

Photograph (front cover): Biologist launching a boat in the Cache Creek watershed, California, for the purpose of collecting aquatic organisms for mercury analysis.

Summary and Synthesis of Mercury Studies in the Cache Creek Watershed, California, 2000–01

By Joseph L. Domagalski, Darell G. Slotton, Charles N. Alpers, Thomas H. Suchanek,
Ronald Churchill, Nicolas Bloom, Shaun M. Ayers, and John Clinkenbeard

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Conversion Factors and Datum

CONVERSION FACTORS)

	Multiply	By	To obtain
	gram (g)	0.03527	ounce, avoirdupois
	gram per day (g/d)	0.03527	ounce, avoirdupois, per day
	gram per year (g/yr)	0.03527	ounce, avoirdupois, per year
	kilogram (kg)	2.205	pound, avoirdupois
	hectare (ha)	2.471	acre
	kilogram per day (kg/d)	2.205	pound, avoirdupois, per day
	kilogram per year (kg/yr)	2.205	pound, avoirdupois, per year
	metric ton per year (t/yr)	1.102	ton per year
	millimeter (mm)	0.03937	inch
	square kilometer (km ²)	0.3861	square mile
	square meter (m ²)	10.76	square foot
	square kilometer (km ² /yr)	0.3861	square mile per year

CHEMICAL-CONCENTRATION INFORMATION

Concentrations in water are given in nanograms per liter (ng/L); one million nanograms per liter is equivalent to 1 milligram per liter (mg/L). Concentrations in soil and rock are given in milligrams per kilogram (mg/kg) or the equivalent units of parts per million (ppm). Concentrations in fish tissue are given in micrograms per gram ($\mu\text{g/g}$) or milligrams per kilogram (mg/kg), or the equivalent units of parts per million. Concentrations in aquatic insects are given in nanograms per gram (ng/g) or the equivalent units of parts per billion (ppb).

ABBREVIATIONS

μm , micrometer

CALFED, California Federal Bay–Delta Drinking Water Program (a Cooperative Program of State and Federal Agencies)

CH_3Hg^+ , methylmercury

Hg, mercury

Hg(0), elemental mercury

Hg^{++} , oxidized mercury (mercuric ion)

HCl, hydrochloric acid

HOAc, acetic acid

HNO_3 , nitric acid

KOH, potassium hydroxide

MeHg, methylmercury

NAWQA, National Water-Quality Assessment (Program)

RUSLE2, Revised Universal Soil Loss Equation

SSE, sequential-selective extraction

TMDL, total maximum daily load

USEPA, U.S. Environmental Protection Agency

USGS, U.S. Geological Survey

Summary and Synthesis of Mercury Studies in the Cache Creek Watershed, California, 2000–01

By Joseph L. Domagalski¹, Darell G. Slotton², Charles N. Alpers¹, Thomas H. Suchanek³, Ronald Churchill⁴, Nicolas Bloom⁵, Shaun M. Ayers², and John Clinkenbeard⁴

Introduction

This report summarizes the principal findings of the Cache Creek, California, components of a project funded by the CALFED Bay–Delta Program entitled “An Assessment of Ecological and Human Health Impacts of Mercury in the Bay–Delta Watershed.” A companion report summarizes the key findings of other components of the project based in the San Francisco Bay and the Delta of the Sacramento and San Joaquin Rivers. These summary documents present the more important findings of the various studies in a format intended for a wide audience. For more in-depth, scientific presentation and discussion of the research, a series of detailed technical reports of the integrated mercury studies is available at the following website:

<http://oer.tamug.tamu.edu/calfed/>.

The overall study was a scientific cooperation and collaboration among several federal and state agencies and universities and one commercial laboratory. These agencies included the U.S. Geological Survey (USGS), the U.S. Fish and Wildlife Service, the California Department of Fish and

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Game, the California Central Valley Regional Water Quality Control Board, the California Geological Survey, the University of California Davis, the San Jose State University Foundation, and Frontier Geosciences, Inc.

Environmental Setting

The Cache Creek watershed encompasses about 2,900 km² (square kilometers) within the Coast Ranges and Sacramento Valley of northern California ([fig. 1](#)) (Domagalski and Dileanis, 2000). The watershed has a diverse geography consisting of low hills and fertile farmland and some exceptional features, including Clear Lake, which is one of the oldest natural lakes in North America. The lake supports a diverse tourism industry and hosts several bass fishing tournaments of regional, state, and national importance. The larger streams, Cache Creek and the North Fork of Cache Creek, are popular white-water rafting and kayaking streams in years having sufficient runoff. A resort that includes hot springs from a geothermal source, Wilbur Springs, hosts a year-round spa and hotel. The valley part of the watershed (downstream of Rumsey) has a predominantly farming economy. This farming region, known as the Capay Valley, supports orchards as well as established farms that supply organic produce to specialty stores in both the San Francisco Bay area and Sacramento.

The diverse geology of the area includes sedimentary, metamorphic, and volcanic rocks. Volcanoes in the area are considered dormant; however, numerous hot springs, as well as commercial geothermal energy production, occur in the area. Geothermal waters are frequently associated with ore-forming processes. An important ore-forming process within the Cache Creek watershed was the emplacement of economically recoverable deposits of mercury.

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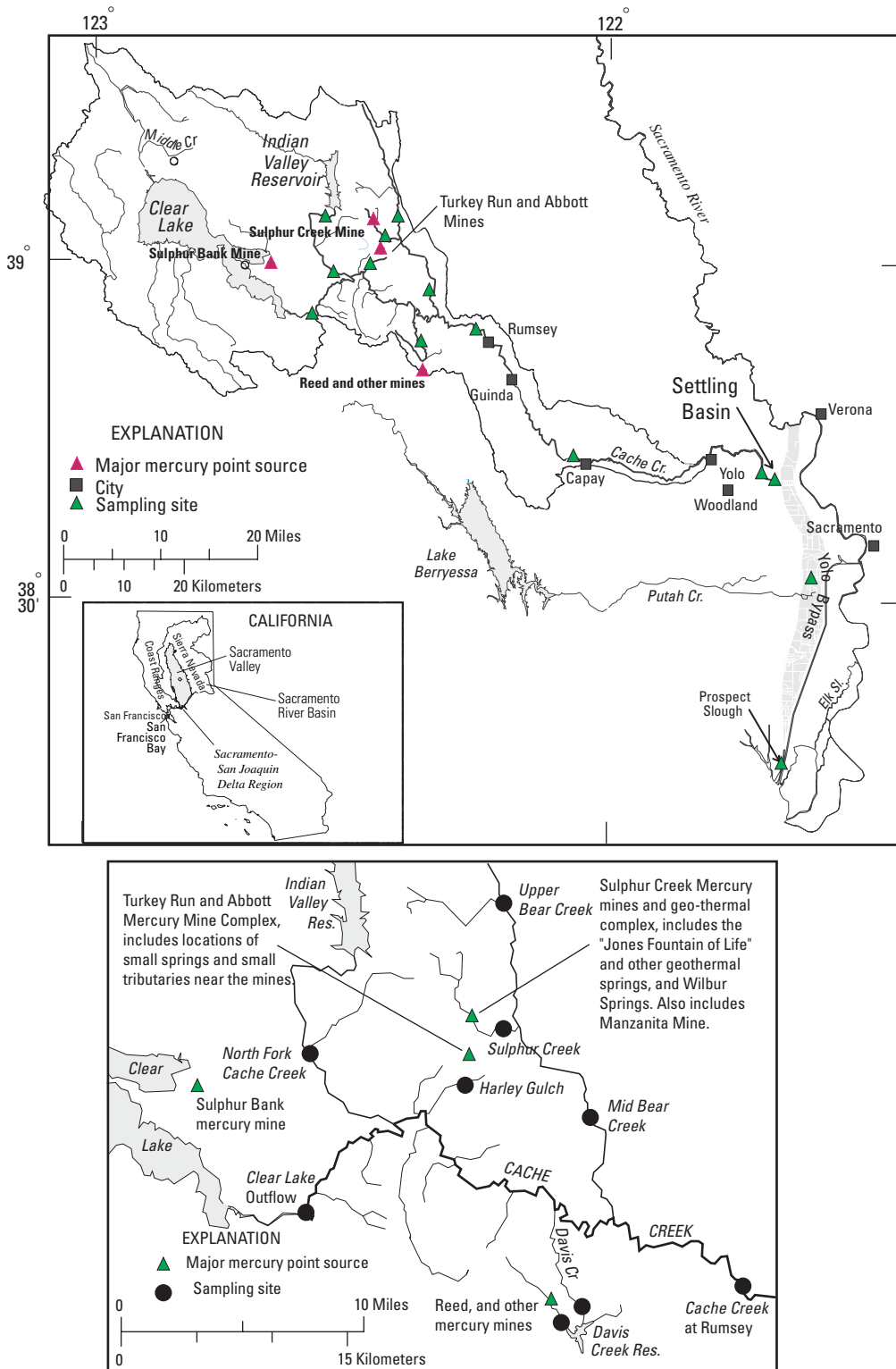


Figure 1. The Cache Creek, California, watershed, mercury sampling sites, and primary known mercury point sources.

The mercury deposits in the Cache Creek area, and elsewhere in the Coast Ranges, were actively mined in the latter part of the 19th century after the discovery of the gold deposits of the Sierra Nevada; mercury production continued until the 1950s (Domagalski and others, 2000). Mercury, in the elemental form known as quicksilver, has long been useful in recovering gold from lode gold and silver ores and placer deposits. The miners of the Sierra Nevada needed quicksilver, and the mercury deposits of the Coast Ranges were quickly developed to fill that need. Peak mercury production in California occurred in 1877 when the various mines of the California Coast Ranges produced approximately 2,776,000 kg (kilograms) of quicksilver (Bradley, 1918).

Statement of the Problem

Very few, if any, environmental constraints were placed on the mercury mines and mineral-processing facilities in those times. In general, hard-rock mining activities leave behind waste materials including waste rock and mill tailings. Recovery of mercury was different from that of other metals in that the quicksilver was commonly extracted by heating or retorting the ore. The residual material from the retorting process is known as calcined tailings. Mercury-mining waste may become an environmental problem when it contacts water and is mobilized and transported away from the mine sites, where it may be acted upon biologically, such as by methylating bacteria. The contaminants become a societal problem if they affect the beneficial uses of receiving bodies of water by causing toxicity to aquatic organisms or if they bioaccumulate in fish to levels that are potentially harmful to people who consume the fish. Mercury is a potent neurotoxin and can cause adverse effects, especially to young children and developing fetuses.

The bioaccumulation of mercury in fish is one of the most widely recognized environmental problems of the current era. Nearly every State in the country has one or more water bodies that have fish with unsafe levels of mercury. Fish-consumption advisories have been posted for certain species in about 12 water bodies in California, including Clear Lake and San Francisco Bay. The U.S. Environmental Protection Agency (USEPA) has proposed a criterion of 0.3 mg/kg (milligrams per kilogram [or parts per million, ppm]) of methylmercury (the bioaccumulative form of mercury) in wet/fresh edible fish tissue (primarily fillet muscle) as a basis of deciding which water bodies are considered impaired because of mercury contamination. Water bodies that have a significant fraction of fish over the criterion would require management using a total maximum daily load (TMDL) plan to bring the levels of mercury down.

Of all the possible contaminants for which TMDL plans are being developed, mercury is arguably the most difficult for the regulatory community. Mercury can be transported in air with subsequent wet or dry deposition to water bodies; by river systems, dissolved in water or attached to sediment or biological particles; and in the tissues of aquatic organisms. Methylmercury bioaccumulates to proportionally higher concentrations as it moves up the aquatic food chain, a process known as biomagnification. As a consequence, tissue concentrations are greatest in predatory (fish-eating) fish and in fish consumers. Because of the atmospheric transport and deposition of mercury, many lakes in the midwestern and eastern United States have elevated mercury in fish even though there are no point sources of mercury in the watershed and no likely nearby geological sources.

Before mercury can bioaccumulate, the inorganic form must be converted to the organic (methylmercury, CH_3Hg^+) form. Methylmercury can also degrade to inorganic mercury, which later may be converted back to methylmercury. The processes of mercury methylation and demethylation are controlled primarily by bacterial activity; however, transformation processes and the environmental factors that control their rates are only partly understood.

In the Cache Creek watershed, both anthropogenic sources of inorganic mercury (abandoned mine sites) and natural sources (geothermal springs and native soils) contribute mercury to the environment (Rytuba, 1996). Superimposed on these point-source inputs is the general atmospheric input from the global mercury cycle. There is no question that the Cache Creek watershed exports significant amounts of inorganic mercury to the Bay-Delta region. Initial studies by the California Regional Water Quality Control Board (Foe and Croyle, 1998) have shown that in very wet years as much as 1,000 kg of inorganic mercury can be exported. Studies by University of California Davis (Slotton and others, 2001) in one small tributary watershed have documented the annual erosion and transport of as much as 225 kg of mercury from a single mid-sized abandoned mercury mine during large storm years. The USGS confirmed that Cache Creek is a significant source of inorganic mercury on the basis of the studies of the National Water-Quality Assessment (NAWQA) Program during 1996–98 (Domagalski, 2001). Much less is known about the fate of this inorganic mercury, either after deposition in the Cache Creek watershed or following transport and deposition in the Yolo Bypass and Bay-Delta. However, early studies by University of California Davis indicate that elevated levels of mercury bioaccumulation occurred in the watershed in relation to the upstream point sources (Slotton and others, 1997), as well as downstream in the part of the Delta influenced by Cache Creek inflows (Slotton and others, 2000).

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The regulatory community and other stakeholders must decide if mine remediation or even control of natural sources of mercury, or other constituents such as sulfate, within the Cache Creek watershed will result in an eventual reduction of fish mercury concentrations in downstream water bodies. The phrase “eventual reduction” is used because of the long time-frame expected for mercury to be removed from the regional system as a result of a localized reduction in an anthropogenic or natural source input.

Accordingly, CALFED commissioned the present study, which has brought together a diverse group of researchers to explore and document the locations and potential remediation of mine wastes; to document the current loads of both total mercury and methylmercury from major anthropogenic and natural point sources; to test the potential for exporting sediment that contains mercury, which transform to methylmercury in downstream environments; and to explore the factors controlling bioaccumulation of mercury in aquatic organisms within the Cache Creek watershed. Some key questions that were addressed are:

- What are the annual loads of mercury and methylmercury from abandoned mine sites and geothermal areas, and which sites might be managed to reduce the loads to downstream regions?
- What are the forms of the transported mercury in the Cache Creek watershed and are those forms subject to methylation in either the Cache Creek watershed or downstream waters?
- Is mercury methylation and bioaccumulation of mercury occurring in the Cache Creek watershed and what are the consequences to human and ecological health in that watershed and downstream in the Bay–Delta?

A more thorough understanding of these relations and inter-relations will allow the regulatory agencies and stakeholder groups to evaluate the costs and benefits of remedial activities in the Cache Creek watershed and how these activities would contribute to the effectiveness of a TMDL plan for the reduction of fish-tissue mercury concentrations, both within the watershed and in downstream water bodies.

Mine-Site Studies

Information on mine-site studies has been summarized from Churchill, 2002, and Suchanek and others, 2002 (<http://loer.tamug.tamu.edu/calfed/>).

