CACHE CREEK WATERSHED PRELIMINARY MERCURY ASSESSMENT, USING BENTHIC MACRO-INVERTEBRATES

By

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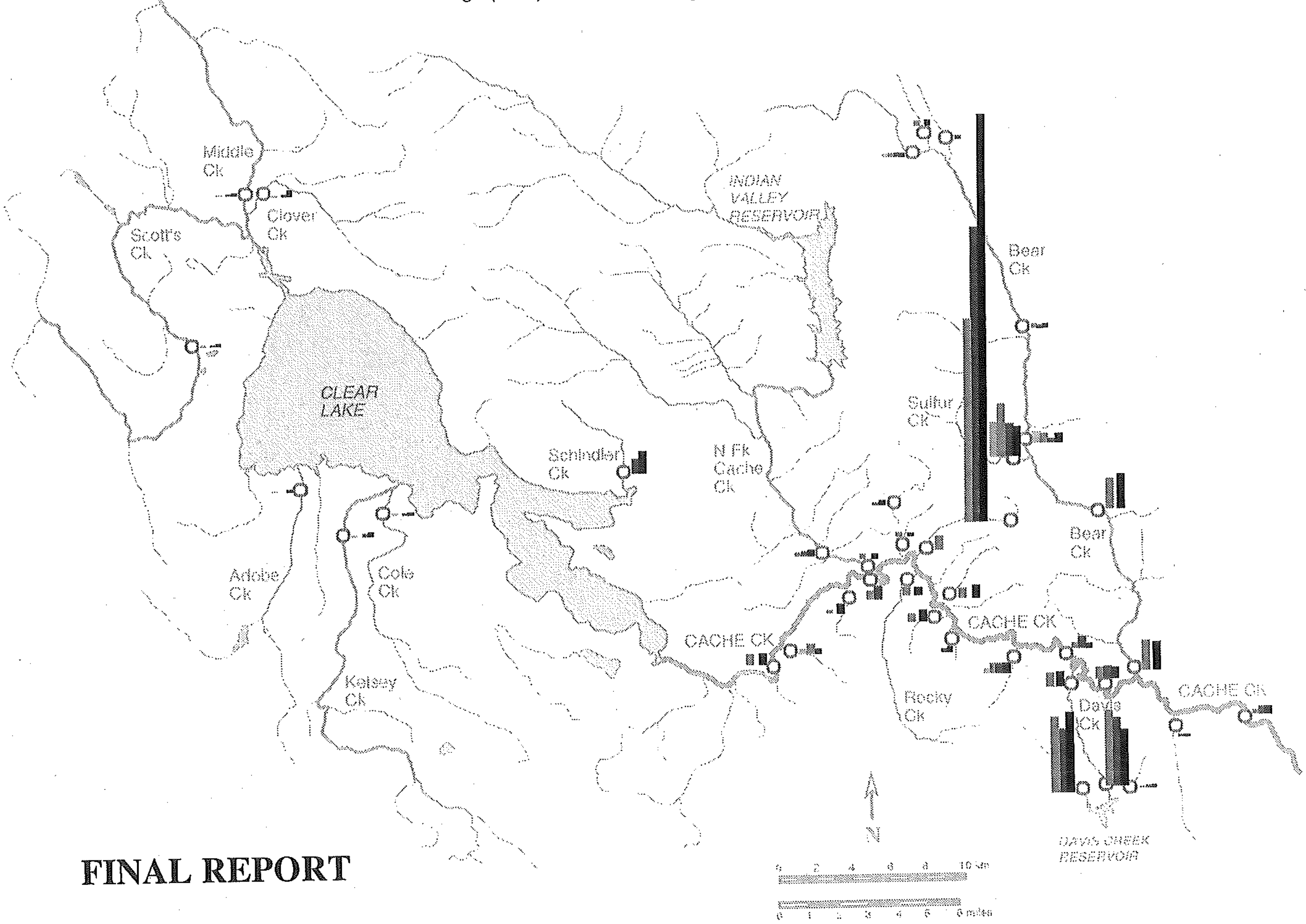

FINAL REPORT

June 1997

The research leading to this report was supported by:

The Cental Valley Regional Water Quality Control Board

and

The National Science Foundation

ABSTRACT

Native benthic macroinvertebrates were used as indicators of biologically available mercury in this Spring 1996 preliminary study of the upper Cache Creek watershed. Thirty-eight sites were sampled above Rumsey, including the Bear Creek and Davis Creek drainages, all significant tributaries to Clear Lake, the main channel of Cache Creek between Clear Lake and Rumsey, and all significant inflowing tributaries to Cache Creek throughout this reach. Biotic mercury was low in most of the Clear Lake tributaries, the headwater regions of the Bear Creek drainage, and in several additional tributaries that did not contain historic mercury mining activity. Dramatic spike concentrations of mercury in bioindicator organisms were present near abandoned mercury mines, with dry weight concentrations of >1.00 $\mu g\ g^{-1}$ and maximal concentrations to over 20 $\mu g\ g^{-1}$. Every significantly elevated set of samples was associated with a known mercury mine source or a stream that drained a mercury mining zone, including Sulfur Creek, Harley Gulch, Davis Creek, Schindler Creek, and Brushy Creek. The highly localized nature of these zones was demonstrated by the dramatically lower biotic mercury accumulations in adjacent streams without historic mercury mining activity. Samples from the main stem of Cache Creek were elevated above background levels throughout the stretch between Clear Lake and Rumsey, but exhibited a slight decline throughout this reach. Tributary inputs with highly elevated biotic mercury did not correspond to increases in main stem Cache Creek invertebrate mercury levels. The findings of this study suggest that much of the large bulk load of mercury in Cache Creek may be relatively inert biologically. However, abandoned mercury mines are clearly sources of mercury that is, at least initially, highly bioavailable. Though this mercury appears to become relatively unavailable in the downstream environment, data suggests that it can be an important substrate for bacterial mercury methylation under conditions of decreased flow, lowered dissolved oxygen, and increased temperature. Mine-derived, surface-adsorbed mercury which has coprecipitated with iron and other metal and mineral flocs may represent a dominant component of the portion of the mercury load that is biologically available to mercury methylating organisms and, subsequently, aquatic food webs.

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INTRODUCTION AND BACKGROUND

Mercury pollution and, particularly, the bioaccumulation of toxic methyl mercury in food webs is a global problem impacting aquatic ecosystems and consumers of aquatic organisms. In California, the threat is compounded by the legacy of mining-related mercury across wide areas of the state. Abandoned mercury mines in the Coast Range continue to leach mercury into their watersheds. On the other side of the state, millions of kilograms of refined elemental mercury were lost into Sierra Nevada drainages in the course of gold mining. Both of these regions supply an ongoing loading of mercury to the Bay-Delta and its watershed. Mercury has been clearly identified by many California state agencies as an aquatic pollutant of great concern. Its toxicity to higher order consumers of aquatic organisms is well established, while the effects on reproduction, development, and juveniles of all aquatic and aquatic-feeding species is only poorly understood. If individual point sources of mercury contamination from the upper watershed regions of the Sierra Nevada and Coast Ranges can be identified as contributing a significant fraction of the downstream bioavailable mercury load, a targeted implementation plan of remediation can be successful in reducing the loading of mercury which ultimately flows into the Bay-Delta system. The work reported here represents a preliminary step toward the identification and ranking of key source regions of bioavailable mercury in the Cache Creek watershed, which has been identified as contributing significantly to the statewide downstream loading of mercury on a bulk basis.

In recent years, the Central Valley Regional Water Quality Control Board has conducted preliminary studies of bulk mercury loading in the Cache Creek watershed, Yolo Bypass, and Delta receiving waters during winter storm flows. The data generated in that work indicated that large quantities of bulk, presumably inorganic mercury move down the drainage in association with high flows and that this source apparently represents a major input of mercury to the San Francisco/San Joaquin Bay-Delta. In our ongoing UC Davis research work at Davis Creek Reservoir, along a tributary to Cache Creek, we have quantified the annual loading of new mercury to the reservoir in the range of 100-300 kg mercury per year (Slotton 1991, Reuter *et al.* 1996). While this mercury is now largely trapped behind the Davis Creek Dam, these data suggest the magnitude of loads potentially moving down Cache Creek, as Davis Creek is but one of several major tributaries to Cache Creek that have abandoned mercury mines along them. Clear Lake, which is the primary source of Cache Creek water, contains an EPA Superfund mercury cleanup site at the Sulphur Bank Mercury Mine, which has been the focus of a large UC Davis research project since 1992 (Suchanek *et al.* 1993, 1997).

We have found much of the bulk load of mercury in Clear Lake to be largely unavailable to the mercury methylation process (Suchanek *et al.* 1997). Bacterially mediated mercury methylation is the source of the toxic form of mercury (methyl mercury) which enters the food web and can become greatly concentrated at the higher trophic levels. Our preliminary studies of fish mercury levels in the lower reaches of Cache Creek near Woodland (Slotton *et al.* 1996b and reported here) also suggest that much of the large bulk mercury load moving through and depositing in this system may be relatively inert biologically.

To supplement the Central Valley Regional Water Quality Control Board's aqueous bulk mercury data, we conducted the project reported here throughout the upper watershed of Cache Creek in the Spring of 1996 (with some supplementary data from earlier years). In this work, we utilized primarily native benthic macroinvertebrates as indicators of bioavailable mercury levels. The mercury present in these organisms at the time of sampling represents an integrated accumulation of, specifically, the bioavailable fraction of mercury that they have been exposed to during their lives, at or very near the site of collection. This technique has been extensively tested and refined in similar work throughout the Sierra Nevada foothill gold mining region (Slotton *et al.* 1995a, 1997) and in the Marsh Creek watershed near Mt. Diablo (Slotton *et al.* 1996a).

Our objective in this preliminary biotic assessment of mercury in the upper Cache Creek watershed has been to obtain measures of relative mercury bioavailability for each of the major tributaries and at sites distributed along the length of the main channel. We believe we have been successful in that objective and feel that the data presented here will be a very useful supplement to the aqueous bulk mercury data being collected in parallel work.

METHODOLOGY

Site Selection

Sampling sites were distributed throughout the watershed of Cache Creek, with all major tributaries sampled near their confluence with Clear Lake or the main stem of Cache Creek (Figure 1, Table 1). Scott's Creek (site 4) was an exception, requiring sampling approximately 11 miles upstream from the confluence with Clear Lake, due to the very low gradient and lack of riffle habitat below that point. Where relatively elevated mercury levels were found at the downstream reaches of tributaries, additional sampling was conducted upstream. Thus, Bear Creek was sampled extensively, while the North Fork Cache Creek drainage was not. Sampling was generally conducted near road crossings where possible. The inflowing tributaries and main stem of Cache Creek throughout the wilderness stretch between Clear Lake and Bear Creek were reached by kayak in a multi-day expedition. Tributaries in this section were sampled $\geq$ 100 m upstream of their confluence with Cache Creek. A total of 38 sites were sampled in this project.

Collection Techniques

Stream invertebrates were taken from riffle habitat at each of the sites, i.e. from rapids or cobble bottomed stretches with maximal flow, where aquatic insects tend to be most concentrated among the rock interstices. Felt-soled boots were used to permit effective movement in this habitat. Stream invertebrates were collected primarily with the use of a kick screen. Screens were constructed with a 1 m x 1.6 m section of heavy duty stainless steel screening which was fastened securely to 4 cm x 1.2 m wooden dowels at both sides with brass wire. A 1.5 mm mesh size was used, trapping invertebrates thicker than this in cross section. One researcher spread and positioned the screen perpendicular to the flow, bracing the side dowels against the bottom, while the other researcher overturned boulders and cobble directly upstream of the screen. These rocks were hand scrubbed into the flow, dislodging any clinging biota. Following the removal of the larger rocks to the side of the stretch, the underlying cobble/pebble/gravel substrate was disrupted by shuffling the boots repeatedly. Invertebrates were washed into the screen by the current. The screen was then lifted out of the current and taken to the shore, where teflon coated forceps were used to pick macro-invertebrates from the screen into pre-washed jars with teflon-lined caps. This process was repeated until a sufficient sample size of each taxon of interest was accumulated to permit future analysis for mercury. Whenever possible, we attempted to collect consistent samples from the following four invertebrate trophic levels: herbivores, drift feeders, small-item predators, and top insect predators (Figure 2). When present, we took a variety of mayfly nymphs for the herbivore trophic level and Hydropsychid caddisfly nymphs for the drift feeder group. The small-

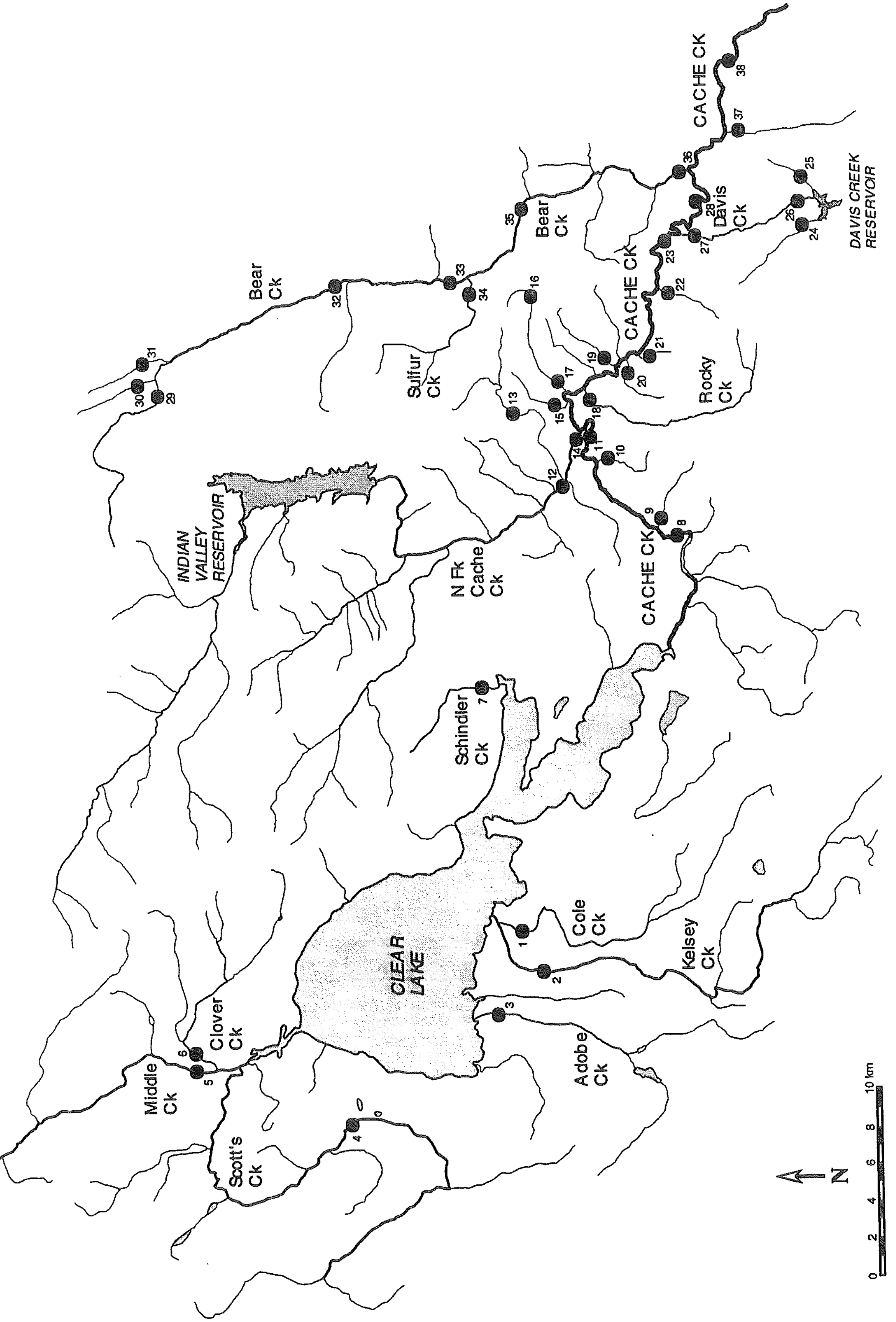


Fig. 1. UPPER CACHE CREEK WATERSHED AND SAMPLING SITES UTILIZED IN THIS PROJECT

Table 1. UC Davis Cache Creek Watershed Biotic Mercury Sampling Sites

CLEAR LAKE TRIBUTARIES

1. Cole Creek (tributary to Clear Lake), 1 mile above Clear Lake.
2. Kelsey Creek (tributary to Clear Lake), 4 miles above Clear Lake.
3. Adobe Creek (tributary to Clear Lake), 3 miles above Clear Lake.
4. Scott's Creek (tributary to Clear Lake), 11 miles above Clear Lake.
5. Middle Creek (tributary to Clear Lake), 4 miles above Clear Lake.
6. Clover Creek (tributary to Middle Creek), 2 miles above confluence.
7. Schindler Creek (tributary to Clear Lake), .5 miles above Clear Lake.

