concentrations of total recoverable mercury in water are maintained below about 5 ng/L.

As discussed in DSCSOC reports (http://www.gfredlee.com/dscsoc/doc.htm), concentrations of total recoverable mercury in stormwater runoff from the LEHR site have been found to repeatedly exceed 500 ng/L. This has caused the CVRWQCB to require that UCD develop stormwater runoff management programs in an attempt to keep the mercury concentration in LEHR site runoff below the current 50 ng/L CTR criterion. When the CTR value is adjusted to provide better protection against excessive bioaccumulation, the target Hg level in the runoff will need to be adjusted to about 5 ng/L of Hg. At this time, UCD is attempting to manage the Hg-containing runoff from the LEHR site to Putah Creek by placing straw bales/rolls in front of stormwater inlets. It has been the experience of the authors that such measures will not be adequate to prevent violations of excessive mercury discharges in stormwater runoff from the LEHR site.

FISH-CONSUMPTION GUIDANCE

The California Office of Environmental Health Hazard Assessment (OEHHA, 2006) published concentrations of mercury in legal and/or edible-size fish and shellfish from Putah Creek and Lake Berryessa (Exhibits 5 and 6), and issued fish-consumption guidelines for fish from Putah Creek upstream and downstream of Lake Berryessa, as well as within the lake (http://oehha.ca.gov/fish/so_cal/putahcreek.html).

It is believed that excessive bioaccumulation will be minimized if concentrations of total recoverable mercury in water are maintained below about 5 ng/L.

CALFED MERCURY STUDIES

In August 2008, the final reports from the multiyear, CALFED-supported mercury project were released (Stephenson et al., 2008). That project included monitoring of Putah Creek water for total recoverable mercury and methyl mercury at Mace Blvd. The location of Putah Creek at Mace Blvd. is shown in Exhibit 1. Exhibit 7 shows that the total recoverable mercury concentrations measured in Putah Creek in that study averaged 24 ng/L, with some high-flow values exceeding 100 ng/L. The methyl mercury concentration in Putah Creek was found to be about 0.15 ng/L.

CVRWQCB Senior Scientist Dr. Chris Foe (personal communication, 2008) indicated that the CVRWQCB staff will propose a fish tissue–based Basin Plan amendment for mercury as follows:

- Our proposed basin plan amendment tissue objectives for large trophic level 3 and 4 fish are 0.08 and 0.24 ppm wet weight. This will allow people to safely eat a meal a week.

Exhibit 5. Summary mean Hg concentrations for legal and/or edible-size fish and shellfish from Putah Creek (OEHHA, 2006)

Species	Hg (ppm)*
Channel Catfish	**0.15**
White Catfish	**0.14**
Catfish	**0.14**
Largemouth Bass	**0.46**
Sacramento Blackfish	**0.09**
Sacramento Sucker	**0.16**
Bluegill	**0.14**
Green Sunfish	0.17
Redear Sunfish	0.15
Hybrid Sunfish	0.19
Sunfish	**0.14**
Carp	**0.18**
Rainbow Trout	0.08
Brown Trout	0.06
Trout	**0.07**
White Crappie	0.28
Black Crappie	0.33
Crappie	0.29
Hitch	0.09
Sacramento Pikeminnow	0.50
Crayfish	**0.21**

***BOLD:** Samples with Sufficient Numbers.

Exhibit 6. Summary mean Hg concentrations for legal and/or edible-size fish from Lake Berryessa (OEHHA, 2006)

Species	Hg (ppm)*
Channel Catfish	**0.52**
White Catfish	**0.77**
Catfish	**0.56**
Largemouth Bass	**0.75**
Smallmouth Bass	0.93
Black Bass	**0.76**
Rainbow Trout	**0.17**
Chinook (King) Salmon	**0.48**
Bluegill	0.39
Carp	0.54

***BOLD:** Samples with Sufficient Numbers.

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Exhibit 7. CALFED mercury project concentrations of Hg in water (based on data in Stephenson et al., 2008)

Location	Concentration Mean ± SD (ng Hg/L)
Putah Creek at Mace Blvd. (63 samples, 2003–2006)	23.82 ± 16.64
Creek During Some High Creek Flows	100
MeHg in Putah Creek	0.15 ± 0.03
MeHg in Cache Creek	0.26 ± 0.09

MeHg is methyl mercury.