One major hypothesis was that mining wastes are a source of total mercury and a potential source of methylmercury. Accordingly, in one component of the study, 14 historical mercury and gold mines were examined in the Sulphur Creek mining district (including the Turkey

Run/Abbott mining area) to evaluate their mercury contributions to the Cache Creek watershed. During field examinations, mine-site materials were inventoried and samples were collected for laboratory analysis to establish the concentration and characteristics of mercury in these materials. In situations where mine materials were eroding into waterways, estimates of erosion rates were made. These estimates were made using the Revised Universal Soil Loss Equation (RUSLE2) model, which evaluates slopes with segments of various angles and lengths and incorporates information on particle size, surface cover, and long-term local rainfall and temperature data. The estimated erosion rates and mercury concentrations for mine materials were then used to estimate the average annual mercury contributions from the mine-site materials to local waterways. Information compiled from previous published and unpublished studies was used to make preliminary estimates of mercury availability from non-mine sources in the project area, for comparison with mercury contributions from mine-site sources. Finally, general recommendations were made for mine-site remediation approaches, which will be evaluated for engineering feasibility, effectiveness, and cost.

The mine-site materials identified during site evaluations included calcined tailings, waste rock, ore, miscellaneous small material piles, and processing-site soil. Naturally elevated mercury in soil resulting from weathering of hydrothermally altered bedrock also was present at the mine sites. The mercury contents of these materials, including the naturally elevated mercury in soils, typically ranged from 10 and 300 mg/kg (milligram per kilogram [or parts per million, ppm]). Ore piles and processing-site soils had higher mercury levels but were much less common and volumetrically less important than other materials and did not occur at all mines. In previous studies (Bradley, 1918; Rytuba, 1996) it was found that mercury occurs principally in the form of cinnabar and metacinnabar in ore and calcined tailings at Sulphur Creek district mines.

In this study, leach analyses with a reducing agent (hydroxylamine hydrochloride) were used to evaluate the mercury associated with iron and manganese oxides. The reductive leach analysis of selected samples found that only a very small percentage of total mercury in ore, waste rock, calcined tailings, and naturally elevated mercury soils was mobilized during leaching. These results are consistent with the occurrence of mercury as cinnabar and metacinnabar and suggest that most mercury moves from mine sites to adjacent waterways in particulate form rather than as dissolved mercury. This is in agreement with findings from other components of this study. Finally, occurrences of acid mine drainage were not observed during the mine-site investigations. The only significant occurrence of low-pH material found during this study is an area of naturally occurring argillic alteration near Wilbur Springs.

Mercury-concentration data and erosion-rate estimates for mine-site materials were used to estimate average annual mercury contributions from mine sites to the Sulphur Creek, Harley Gulch, and Bear Creek sub-watersheds. The resulting estimates of annual mine-site mercury contributions owing to erosion were 4 to 19 kg/yr (kilogram per year) and 1.2 to 11 kg/yr to the Sulphur Creek and Harley Gulch watersheds, respectively. It is estimated that 0.7 to 23.5 kg/yr of mercury is moving offsite from mine-waste piles within the Bear Creek watershed. However, it is uncertain how much, if any, of this waste-pile sediment actually reaches Bear Creek because this material is being deposited in dry ravines adjacent to the mines, several miles from Bear Creek. Sediment along the drainages between these ravines and Bear Creek has not been sampled. It is very important to note that these estimates are based on long-term average climatic conditions for the area. Mercury contributions to the watershed from mine-site materials as a result of severe storms may be substantially greater than the average annual contributions estimated here.

Estimates of the annual amounts of regional background mercury mobilized within these watersheds have been made for comparison with the estimates for mine materials and are as follows: 0.45 to 9.8 kg for Sulphur Creek, 0.04 to 0.8 kg for Harley Gulch (west tributary), and 3.7 to 74.7 kg for Bear Creek. These regional mercury contributions assume lower and upper annual erosion rates of 0.2 and 4 metric tons per hectare for each watershed. The amount of regional background mercury actually entering waterways in the project area on an annual basis is unknown, and these estimates should be viewed as upper limits.

In order to further identify localized mercury hot spots, stream waters were collected, in another component of the overall project, from several locations within the Harley Gulch and the Sulphur Creek mining districts ([fig. 1](#)) during storms in February 2000 and 2001. All samples were analyzed for total mercury and, in some cases, methylmercury. Water from geothermal springs within each district also was sampled and analyzed for mercury. Graphical results on the concentrations of mercury from specific localized sites in the Harley Gulch region are presented in [figure 2](#). The highest observed concentration (6,800 ng/L) was in a sample collected from an erosional ditch emanating from the Turkey Run processing facility during February 2000. The lowest concentration was in water from a geothermal spring near the Turkey Run mine. Water samples collected in February 2001, when runoff was lower than in 2000, indicated significantly less mercury at these same sites; total mercury concentrations ranged from 6 to 933 ng/L.

Under the (low) precipitation conditions of these particular sampling years, water samples from the Sulphur Creek sites yielded significantly higher total mercury concentrations than those from the Harley Gulch region. Sulphur Creek concentrations ([fig. 3](#)) ranged from 230 to 24,262 ng/L in 2000 and from 137 to 35,000 ng/L in

2001; most of the mercury was in the particulate fraction. It is notable that the geothermal springs in this region contributed the highest mercury concentrations in water, in sharp contrast with the Harley Gulch region. Although the geothermal flows were low relative to winter stream runoff flows, they were fairly continuous throughout the year, and a substantial part of the mercury in geothermal water occurred in dissolved form.

The focus of these parts of the study was the potential role of mine-site materials and geothermal waters as sources of total mercury in the Sulphur Creek, Harley Gulch, and Bear Creek watersheds ([fig. 1](#)). However, additional sources of mercury are present in these watersheds, including precipitates associated with thermal-spring waters, deposits of elevated-mercury alluvium along creek banks, elevated mercury in streambed sediments, soil mercury emissions to the air (local sources), and atmospheric mercury (regional and global sources). The annual mercury contributions from these sources to waterways in the project area are incompletely or poorly known and should be considered for investigation in future studies. However, this study provides a foundation for estimating the concentrations and loadings of mercury during relatively dry years. Available information from previous studies within the project area, and from the nearby Knoxville mercury district, suggest that the significance of these sources is as follows:

- Geothermal-spring waters probably contribute only a few hundred grams of mercury annually to the watersheds, but contribute large amounts of sulfate (50 to 160 metric tons to Harley Gulch and 7 to 16 metric tons to Sulphur Creek).
- Precipitates deposited in mud at geothermal springs contain mercury at concentrations ranging from 10s to 100s of ppm. However, the annual rate of production of these precipitates is unknown and, therefore, the amount of mercury they add to watershed loads is unknown.
- Streambank alluvium and streambed sediment near mines or other mercury source areas may contain 10s of ppm mercury. Virtually no information currently is available on the location, extent, or conditions necessary for erosion and downstream transport of these sediments.
- Preliminary estimates suggest that total annual mercury emissions to the air from all mine-site material in the project area are about 3 kg. This estimate was obtained by applying mercury flux rates determined by Gustin and others (2000) for mine-site features in a nearby mercury district to mine-related features in the Sulphur Creek district. The estimates obtained for the annual mercury emission from each mine-site feature were summed to obtain an estimate of the annual mercury emissions from mine-site features for the district as a whole.

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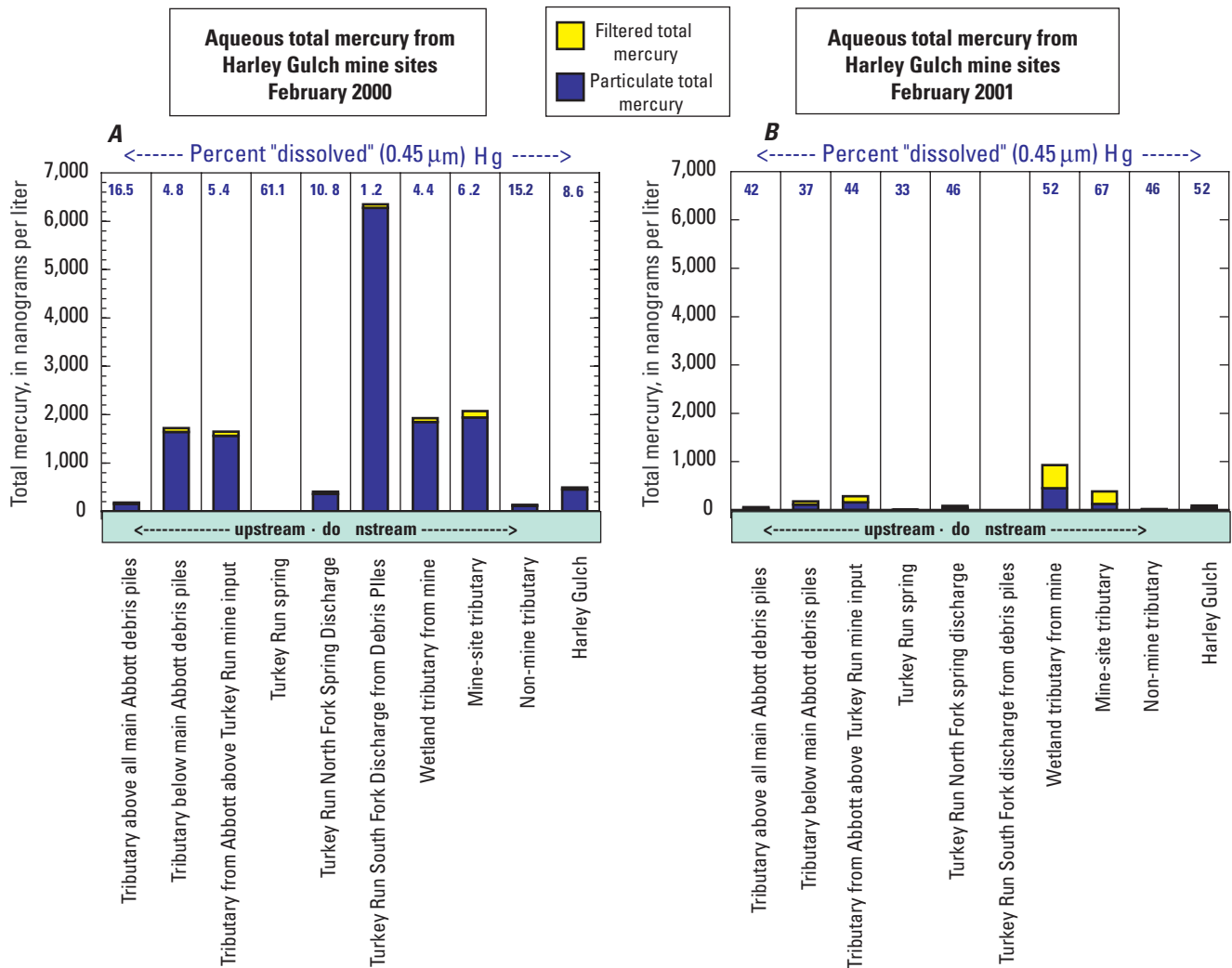


Figure 2. Total mercury in water from the Harley Gulch, California, mining district sites in (A) February 2000 and (B) February 2001.

From Suchanek and others, 2002. Blue portions of bars represent total mercury (Hg) in raw (unfiltered) water; yellow portions indicate total Hg in the dissolved fraction (0.45 μm [micrometer] pore size).

- Estimates of mercury emissions from soils with elevated mercury in mineralized areas (areas of high total mercury in soil and bedrock, but in drainages that have not been developed for mining) may exceed mine-materials emissions by 10 times or more. These soil occurrences may constitute an important watershed mercury source if a significant percentage of this mercury is deposited in waterways. These estimates were made using flux rates for background and disturbed soils with elevated mercury in a nearby mining district determined by Gustin and others (2000) and estimates of the areas of background and disturbed soils with elevated mercury in the Sulphur Creek district.
- If atmospheric mercury deposition occurs in the study area at about the same rate as in the San Francisco area (2.2 nanograms per square meter per hour), then the annual mercury contribution from this source is relatively small in comparison with the previously mentioned sources (about 0.55 kg to Sulphur Creek and the Harley Gulch [west tributary area] watersheds combined, and 4.6 kg to the Bear Creek watershed).
- Additional studies would be necessary to determine the amount of mercury and methylmercury loading that occur from the mining and geothermal sites in relatively wet years.

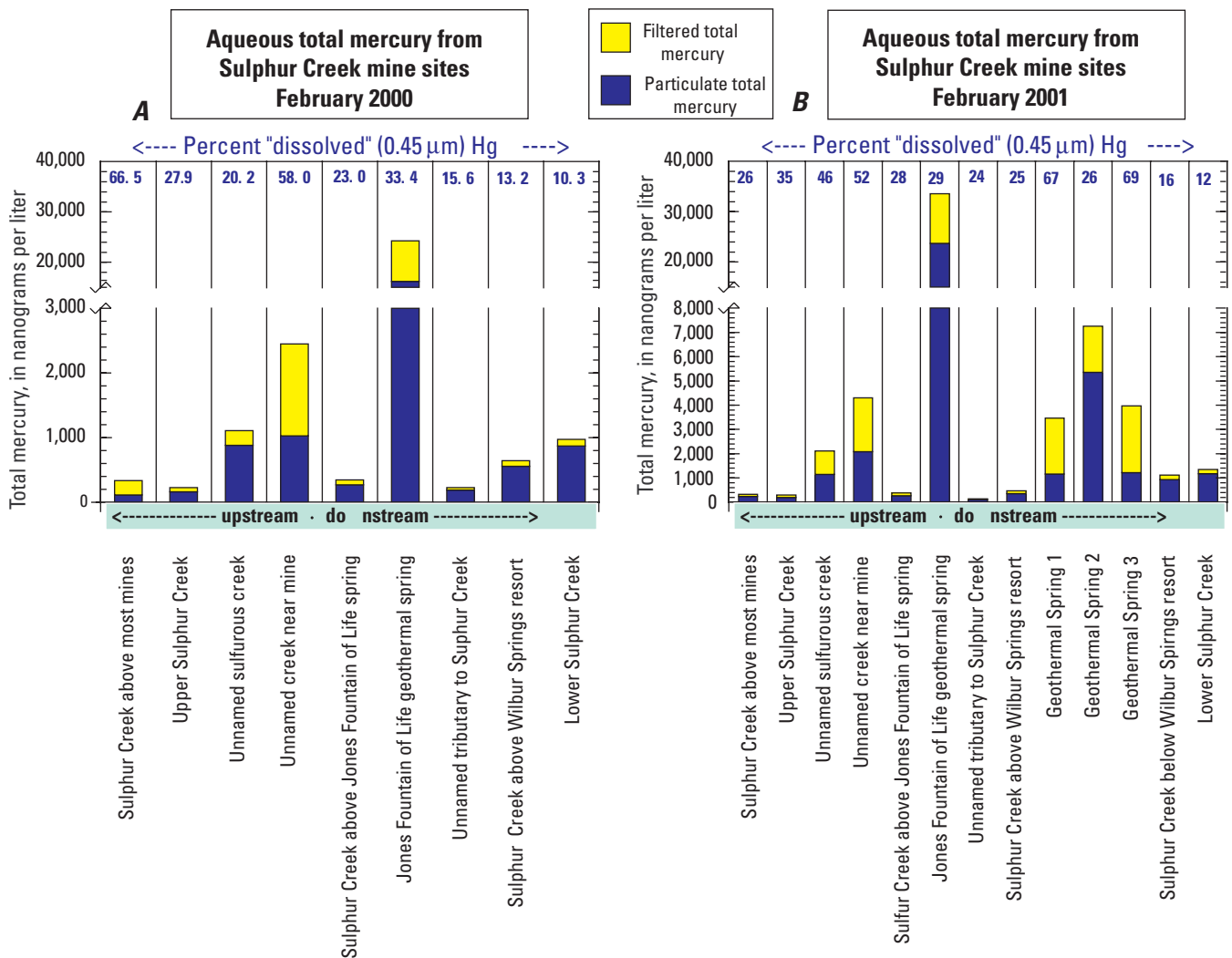


Figure 3. Mercury in water from the Sulphur Creek, California, mining district sites in (A) February 2000 and (B) February 2001. From Suchanek and others, 2002. Blue portions of bars represent total Hg in raw (unfiltered) water; yellow portions indicate total Hg in the dissolved fraction (0.45 μm [micrometer] pore size). ppm, parts per million; kg, kilogram.