CACHE CREEK MAIN STEM AND TRIBUTARIES (between Clear Lake and Bear Creek)

8. Cache Creek below Clear Lake Dam.
9. Dry Creek (tributary to Cache Ck.), above confluence.
10. Deadman Creek (tributary to Cache Ck.), above confluence.
11. Cache Creek upstream of North Fork Cache Creek confluence.
12. North Fork Cache Creek at Hwy. 20 (trib. to Cache Ck.), 2 miles above confl.
13. Highway 20 Creek (tributary to N. Fk. Cache Ck.), 1 mile above confluence.
14. North Fork Cache Creek (tributary to Cache Creek), above confluence.
15. Stemple Creek (tributary to Cache Creek), above confluence.
16. Harley Gulch (tributary to Cache Creek), at Hwy. 20, 4 miles above confluence.
17. Harley Gulch (tributary to Cache Creek), above confluence.
18. Rocky Creek (tributary to Cache Creek), above confluence.
19. Brushy Creek (tributary to Cache Creek), above confluence.
20. Petrified Creek (tributary to Cache Creek), above confluence.
21. Trout Creek (tributary to Cache Creek), above confluence.
22. Crack Creek (tributary to Cache Creek), above confluence.

(continued)

Table 1. (continued)

23. Cache Creek, 1 mile above Davis Creek confluence.
24. Davis Creek (tributary to Cache Creek), above Davis Creek Reservoir.
25. Rayhouse Creek (tributary to Davis Creek Reservoir), 1/2 mile above reservoir.
26. Davis Creek (tributary to Cache Creek), below Davis Creek Reservoir.
27. Davis Creek (tributary to Cache Creek), above confluence with Cache Creek.
28. Cache Creek, 2 miles below Davis Creek.

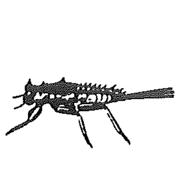
BEAR CREEK DRAINAGE

29. Mill Creek (tributary to upper Bear Creek), 1 mile above confluence.
30. West Upper Bear Creek, 1mile above confluence with Mill Creek.
31. East Upper Bear Creek, 1 mile above confluence with main stem.
32. Bear Creek at Valley Xing, first road crossing in Bear Valley.
33. Bear Creek, 1/2 mile above Sulfur Creek confluence.
34. Sulfur Creek (tributary to Bear Creek), above confluence.
35. Bear Creek at Hwy. 20 Xing.
36. Bear Creek, above confluence with Cache Creek.

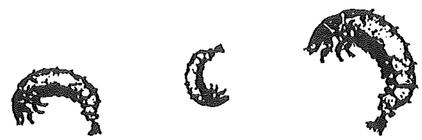
CACHE CREEK MAIN STEM AND TRIBUTARIES (downstream of Bear Creek confluence)

37. Fiske Creek (tributary to Cache Creek), above confluence.
38. Cache Creek at Scout Camp, above Rumsey at head of Capay Valley.

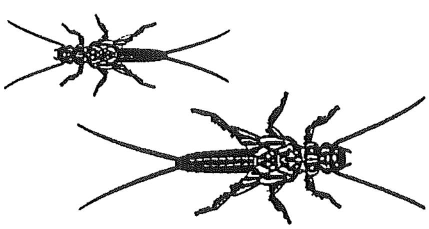
Figure 2. Primary Stream Invertebrates Analyzed in This Project
(illustrations taken from McCafferty 1981, Merritt and Cummins 1984)



HERBIVORES
Mayflies (Ephemeroptera)
(5-15 mm)
Ephemerellidae
Siphloneuridae

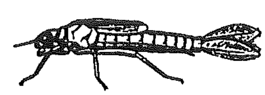


DRIFT FEEDERS / OMNIVORES
Caddisflies (Trichoptera)
(5-15 mm)
Hydropsychidae

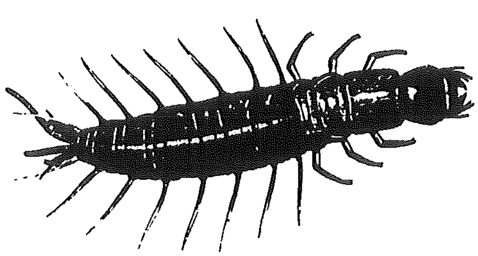


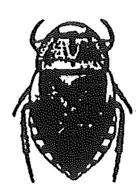
Stoneflies (Plecoptera)
Perlodidae (10-30 mm)

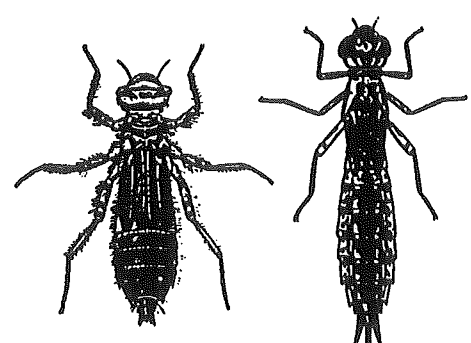
FIRST ORDER PREDATORS



Damselflies (Zygoptera)
Coenagrionidae (10-20 mm)







SECOND ORDER PREDATORS

Hellgrammites (Megaloptera)
Corydalidae (20-100 mm)

Water Bugs (Hemiptera)
Naucoridae (10-15 mm)

Dragonflies (Anisoptera)
Libellulidae (15-30 mm)
Aeschnidae (15-40 mm)

item predator group was represented by Perlid and Perlodid stoneflies at some of the sites and damselfly nymphs at others. Hellgrammites (Megaloptera) were the primary top predator stream insect in some of the streams while, at many of the sites, predaceous Naucorid water bugs were the major representatives. We endeavored to obtain samples of all major macroinvertebrate groups present at each of the sample sites, though diversity was frequently quite meager.

Sample Preparatory Techniques

Stream insects were analyzed for mercury in homogenized composite samples of multiple whole individuals. Typically, ≥ 10 individuals were composited for each of the trophic levels excepting Hellgrammite and dragonfly samples, which generally consisted of 2-5 individuals, based on availability. Samples were pooled by taxa into separate jars. The insects were maintained live on ice. Within 24 hours of collection, the contents of each jar were carefully cleaned and sorted. This was accomplished by resuspending the jar contents in a tray of clean water and, with teflon-coated forceps, individually rinsing and shaking each individual insect in the clean water to remove any extraneous material. Insects were keyed to at least the family level, using a variety of aquatic insect texts and manuals. Trophic feeding category of organisms was determined based on the recommendations of Merritt and Cummins (1984). In uncertain cases, the magnified examination of mouthparts was used to help make this determination. Cleaned insects were placed in well rinsed jars and frozen. At the onset of sample analysis, the jar contents were dried at 50-60 °C for 24 hours and then ground with teflon coated instruments or glass mortar and pestle to a homogeneous powder. The resulting powder was dried a second time to constant weight before analytical sub-samples were taken for digestion. All aquatic insect mercury analytical work was performed with dry powdered sample, both to ensure homogeneity of sample and to enhance mercury detection capacity.

Analytical Methodology

Mercury analytical methodology followed the protocols developed at UC Davis (Slotton 1991) and summarized in Slotton *et al.* (1995b). The method combines features of a number of previous techniques, and is notable for allowing excellent reproducibility, low detection levels, high numbers of samples per batch and thus room for high numbers of QA/QC samples, and the ability to re-analyze digests.

The method can be summarized as follows: digestion is performed in teflon-capped pyrex test tubes in a two stage process. Environmental samples are broken down in a 2:1 mixture of concentrated sulfuric acid to concentrated nitric acid, the digest mixture found to be most effective in a comparative study (Sadiq and Zaidi 1983). This first stage utilizes a temperature of 90-100 °C and pressure (sealed tubes) for 1.5 hrs, resulting in clear solutions. In the second stage, also 1.5 hrs, potassium permanganate is added for additional oxidation and digest stabilization. This portion of the digest procedure is performed at 80-95 °C with the tubes refluxing, uncapped. The resulting digests can be diluted or not, depending on the mercury concentrations and required level of detection, and are stable indefinitely, both before and following detection. Detection utilizes typical cold vapor atomic absorption techniques with a mercury lamp of 253.7 nm wavelength. The method differs from standard flow-through systems which reduce the entire digest in a one-time detection. A long path length, minimum volume gas cuvette and holder have been manufactured for positioning in the beam path and a specialized injection port allows direct introduction of reduced mercury in vapor. Reduction of digest mercury is performed inside a 12 cc calibrated syringe on a 2.0 cc aliquot of digest together with 2.0 cc of stannous chloride/hydroxylamine sulfate/sodium chloride reductant. A 6.00 cc airspace is utilized for partitioning of the volatile reduced mercury within the syringe and, after partitioning is complete, this airspace is injected directly into the low volume cuvette mounted in the beam path for detection. The amount of digest and, thus, proportion of sample detected is accurately determined through difference, with the digest tubes weighed to ± 0.001 g both before and immediately after removal of the analytical aliquot. Weight of total digest is initially determined by weighing the empty tube and then the full tube of digest. Level of detection was approximately 0.01 $\mu g\ g^{-1}$ (ppm).

QA/QC was quite extensive, with approximately 16 of the 40 tubes in each run dedicated to this purpose. QA/QC samples in each run included an extensive set of aqueous mercury standards, a minimum of 3 certified reference material samples in an appropriate matrix, duplicates, and spike recovery samples. QA/QC samples passed through all phases of the digest and were treated identically to analytical samples. Replication was typically ≤ 5% difference between duplicates, recoveries of certified reference materials were uniformly within 20% of certified values, spike recoveries were within 15% of predicted concentrations, and standard curves generally had R^2 values in excess of 0.98.

RESULTS

Mercury data from sampled stream benthic macroinvertebrates are presented graphically on maps of the regions in Figure 3 (Clear Lake tributaries), Figure 4 (Cache Creek main stem and tributaries), Figure 5 (Bear Creek drainage), and Figure 6 (whole watershed, expanded scale, showing high spike concentrations at point sources). The raw data for all samples from each of the 38 collection sites are additionally presented in tabular and bar graph format in Table 2. In Table 3, reduced data are presented for each of the 4 trophic levels of interest, together with summary statistics. Table 4 compares the mean data for each site with those from a group of Cache Creek main stem sites and near-main-stem tributaries.

Clear Lake Tributaries

All significant tributaries to Clear Lake were sampled (sites 1-7), including the dominant sources of the lake's inflow volume, Scott's Creek, Middle Creek, and Kelsey Creek, and the larger of the remaining tributaries, Clover Creek, Cole Creek, Adobe Creek, and Schindler Creek. Mercury data are presented in Figure 3 and Table 2.

It was possible to obtain very similar samples from most of these sites, including herbivorous Ephemerellid maylies, small item predator Perlodid and Perlid stoneflies, and top invertebrate predator Corydalid hellgrammites. Throughout these upper watershed sites, macroinvertebrate mercury levels increased fairly regularly with trophic level of organism. Concentrations were uniformly quite low from the major water sources to Clear Lake: Kelsey Creek, Middle Creek, and Scott's Creek, as well as from Cole and Adobe Creeks. Dry weight mercury concentrations in all samples from these tributaries were less than or equal to 0.18 $\mu g\ g^{-1}$. Ephemerellid mayflies from these sites averaged 0.05 $\mu g\ g^{-1}$, Perlodid and Perlid stoneflies averaged 0.10 $\mu g\ g^{-1}$, and Corydalid hellgrammites and Libellulid dragonflies had a mean level of 0.14 $\mu g\ g^{-1}$. Hellgrammites from Clover Creek were somewhat elevated, at 0.29 $\mu g\ g^{-1}$ Hg. Among Clear Lake tributary sites 1-6, 14 of the 17 total trophic level comparisons (82%) exhibited mercury levels that were at least one standard deviation below the Cache Creek main stem and near-main-stem sites used for normalization (Table 4). Only small Schindler Creek, near the back of the Oaks Arm and the Sulphur Bank Mercury Mine, demonstrated invertebrate mercury levels that were significantly elevated. Perlodid stoneflies from this stream contained 0.58 $\mu g\ g^{-1}$ Hg and Corydalid hellgrammites exhibited a level of 0.93 $\mu g\ g^{-1}$.