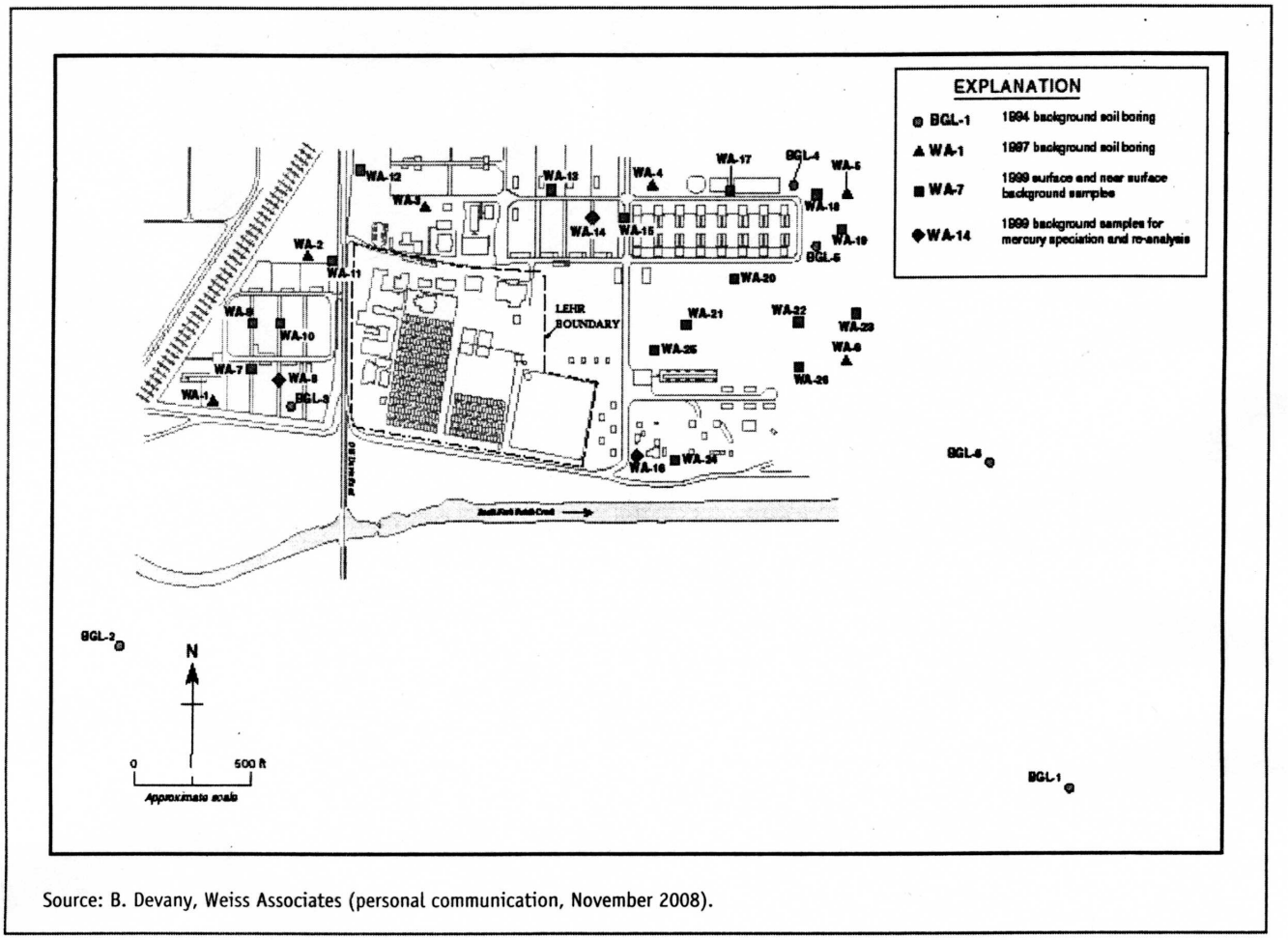
- We are also proposing a small fish (up to 50 mm length) tissue objective of 0.03 ppm wet weight. This is to protect fish eating wildlife. The small fish number comes from recommendations by the US FWS (United States Fish and Wildlife Service) to protect, among other animals, least terns. There is a least tern nest colony near Antioch.
- You can read the details in our TMDL report to the US EPA. The unfiltered methyl mercury concentrations needed to meet these tissue numbers are site-specific. The value for the Delta appears to be around 0.06 ng/L.