The current conceptual model developed in these components of the project for the sources and fate of mercury in the Cache Creek mining district are summarized in [figure 4](#). Information developed regarding the abundance and characteristics of mercury in mine-site materials, and estimates of mine-site mercury contributions to waterways, suggests that effective mine-site remediation should be based on general site erosion-control measures. Because of the important role of sulfate-reducing bacteria in the methylation of inorganic mercury, a further understanding of the role of sulfate from either geothermal or mining sites in mercury

methylation is needed. Although increasing sulfate concentrations can increase the rate of mercury methylation, an excess of sulfate can result in a net decrease in methylation. In some locations, controls on sulfate transport may reduce the amount of methylation and bioaccumulation, whereas in other locations excess sulfate may actually be limiting methylation. It should be emphasized that currently available information is insufficient to assess the actual amount of erosion that occurs to streams under a variety of flow conditions. The actual amount of erosion that occurs during storm-water runoff may be different than predicted.

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Sources, transport, and fate of mercury (Hg) in the Cache Creek Watershed

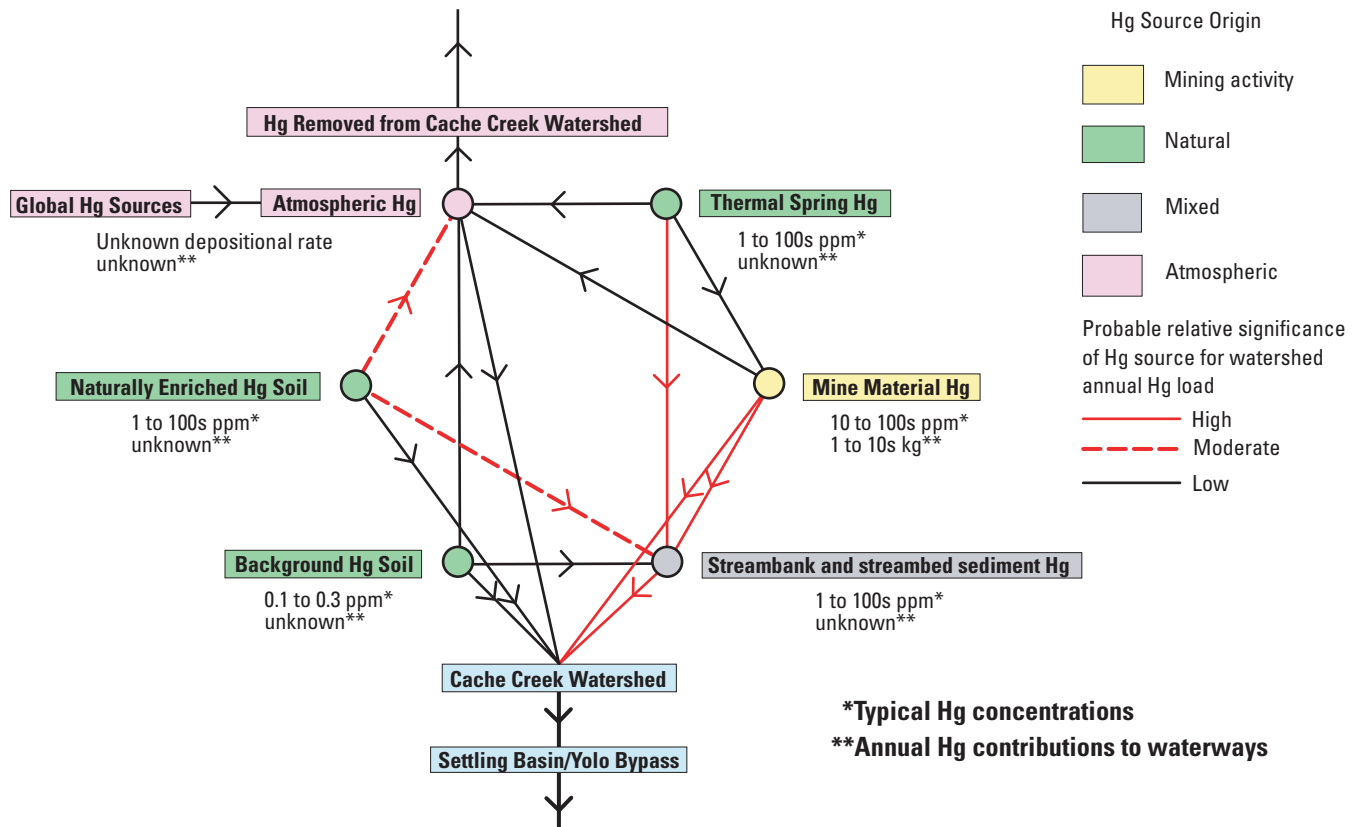


Figure 4. Conceptual model of sources, transport, and fate of mercury in the Sulphur Creek mining district of the Cache Creek watershed, California. From Churchill and others, 2002.

Mercury-Speciation Studies

Information on mercury speciation studies has been summarized from Bloom, 2002 (<http://loer.tamug.tamu.edu/calfed/>).

Another major hypothesis was that the chemical form of mercury from different sources may have an effect on the rate of mercury methylation and subsequent bioaccumulation. The combined uses of sequential-selective extractions and sediment incubations have provided some insights into the behavior of mercury derived from mine sites when it is introduced to the aquatic environment. Sequential-selective

extraction experiments (SSE) provide a means to determine what types of water chemistry will allow the mercury to dissolve. This provides some insight into the geochemical form of the extracted mercury, such as mineral or natural organic matter. Incubations of the inorganic mercury provide insight into the amount of mercury that can be changed to methylmercury, primarily through microbiological processes. However, because of the complex dependencies involved in the methylation incubations and the poor resolution of the SSE speciation profiles, these insights are limited to qualitative rather than quantitative treatment.

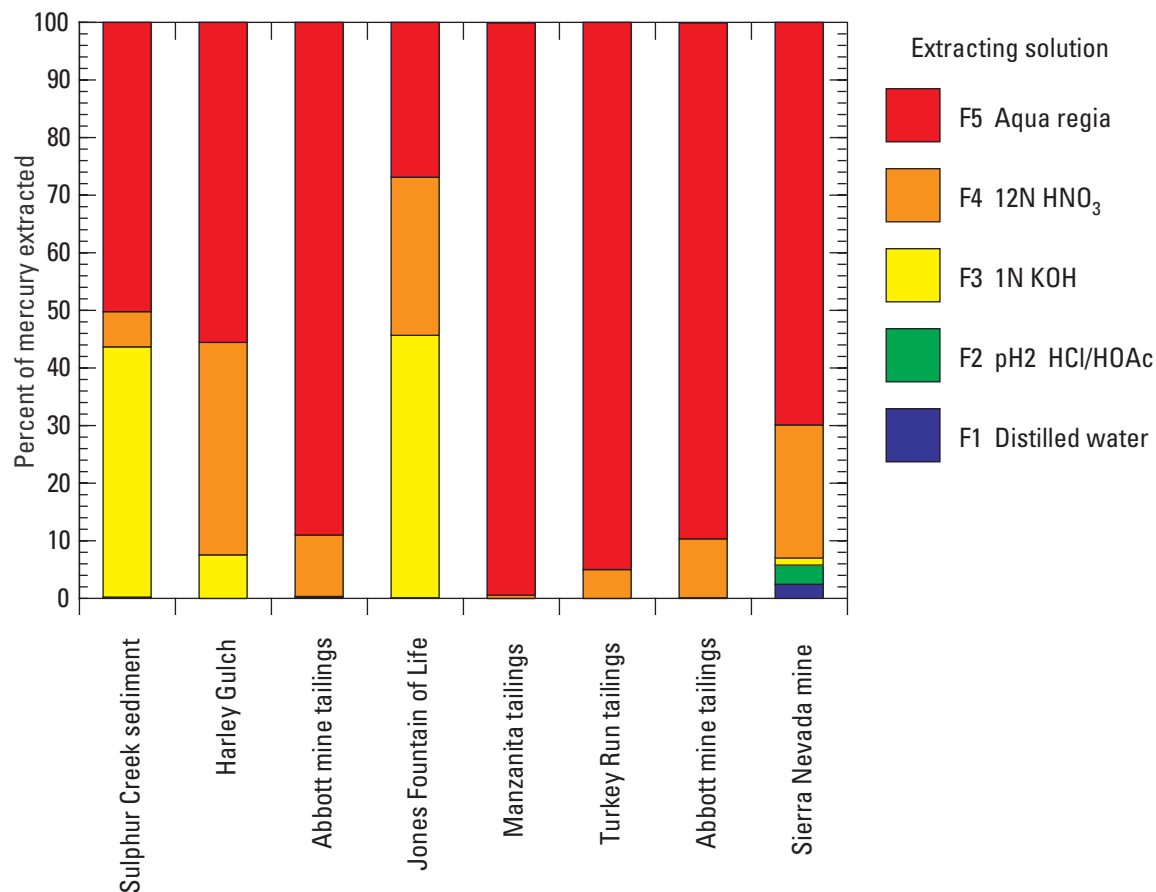


Figure 5. Speciation of solids from mine or geothermal sites. The solids were extracted with solutions (F1–F5) of increasing strength. Extracting solution F5 is a strong acid. From Bloom, 2002.

Of greatest significance was the verification that the mine-site-derived solids are approximately 20 times less bioavailable for methylation than is dissolved mercury (Hg^{++}). This observation is supported by the speciation profiles, which showed that these solids have more than 90 percent of the mercury present as cinnabar-like compounds. The results of SSE on mine-site solids are shown in [figure 5](#). In an SSE experiment, five different solutions are allowed to contact the mercury. The strength of the extracting solution increases from F1 to F5. The F3 fraction is thought

to recover mercury primarily from naturally occurring organic matter. Most of the extracted mercury from the actual mine-pile materials was recovered only with the F5 fraction, which is a strong acid. In contrast, extraction of mercury from the sediments of the tributary sites tended to occur more readily with the F3 fraction ([fig. 6](#)). The mercury from the geothermal sources (Sulphur Creek or Jones Fountain of Life) and Harley Gulch below the Turkey Run and Abbott mines was extracted with weaker solutions probably owing to the discharge of more labile forms of mercury.

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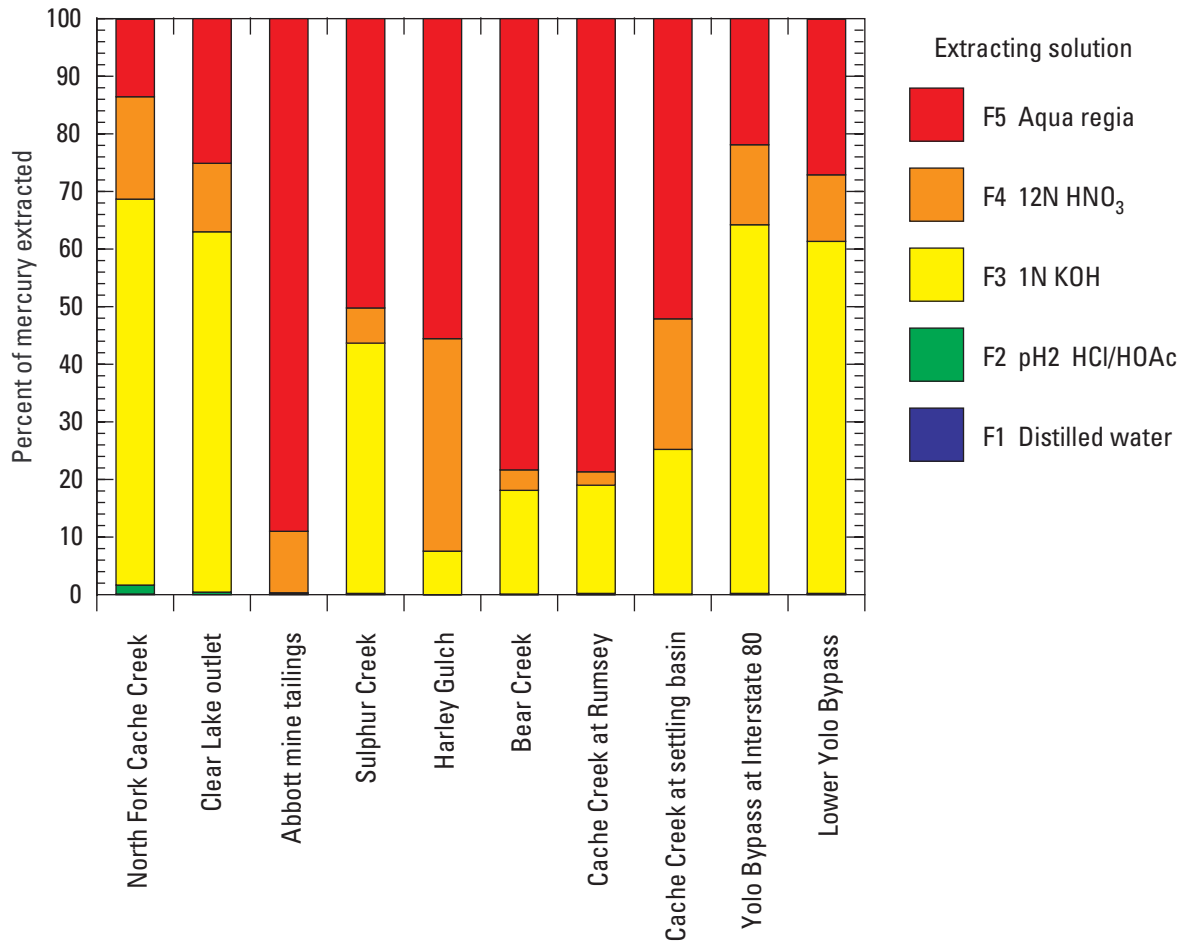


Figure 6. Speciation of solids from stream sites.

The solids were extracted with solutions (F1–F5) of increasing strength. Extracting solution F5 is a strong acid. From Bloom, 2002.

When a long-term incubation was completed, very little of the cinnabar-dominated solids added to a receiving sediment was ultimately methylated, even after 1 year, whereas all of the more labile mercury compounds ultimately were methylated to the same degree as was the dissolved mercury addition (fig. 7). When sediment from mine sites was added to sediment collected from Cache Creek near Capay (downstream of the Capay Dam), very little change in the net amount of methylmercury resulted. When more labile mercury compounds were added, much more methylmercury was generated. These experiments indicate that solid-phase cinnabar-containing minerals do not represent a major

methylation source to the main stem of the river, and thus other sources (such as soluble mercury resulting from weathering of the tailings piles and geothermal discharge) may be more significant. Although this is true for the timeframe of the experiments, the cinnabar may be a significant source of methylmercury under longer timeframes such as decades to centuries. The fact that added elemental mercury (quicksilver) was ultimately just as bioavailable as was dissolved mercury further suggests that mercury from the gold mining sites of the Sierra Nevada may be more bioavailable than is mercury from the cinnabar mining sites of the Coast Ranges.