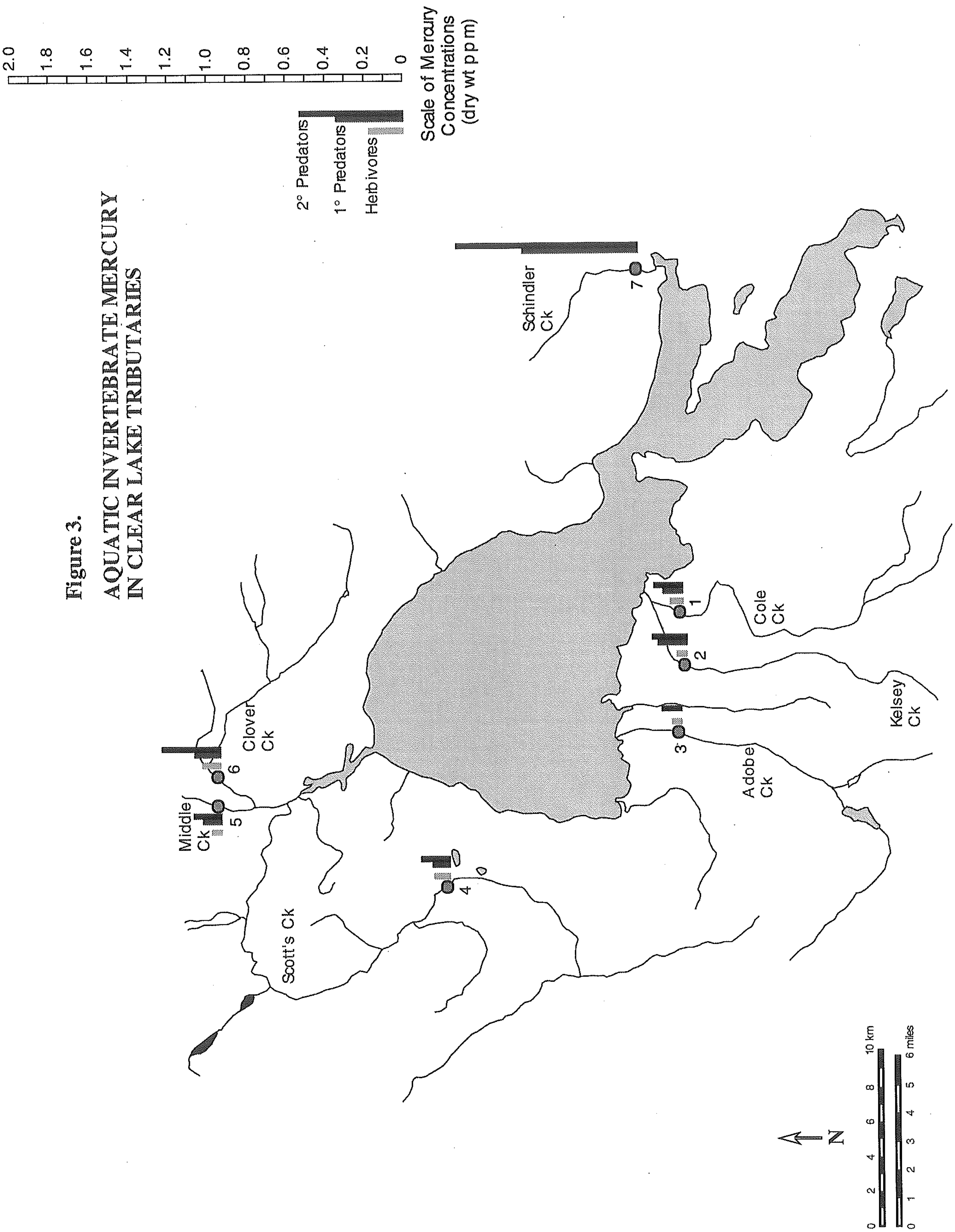


Figure 3.
AQUATIC INVERTEBRATE MERCURY IN CLEAR LAKE TRIBUTARIES

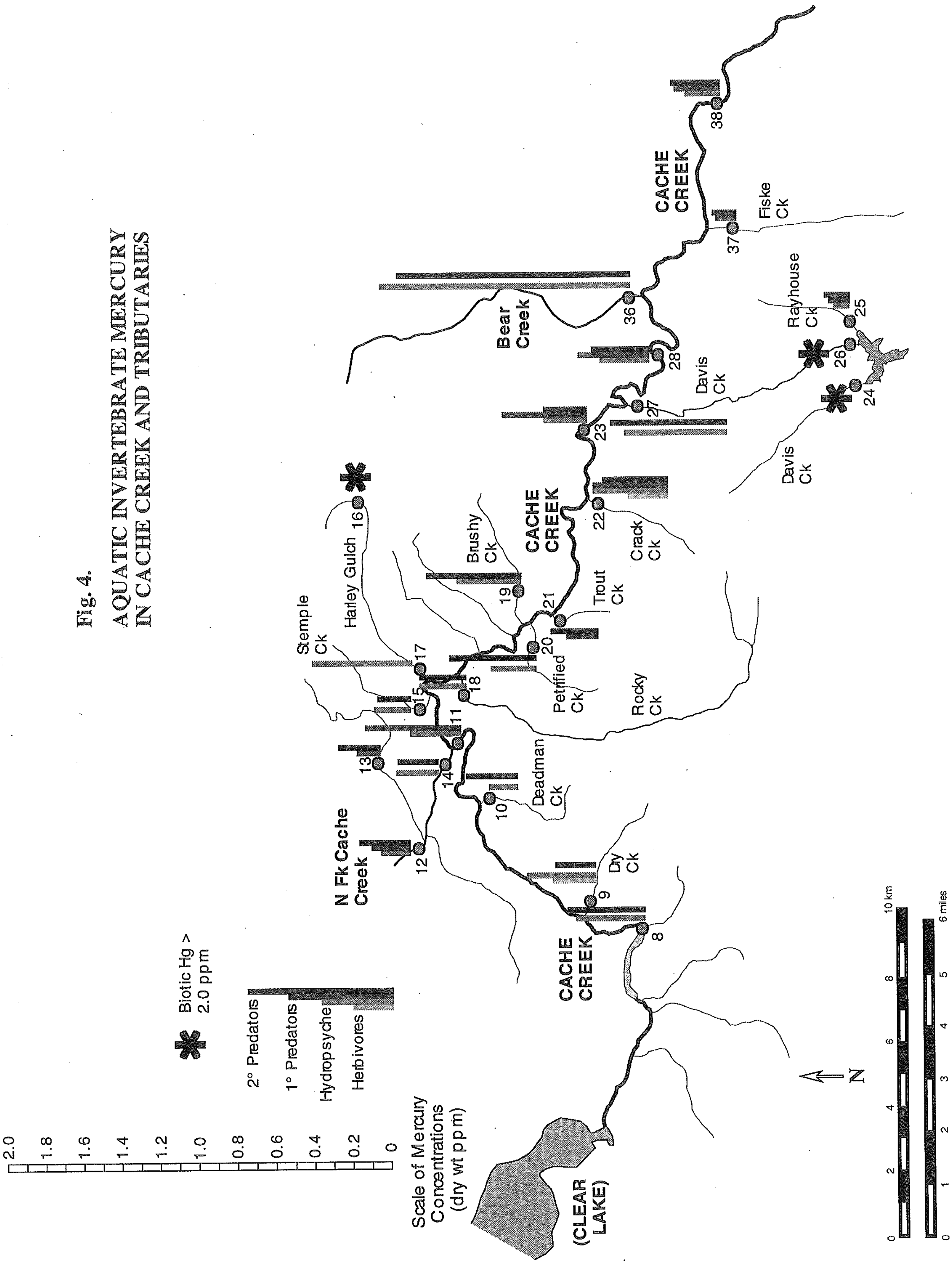


Fig. 4.
AQUATIC INVERTEBRATE MERCURY IN CACHE CREEK AND TRIBUTARIES

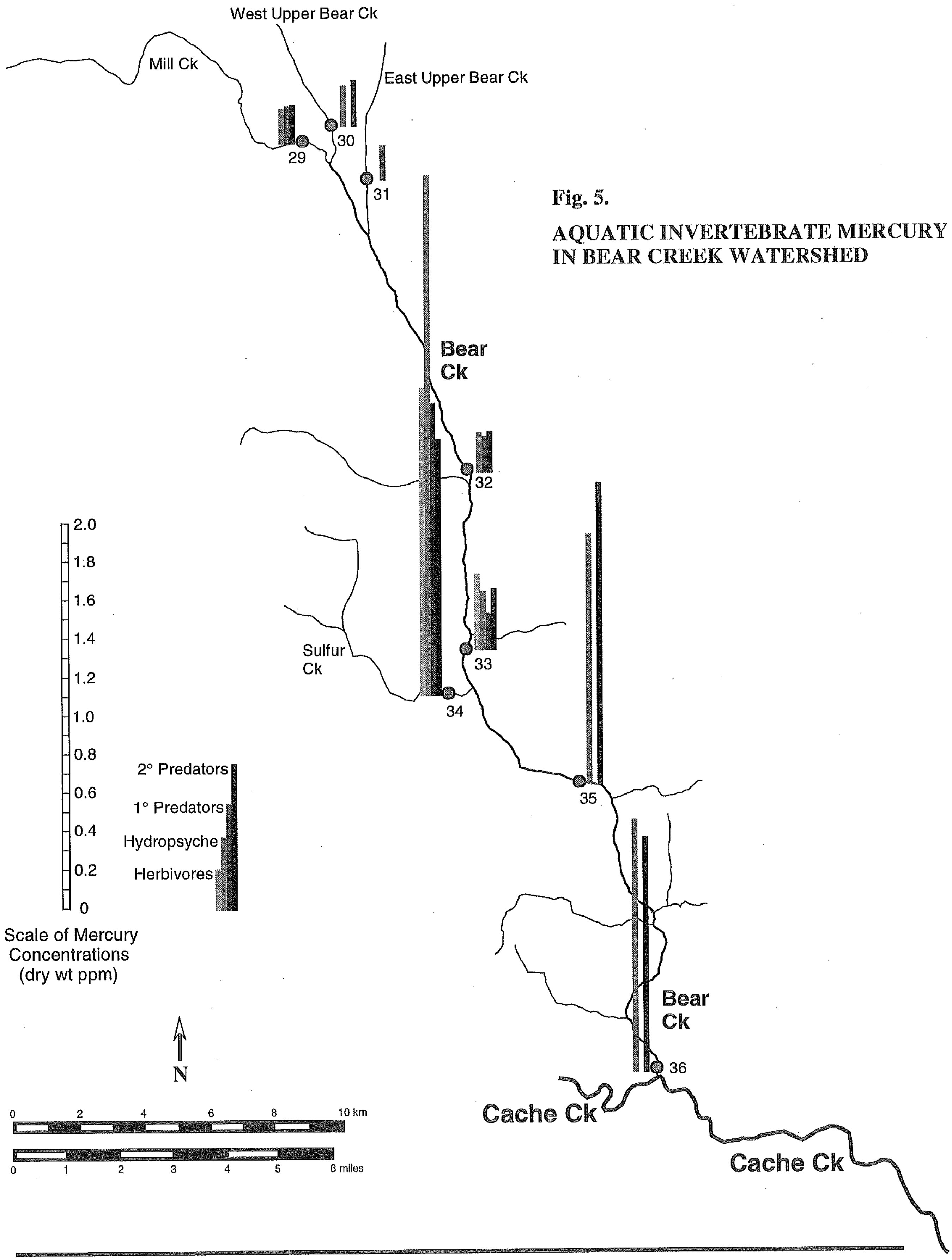


Fig. 5.

AQUATIC INVERTEBRATE MERCURY IN BEAR CREEK WATERSHED

Figure 6.

AQUATIC INVERTEBRATE MERCURY THROUGHOUT THE UPPER CACHE CREEK WATERSHED (large scale)

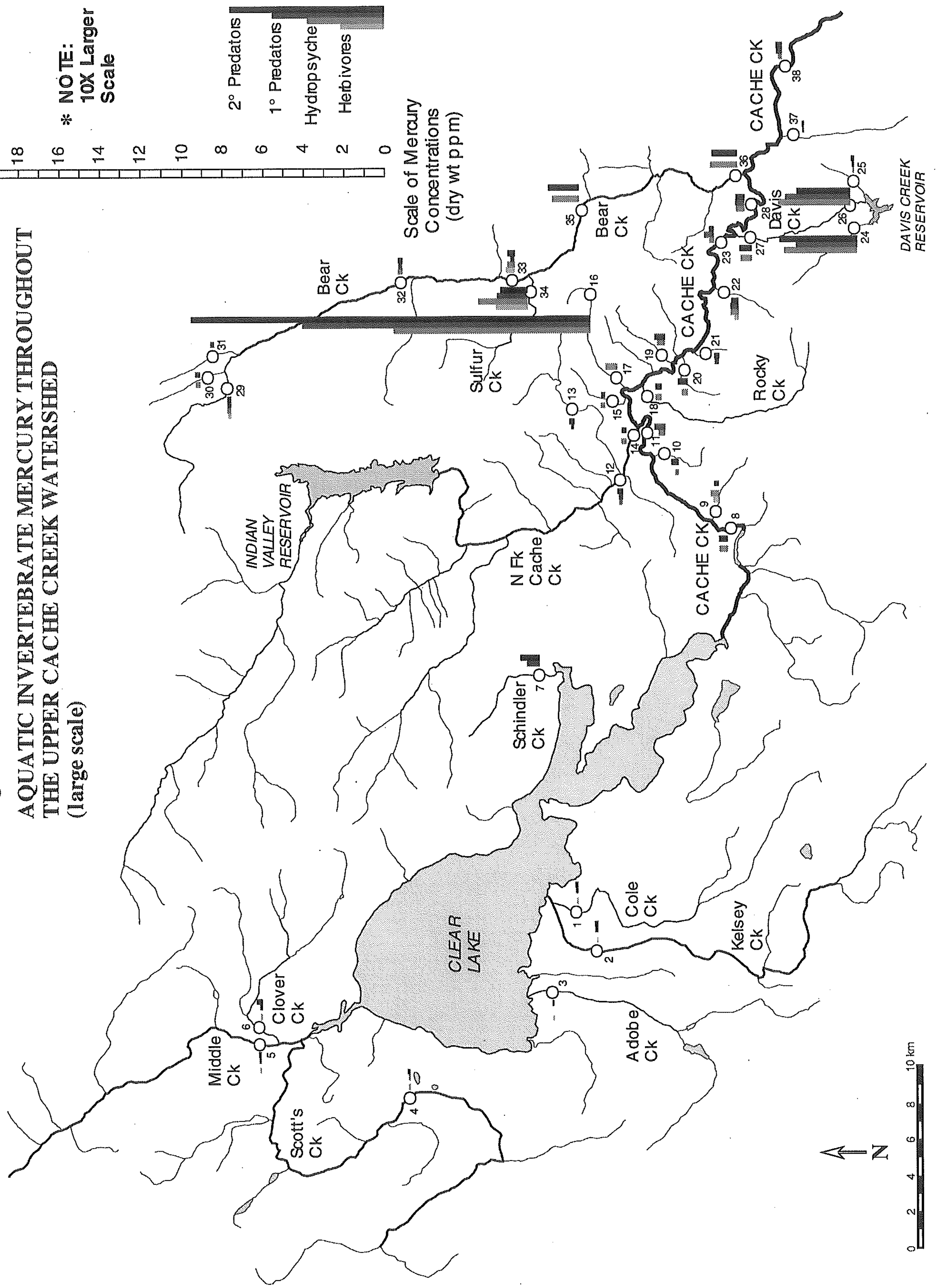


Table 2. Mercury data for all invertebrate samples analyzed in this work

identification	trophic level	Hg
1. Cole Ck. (4/95)		
Ephemerellidae (mayfly)	herbivore	0.06
Perlodidae (stonefly)	small predator	0.10
Corydalidae (hellgrammite)	large predator	0.15
2. Kelsey Ck. (4/95)		
Ephemerellidae (mayfly)	herbivore	0.04
Siphlonuridae (swimming mayfly)	herbivore	0.06
Perlidae (golden stonefly)	small predator	0.15
Libellulidae (dragonfly)	large predator	0.18
3. Adobe Ck. (4/95)		
Ephemerellidae (mayfly)	herbivore	0.03
Siphlonuridae (swimming mayfly)	herbivore	0.05
Corydalidae (hellgrammite)	large predator	0.10
4. Scott's Ck. (4/95)		
Ephemerellidae (mayfly)	herbivore	0.08
Siphlonuridae (swimming mayfly)	herbivore	0.07
Perlodidae (stonefly)	small predator	0.08
Libellulidae (dragonfly)	large predator	0.15
5. Middle Ck. (4/95)		
Ephemerellidae (mayfly)	herbivore	0.04
Perlodidae (stonefly)	small predator	0.09
Corydalidae (hellgrammite)	large predator	0.14
6. Clover Ck. (4/95)		
Ephemerellidae (mayfly)	herbivore	0.09
Perlodidae (stonefly)	small predator	0.13
Corydalidae (hellgrammite)	large predator	0.29