From this, it appears that the edible flesh of some fish in Putah Creek would be expected to contain excessive mercury since the mercury concentrations in Putah Creek are well above the proposed Basin Plan water-quality objective for mercury. Information on the CVRWQCB-proposed TMDL for the Delta may be found at http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/index.shtml.

LEHR SITE AND AREA SURFACE SOIL MERCURY

Exhibit 8 (a sample location figure) and Exhibits 9 and 10 (data tables) show that surface soils at and near the LEHR site typically contain mercury concentrations of 1 to 2 mg/kg of Hg, with some measurements somewhat higher than these concentrations. The mercury concentrations in the deeper soils near the LEHR site were typically a factor of five to ten times less than those in the surface soils.

The elevated mercury concentrations in the surface soil are likely related to the historic periodic flooding of the area by high flows of Putah Creek. Prior to the mid-1940s, Putah Creek used to flood the lands near the channel. Those flood waters brought particulate-associated mercury with them from the upstream mining areas, which was deposited in the floodplain. This flooding was reduced in the mid-1940s when high levees were constructed as part of the Corps of Engineers' Putah Creek project. Since the completion of the Morrison Dam on Putah Creek forming Lake Berryessa in 1957, particulate mercury derived from the erosion of mine tailings at the mercury mines has been trapped in Lake Berryessa. Thus, at this time the source of the mercury that is



Source: B. Devany, Weiss Associates (personal communication, November 2008).

Exhibit 8. Map of the mercury near LEHR surface soil sampling locations (Dashed area is LEHR site)

Exhibit 9. Hg concentrations in near-LEHR area soils

Sample Depth	Mean ± SD (mg/kg of Hg)
Surface	1.3 ± 1.1
2 ft	1.9 ± 1.3
3–4 ft	0.25 ± 1.7
8–22 ft	0.16 ± 0.16
30–40 ft	0.19 ± 0.09

Source: B. Devany, Weiss Associates (personal communication, November 2008).

bioaccumulating in Putah Creek fish is mercury originally derived from the mines upstream of Lake Berryessa prior to the construction of the dam and now accumulated in the Putah Creek stream sediments and banks, as well as mercury that has been added to the creek from runoff from the near-creek areas.

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Exhibit 10. Average concentrations of Hg in soil at selected locations at LEHR site

	Soil Depth: ≤2 ft			Soil Depth: >2–4 ft		
		Hg Concentration (mg/kg of Hg)			Hg Concentration (mg/kg of Hg)	
Area	No. Samples	Mean	SD	No. Samples	Mean	SD
Eastern Dog Pens	25	1.7	3.1	19	1.7	2.5
Western Dog Pens	163	1.1	0.92	28	1.1	1.1
Landfill No. 1	11	1.4	0.81	2	0.6	0.57
Landfill No. 2	11	0.5	0.29	5	0.93	0.69
Landfill No. 3	9*	1.1	0.8	1	0.75	n/a
Non OU Area	71	0.89	0.77	18	1.2	0.72
Old Davis Road Stormwater Runoff Ditch	5	0.8	0.59	0		

Source: B. Devany, Weiss Associates (personal communication, November 2008).

* One anomalous sample (49.5 mg/kg) excluded.

CONTROL OF MERCURY IN PUTAH CREEK FISH

The CVRWQCB has scheduled the development of a TMDL for control of mercury in Putah Creek by 2015. As part of implementing this TMDL, it will be necessary for studies to be conducted to determine if there are locations along Putah Creek that are major sources of the total recoverable and methyl mercury currently in the creek. Similarly, studies need to be conducted to define the contributions of mercury to Putah Creek from the surface soils along Putah Creek, including at and near the LEHR site, and within the city of Davis. Such studies could define hot spots that need attention for mercury control as part of implementing the TMDL. Additional information on the implementation of this TMDL is provided below.

