CACHE CREEK NATURE PRESERVE
MERCURY MONITORING PROGRAM

YOLO COUNTY, CALIFORNIA

THIRD SEMI-ANNUAL DATA REPORT
(FALL 2001 – WINTER 2001/2002)

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prepared for

Yolo County, California

Study and Report by

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EXECUTIVE SUMMARY

This third semi-annual report marks the midpoint of this mercury study at the Cache Creek Nature Preserve and environs. In this work, which began in the fall of 2000, mercury bioaccumulation has been characterized within the Nature Preserve wetlands in six quarterly samplings to date. A more extensive additional series of collections was made semi-annually at strategically located adjacent sites (three events to date). The data collected thus far indicate that Gordon Slough is a significantly lower mercury environment than adjacent Cache Creek. Mercury bioaccumulation in the Nature Preserve has been substantially elevated over that in its source water environment (Gordon Slough), bringing it to a level similar to that found in Cache Creek. The Nature Preserve has thus functioned to some extent as a source of methylmercury. This is consistent with most wetland environments. A possible localized elevation in invertebrate mercury bioaccumulation has been noted in Cache Creek immediately downstream of the Nature Preserve outlet. However, a short distance downstream of that location, in Cache Creek below Gordon Slough, mercury bioaccumulation has consistently been similar to or lower than corresponding levels in Cache Creek upstream of the project.

A fascinating seasonal trend is becoming apparent in the long-term data. The small fish exhibited a pronounced drop in their mercury levels in the spring 2001 sampling relative to fall collections both before (2000) and after (2001). The fall concentrations were generally between 50% and over 400% greater than corresponding spring levels. We believe that these trends in the fish data are actually offset by a period of one to several months from the underlying cycles of mercury methylation and bioavailability. Other project data are consistent with these cycles being maximal in the mid-summer and lowest in the winter. The invertebrate data did not capture these apparent seasonal trends. This may be due to a more rapid equilibration between mercury exposure conditions and bioaccumulation in these organisms.

In this last semi-annual period, organic (methyl) mercury analyses have been added to the standard total mercury assays for biological samples. These new data closely followed the total mercury values, at high percentages of the total mercury concentrations. At this point, data interpretation would be very similar using either mercury parameter as a monitoring tool.

BACKGROUND AND INTRODUCTION

The Cache Creek Nature Preserve is a constructed wetland reserve in Yolo County, built in 1999-2000 at the site of a former gravel mining operation. It is located between Gordon Slough and Cache Creek, just west of County Road 94B and the Gordon Slough-Cache Creek confluence, on the north side of Cache Creek. The Preserve was built to provide new habitat for wildlife and recreational and educational opportunities for the public. A contoured pond system with several islands was created and landscaped with native vegetation. A visitor's center and a system of walkways and overlooks were built. The Preserve has attracted numerous wildlife species and is becoming a popular educational and recreational destination.

As constructed, the wetland is intended to occasionally have its water exchanged between the months of approximately April and September (irrigation season). During these months, water is periodically diverted from Gordon Slough to the wetland, exiting the wetland to Cache Creek approximately 0.5 km upstream of the Gordon Slough - Cache Creek confluence. Gordon Slough is a seasonally operated irrigation drainage canal, which contains agricultural return flows of water that originates from upstream Cache Creek. Wetland water exchanges typically occur for 1/2 – 2 days and are conducted one or two times per month during irrigation season.

Cache Creek is known to transport seasonally elevated loads of mercury (Hg) from historic mining districts in the upper watershed (Slotton et al. 1997, Foe and Croyle 1998). Consequently, there is a general interest in mercury and mercury bioaccumulation throughout the watershed. Because wetland habitats have been demonstrated to enhance the conversion of inorganic mercury to bioaccumulating methylmercury in certain environments (Rudd 1995), it was felt that the issues of mercury and mercury bioaccumulation should be investigated at the Cache Creek Nature Preserve, both within the Preserve wetlands and in adjacent Cache Creek upstream and downstream of the Nature Preserve outlet. Mercury dynamics in this wetland are additionally of interest as a model that may help in the planning of potential future wetland preserves at other sites in the region.

A three-year mercury monitoring study was initiated in the fall of 2000. The primary purpose of this monitoring program is to indicate the potential role, if any, that Nature Preserve water discharges may have on mercury levels in adjacent Cache Creek. The monitoring includes a series of quarterly collections, with data reports issued semi-annually. This is the third of these reports. In it, we discuss findings from collections made in Fall 2001 and Winter 2001/2002, and compare to results from previous sampling for the project (Fall 2000 through Summer 2001).