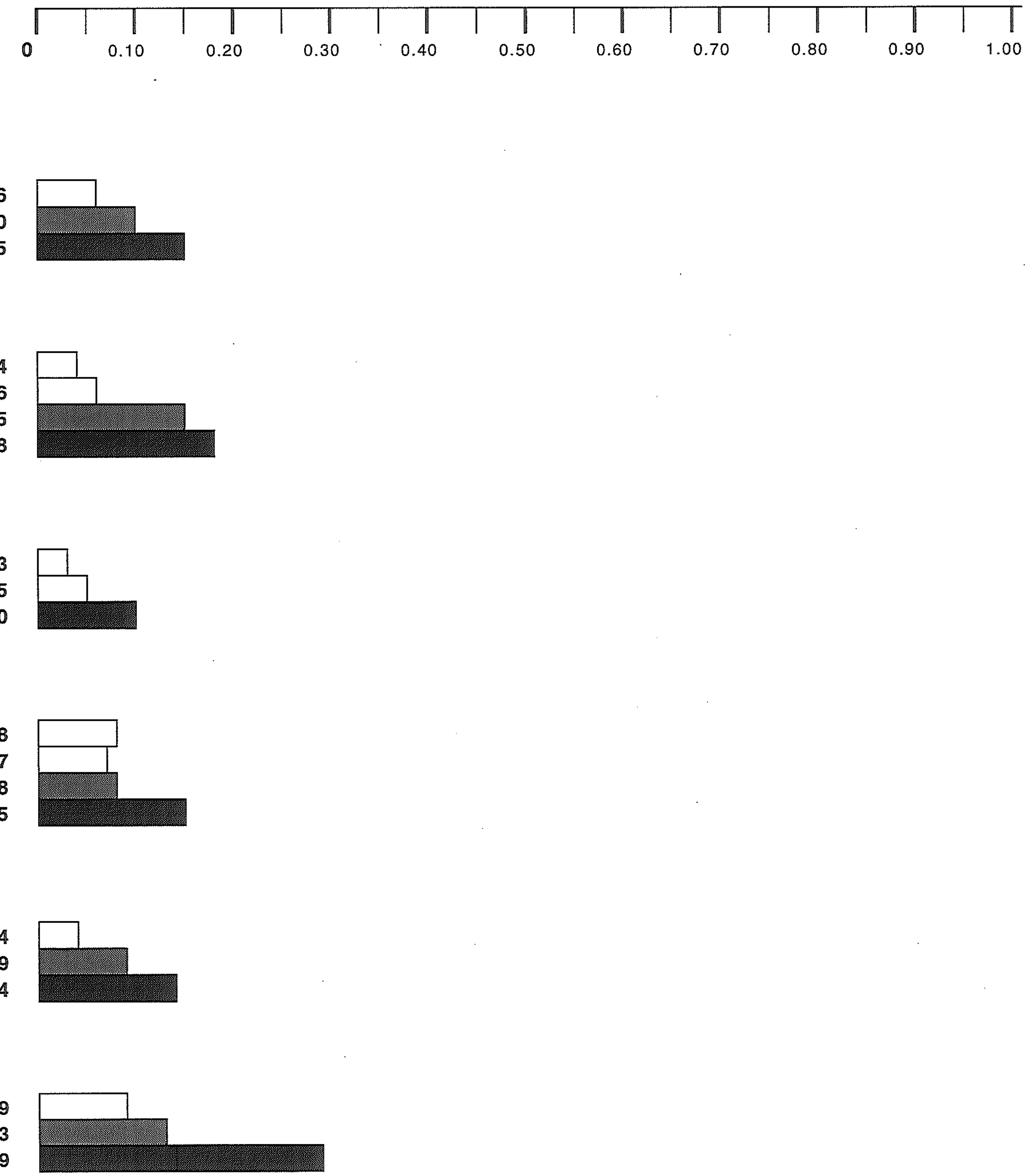


Table 2. (continued)

identification	trophic level	Hg
7. Schindler Ck. (4/95)		
Perlodidae (stonefly)	small predator	0.58
Corydalidae (hellgrammite)	large predator	0.93
8. Cache Ck. below Dam (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.36
Naucoridae (creeping water bug)	large predator	0.40
9. Dry Ck. (5/96)		
Ephemerellidae (mayfly)	herbivore	0.22
Hydropsychidae (net caddis)	drift feeder	0.35
Corydalidae (hellgrammite)	large predator	0.21
10. Deadman Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.15
Naucoridae (creeping water bug)	large predator	0.30
Corydalidae (hellgrammite)	large predator	0.34
11. Cache Ck. above North Fork (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.28
Coenagrionidae (damselfly)	small predator	0.50
12. North Fork Cache Ck. @ Hwy. 20 (5/96)		
Pteronarcyidae (giant stonefly)	leaf shredder	0.10
Hydropsychidae (net caddis)	drift feeder	0.16
Perlodidae (yellow sally stonefly)	small predator	0.20
Libellulidae (dragonfly)	Large predator	0.27

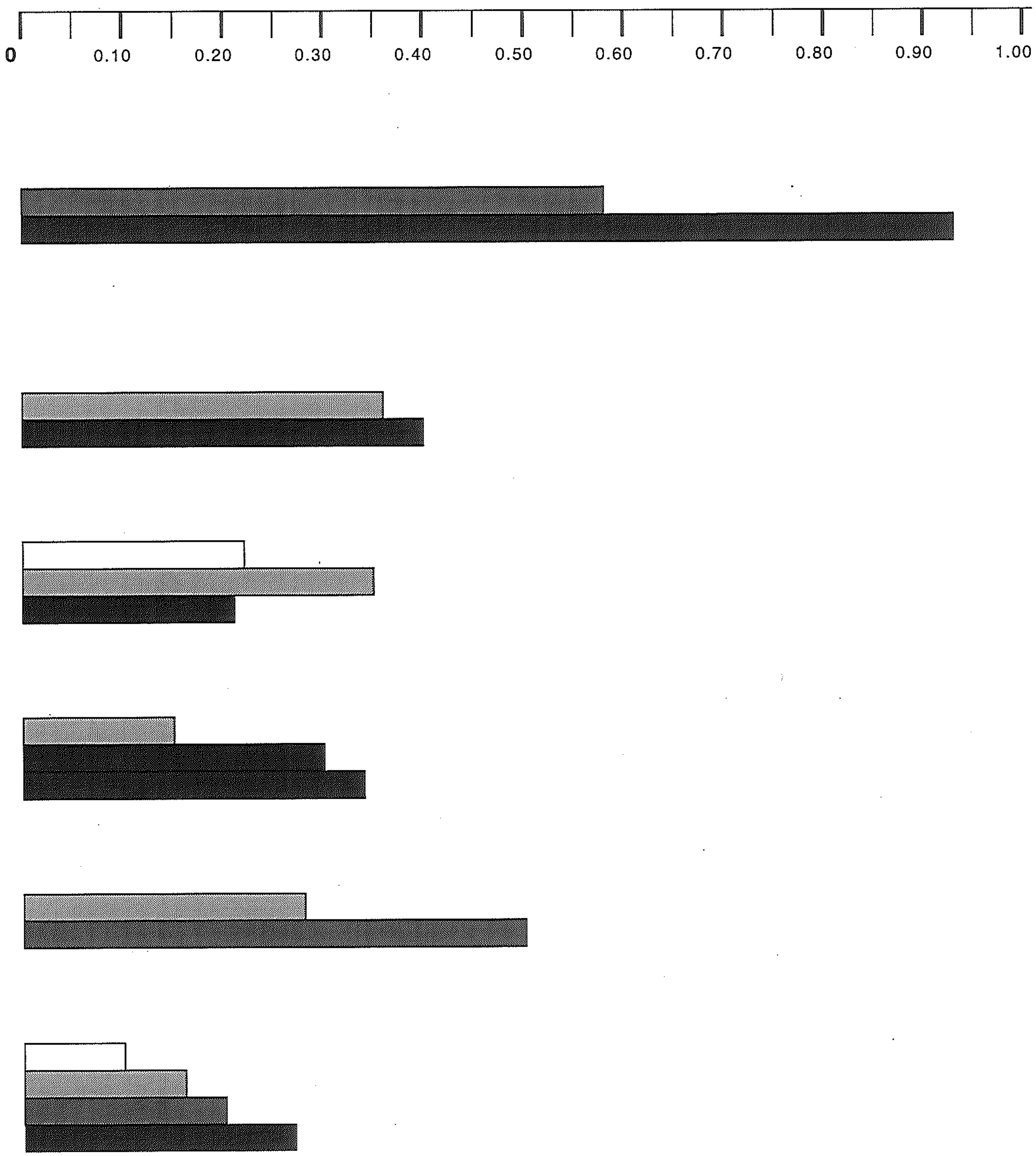


Table 2. (continued)

identification	trophic level	Hg
13. Highway 20 Ck. (5/96)		
Perlodidae (yellow sally stonefly)	small predator	0.09
Sialidae (alderfly)	small predator	0.16
Corydalidae (hellgrammite)	large predator	0.22
14. North Fork Cache Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.22
Naucoridae (creeping water bug)	large predator	0.21
15. Stemple Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.19
Corydalidae (hellgrammite)	large predator	0.17
16. Harley Gulch @ Hwy 20 (5/96)		
Hydropsychidae (net caddis)	drift feeder	9.64
Coenagrionidae (damselfly)	small predator	14.20
Hydrophilidae (beetle larvae)	large predator	15.75
Corydalidae (hellgrammite)	large predator	22.74
17. Harley Gulch @ Cache Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.52
18. Rocky Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.24
Corydalidae (hellgrammite)	large predator	0.24

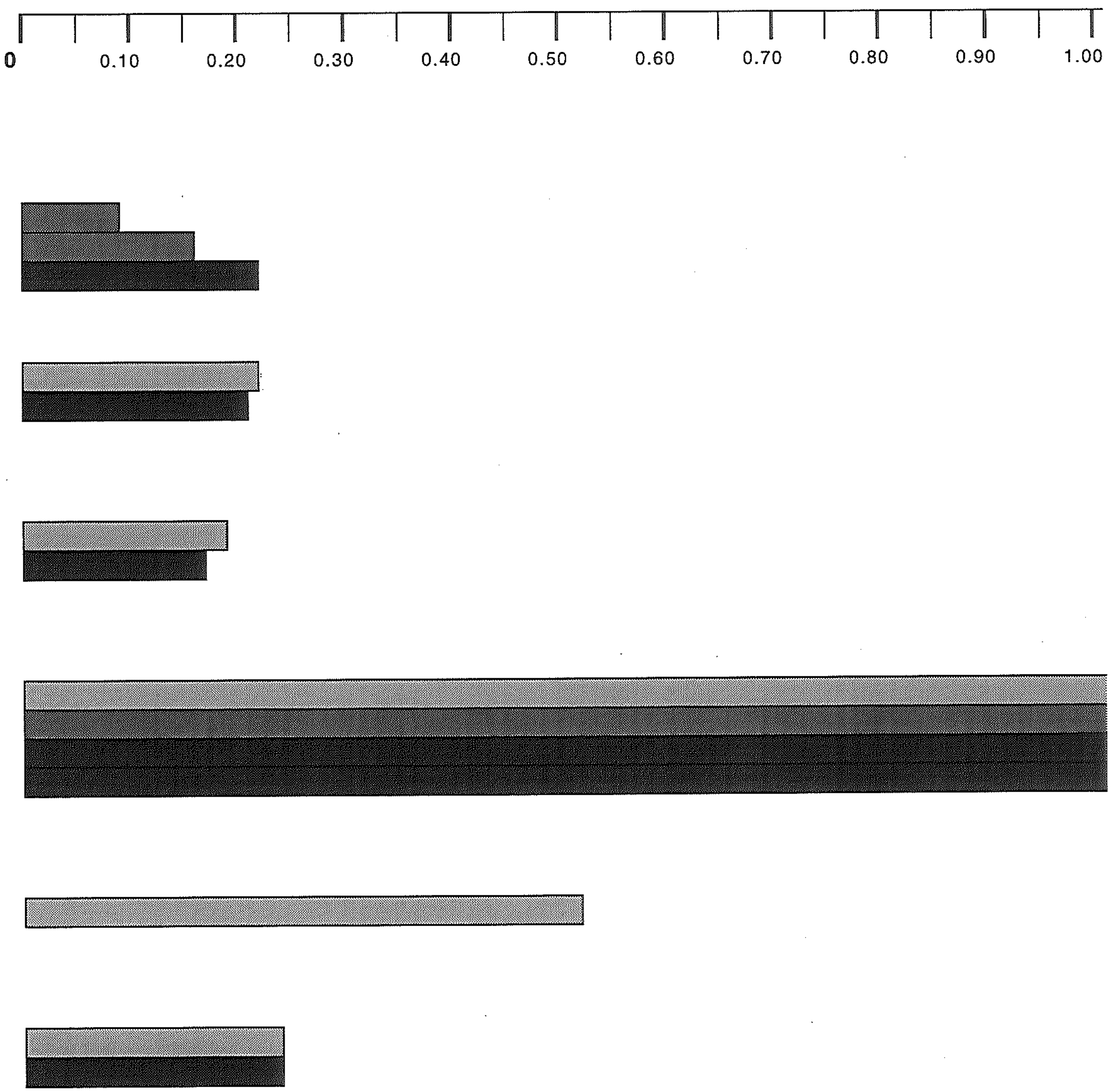


Table 2. (continued)

identification	trophic level	Hg
19. Brushy Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.33
Corydalidae (hellgrammite)	large predator	0.49
20. Petrified Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.25
Corydalidae (hellgrammite)	large predator	0.45
21. Trout Ck. (5/96)		
Perlidae (golden stonefly)	small predator	0.17
Naucoridae (creeping water bug)	large predator	0.20
Tipulidae (cranefly)	large predator	0.20
Corydalidae (hellgrammite)	large predator	0.29
22. Crack Ck. (5/96)		
Ephemerellidae (mayfly)	herbivore	0.20
Hydropsychidae (net caddis)	drift feeder	0.38
Perlodidae (yellow sally stonefly)	small predator	0.38
Naucoridae (creeping water bug)	large predator	0.31
Libellulidae (dragonfly)	large predator	0.32
Corydalidae (hellgrammite)	large predator	0.36