FATE OF MERCURY IN PUTAH CREEK

An issue of concern is the fate of the mercury that is transported downstream in Putah Creek to the areas near the Yolo Bypass. Exhibit 7 showed that the average concentration of mercury in Putah Creek waters at Mace Blvd., several miles upstream of the point at which Putah Creek enters the Yolo Bypass (see Exhibit 1), was about 24 ng/L between 2003 and 2006. Between Mace Blvd. and the Yolo Bypass, agricultural interests divert Putah Creek water to irrigate crops. According to Dave Feliz (personal communication, 2008), during Putah Creek high flows, creek waters flood agricultural lands west of the Bypass. Both the irrigation diversion and the flooding cause mercury to be deposited on agricultural lands. Some of that mercury is transported from the irrigated lands in the tail water discharges to the Yolo Bypass.

The flow into parts of the Yolo Bypass is controlled by the Los Rios Check Dam. The California Department of Fish and Game (DFG) et al. (2008) discussed the influence of

that check dam on Putah Creek flow into the Yolo Bypass. Seasonally, that dam is operated to increase the elevation of Putah Creek to assist in the diversion of water from the creek for irrigation. During the fall/winter, the boards controlling the spillway elevation at the dam are removed to facilitate the migration of Chinook salmon and steelhead trout from the Yolo Bypass to upstream Putah Creek for spawning. When the boards have been removed, the flow to Putah Creek is via a channel to the Toe Drain. When the boards are in place, some of the Putah Creek water and its associated mercury is diverted into the Yolo Bypass near its west side.

Chris Foe of the CVRWQCB (personal communication, 2008) suggested the development of a settling basin to settle particulate mercury in Putah Creek water before it enters the Yolo Bypass. A major issue is the development of a fund for this and an approach for the removal and disposal of the mercury-containing sediments from the settling basin.

The implementation of the TMDL for controlling mercury in Putah Creek will need to include consideration of the potential significance of the mercury in stormwater runoff from the areas along Putah Creek that used to flood during the periods of high Putah Creek flows.

MERCURY TMDL IMPLEMENTATION

The implementation of the TMDL for controlling mercury in Putah Creek will need to include consideration of the potential significance of the mercury in stormwater runoff from the areas along Putah Creek that used to flood during the periods of high Putah Creek flows. Further, it will need to address the fact that urban areas such as Davis, California, are not required to monitor stormwater runoff and, therefore, are not required to control discharges of mercury to Putah Creek in stormwater runoff. At the LEHR site, runoff of stormwater from the east (LEHR) side of Old Davis Road is regulated; it is not to contain mercury in excess of the CTR criterion. However UCD's Phase II NPDES stormwater permit does not require that the stormwater runoff from the west side of Old Davis Road (which has the same elevated levels of mercury in surface soils as the LEHR side) be monitored for any pollutant, including mercury, although samples of that stormwater have been found to contain more than 500 ng/L of total recoverable mercury.

A similar situation exists for the regulation of mercury in tail water discharges and stormwater runoff from irrigated agriculture. The CVRWQCB does not require monitoring for mercury in streams impacted by runoff/discharges from irrigated lands. Since many of the waters that are used by irrigated agriculture contain mercury, the irrigated agriculture tail water discharges and stormwater runoff are sources of mercury. At this time, there is no information on how much of the mercury that becomes associated with irrigated lands subsequently contributes to the excessive bioaccumulation of mercury in waters downstream of runoff/discharge from that land. The changes in the behavior of soil-associated mercury and transformations of mercury that occur on the agricultural lands need to be investigated to determine if additional mercury bioaccumulation problems occur because of the discharge of mercury from irrigated lands.

Under the Phase II Stormwater NPDES permits and in accordance with the US EPA requirements for implementing Phase II permits, the CVRWQCB is not, at this time, requiring that permittees monitor stormwater runoff for violations of water-quality standards/objectives, such as for mercury discharges to Putah Creek. However with the implementation of the Putah Creek mercury TMDL in 2015, the CVRWQCB will have the regulatory authority to require Phase II permittees to prevent violations of water-quality objectives that are considered in the TMDL. This requirement could also

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apply to discharges from agricultural lands, such as those from areas of lower Putah Creek, where mercury-containing water from the creek is used for irrigation of crops and where lands are flooded during periods of high creek flow.

Photographs of Putah Creek are available at http://www.gfredlee.com/SJR-Delta/PutahHgMinesli.pdf.

ACKNOWLEDGMENTS

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