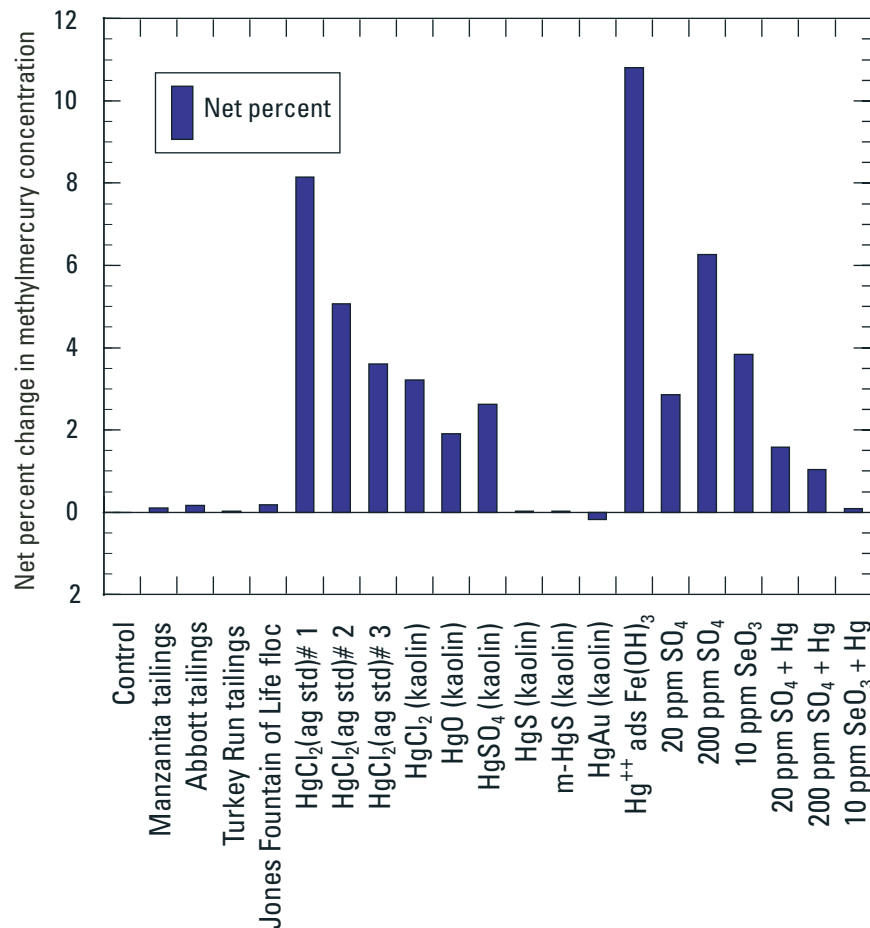


Figure 7. Net methylation, in percent, of mine solids and reactive forms of mercury spiked to sediments collected from Cache Creek near Capay, California. From Bloom, 2002. ads, adsorbed to; floc, flocculent precipitate; HgS, cinnabar; m-Hgs, metacinnabar; ppm, part per million.

Mercury-Loading Studies

Information on the loading studies is summarized from Domagalski and others, 2002, and Suchanek and others, 2002 (<http://loer.tamug.tamu.edu/calfed/>).

The present studies of mercury loading were designed to document both wet-season and dry-season mercury and methylmercury concentrations and loads with the intention to determine annual amounts of transport. Mercury and methylmercury transport was assessed from Clear Lake and Indian Valley Reservoir as well as from the important tributaries downstream from either mining-discharge sites

(Harley Gulch and Davis Creek Reservoir), geothermal sites (Sulphur Creek), and sites with a mixture of mercury inputs (Bear Creek). Finally, several locations on Cache Creek were assessed to document transport through and out of the basin.

Three key hypotheses, related to loading and transport of total mercury were that (1) geothermal sources were relatively constant throughout the year because the water discharges from springs; (2) the transport from mine-waste sites would occur primarily in response to seasonal rainfall because most of the mercury is associated with solid material that is mobilized only by flowing water, and; (3) previously deposited mercury in the larger streams is a source to downstream locations.

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Mine site research has shown that large amounts of erosional material from mine sites can be deposited each year at various sites. Once deposited, these sediments can be moved only as a result of local hydrodynamic forces. Erosional materials greater than 63 μm (micrometers) in diameter—that is, sand-sized particles—require higher flow regimes for transport in comparison with smaller particles. The sand particles will move mainly as bedload under relatively high-flow conditions, but smaller particles less than 40 μm in diameter will stay in suspension and be transported out of the basin. As mentioned, previous studies have shown that the amount of inorganic mercury that can be transported out of the basin ranges from about 300 kg in a relatively normal rainfall year to about 1,000 kg in an extremely wet year. Although high concentrations of sediment and mercury in storm-water runoff were known to be present in previous studies, the loads could not be assessed because no stream-discharge gaging stations were present. This study allowed for the installation of new gaging stations at two mine-waste locations and one geothermal site (Sulphur Creek at Wilbur Springs, Harley Gulch near Wilbur Springs, and Davis Creek Reservoir at dam, near Knoxville).

Rainfall amounts in northern California are variable from year to year. Although not considered drought years, the two years of this study had low streamflow. Gaging-station records for the location near the mouth of the basin indicate that the annual discharge was about 55 percent of the long-term average. The low rainfall amounts resulted in limited opportunities to assess mercury transport from mine-waste sites. For example, discharge from Davis Creek Reservoir will occur only if rainfall is sufficient to fill the reservoir. In the first year of the study a small amount of water discharged, but in the second year virtually no discharge occurred. Streamflow on Harley Gulch, one of the tributaries receiving runoff from a large abandoned mercury mine, accounted for 0.15 percent of the total streamflow leaving the basin in the first year of the study but only 0.005 percent in the second. The principal geothermal source, Sulphur Creek, accounted for 1 percent in the first year and 2 percent in the second.

Most of the transport of mercury out of the Cache Creek watershed occurs in response to rainfall. As storms generate runoff, and associated suspended sediment, concentrations and associated loads of mercury and methylmercury increase in the tributaries and main stem of Cache Creek. Mercury loads for one storm sampling in February 2001 are shown in [figure 8](#). During that storm, most, but not all, of the mercury load measured at the Rumsey site (centrally located in the watershed) originated from Sulphur Creek and Bear Creek. Mercury loads increased at the lower site on Cache Creek, at the Cache Creek settling basin, and that increase can be

attributed to re-suspension of previously deposited mercury within the bed sediments of Cache Creek. Methylmercury loading patterns were similar to those for total mercury, although the amounts were much smaller. The Cache Creek settling basin was shown to be largely ineffective in decreasing the amount of mercury transported out of the Cache Creek watershed. However, previous studies have shown that the settling basin can be effective in reducing the amount of total suspended sediment and associated mercury occurring in downstream areas.

Annual loads for each year (water years 2000 and 2001) of the study, for sites that have continuous streamflow records, are shown in [figure 9](#). For both water years, the loads from Sulphur Creek are greater than those from either Clear Lake or the Indian Valley Reservoir. Loads from Sulphur Creek are also much greater than those from Harley Gulch, which is immediately downstream from a large mercury mine. Owing to the lower than normal rainfall, mercury loads from Harley Gulch were relatively low. Mercury loads from Bear Creek increase slightly from those of Sulphur Creek, probably from re-suspension of previously deposited mercury from Sulphur Creek. When the loads of the upstream tributaries—Clear Lake outflow, Indian Valley Reservoir outflow, Bear Creek, and Harley Gulch—are summed, the resulting combined load is less than that calculated for the most downstream site, Cache Creek at Yolo (Cache Creek settling basin). Once again, this increase in loads between the mine and geothermal sites and the most downstream site can be attributed to re-suspension of previously deposited mercury. Erosion of mercury from these mine-waste piles has been ongoing for over 100 years. As a result, the bed sediments of Cache Creek also can be considered a source of mercury to downstream water bodies. Because of the low rainfall amounts during this study, it is not known if the re-suspension of previously deposited mercury, within the mainstem of Cache Creek, would be significant relative to the high erosion rates from the mining regions associated with major storms.

Because one goal of these studies was to evaluate the potential value of remediating localized contaminant piles or hot spots, it was important to quantify the differences between the contributions from various topographic or historical features at specific source areas. Using flow rates of streams passing through or near these mines and geothermal springs, and multiplying those flow rates by the mercury concentrations in those waters, we were able to compare the mercury-loading factors from localized sites to evaluate which sites might benefit the most from remediation. These loading factors relate directly to the same sites for which mercury concentrations were reported in [figures 2](#) and [3](#).

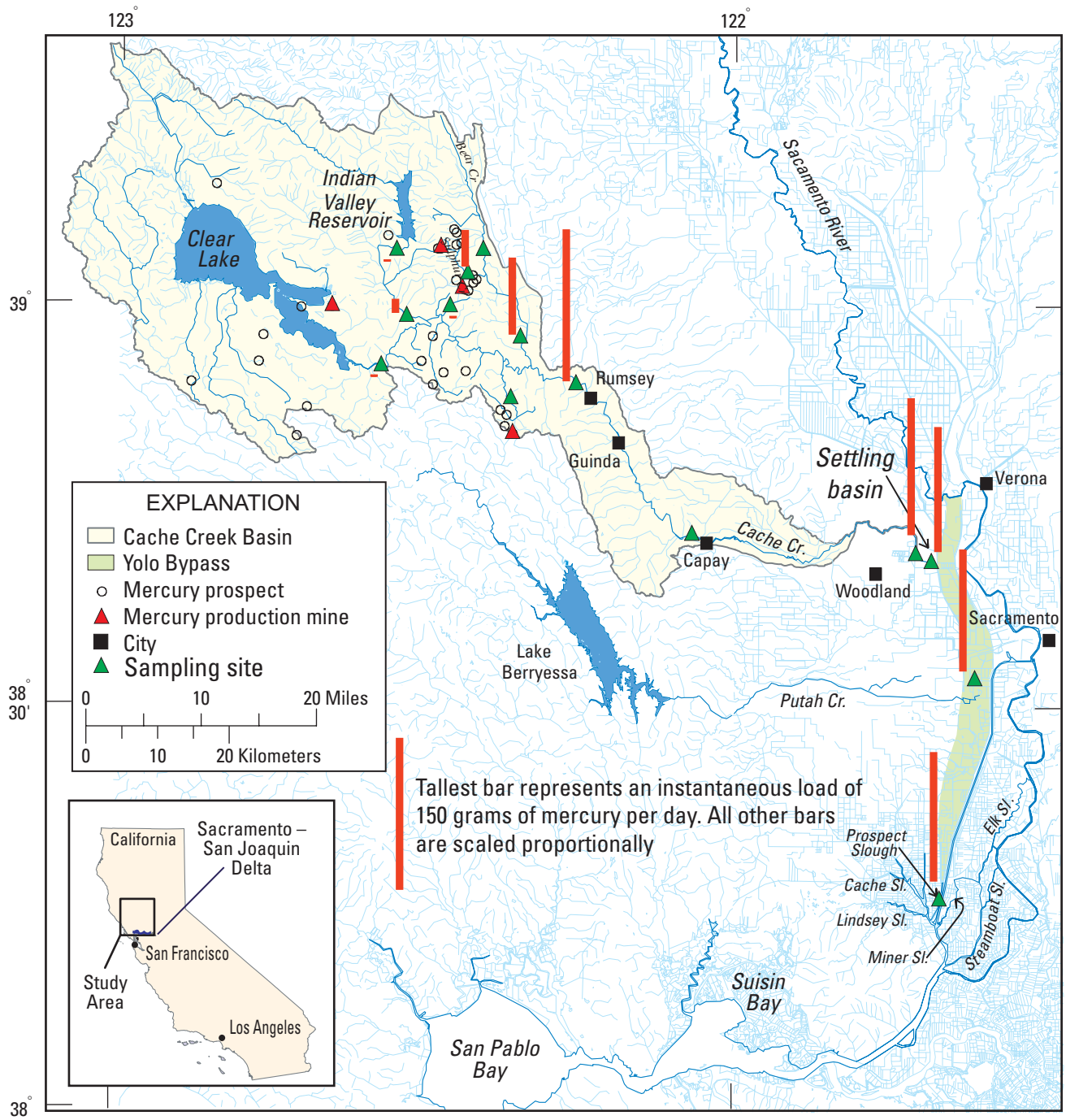


Figure 8. Mercury loads at selected sites in the Cache Creek watershed, California, for February 20–23, 2001, sampling. From Domagalski and others, 2002.

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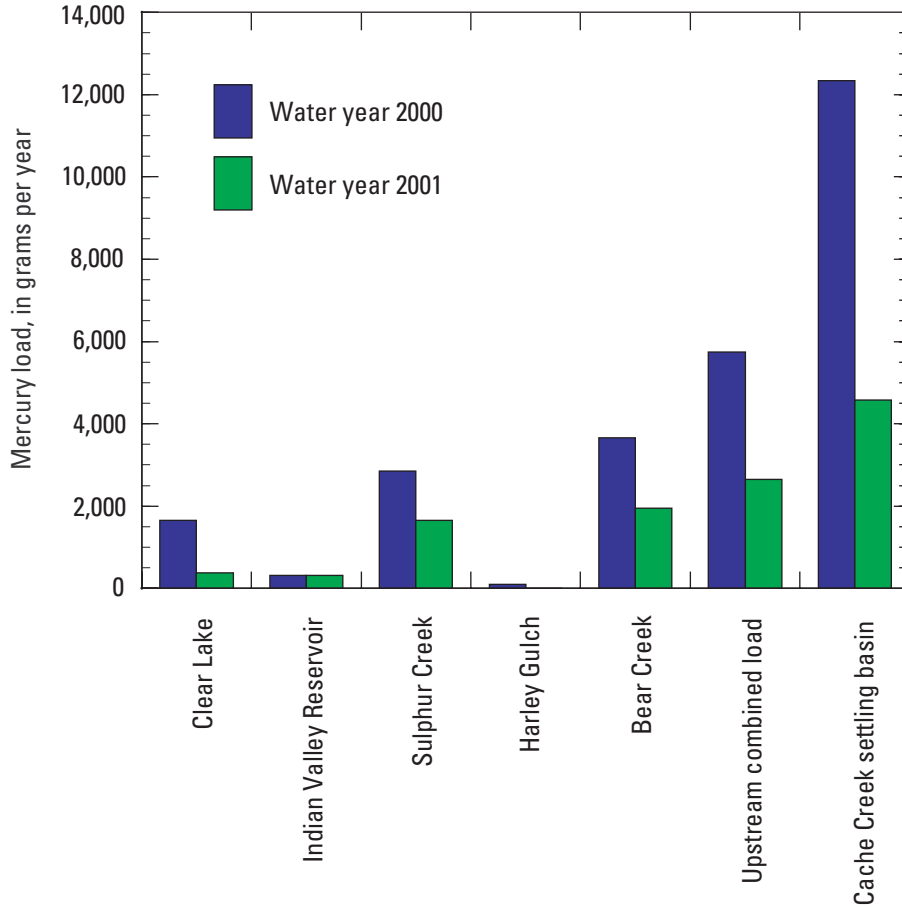


Figure 9. Annual loads of mercury for selected sites and combined upstream loads to lower Cache Creek, California. From Domagalski and others, 2002.

A comparison of localized, wet-season mercury loading from specific sites in the Harley Gulch mining district is shown in [figure 10A](#), for both raw (unfiltered) and filtered water sampled during the 2000 water year (October 1, 1999, through September 30, 2000). These data indicate that (1) the vast majority of the loading is in the particulate form, (2) the highest loading derives from the sites where the two mine sub-drainages converge, and (3) the geothermal spring in this region is nearly devoid of mercury. Results from the 2001 water year were very comparable in the proportional contribution from each local site, but the magnitude of the loading was significantly reduced (as was the streamflow).

Comparable values for loading contributions of total and methylmercury from raw and filtered water from the local Sulphur Creek sites, calculated from the mercury concentrations measured during the 2001 water year, are shown in [figure 10B](#). Although the Jones Fountain of Life geothermal spring had by far the highest concentrations of mercury, its relative contribution appears to be very small in comparison with other sources (primarily because of its low flow rate). The highest estimated loading was at the index station downstream.