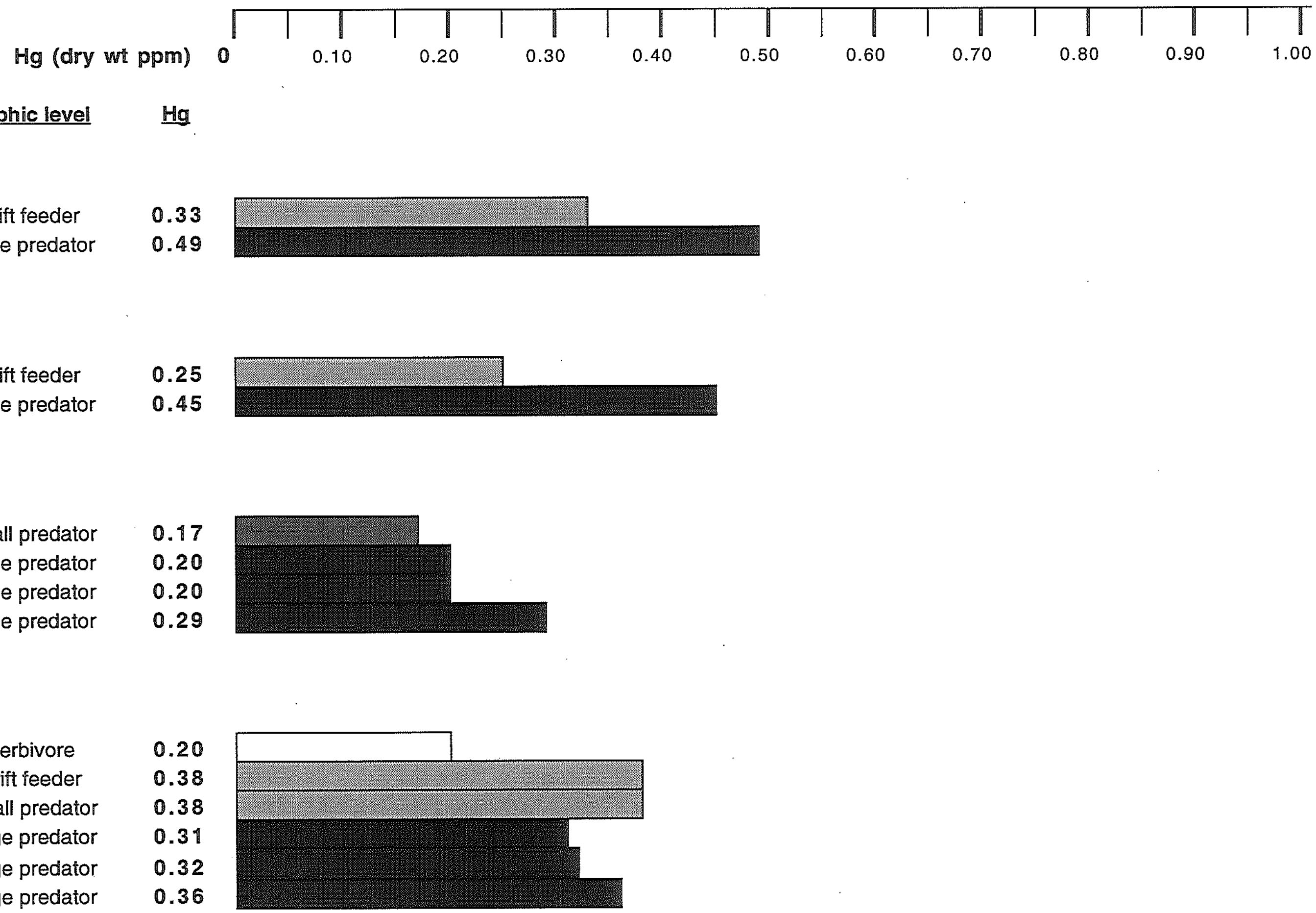


Table 2. (continued)

identification	trophic level	Hg
23. Cache Ck. above Davis Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.22
Perlodidae (yellow sally stonefly)	small predator	0.44
Naucoridae (creeping water bug)	large predator	0.22
24. Davis Ck. above Reservoir (Composite values from several 1993-1996 dates)		
Hydropsychidae (net caddis)	drift feeder	3.61
Perlodidae (yellow sally stonefly)	small predator	2.94
Corydalidae (hellgrammite)	large predator	3.78
25. Rayhouse Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.07
Perlodidae (yellow sally stonefly)	small predator	0.11
Corydalidae (hellgrammite)	large predator	0.14
26. Davis Ck. below Reservoir (Composite values from several 1993-1996 dates)		
Hydropsychidae (net caddis)	drift feeder	3.50
Coenagrionidae (damselfly)	small predator	3.15
Aeschnidae (dragonfly)	large predator	2.63
27. Davis Ck. @ Cache Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.53
Corydalidae (hellgrammite)	large predator	0.60
27*. Davis Ck. @ Cache Ck. (11/95)		
Hydropsychidae (net caddis)	drift feeder	(1.20)
Coenagrionidae (damselfly)	small predator	(0.90)
Corydalidae (hellgrammite)	large predator	(0.92)
28. Cache Ck. below Davis Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.26
Perlodidae (yellow sally stonefly)	small predator	0.37
Naucoridae (creeping water bug)	large predator	0.30

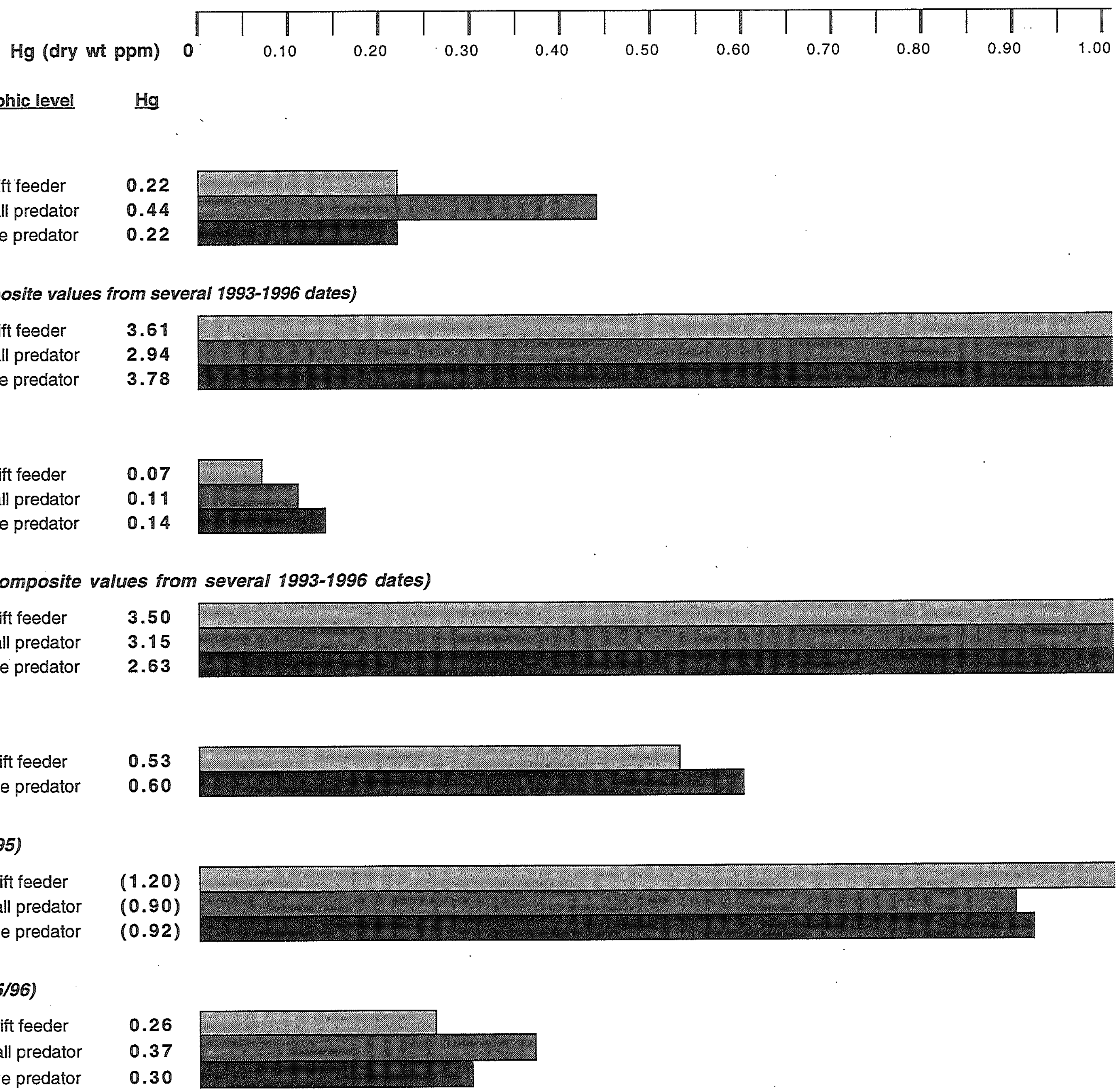


Table 2. (continued)

identification	trophic level	Hg
29. Mill Ck. (5/96)		
Ephemerellidae (mayfly)	herbivore	0.12
Hydropsychidae (net caddis)	drift feeder	0.18
Perlidae (golden stonefly)	small predator	0.19
Libellulidae (dragonfly)	large predator	0.16
Naucoridae (creeping water bug)	large predator	0.20
30. West Upper Bear Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.22
Tipulidae (cranefly)	large predator	0.25
Naucoridae (creeping water bug)	large predator	0.22
31. East Upper Bear Ck. (5/96)		
Sialidae (alderfly)	small predator	0.17
32. Bear Ck. @ Valley Xing (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.20
Perlidae (golden stonefly)	small predator	0.18
Libellulidae (dragonfly)	large predator	0.20
Tipulidae (cranefly)	large predator	0.24
Naucoridae (creeping water bug)	large predator	0.20
33. Bear Ck. above Sulfur Ck. (5/96)		
Siphlonuridae (swimming mayfly)	herbivore	0.39
Hydropsychidae (net caddis)	drift feeder	0.30
Calopterygidae (damselfly)	small predator	0.18
Libellulidae (dragonfly)	large predator	0.32
Tipulidae (cranefly)	large predator	0.31
Naucoridae (creeping water bug)	large predator	0.34

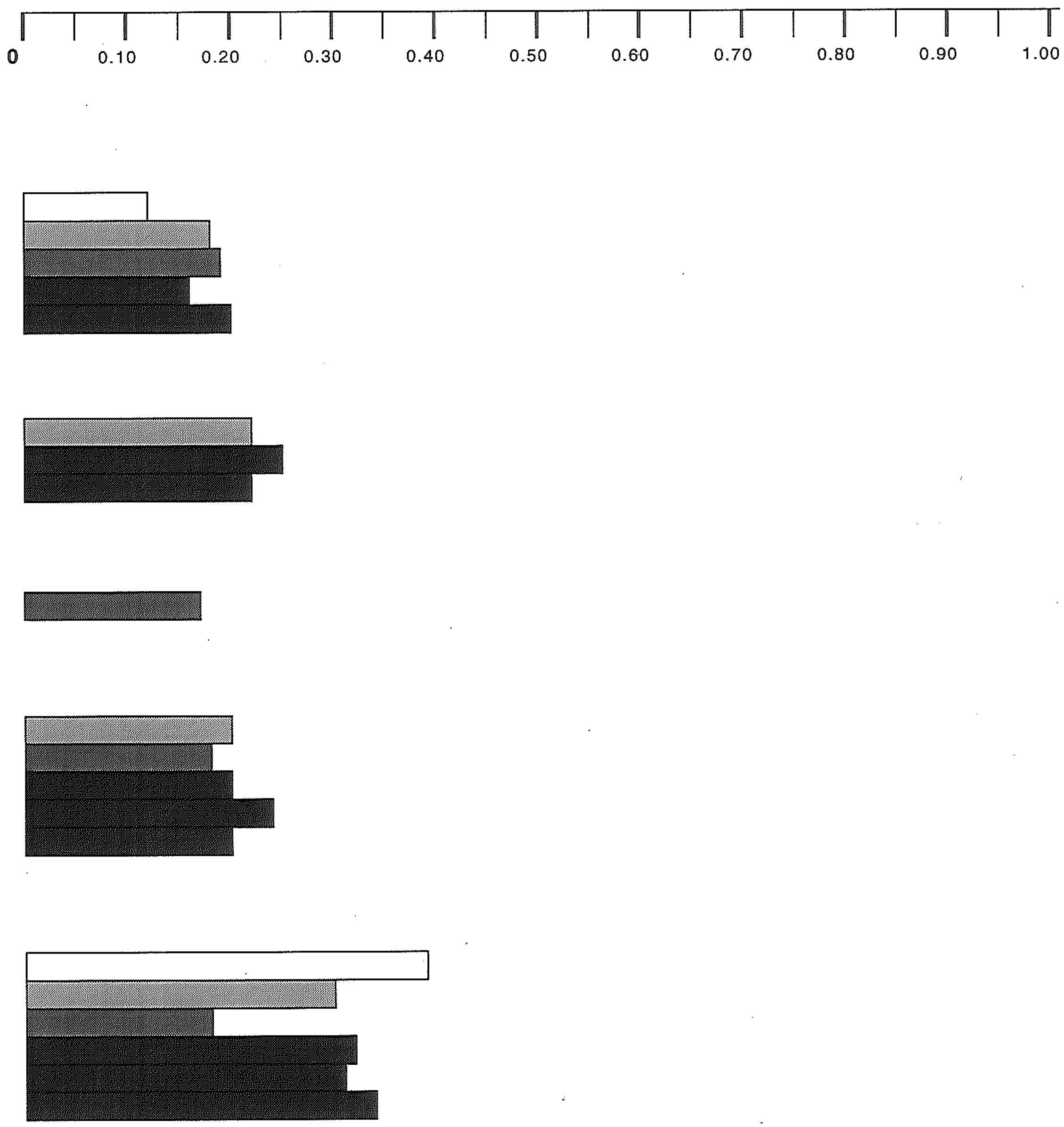


Table 2. (continued)

identification	trophic level	Hg
34. Sulfur Ck. (5/96)		
Ephemerellidae (mayfly)	herbivore	1.17
Siphlonuridae (swimming mayfly)	herbivore	2.01
Hydropsychidae (net caddis)	drift feeder	2.69
Sialidae (alderfly)	small predator	1.51
Naucoridae (creeping water bug)	large predator	1.33
35. Bear Ck. @ Hwy. 20 (5/96)		
Hydropsychidae (net caddis)	drift feeder	1.29
Naucoridae (creeping water bug)	large predator	1.56
36. Bear Ck. @ Cache Ck. (5/96)		
Hydropsychidae (net caddis)	drift feeder	1.30
Naucoridae (creeping water bug)	large predator	1.22
37. Fiske Ck. (5/96)		
Perlodidae (yellow sally stonefly)	small predator	0.10
Corydalidae (hellgrammite)	large predator	0.12
38. Cache Ck. @ Scout Camp (5/96)		
Hydropsychidae (net caddis)	drift feeder	0.18
Perlodidae (yellow sally stonefly)	small predator	0.22
Coenagrionidae (damselfly)	small predator	0.27
Libellulidae (dragonfly)	large predator	0.21
Naucoridae (creeping water bug)	large predator	0.33
Corydalidae (hellgrammite)	large predator	0.25

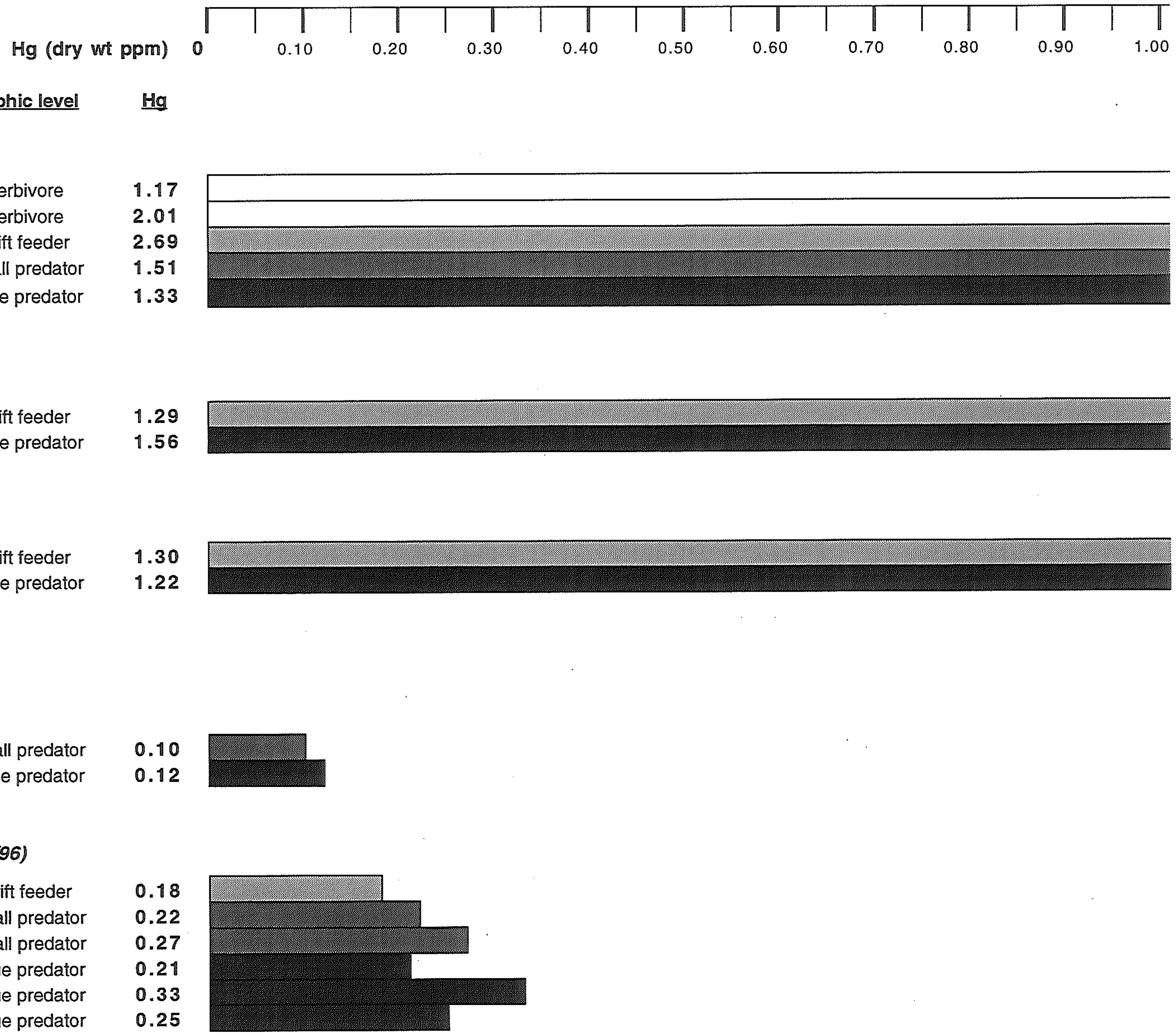


Table 3. Reduced mercury data, by trophic level.

mayflies (M), Hydropsyche (H), 1° Predators (1°), and 2° Predators (2°)

	Site		M	H	1°	2°
Clear Lake Tributaries						
1	Cole Ck		0.06		0.10	0.15
2	Kelsey Ck		0.05		0.15	0.18
3	Adobe Ck		0.04			0.10
4	Scott's Ck		0.08		0.08	0.15
5	Middle Ck		0.04		0.09	0.14
		mean:	*0.053*		*0.105*	*0.144*
		std. dev.:	*± .015*		*± .031*	*± .029*
6	Clover Ck		0.09		0.13	0.29
		mean:	*0.059*		*0.11*	*0.168*
		std. dev.:	*± .020*		*± .029*	*± .065*
			(sites 1-6)		*(sites 1-6)*	*(sites 1-6)*
7	Schindler Ck				0.58	0.93
Cache Creek Main Stem and Near-Stem Tributaries (- High Hg Anomalies: Harley, Davis, Bear Cks)						
8	Cache Ck below Clear Lake			0.36		0.40
9	Dry Ck		0.22	0.35		0.21
10	Deadman Ck			0.15		0.32
11	Cache above N Fk			0.28	0.50	
12	N Fk Cache Hwy 20			0.16	0.20	0.27
13	Hwy 20 Ck				0.13	0.22
14	N Fk Cache Ck			0.22		0.21
15	Stemple Ck			0.19		0.17
18	Rocky Ck			0.24		0.24
19	Brushy Ck			0.33		0.49
20	Petrified Ck			0.25		0.45
21	Trout Ck				0.17	0.23
22	Crack Ck		0.20	0.38	0.38	0.33
23	Cache Ck above Davis Ck			0.22	0.44	0.22
28	Cache Ck below Davis Ck			0.26	0.37	0.30
37	Fiske Ck				0.10	0.12
38	Cache Ck at Scout Camp			0.18	0.25	0.26
		mean:	*0.21*	*0.255*	*0.281*	*0.278*
		std dev.:	*± .014*	*± .076*	*± .145*	*± .100*
Harley Gulch						
16	Harley Gulch at Hwy 20			9.64	14.2	19.24
17	Harley Gulch at Cache Ck			0.52		

(continued)

(Table 3. continued)

	Site	M	H	1°	2°
	Davis Creek Drainage				
24	Davis Ck Above DCR		3.61	2.94	3.78
25	Rayhouse Ck		0.07	0.11	0.14
26	Davis Ck Below DCR		3.50	3.15	2.63
27	Davis Ck at Confluence		0.53		0.60
	Bear Creek Drainage				
29	Mill Ck	0.12	0.18	0.19	0.18
30	W Upper Bear Ck		0.22		0.24
31	E Upper Bear Ck			0.17	
32	Bear Ck at Valley Xing		0.20	0.18	0.21
	mean:	*0.12*	*0.20*	*0.18*	*0.208*
	std. dev.:		*± .020*	*± .010*	*± .028*
33	Bear Ck above Sulfur	0.39	0.30	0.18	0.32
34	Sulfur Ck	1.59	2.69	1.51	1.33
35	Bear Ck at Hwy 20		1.29		1.56
36	Bear Ck at Cache Ck		1.30		1.22
	mean:		*1.295*		*1.39*
	std. dev.:		*± .007*		*± .240*

Table 4. Reduced trophic mercury data, demonstrating variation from mean levels, relative to Cache main stem and near-stem tributary sites 8-15, 18-23, 28, and 37-38.

mayflies (M), Hydropsyche (H), 1° Predators (1°), and 2° Predators (2°)

"<" = std. devs. below mean (to 2+) "+" = std. devs. above mean
"=" = within ± 1 std dev. of mean "+++++" = ≥5 std. devs. above mean

		M	H	1°	2°
Clear Lake Tributaries					
1	Cole	<<		<	<
2	Kelsey	<<		=	=
3	Adobe	<<			<
4	Scott's	<<		<	<
5	Middle Ck	<<		<	<
6	Clover Ck	<<		<	=
7	Schindler Ck			++	+++++
Cache Ck Main Stem and Near-Stem Tributaries (- High Hg Anomalies: Harley, Davis, Bear Cks)					
8	Cache Ck below CL		+		+
9	Dry Ck	=	+		=
10	Deadman Ck		<		=
11	Cache above N Fk		=	+	
12	N Fk Cache Hwy 20		<	=	=
13	Hwy 20 Ck			<	=
14	N Fk Cache Ck		=		=
15	Stemple Ck		=		<
18	Rocky Ck		=		=
19	Brushy Ck		+		++
20	Petrified Ck		=		+
21	Trout Ck			=	=
22	Crack Ck	=	+	=	=
23	Cache Ck above Davis Ck		=	+	=
28	Cache Ck below Davis Ck		=	=	=
37	Fiske Ck			<	<
38	Cache Ck at Scout Camp		<	=	=
Harley Gulch					
16	Harley Gulch at Hwy 20		+++++	+++++	+++++
17	Harley Gulch at Cache Ck		+++		
Davis Ck Drainage					
24	Davis Ck Above DCR		+++++	+++++	+++++
25	Rayhouse Ck		<<	<	<
26	Davis Ck Below DCR		+++++	+++++	+++++
27	Davis Ck at Confluence		+++		+++
Bear Ck Drainage					
29	Mill Ck	<<	<	=	<
30	W Upper Bear Ck		=		=
31	E Upper Bear Ck			=	
32	Bear Ck at Valley Xing		=	=	=
33	Bear Ck above Sulfur	+++++	=	=	=
34	Sulfur Ck	+++++	+++++	+++++	+++++
35	Bear Ck at Hwy 20		+++++		+++++
36	Bear Ck at Cache Ck		+++++		+++++

Main Stem Cache Creek And Tributaries

Data for the main stem Cache Creek and tributary sites are presented in Figure 4 and Table 2. The main stem of Cache Creek was sampled at 5 locations between the Clear Lake outflow and Rumsey (sites 8, 11, 23, 28, and 38). Twelve tributaries (in addition to Bear Creek and the Clear Lake tributaries) were sampled near their confluences with Cache Creek, plus 6 additional sites upstream of the confluences.

Invertebrate mercury levels were notable for their relative similarity throughout the main stem sites and most of the near-confluence tributary sites, with the exception of Harley Gulch, Davis Creek, and Bear Creek (Figures 4 and 6). Consequently, these 17 sites (8-15, 18-23, 28, and 37-38) were pooled to produce a comparative baseline against which each of the study sites could be compared. Mean mercury levels for this and other subsets of the database, with standard deviations, are presented for each of the trophic levels in Table 3. In Table 4, mean mercury, by trophic level for each of the 38 project sampling sites, is compared to the range of levels seen in this "baseline" set. Among the baseline set of 17 sites, 25 of the 41 total trophic comparisons (61%) were within ± 1 standard deviation of the mean. Seven trophic mercury comparisons (17%) were 1-2 standard deviations below the mean. These were distributed among 6 sites: Site 10--Deadman Creek, Site 12--N Fk Cache Ck at Hwy 20, Site 13--Creek along Hwy 20, Site 15--Stemple Creek, Site 37--Fiske Creek (which was low for all samples), and Site 38--Cache Creek at the Scout Camp 3 miles above Rumsey. Nine trophic mercury comparisons (22%) were 1-2+ standard deviations above the mean. These were distributed among 7 sites: Site 8--Cache Creek near Clear Lake outflow (both samples elevated), Site 9--Dry Creek, Site 11--Cache Creek above confluence with N Fk Cache Ck, Site 19--Brushy Creek (both samples elevated, hellgrammites >2 std deviations elevated), Site 20--Petrified Creek, Site 22--Crack Creek, and Site 23--Cache Creek above Davis Creek.

Highly elevated mercury levels, of 3 to greater than 5 standard deviations above the baseline means, were present at the near-confluence sites of Harley Gulch (site 17), Davis Creek (site 27), and Bear Creek (site 36). Of these downstream sites near the confluence with Cache Creek, Bear Creek demonstrated the most dramatically elevated concentrations in benthic macroinvertebrates, with levels of 1.22-1.30 $\mu g\ g^{-1}$ Hg. Harley Gulch, the Davis Creek drainage, and the Bear Creek drainage are discussed below in separate sections.

Harley Gulch

At the time of sampling, the region of Harley Gulch near the confluence with Cache Creek (Site 17) was severely impacted by a whitish precipitate which thickly coated all bottom substrate. Water flowing across this coated bottom material was relatively clear at the time of the spring sampling effort. A typical benthic macroinvertebrate fauna was not present at this site; extensive collection attempts yielded only a small sample of Hydropsychid caddisfly larvae. This sample was relatively elevated in mercury, at 0.52 $\mu g\ g^{-1}$. This value was > 3 standard deviations above the mean Hydropsychid mercury level in baseline samples ($0.255 \pm 0.076\ \mu g\ g^{-1}$). Harley Gulch was of particular interest because it drains the large, abandoned Abbott and Turkey Run mercury mine complexes alongside Highway 20, approximately 4 miles upstream.