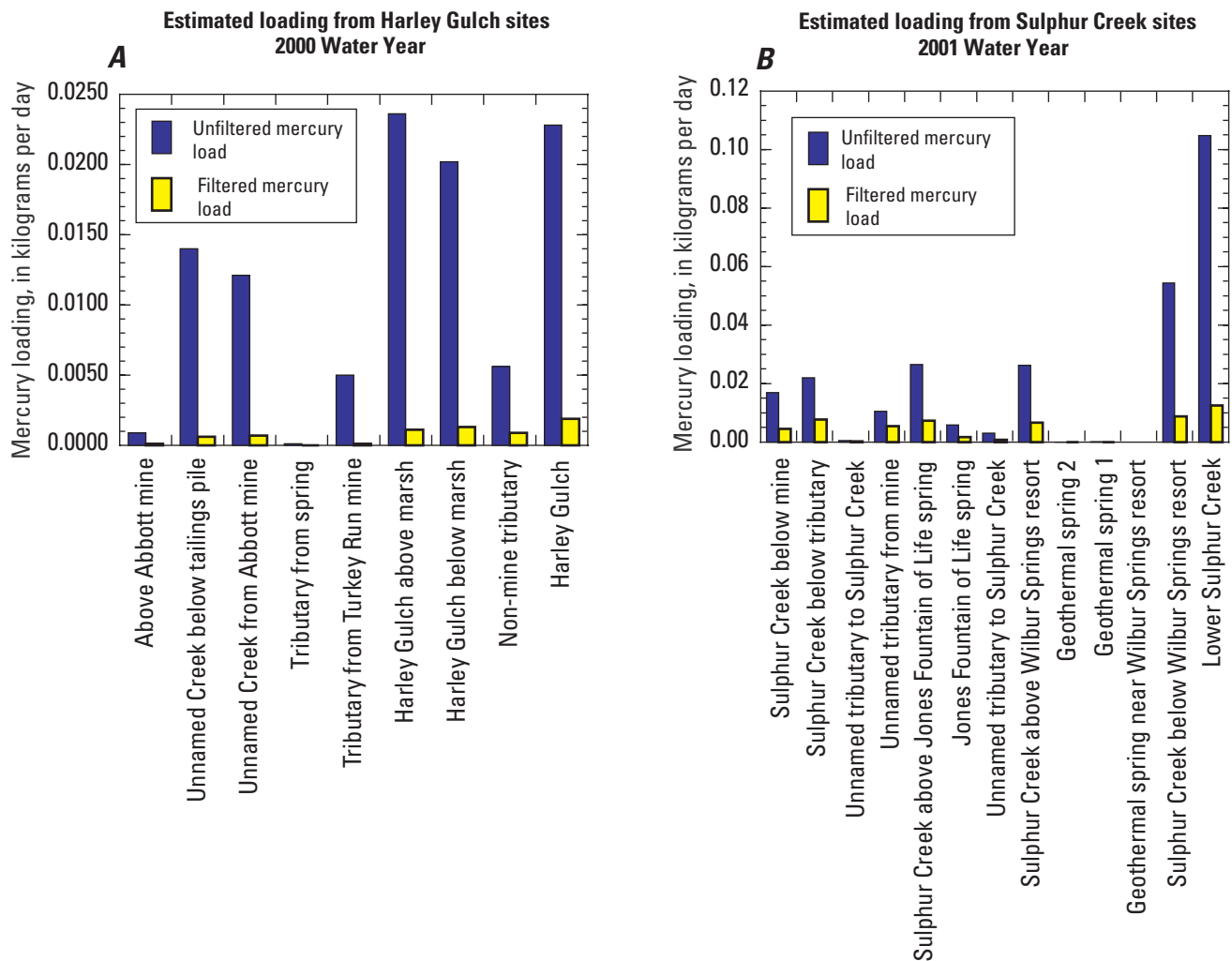


Figure 10. Comparison of daily mercury loading from specific sites in California in the mining districts of (A) Harley Gulch and (B) Sulphur Creek. From Suchanek and others, 2002. Sites are arranged from left to right in relation to their upstream to downstream locations.

Studies of Mercury Bioaccumulation Into and Through the Aquatic Food Chain in the Cache Creek Watershed

Information on bioaccumulation studies was summarized from Slotton and others, 2002 (<http://loer.tamug.tamu.edu/calfed/>).

The studies of mercury in the tissues of aquatic organisms were designed to measure concentrations at different locations throughout the Cache Creek watershed and to determine the relations between these concentrations and mercury or methylmercury concentrations in water, and the relations between different trophic levels of the aquatic ecosystem.

As mentioned previously, it is known that mercury concentrates or bioaccumulates among successive trophic levels of an ecosystem with the top-level predatory organisms having the highest concentrations. Therefore, the analysis of mercury in predatory fish at various sites within the

watershed provided a good indication of whether the mercury from abandoned mines or geothermal sources is affecting the aquatic food web. Mercury concentrations in fish usually increase as the fish grows, assuming that mercury in the fish's diet remains more or less constant. Concentrations of mercury in bass are shown in [figure 11](#) for sites on the main stem and North Fork of Cache Creek. At the most upstream location, near the outflow of Clear Lake, mercury concentrations in bass were generally below the USEPA criterion of 0.3 ppm. The USEPA criterion is designed for determining whether a given stream or lake is impaired by mercury, necessitating remedial action through the TMDL process. At the upper Cache Creek site, all but the largest fish caught had tissue concentrations of mercury below 0.3 ppm. Smaller fish that were caught at downstream locations, below mining or geothermal sites, exceeded the criterion, indicating that mercury from the abandoned mine sources or geothermal sources is affecting the aquatic ecosystem. At the smaller tributaries nearer these identified point sources, such as Bear Creek, the effect was more dramatic ([fig. 12](#)).

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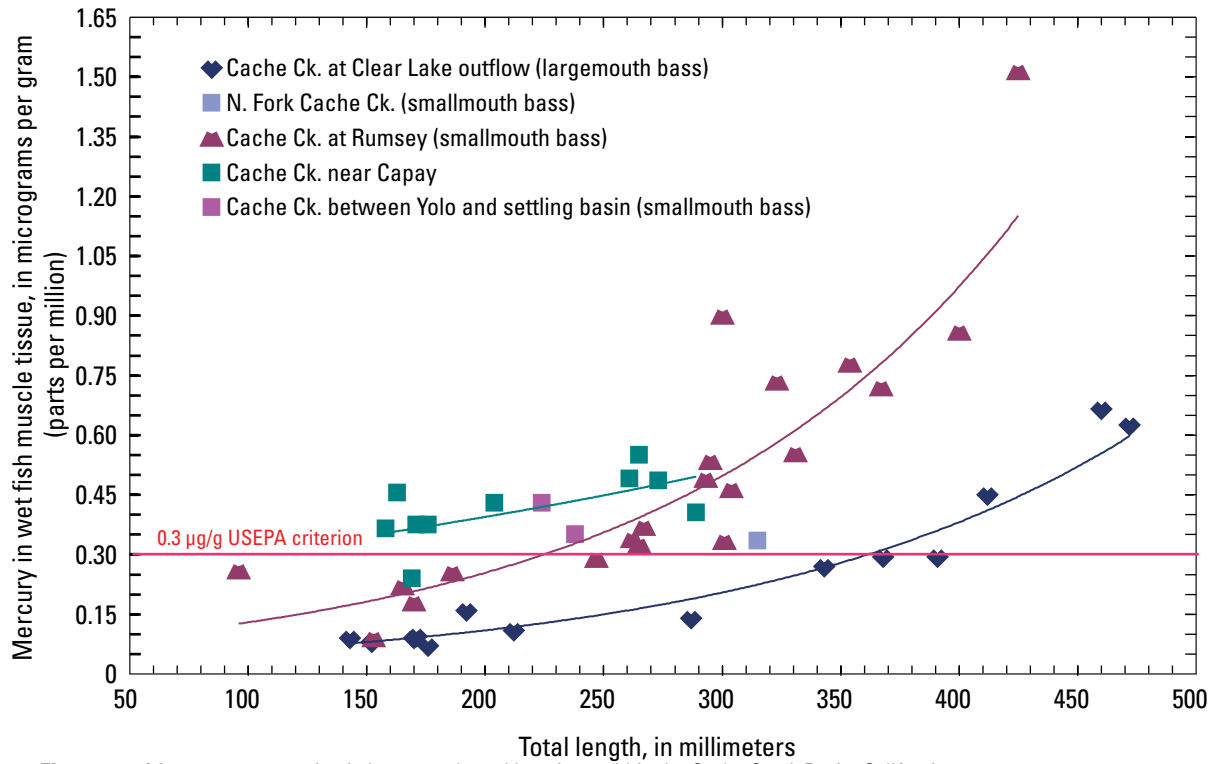


Figure 11. Mercury concentration in bass at selected locations within the Cache Creek Basin, California. From Slotton and others, 2002. µg/g, microgram per gram; USEPA, U.S. Environmental Protection Agency. Cr., creek.

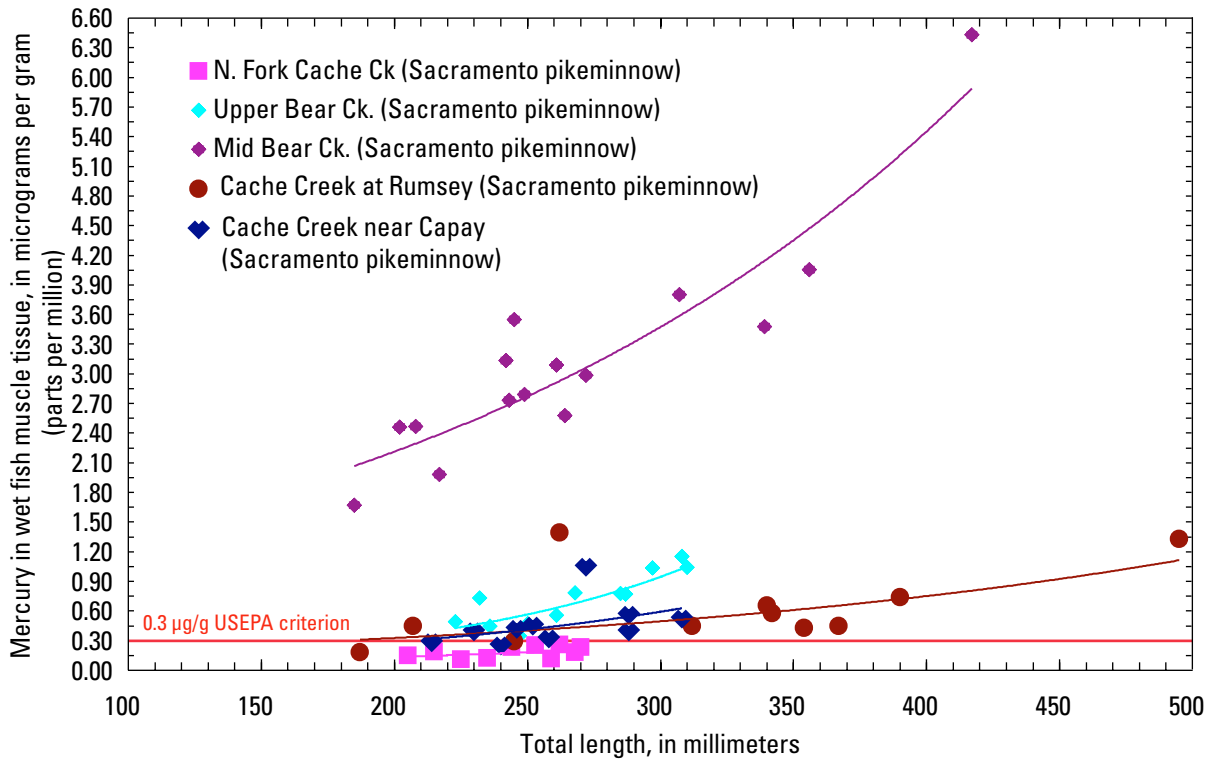


Figure 12. Mercury concentration in pikeminnows at selected locations within the Cache Creek Basin, California. From Slotton and others, 2002. µg/g, microgram per gram; USEPA, U.S. Environmental Protection Agency. Cr., creek.

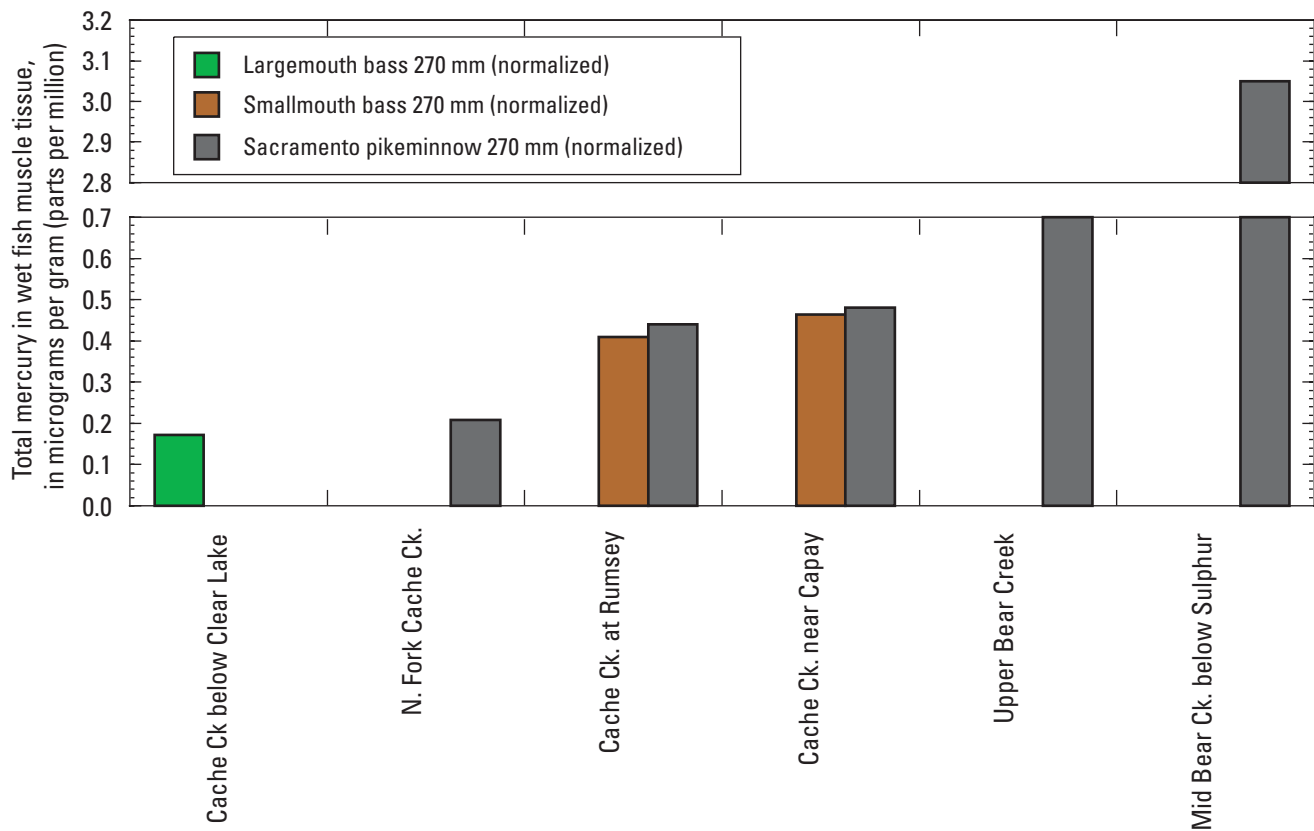


Figure 13. Normalized muscle-tissue mercury (Hg) in piscivorous fish collected throughout the Cache Creek, California, watershed. From Slotton and others, 2002. mm, millimeter; Cr., creek. Normalization = intersection of normalizing length with length: Hg regressions.