Site 16 was located approximately 3/4 mile below the abandoned mines, on the west side of Highway 20 and just before the confluence with a small stream flowing along Highway 20 from the south. In 1992, the first author took a sample of predaceous Hydrophilid beetle larvae from small pools closer to the mine site and found highly elevated mercury levels in the range of 8.50 $\mu g\ g^{-1}$ (unpublished data). In our 1996 sampling, we collected substantial samples from 4 macroinvertebrate families in 3 trophic levels: Hydropsychid caddisfly larvae, Coenagrionid damselfly nymphs, Hydrophilid beetle larvae, and Corydalid hellgrammites. These samples were taken from a reach of stream which contained marshy, pooling regions directly upstream and exhibited none of the precipitate phenomenon seen downstream. Signs of precipitate appeared shortly below the confluence downstream with the other small creek and were attributed to a neutralization of mine-derived water, which held metals in solution prior to mixing with the other water. This is typical of acid mine drainage, as well as anoxic, mine-derived waters which can produce dramatic precipitates when aerated upon mixing with typical surface waters (e.g. Davis Creek near the Reed Adit; Slotton 1991, Reuter *et al.* 1996). Macroinvertebrates taken from the mine-derived reach of Harley Gulch upstream of the onset of precipitate development (Site 16) exhibited extremely elevated mercury concentrations of 9.6-22.7 $\mu g\ g^{-1}$. The Hydropsychid caddisfly sample contained 9.64 μg Hg g^{-1}. Coenagrionid damselfly nymphs (similar in trophic level to stoneflies) had 14.20 μg Hg g^{-1}. The top predators contained 15.75 μg Hg g^{-1} (Hydrophilid beetle larvae) and 22.74 μg Hg g^{-1} (Corydalid hellgrammites). These biotic mercury concentrations were higher than any found by this research team throughout this region of the California Coast Range, though they were not quite as high as the maximal concentrations noted directly below the Mt. Diablo mercury mine in the Marsh Creek watershed in Contra Costa County (Slotton *et al.* 1996a).

Davis Creek Drainage

The Davis Creek watershed has been the site of a continuous mercury research effort by this UC Davis team since 1985 (Slotton 1991, Slotton *et al.* 1995b, Reuter *et al.* 1996). That work has focused on mercury dynamics in Davis Creek Reservoir, located ~8 miles upstream of Cache Creek, and the near-reservoir stretches of Davis Creek above and below the reservoir. Davis

Creek Reservoir was built in 1984 by the Homestake Mining Company, for use as a water supply to the large gold mining operation it ran in the upper Putah Creek watershed. While the recent gold mining effort utilized no mercury and was located in a different watershed, the dam on Davis Creek created the reservoir immediately downstream of a concentration of abandoned historic mercury mining sites, including the Reed Mine which is located along Davis Creek directly above the inflow to the reservoir. Large quantities of mercury have been documented to sediment out in the reservoir in conjunction with winter runoff (Reuter *et al.* 1996). The reservoir has been clearly demonstrated to act as a trap for a large portion of the annual bulk load of mercury moving down Davis Creek from historic mercury mining sites. During the past several years, we have conducted an intensive sampling effort at sites above, below, and within the reservoir for benthic macroinvertebrates comparable to those utilized in this study (to be published in the upcoming 1997 annual report for Yolo County). Composite averages from several dates were used for the current (Cache Creek watershed) report for sites immediately above and below the reservoir (sites 24 and 26). We additionally sampled the creek which flows into the dam arm of the reservoir and which we have named Rayhouse Creek (after Rayhouse Road, County Road 40, along which it flows). This creek, which contains no mercury mines, has been identified as contributing large seasonal loads of very low-mercury sediment to the dam arm of the reservoir.

The primary Davis Creek site upstream of the reservoir (site 24) is located alongside the abandoned Reed Mercury Mine tailings and 1/2 mile downstream of a mineshaft adit which deposits a flow of metals-rich, anoxic groundwater into Davis Creek. An orange precipitate floc, composed largely of iron oxides, typically forms in the water below this point, making the water opaque orange and depositing on all bottom substrate. Invertebrate mercury from this reach has typically been highly elevated. The composite values used for this report fall within the range of 2.94-3.78 $\mu g\ g^{-1}$ in Hydropsychid caddisflies, Perlid and Perlodid Stoneflies, and Corydalid hellgrammites.

In sharp contrast to upper Davis Creek, samples of identical invertebrates from Rayhouse Creek (site 25) contained among the lowest mercury levels found in this study, similar (at 0.07-0.14 $\mu g\ g^{-1}$ across 3 trophic levels) to those found in the cleaner tributaries to Clear Lake (sites 1-5).

Interestingly, samples from below Davis Creek Reservoir (site 26) exhibited elevated mercury concentrations similar to those above the reservoir, with concentrations of 2.63-3.50, despite the documented mercury-trapping action of the reservoir. Mercury bioavailability apparently declined dramatically downstream, as was seen at Harley Gulch, with mercury concentrations of 0.53 $\mu g\ g^{-1}$ in Hydropsychid caddisflies from site 27--nearly identical to the 0.52 $\mu g\ g^{-1}$ level found at the downstream Harley Gulch site (site 17). Corydalid hellgrammites were also taken at this site near the confluence with Cache Creek, and these had mercury in a similar range, at 0.60 $\mu g\ g^{-1}$.

However, similar collections made in November of 1995 exhibited markedly higher concentrations, with Hydropsychid caddisflies containing 1.20 $\mu g\ g^{-1}$, Coenagrionid damselflies having 0.90 $\mu g\ g^{-1}$, and Corydalid hellgrammites at 0.92 $\mu g\ g^{-1}$. We note that, relative to the conditions prior to the May 1996 collections, water conditions in the months prior to the fall collection were characterized by pooling, stagnant, warm water conditions, all of which are conducive to enhanced microbial methylator populations and enhanced mercury methylation.

Bear Creek Drainage

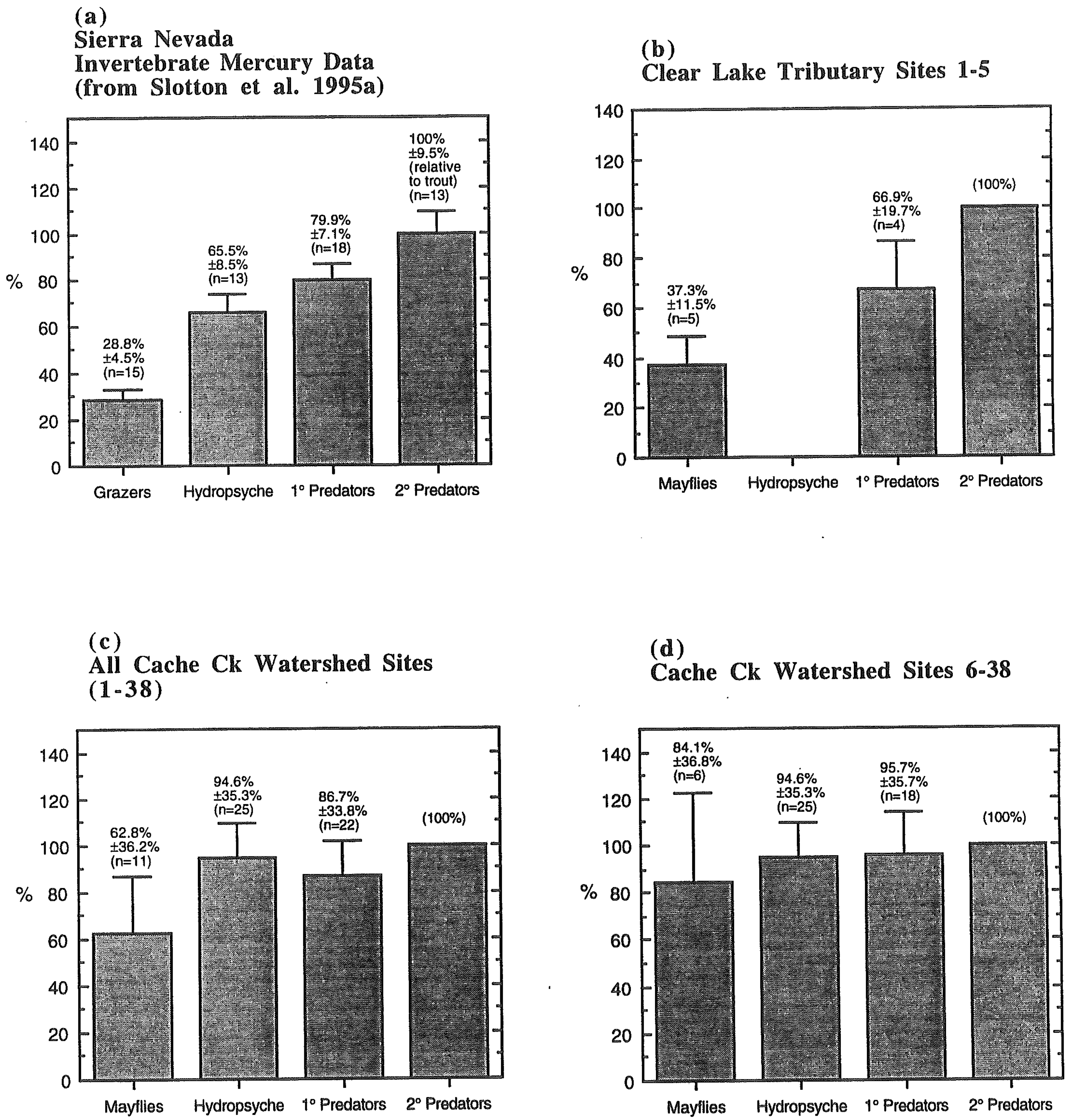
Eight sites were sampled in the Bear Creek drainage (sites 29-36). Mercury data are presented in Figure 5 and Table 2. At the lower two sites, closer to the confluence with Cache Creek, Hydropsychid caddisfly larvae (drift feeders) and Naucorid water bugs (predaceous, primarily on medium to large invertebrates) were the only macroinvertebrates well represented at the time of these collections. These samples exhibited dramatically elevated mercury concentrations of 1.22-1.56 $\mu g\ g^{-1}$. In subsequent collections, the primary source of elevated levels of bioavailable mercury in Bear Creek was found to be Sulfur Creek, which enters Bear Creek approximately 20 km (12 miles) above the confluence with Cache Creek. Sulfur Creek macroinvertebrate samples were very high in mercury, at 1.17-2.69 $\mu g\ g^{-1}$. Immediately above Sulfur Creek, invertebrate mercury levels were dramatically lower, at 0.18-0.39 $\mu g\ g^{-1}$. Samples from the 4 sites upstream of this point (29-32) contained still lower levels of 0.12-0.25 $\mu g\ g^{-1}$. Though dramatically lower than the heavily contaminated samples from Sulfur Creek and downstream Bear Creek, it is notable that these samples from the upper portions of the Bear Creek drainage were higher on average than similar samples from Clear Lake tributary sites 1-5. Except for Mill Creek, where 3 of 4 trophic comparisons were ≥ 1 standard deviation below the comparative Cache Creek main stem and near-main-stem tributary sites, all other upper Bear Creek drainage sites exhibited invertebrate mercury levels that were comparable (Table 4). At site 33, immediately above Sulfur Creek, levels were also within this comparable range, except for the mayfly sample which was elevated. All trophic comparisons to the Cache Creek baseline were highly elevated (by greater than 5 standard deviations) from Sulfur Creek and the Bear Creek sites between Sulfur Creek and the Cache Creek confluence.

Trophic Mercury Relationships

Figure 7(a-d) demonstrates the pooled, relative mercury concentration relationships between the four trophic levels of invertebrates utilized in this study: herbivores (primarily mayflies), drift feeding Hydropsychid caddisflies, small item (first order) predators (stoneflies, damselflies), and large item (second order) predators (hellgrammites, dragonflies). Mean pooled relative mercury

Fig. 7. Relative mercury in pooled invertebrate trophic levels.

Mean pooled relative mercury concentration (as a percentage of mean second order predator mercury), together with 95% confidence intervals.



concentration (as a percentage of mean second order predator mercury) is presented for each trophic level, together with 95% confidence intervals. Figure 7a is modified from Slotton *et al.* (1995a) and depicts the trophic mercury relationships for corresponding invertebrates from Sierra Nevada gold mining streams. A fairly consistent increase in mercury concentration with trophic level is apparent in that data. A similar, regular pattern was observed in the low mercury Clear Lake tributaries (sites 1-5, Figure 7b) and Rayhouse Creek (site 25) another notably low mercury site.

In contrast, the Cache Creek watershed sites as a whole (Figure 7c) and, particularly, the Cache Creek watershed sites not including the cleaner Clear Lake tributaries 1-5 (Figure 7d) demonstrated a notable lack of any clear trophic mercury concentration relationship. Variation in the trophic relationship percentage was high and mean concentrations were similar among all 4 trophic levels. This somewhat anomalous relationship has been noted by our mercury research group at other mercury contaminated Coast Range sites including Marsh Creek near the Mt. Diablo Mercury Mine (Slotton *et al.* 1996a).

Cache Creek Fish Mercury

In October 1995, we made a series of fish collections in Cache Creek, well downstream of the upper watershed reaches utilized in this study. Fish of six species were taken from the region of Cache Creek between County Road 102 and Interstate Highway 5, near Woodland. Those data, reported in Slotton *et al.* 1996b, are reproduced here in Figure 8 and Table 5.