Sacramento pikeminnows exceeded the 0.3-ppm criterion among all size classes sampled and reached concentrations as high as 6.5 ppm; such high concentrations are rarely observed in natural populations. These very high concentrations might be attributable to more labile forms of mercury present in the geothermal discharge of Sulphur Creek, a tributary to Bear Creek. The highest concentrations of dissolved mercury observed during this study were in Sulphur Creek samples.

A convenient way to demonstrate relations among the sites is to normalize the mercury concentrations by fish size. This does not indicate highest or even average fish-mercury levels, but instead provides a consistent relative measure between sites. Normalized concentrations for predatory fish are shown in [figure 13](#). This plot shows the same spatial trend of lower mercury in the upper Cache Creek and North Fork

Cache Creek sites and substantially higher concentrations in and downstream from the tributary sites that have identified point sources of mercury. Although a large abandoned mercury mine is located on the shores of Clear Lake, runoff from that mine is apparently not dramatically affecting fish directly downstream from the Clear Lake outlet. The upper Bear Creek site presents an apparent anomaly with regard to fish-tissue mercury. That site is also above the primary geothermal and abandoned mine sources, but predatory fish there were found to have tissue mercury concentrations in excess of 0.3 ppm. Although fish migration from the downstream Bear Creek site is one possibility, the bulk of the evidence indicates that these were local fish. The upper Bear Creek site may have physical, chemical, or biological conditions that are more conducive to mercury methylation.

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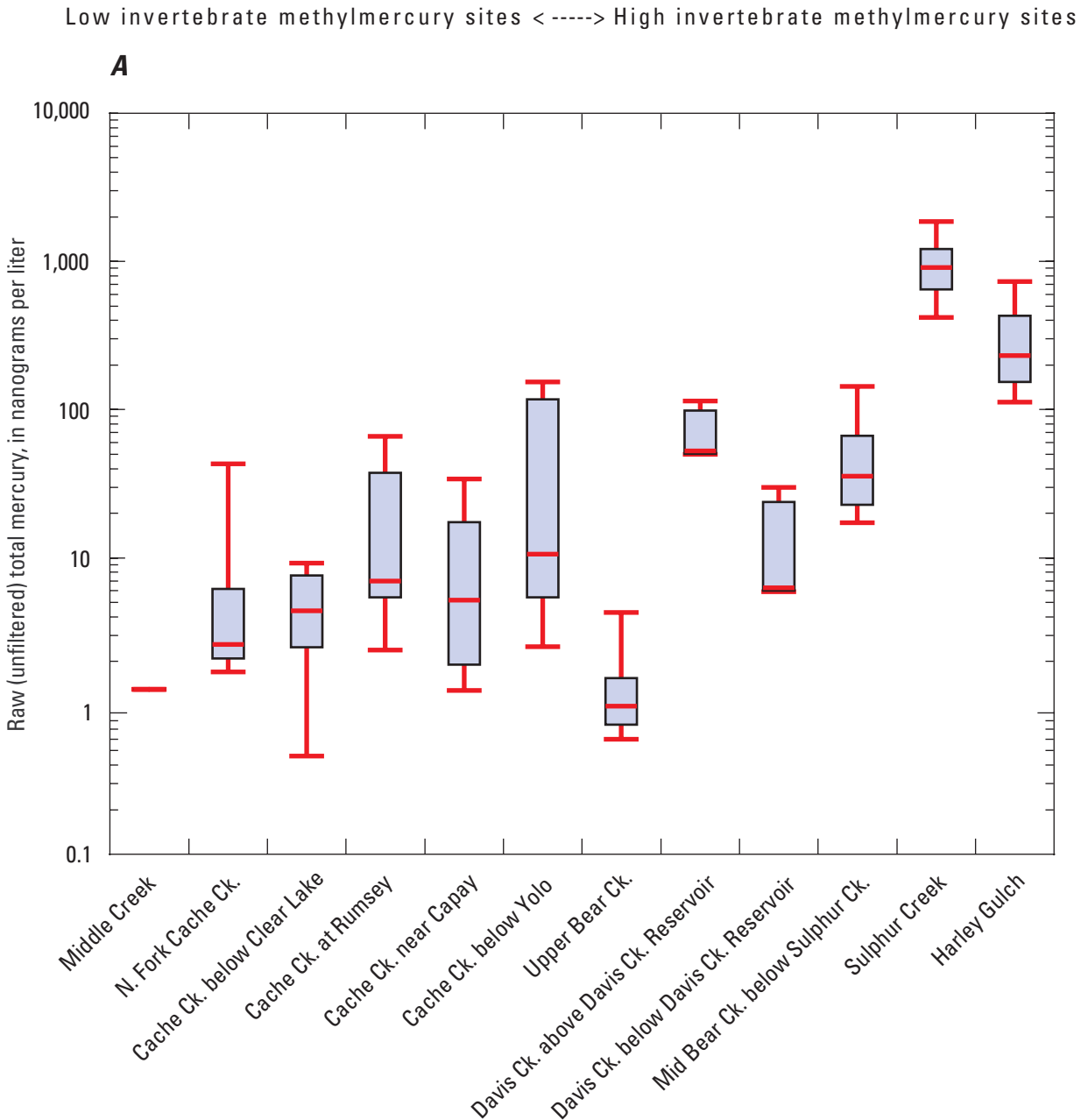


Figure 14A. Concentrations of total mercury in water at selected sites of the Cache Creek, California, watershed. From Slotton and others, 2002. Cr., creek. Each box represents the 25th to 75th percentile of data for a given site; median (50th percentile) value is represented by horizontal red line within box; horizontal bars below and above box represent 10th and 90th percentile values, respectively.

Relations Between Mercury in Fish and Mercury in Water

Understanding relations between mercury in fish and mercury and methylmercury in water is not straightforward. Boxplots of mercury and methylmercury in water are shown in [figure 14](#). The mining and geothermal sites all contained

dramatically higher water concentrations. The upper Bear Creek site, however, had extremely low total mercury and moderate methylmercury concentrations in water, but relatively high mercury concentrations in fish. Although the effect of the mining and geothermal sources of mercury on the level of mercury in fish is undeniable, local conditions at individual sites may also have a substantial effect on mercury methylation and subsequent bioaccumulation.

Low invertebrate methylmercury sites <----->High invertebrate methylmercury sites

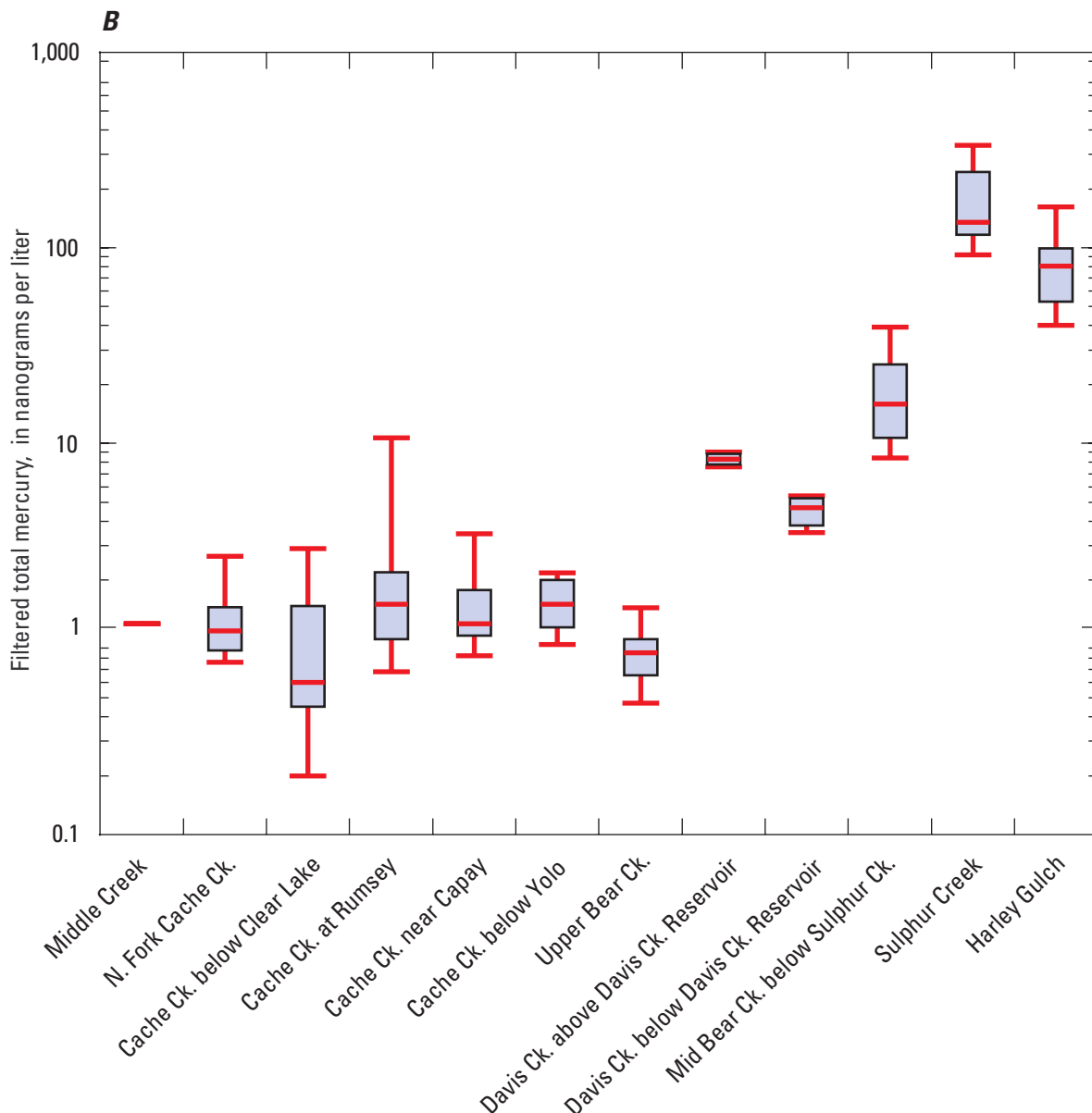


Figure 14B. Concentrations of filtered mercury in water at selected sites of the Cache Creek, California, watershed.

From Slotton and others, 2002. Cr., creek. Each box represents the 25th to 75th percentile of data for a given site; median (50th percentile) value is represented by horizontal red line within box; horizontal bars below and above box represent 10th and 90th percentile values, respectively.

When the watershed was looked at as a whole, a general correspondence was seen between total mercury in water and the other aqueous mercury fractions, including methylmercury. This indicates that reductions in overall mercury loading may result in general reductions in aqueous methylmercury. However, the study also yielded evidence for additional local methylmercury production at some of the sites, apparently unrelated to corresponding concentrations of total mercury in the water. The levels of aqueous methylmercury at mid Bear Creek generally correspond to

levels of total mercury in most samples, but to greatly elevated methylmercury in others (fig. 15). These representative results, all from the same spring-to-summer time of year, indicate that substantial methylmercury was being produced locally, supplementing methylmercury transported from upstream or in quasi-equilibrium with the inorganic mercury in the water. Local methylmercury production likely occurs beneath the water column in the sediment or algal layers, utilizing mercury that was previously deposited.

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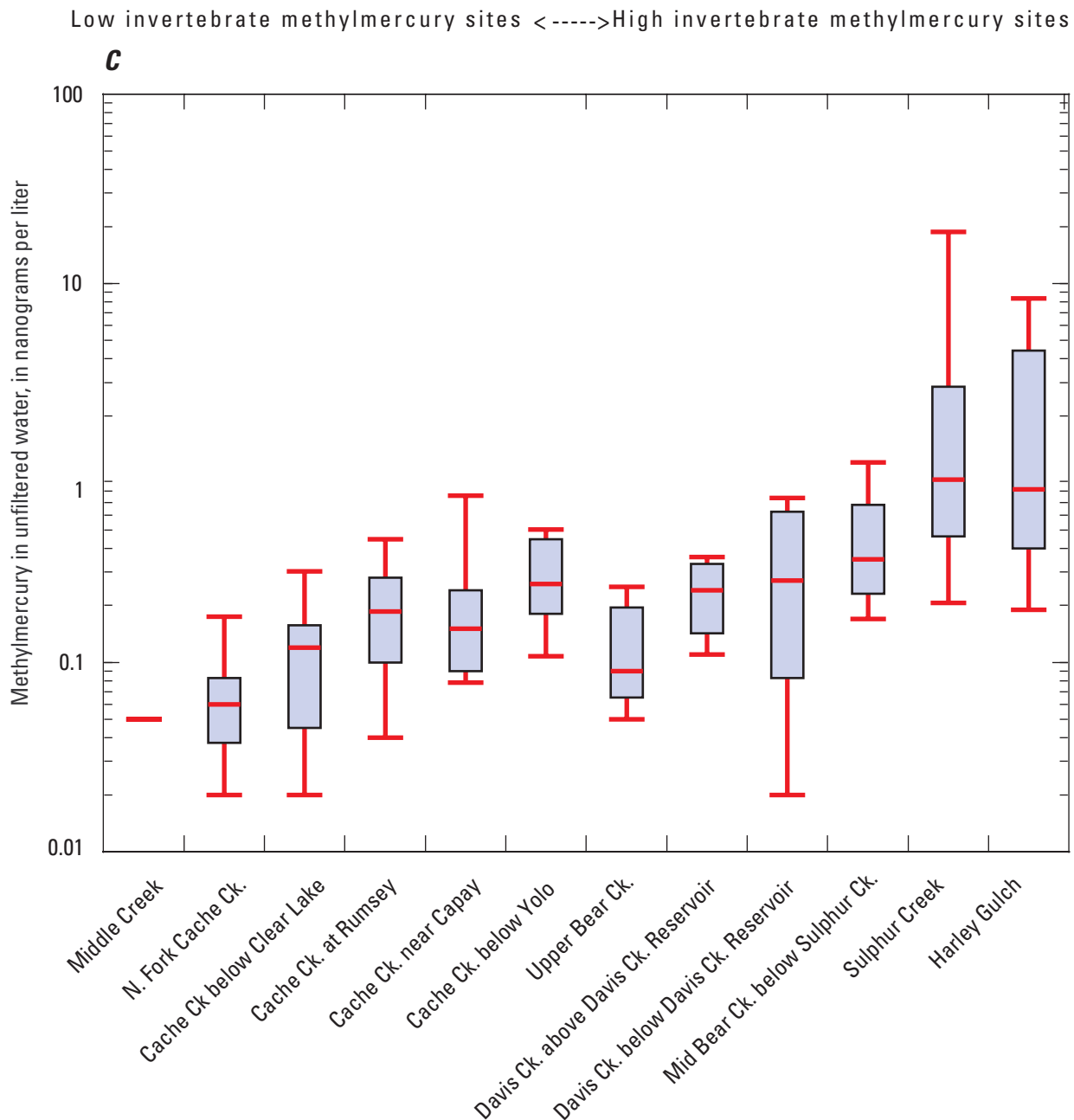


Figure 14C. Concentrations of methylmercury in unfiltered water at selected sites of the Cache Creek, California, watershed.

From Slotton and others, 2002. Cr., creek. Each box represents the 25th to 75th percentile of data for a given site; median (50th percentile) value is represented by horizontal red line within box; horizontal bars below and above box represent 10th and 90th percentile values, respectively.

Links Between Water and Mercury Bioaccumulation

Mercury concentrations were also studied in small fish and aquatic insects. These lower-trophic-level organisms are often easier to sample than are large fish and can be better indicators of potential differences in mercury-exposure conditions between sites or through time. Mercury levels in the lower-trophic-level organisms are also of interest in

relation to their being food items for other wildlife. Boxplots summarizing mercury concentrations in aquatic-insect samples are shown in [figure 16](#). Samples collected near mine or geothermal sites were clearly elevated relative to other locations. Levels in the main stem of Cache Creek, although at much lower concentrations, also were elevated downstream from these sources, as compared to concentrations upstream from Rumsey. Levels in upper Bear Creek, again, were anomalously elevated.

Low invertebrate methylmercury sites <---->High invertebrate methylmercury sites

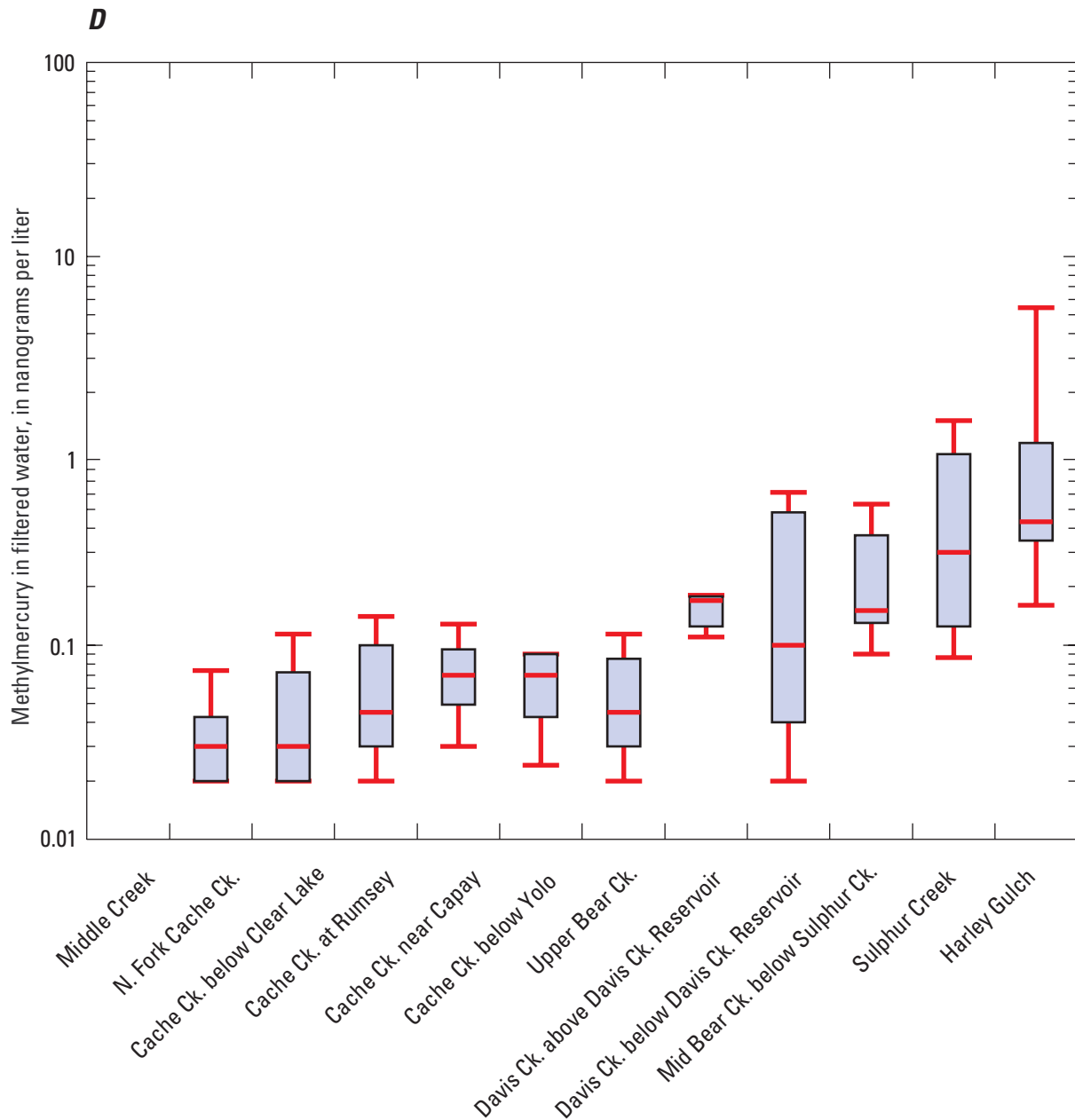


Figure 14D. Concentrations of methylmercury in filtered water at selected sites of the Cache Creek, California, watershed.

From Slotton and others, 2002. Cr., creek. Each box represents the 25th to 75th percentile of data for a given site; median (50th percentile) value is represented by horizontal red line within box; horizontal bars below and above box represent 10th and 90th percentile values, respectively.

Plots of insect mercury levels against total mercury or methylmercury in water for all sites of the Cache Creek watershed generally resulted in a good correlation. However, when examined at individual sites, most of the correlations broke down (fig. 17). The apparent relations between the water fractions of mercury and biota mercury across the watershed were determined to be mostly the result of a

statistical artifact of the large range of mercury concentrations. However, one fraction of mercury in the water—raw aqueous methylmercury— was found to be consistently predictive of corresponding invertebrate methylmercury concentrations, even at the level of individual sites. Similar results were found in the studies of small fish.

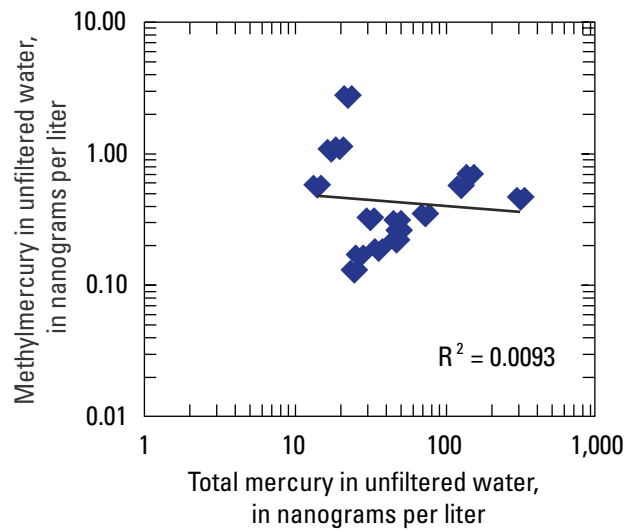


Figure 15. Methylmercury in unfiltered water relative to total mercury in unfiltered water (representative data from mid Bear Creek, California). From Slotton and others, 2002.

Links to Large-Fish Mercury

Although unfiltered methylmercury levels in the water were determined to be predictive of methylmercury bioaccumulation in the lower-trophic-level bioindicator species, they were not predictive of concentrations in large fish. A relation was found, though, between mercury in insects and small fish and mercury in large fish (fig. 18).

Because of the various and complex dynamics of methylmercury formation and transport, the levels of mercury in insects or small fish were better indicators (than methylmercury levels in water) of the mercury concentrations in large fish. When biotic data across the entire 20-month project are averaged for each site and sample type (fig. 19), the various sampled organisms follow similar mercury trends across the watershed.

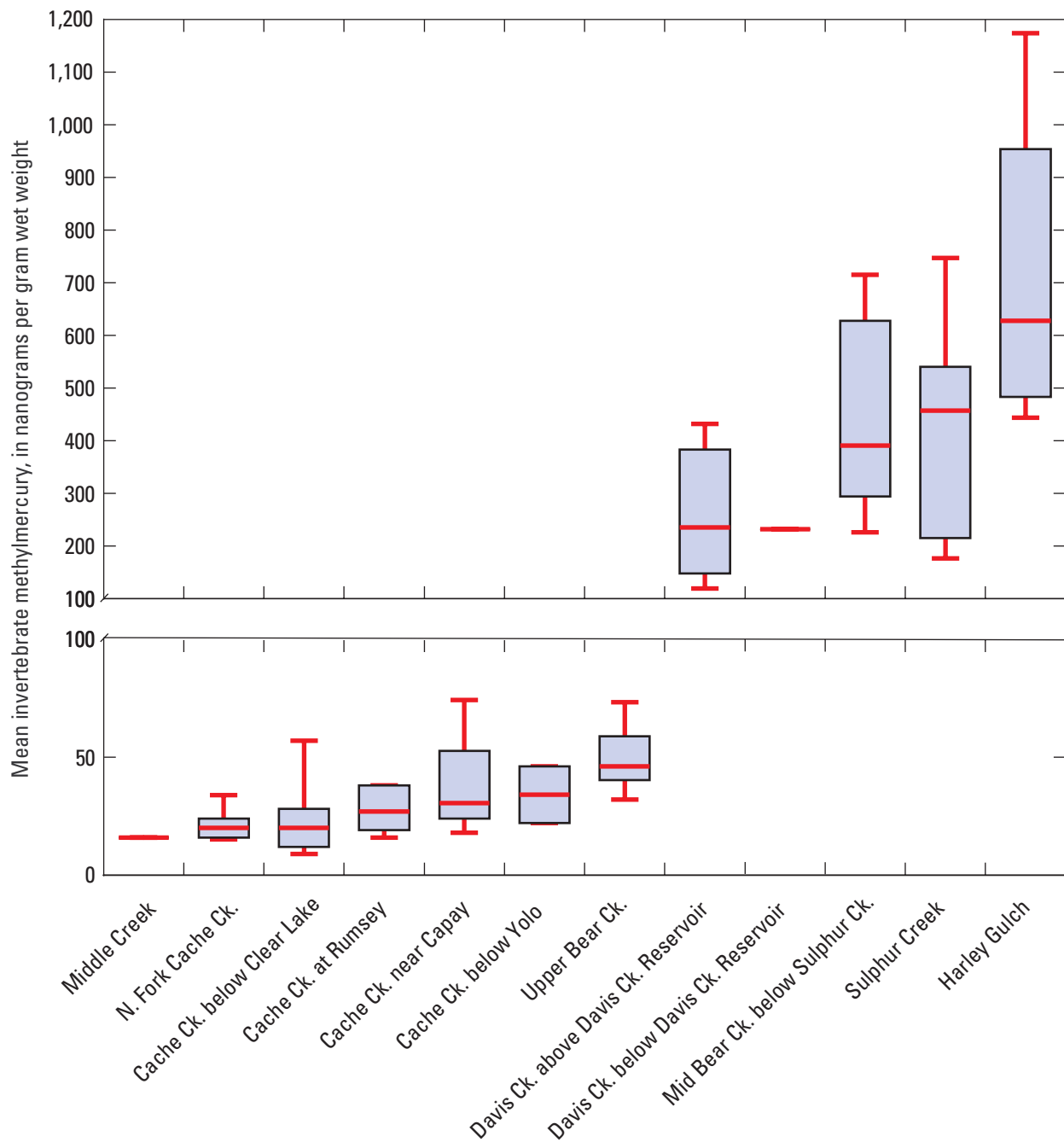


Figure 16. Methylmercury in aquatic invertebrates from study sites in the Cache Creek, California, watershed. From Slotton and others, 2002. Cr., creek. Each box represents the 25th to 75th percentile of data for a given site; median (50th percentile) value is represented by horizontal red line within box; horizontal bars below and above box represent 10th and 90th percentile values, respectively

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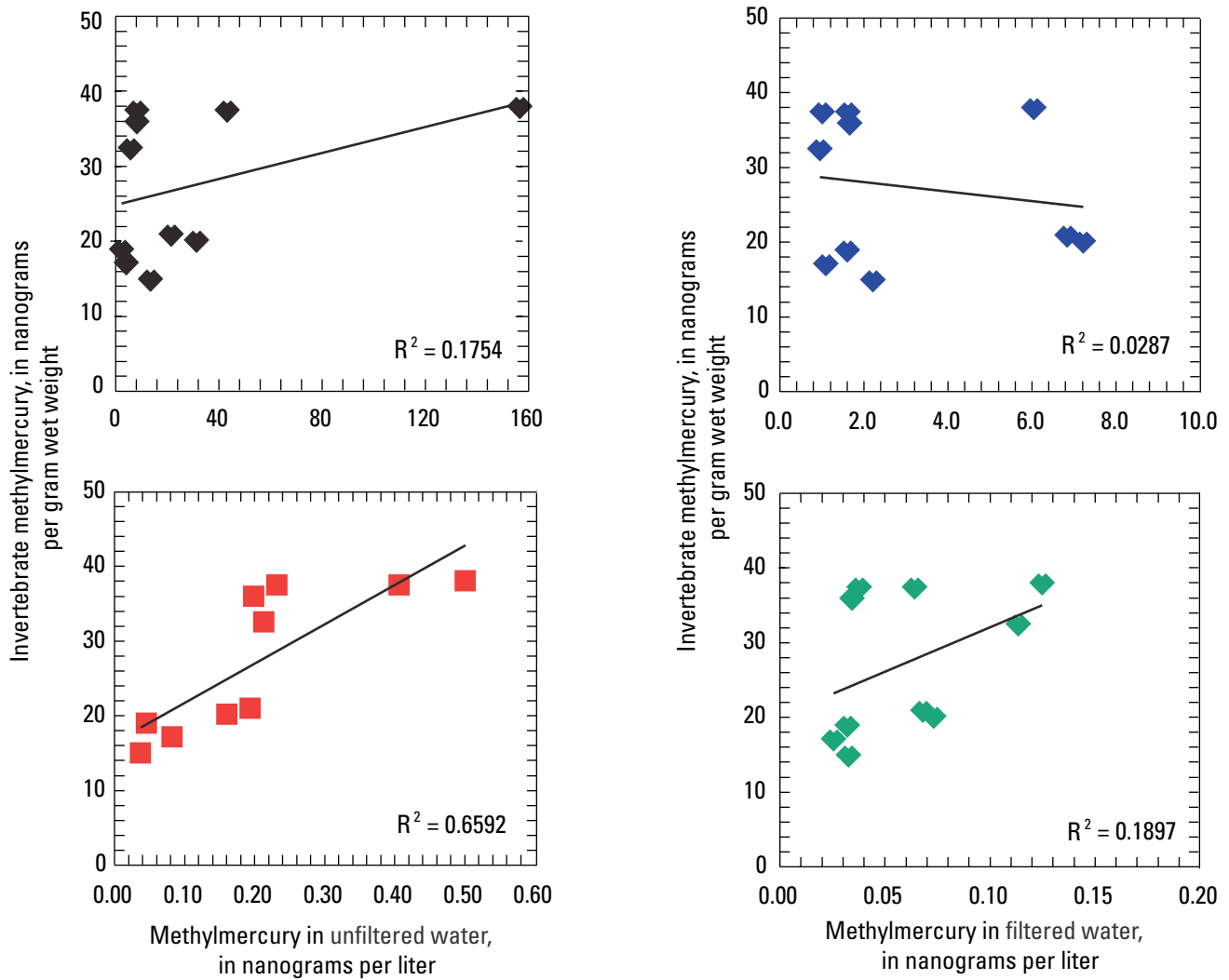


Figure 17. Different fractions of mercury in water versus invertebrate methylmercury at Cache Creek at Rumsey, California. From Slotton and others, 2002.