Figure 8. Fish Muscle Mercury From Lower Cache Creek, October 1995

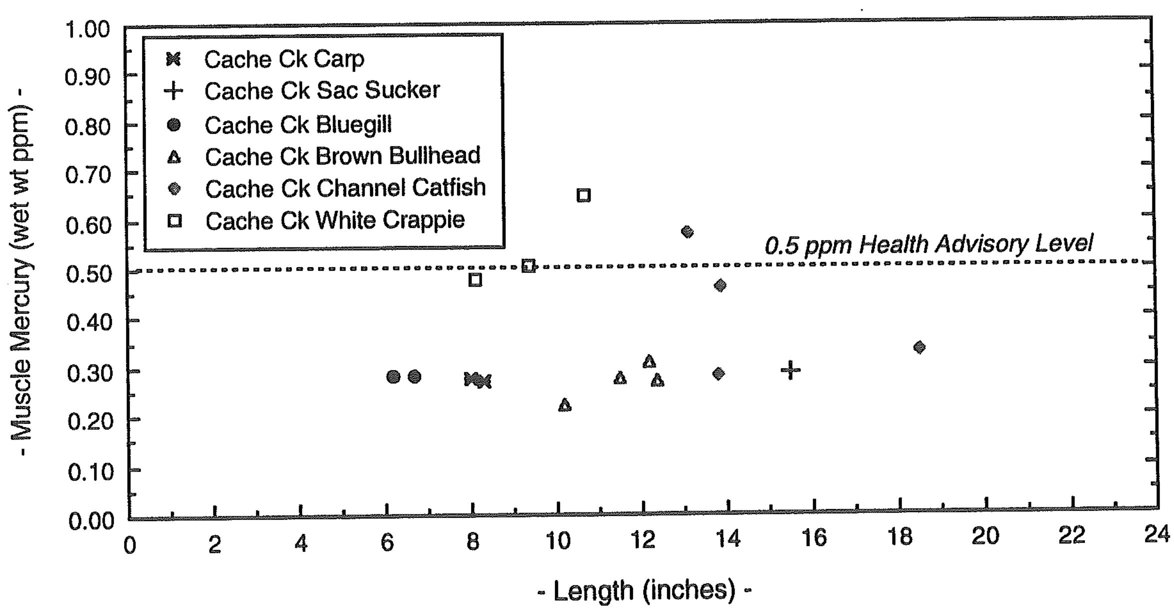


Table 5. Fish Muscle Mercury Concentrations *(wet wt ppm)*; Lower Cache Creek, October 1995

Identification	Length (mm)	Length (inches)	Weight (grams)	Weight (pounds)	ppm Hg (wet wt)
CACHE CREEK (10/95)					
Carp	202	8.0	180	0.4	0.28
Carp	210	8.3	200	0.4	0.27
Sacramento Sucker	393	15.5	660	1.5	0.29
Bluegill Sunfish	157	6.2	105	0.2	0.29
Bluegill Sunfish	169	6.7	118	0.3	0.28
White Crappie	207	8.1	130	0.3	0.48
White Crappie	238	9.4	205	0.5	0.51
White Crappie	272	10.7	275	0.6	0.65
Brown Bullhead	260	10.2	260	0.6	0.22
Brown Bullhead	293	11.5	410	0.9	0.28
Brown Bullhead	310	12.2	438	1.0	0.31
Brown Bullhead	316	12.4	535	1.2	0.27
Channel Catfish	332	13.1	578	1.3	0.57
Channel Catfish	351	13.8	680	1.5	0.28
Channel Catfish	353	13.9	730	1.6	0.46
Channel Catfish	470	18.5	1,380	3.0	0.33

These fish data are quite similar to mercury data for corresponding fishes in Clear Lake (Suchanek et al. 1997, Slotton et al. 1998). While some of the data are above the 0.50 ppm Health Guideline level, they are not notably elevated for this region of Northern California (TSMP 1990, 1992, 1993, 1995).

DISCUSSION AND CONCLUSIONS

Cache Creek Watershed Spatial Variation in Invertebrate Mercury

The results of this preliminary survey of bioavailable mercury, using native benthic macroinvertebrate indicators, indicate similar levels of biotic mercury accumulation along the main stem of Cache Creek, despite inputs of very high mercury material from tributaries between the Clear Lake outflow and Rumsey. Spike accumulations of biotic mercury were present in several of the tributaries (Harley Gulch, Davis Creek, Sulfur Creek) in conjunction with effluent from abandoned mercury mines. It is notable that every significantly elevated set of samples was associated with a known mercury mine source or a stream that drained a mercury mining zone. The Davis Creek watershed contains several mines, notably the Reed. Schindler Creek is very near the Sulphur Bank Mercury Mine, and the Clear Lake outflow to Cache Creek is impacted by that mine. Sulfur Creek, Harley Gulch, and Brushy Creek derive from the same region containing a cluster of abandoned mines. The highly localized nature of these zones is demonstrated by the dramatically lower biotic mercury accumulations in very nearby streams without historic mercury mining activity. These include most of the Clear Lake tributaries (sites 1-6), Rayhouse and Fiske Creeks (sites 25 and 37), Mill Creek and the headwaters of Bear Creek (sites 29-32), and the creek along Highway 20 (site 13) which originates just over a small ridge from the Abbot/Turkey Run mine complex.

Below Sulfur Creek, highly elevated levels were found in Bear Creek throughout the 20 km (12 miles) to the confluence with Cache Creek. In both Harley Gulch and Davis Creek, highly elevated biotic mercury was present only relatively near the mine sources, with levels declining precipitously in the miles below the mines and only somewhat elevated at the confluences with Cache Creek. None of these apparent inputs to Cache Creek translated into a notable elevation in main-stem Cache Creek biotic mercury accumulations. At the most downstream site, just above Rumsey, concentrations were similar to or lower than the range found upstream.

The tributaries feeding Clear Lake, except for small Schindler Creek, do not contain biotic mercury that is elevated to any significant extent. This suggests that the Clear Lake mercury problem results entirely from within-lake processes and, primarily, from historic and ongoing contamination from the Sulphur Bank Mercury Mine. Biotic indicator mercury in Cache Creek directly below the Clear Lake outflow was somewhat elevated. Concentrations either remained similar or declined somewhat along the main stem of Cache Creek below Clear Lake. A wide variety of fishes taken from Cache Creek ~60 miles downstream of Clear Lake near Woodland exhibited mercury levels that were very similar to levels seen in comparable fish from Clear Lake.

It is entirely possible that the form of the mercury being uptaken by biota is quite different throughout the system, moving from Clear Lake outflows to inputs from tributaries containing direct mine drainage and finally to downstream locales where bedload accumulations and speciation may drive the mercury methylation process. Despite the very high concentrations of mercury exhibited in Harley Gulch biota near the Abbott and Turkey Run mine complex, Bear Creek may represent a more important source of bioavailable mercury to the system as a whole, as indicated by the persistent elevation in bioindicator mercury all the way down to the Cache Creek confluence. It is expected that when further sampling is conducted along Sulfur Creek in closer proximity to the several abandoned mercury mines located upstream, spike concentrations of biotic mercury similar to those seen at Harley Gulch will be documented. At Harley Gulch, Davis Creek and, likely, Sulfur Creek, greatly elevated biotic mercury was associated with mine drainage which subsequently exhibited dramatic declines in apparent bioavailability in conjunction with the precipitation of metal and mineral oxides and oxyhydroxides. This phenomenon has also been noted at the Mt. Diablo Mercury Mine (Slotton *et al.* 1996a) and the Sulphur Bank Mercury Mine at Clear Lake (Suchanek *et al.* 1997). We speculate that these colloidal precipitates scavenge dissolved inorganic and organic mercury and are then easily transported, with the associated mercury surface adsorbed and significantly more available to methylating microbes than the bulk of the system's mercury, which may be largely locked in the mineral matrix of cinnabar particles. The similar levels of bioindicator mercury above and below Davis Creek Reservoir, despite the documented mercury trapping action of the dam, may provide additional evidence for this theory. Mercury that is surface adsorbed to colloidal particles can be transported across the reservoir to the spillway more readily than cinnabar particles which tend to drop out into the bottom sediments. The significant elevation in biotic mercury at the Davis Creek site near the Cache Creek confluence in November 1995 relative to May 1996 indicates that this material can be methylated under conditions of decreased water flow and increased temperature and stagnation.

Comparison and Contrast With Sierra Nevada Invertebrate Hg Trends

In the Sierra Nevada, streams which were found to contain elevated biotic mercury tended to be elevated throughout many tens of river miles (Slotton *et al.* 1995a, 1997). Cache Creek demonstrates this general pattern along the section examined in this project. However, extremely elevated and highly localized spike distributions, as seen near abandoned mercury mines in this project, were not found in the Sierra gold region. The refined elemental mercury utilized in the gold mining process may have demonstrated some highly localized concentrations historically, but, apparently, these concentrations were subsequently redistributed throughout the downstream lengths of the streams, primarily through transport during high flow periods. A considerable fraction of the ongoing transport is depositing in Sierra foothill reservoirs. In the Sierra Nevada studies, we found biotic mercury accumulations below these reservoirs to be generally considerably reduced as compared to stream sites above the reservoirs. In the Cache Creek watershed, a large proportion of the bulk mercury load is similarly depositing behind dams, where they exist (e.g. Clear Lake and Davis Creek Reservoir). However, this project provides some evidence that some of the most highly bioavailable fractions of Coast Range mercury are more easily suspended and transported than the bulk of the system's large inorganic mercury load.

Overall, concentrations of mercury in benthic macroinvertebrates were quite similar in the Cache Creek watershed as compared to corresponding levels in Sierra Nevada gold mining streams. Concentrations in the baseline set of main stem and near-main-stem Cache Creek samples were similar to mean levels observed throughout the heavily gold-mined region of the Sierra foothills. Low, apparently background concentrations in this study, found in most Clear Lake tributaries, Rayhouse Creek, and Fiske Creek, were similar to concentrations noted from apparent background sites above the Sierra Nevada gold-mining zone and in watersheds in which historic mining-associated mercury had apparently been transported downstream (American River drainage and much of the Feather River drainage). Maximal concentrations, however, were considerably higher in the Cache Creek watershed as compared to the Sierra Nevada gold region. In the Sierra Nevada, highest concentrations were less than or equal to ~1.00 $\mu g\ g^{-1}$ in the South Fork Yuba River, Bear River, and Deer Creek, with concentrations to ~2.00 $\mu g\ g^{-1}$ in the North Fork Cosumnes River. Similar and slightly higher levels were found in this study in Sulfur Creek and all of Bear Creek downstream of Sulfur Creek (1.22-2.69 $\mu g\ g^{-1}$). Closer to mercury mine sources, significantly higher levels were found in Davis Creek (2.63-3.78 $\mu g\ g^{-1}$) and Harley Gulch (9.64-19.24 $\mu g\ g^{-1}$).

Still higher levels have been reported in comparable biotic samples taken from Dunn Creek just below the Mt. Diablo Mercury Mine (26.83-34.96 $\mu g\ g^{-1}$, Slotton *et al.* 1996a). It is apparent that abandoned mercury mines release mercury in a form that is, at least initially, highly bioavailable. In our Marsh Creek work (Slotton *et al.* 1996a), we found the aqueous mercury in Mt. Diablo Mercury Mine seepage from calcine tailings to be entirely in the dissolved form. Upon mixing with Dunn Creek, ≥75% of the aqueous mercury became associated with freshly precipitated particulates, similar to the pattern observed in Clear Lake Sulphur Bank Mine seepage (Suchanek *et al.* 1997) and apparently similar to the pattern observed in Davis Creek near the Reed Mine and in Harley Gulch below the Abbott/Turkey Run mine complex. Presumably, Sulfur Creek will demonstrate the same pattern in the vicinity of that stream's upstream abandoned mercury mines.

Implications for Downstream Mercury Loading

We suspect that mine-derived, surface adsorbed mercury on colloidal particles may represent a significant portion of the total mercury that is readily available to downstream methylating organisms and, subsequently, aquatic food webs. This may remain the case throughout the system all the way into the Sacramento/San Joaquin Bay-Delta. The data presented in this report is consistent with the bulk of the system's large inorganic mercury load being relatively inert biologically. In proposed and ongoing work, we plan to determine the contribution of dissolved and colloidal mercury from abandoned mine sites to the bioavailable mercury pool of the entire Bay-Delta watershed. If we find that this source is very important, the implications for statewide mercury remediation are great, as these sites are highly localized and thus offer a variety of cost-effective remediation options, as compared to potential generalized regional mercury sources.

REFERENCES

McCafferty, W.P. 1981. *Aquatic Entomology.* Jones and Bartlett Publishers, Boston. 448 pp.

Merritt, R.W. and K.W. Cummins. 1984. *An Introduction to the Aquatic Insects of North America, second edition.* Kendall-Hunt Publishing Company, Dubuque, Iowa. 722 pp.

Reuter, J.E., D.G. Slotton, S.M. Ayers, and C.R. Goldman. 1996. Evaluation of McLaughlin Gold Mine Project in Yolo County as Related to Surface Waters in the Davis Creek Watershed--July 1, 1995 - June 30, 1996. *Report for Yolo County.* 213 pp. (Similar reports from 1987-1995).

Sadiq and Zaidi 1983. A study of various factors affecting digestion of fish tissues prior to mercury determination. *Internat. J. Environ. Anal. Chem.*, 16:57-66.

Slotton, D.G. 1991. Mercury bioaccumulation in a newly impounded Northern California reservoir. *Doctoral dissertation, University of California, Davis, December 1991.* 363 pp.

Slotton, D.G., S.M. Ayers, J.E. Reuter, and C.R. Goldman. 1995(a). Gold mining impacts on food chain mercury in northwestern Sierra Nevada streams. *Technical Completion Report for the University of California Water Resources Center, Project W-816*, August 1995, 46 pp.

Slotton, D.G., J.E. Reuter, and C.R. Goldman. 1995(b). Mercury uptake patterns of biota in a seasonally anoxic northern California reservoir. *Water, Air, and Soil Pollution*, 80:841-850.

Slotton, D.G., S.M. Ayers, and J.E. Reuter. 1996(a). Marsh Creek watershed 1995 mercury assessment project. *Final Report for Contra Costa County*, March 1996, 66 pp.

Slotton, D.G., S.M. Ayers, and J.E. Reuter. 1996(b). Off-channel gravel pit lakes--mercury considerations; lower Cache Creek, Yolo County, California. Preliminary study, April 1996. *Report for Yolo County*, May 2, 1996. 31 pages.

Slotton, D.G., S.M. Ayers, J.E. Reuter, and C.R. Goldman. 1997. Sacramento River watershed mercury control planning project--UC Davis biotic component. *Final Report for the Sacramento Regional County Sanitation District*, March 1997, 74 pp.

Slotton, D.G., T.H. Suchanek, L.H. Mullen, and P.J. Richerson. (1998). Mercury in fishes from the Clear Lake aquatic ecosystem, a mine-impacted EPA Superfund Site in California. (In final stages of preparation; to be submitted this month).

Suchanek, T.H., P.J. Richerson, L.A. Woodward, D.G. Slotton, L.J. Holts and C.E. Woodmansee 1993. Ecological Assessment of the Sulphur Bank Mercury Mine Superfund Site, Clear Lake, California: A survey and Evaluation of Mercury In: Sediment, Water, Plankton, Periphyton, Benthic Invertebrates and Fishes Within the Aquatic Ecosystem of Clear Lake, California. *Phase 1- Preliminary Lake Study Report.* Prepared for EPA-Region IX, Superfund Program. 113 pp., plus 2 attachments.

Suchanek, T.H., P.J. Richerson, L.J. Mullen, L.L. Brister, J.C. Becker, A. Maxson, and D.G. Slotton 1997. The role of the Sulphur Bank Mercury Mine site (and associated hydrogeological processes) in the dynamics of mercury transport and bioaccumulation within the Clear Lake aquatic ecosystem. *A report prepared for the USEPA, Region IX Superfund Program.* 479pp.

TSMP 1990. Toxic Substances Monitoring Program, ten year summary report (1978-1987). *California Water Resources Control Board publication 90-1Q*. Similar reports from 1991 (1988-1989 data), 1992 (1990 data), 1993 (1991 data), and 1995 (1992-1993 data).