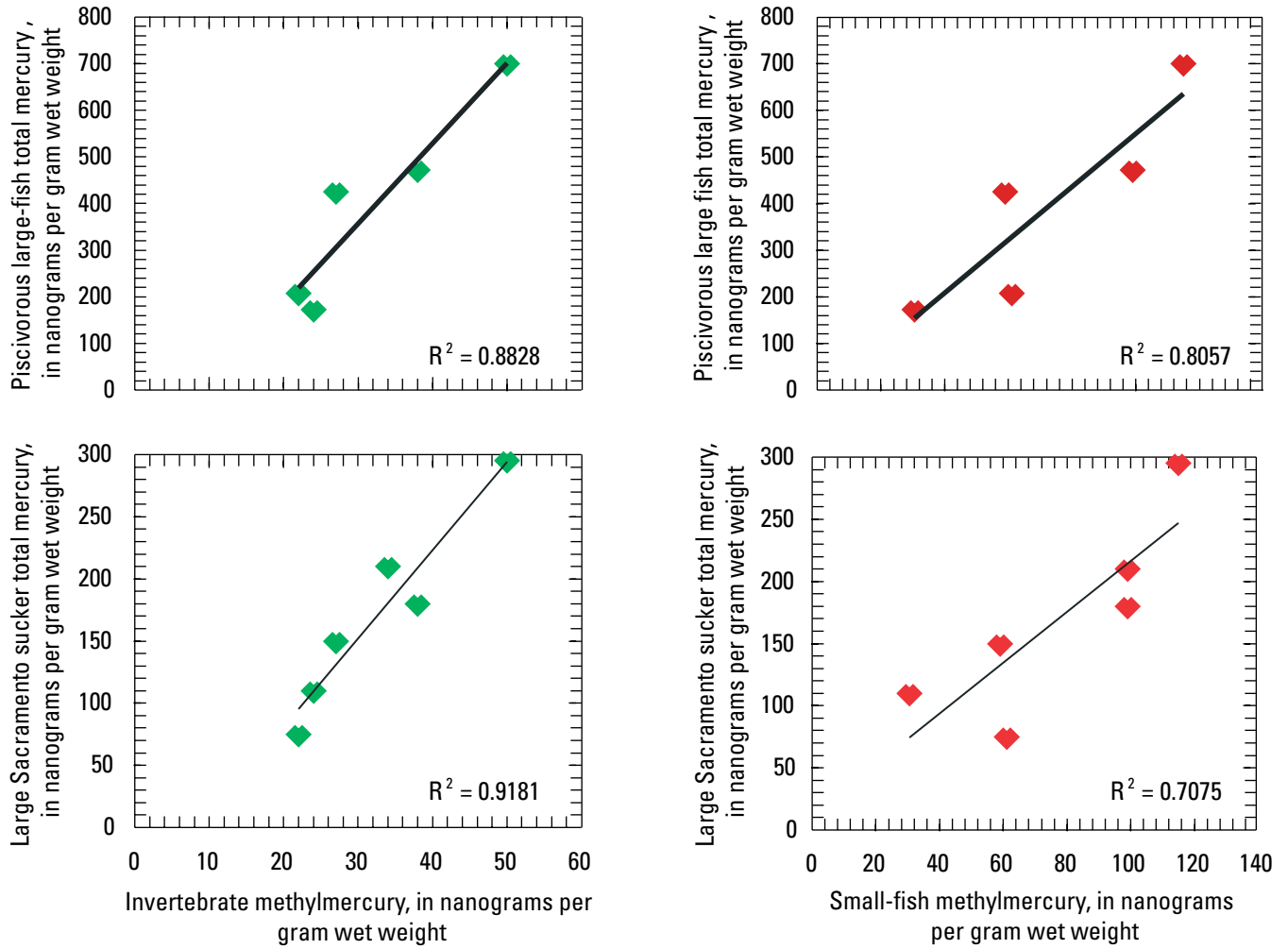


Figure 18. Relation between invertebrate methylmercury or small-fish methylmercury and methylmercury concentrations in large fish at representative individual sites.

Piscivorous large fish, above; adult Sacramento suckers, below. From Slotton and others, 2002.

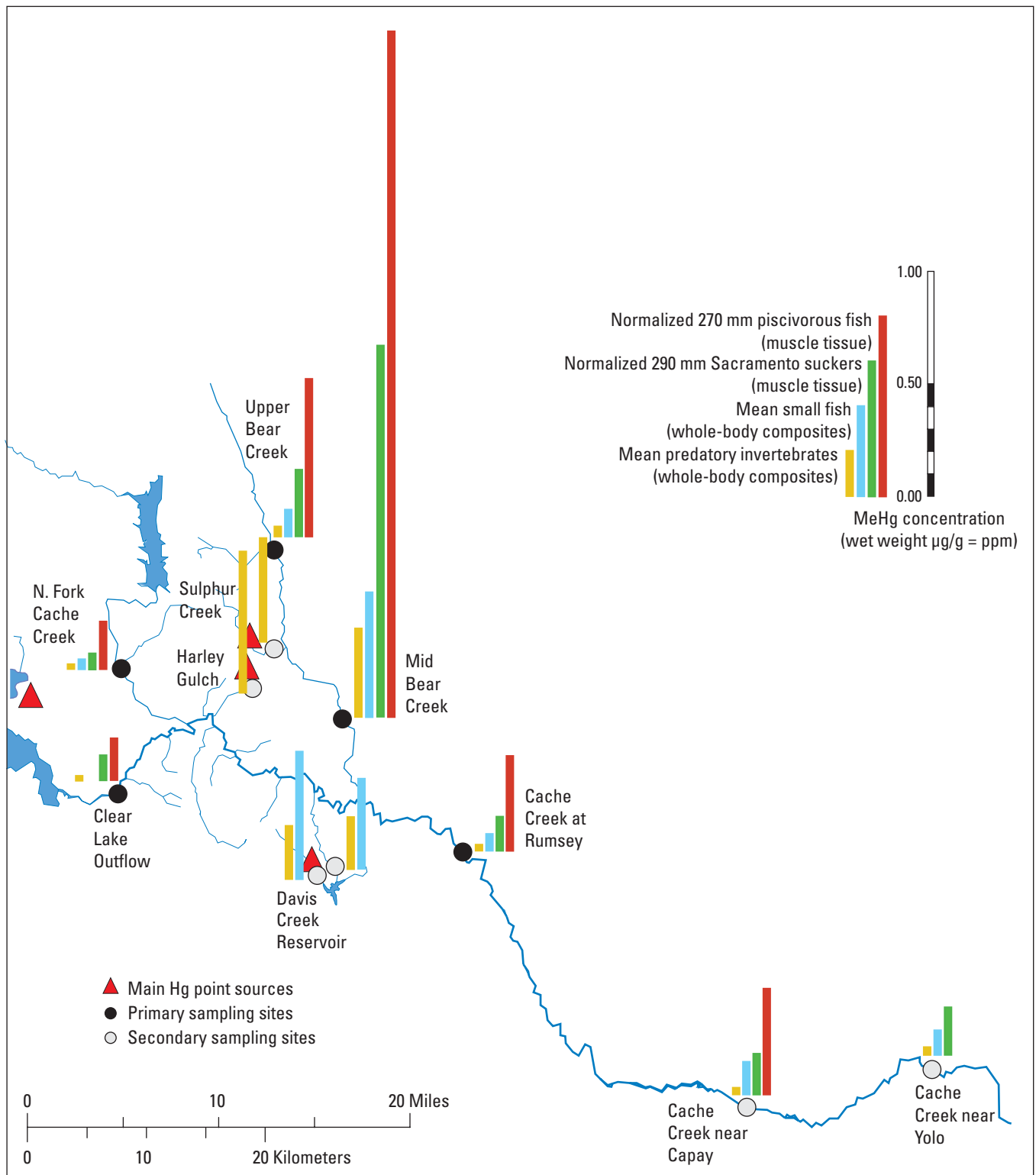


Figure 19. Spatial distributions of condensed project methylmercury biotic data for invertebrates, small fish, normalized Sacramento suckers, and normalized piscivorous fish. From Slotton and others, 2002. mm, millimeter; Hg, mercury; MeHg, methylmercury; $\mu\text{g/g}$, microgram per gram; ppm, part per million.

In summary, the bioaccumulation studies demonstrated a definite effect of the abandoned mine sites and geothermal sources on the aquatic biota of downstream receiving waters. Methylmercury in the water was generally correlated with total mercury, with additional surges of methylmercury apparently produced locally from below the water column, especially at sites nearer the main point sources. This, and the greatly elevated concentrations of mercury in biota of these regions, indicates that at least some fraction of the mercury exported from the identified sources may be readily converted to methylmercury. It also indicates that reductions in overall mercury loading from these sites may indeed be warranted. A predictive relation was found between unfiltered aqueous methylmercury and methylmercury in lower-trophic-level bioindicator organisms. Mercury in the invertebrates and small fish was subsequently determined to be predictive of levels in the larger fish. These techniques can be used in the future to monitor mercury-exposure conditions in the watershed and test the effectiveness of remedial measures.

Conceptual Model of Mercury Cycling and Transport in the Cache Creek Watershed

A conceptual model was developed to depict the major aspects of mercury transport and biogeochemical cycling in the Cache Creek watershed ([fig. 20](#)). Mercury cycling depicted in [figure 20](#) (and outlined below) is based on findings from the present study and known aspects of the transformations of mercury to methylmercury and (or) degradation of methylmercury to inorganic mercury. Major sources of mercury to streams of the Cache Creek watershed include:

- Runoff from abandoned mercury mines
- Geothermal discharge
- Runoff from soils naturally elevated in mercury
- Re-suspension of previously deposited mercury in existing stream channels
- Atmospheric deposition

Major sinks/losses for mercury in the Cache Creek watershed include:

- Transport out of the basin to Yolo Bypass
- Sedimentation within Cache Creek and other creeks
- Use of irrigation water (sedimentation to farmland)
- Evasion from water and soils to atmosphere
- Bioaccumulation into animals and plants

Major internal biogeochemical cycling processes include:

- Microbially mediated production and degradation of methylmercury
- Bioaccumulation of methylmercury by aquatic species and their consumers

Primary environmental impacts include:

- Human health concerns from consumption of fish containing elevated levels of mercury
- Wildlife health concerns from consumption of biota containing elevated levels of mercury

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Figure 20. Conceptual model of mercury cycling and transport in the Cache Creek, California, watershed. Hg, mercury; Hg(0), elemental mercury; Hg(II), oxidized (mercuric) mercury; CH₃Hg⁺, methylmercury.

Working Hypotheses

Our work to characterize the occurrence, loading, and bioaccumulation of mercury within the Cache Creek watershed has led to the following generalized hypotheses:

1. Mine sites and geothermal sources are major sources of mercury, and potentially of methylmercury, to creeks and streams.
2. Geothermal discharge is important in the subsequent production and accumulation of methylmercury within the Cache Creek watershed.
3. Information developed by this project regarding the abundance and characteristics of mercury in mine-site materials and estimates of mine-site mercury contributions to waterways suggests that effective mine-site remediation should be based on general-site erosion-control measures. Measures to reduce the amount of sulfate entering waterways from thermal springs and to reduce interaction between sulfate-rich thermal-spring water and mine materials should also be considered.
4. Sediments of Cache Creek below the mine sites and geothermal sources are also a source of mercury and methylmercury to the aquatic ecosystem because of a greater than 100-year history of erosion from mine sites and because of continuous discharge from geothermal springs.
5. Although much of the cinnabar-based mine-site materials appears to be relatively unavailable for conversion to toxic methylmercury, these sites and the geothermal sites also discharge more labile forms of mercury.
6. Some portion of the mercury derived from the identified point sources can be methylated within the watershed, particularly in the upper tributary environments.
7. Clear Lake and Indian Valley Reservoir do not contribute high concentrations of bioavailable mercury to the aquatic environment.
8. The aquatic food chain below mine sites and geothermal sources is greatly affected by accumulation of methylmercury.
9. A predictive relation exists between unfiltered methylmercury in the water and methylmercury bioaccumulation in invertebrates and small fish.
10. Mercury in lower-trophic-level bioindicator organisms is predictive of mercury bioaccumulation in large fish.

References Cited

- Bloom, N., 2002, Mercury speciation studies for CALFED Hg project: Interim link, <http://loer.tamug.tamu.edu/calfed/>.
- Bradley, W.W., 1918, Quicksilver resources of California, with a section on metallurgy and ore-dressing: California State Minerals Bureau Bulletin.
- Churchill, R., 2002, Mine site studies for CALFED Hg project: Interim link, <http://loer.tamug.tamu.edu/calfed/>.
- Domagalski, J.L., and Dileanis, P.D., 2000, Water-quality assessment of the Sacramento River Basin, California—Water quality of fixed sites, 1996–1998: U.S. Geological Survey Water-Resources Investigations Report 00-4247, 60 p.
- Domagalski, J.L., 2001, Mercury and methylmercury in water and sediment of the Sacramento River Basin, California: Applied Geochemistry, v. 16, p. 1677–1691.
- Domagalski, J.L., Knifong, D.L., Dileanis, P.D., Brown, L.R., May, J.T., Connor, Valerie, and Alpers, C.N., 2000, Water quality in the Sacramento River Basin, California, 1994–98: U.S. Geological Survey Circular 1215, 36 p.
- Domagalski, J.L., Alpers, C.N., Slotton, D.G., Suchanek, T.H., and Ayers, S.M., 2002, Mercury and methylmercury concentrations and loads within the Cache Creek Watershed, California, January 2000 through May 2001, Interim link, <http://loer.tamug.tamu.edu/calfed/>.
- Foe, C. and Croyle, W., 1998, Mercury concentrations and loads from the Sacramento River and from Cache Creek to the Sacramento–San Joaquin Delta Estuary, California: Water Quality Control Board, Central Valley Region, Sacramento, California.
- Gustin, M.S., Coolbaugh, M., Engle, M., Fitzgerald, B., Nacht, D., Zehner, R., Sladek, C., Keislar, R., Rytuba, J., Lindberg, S., and Zhang, H., 2000, Atmospheric mercury emissions from mine waste, Extended Abstracts: U.S. Environmental Protection Agency sponsored meeting—Assessing and Managing Mercury from Historic and Current Mining Activities, November 28–30, 2000, San Francisco, p. 119–124.

30 Summary and Synthesis of Mercury Studies in the Cache Creek Watershed, California, 2000–01

- Rytuba, J.J., 1996, Cenozoic metallogeny of California: In Goyner, A.R., and Fahley, P.L., eds., *Geology and ore deposits of the American Cordillera: Geological Society of Nevada Symposium Proceedings*, Reno, Sparks, Nevada, April 1995, p. 803–822.
- Slotton, D.G., Ayers, S.M., Reuter, J.E., and Goldman C.R., 1997, Cache Creek watershed preliminary mercury assessment, using benthic macro-invertebrates: Final Report for the Central Valley Regional Water Quality Control Board and the National Science Foundation, June 1997, 36 p.
- Slotton, D.G., Ayers, S.M., Suchanek, T.H., Weyland, R.D., and Liston, A.M., 2002, Mercury bioaccumulation and trophic transfer in the Cache Creek Watershed, California, in relation to diverse aqueous mercury exposure conditions, Interim link, <http://loer.tamug.tamu.edu/calfed/>.
- Slotton, D.G., Reuter, J.E., Ayers, S.M., and Goldman, C.R., 2001, Environmental monitoring for mercury in water, sediment, and biota in Davis Creek and Davis Creek Reservoir: Report for Yolo County, 83 p. (and similar reports from 1985–2000).
- Slotton, D.G., Suchanek, T.H., and Ayers, S.M., 2000, Delta wetlands restoration and the mercury question: Interagency Ecological Program Newsletter, v. 13, no. 4, p. 40–50.
- Suchanek, T.H., Slotton, D.G., Nelson, D.C., Ayers, Shaun M., Asher, C., Weyand, R.D., Liston, A.M., and Eagles-Smith, C., 2002, Mercury loading and source bioavailability from the upper Cache Creek mining districts, Interim link, <http://loer.tamug.tamu.edu/calfed/>.