METHODS

As designed, the monitoring program focuses on mercury levels in selected types of localized aquatic biota as the primary indicators of relative mercury conditions at several key locations. These locations are:

- Cache Creek upstream of the Preserve and the Preserve water outlet.
- Gordon Slough, near the Preserve intake and the confluence with Cache Creek.
- The Nature Preserve wetlands.
- Cache Creek downstream of Gordon Slough and the Preserve.

The Cache Creek sites for invertebrate collections are located approximately 0.5 km upstream of the Preserve and 1 km downstream (~0.7 km downstream of the Cache Creek - Gordon Slough confluence). Small fish are taken along the Creek from these points and continuing away from the Preserve for a further 0.3-0.7 km. An additional site was added for invertebrate sampling only at:

- Cache Creek between the Preserve outlet and the Gordon-Cache confluence.

Fish cannot be effectively sampled from this intermediate site because (a) the reach between the Preserve outlet and the Cache-Gordon confluence is too small to contain sufficient, reliable samples and (b) due to fish movement, it is not possible to ensure that samples taken in this location are not derived from adjacent sites upstream and downstream. However, with some effort, it has been possible to collect adequate samples of invertebrate bioindicators that we believe are representative of mercury exposure conditions at the intermediate stretch of Cache Creek just downstream of the Preserve outlet.

By comparing mercury concentrations in similar local biota taken at the different sites, it can be determined whether significant differences exist among the sites. The potential role of Nature Preserve water discharges on mercury levels in Cache Creek can be assessed.

All of the sites are scheduled for sampling on a semi-annual basis, once in the fall and once in the spring. Because aquatic organisms accumulate their mercury burdens over time, biotic sampling can provide information on average conditions throughout the previous months. The fall samplings are intended to integrate relative mercury bioaccumulation throughout the warm season period of irrigation flows. The spring collections monitor conditions during the previous cool season, when the Preserve is not designed to exchange water. Supplementing the primary multi-site, semi-annual collections are additional quarterly samplings from the Nature Preserve wetlands site alone, conducted in summer and winter.

The target biota for use as mercury bioindicators in this project are small or juvenile fishes and aquatic insects that tend to remain within fairly localized ranges. These organisms have been found to be ideal monitoring tools to indicate relative mercury bioaccumulation between locations, in numerous research studies by the authors throughout California and by other researchers elsewhere. Because these organisms are generally well under a year old when collected, they can also reflect potential seasonal changes in mercury exposure more directly than large fish. In contrast, large fish mercury burdens represent the combined mercury accumulations of several years time. Large fish are also far less likely to have remained in the immediate sampling region throughout their lives.

The localized availability of potential mercury bioindicator species was determined at each of the sites in the initial Fall 2000 work. Sampling was directed at taxa that were prevalent and would not be impacted by collections. Efforts have been made to collect similar sample types from the different sites and between collection dates. Whenever possible, composite samples of multiple individuals were collected. For the samples that were most inter-comparable between sites and/or dates, replicate composites were taken when possible. When triplicate identical composites could be taken, each containing multiple small individual fish or invertebrates, statistical confidence intervals of the mean mercury levels were determined.

Benthic aquatic insects were collected with research kick screens and various nets. Small fishes were taken using a backpack electro-shock unit, beach seines, and other nets. Samples were identified, measured, cleaned, and sorted using well-established laboratory protocols. Composite samples were prepared and analyzed for mercury at the UC Davis Environmental Mercury Laboratory. Research-level Quality Assurance / Quality Control (QA/QC) was employed throughout.

We are pleased to report that our laboratory has recently completed development of a modified technique to analyze organic (methyl) mercury in biotic samples, in addition to the standard total mercury that we have long provided. Following over a year of extensive QA/QC testing of the new method, we have added this very important parameter to our standard analytical list. During the past year, the concern was raised that tracking of total mercury alone in project bioindicator samples might not provide an accurate measure of methylmercury trends. We are therefore conducting double analyses of all samples during this monitoring year, generating both organic (methyl) and total mercury data.

RESULTS AND DISCUSSION

This third semi-annual data report discusses samples taken in the fall of 2001 (November 12-16) and the winter of 2001/2002 (February 7). A total of 34 composite fish samples, each consisting of multiple similar individual small fish, were prepared and analyzed from the four fish sampling locations in Fall 2001. Twenty-seven composite samples of aquatic insects were assembled from the fall collections as well. Winter 2001/2002 collections at the Nature Preserve site alone included 14 composite samples of fish. Samples analyzed for both total and methyl mercury during this reporting period are summarized in Table 1 (below). Additional data tables and associated figures are presented together following the text. Figures 6(a-e) and 7(a-c) compare selected parameters seasonally across the entire monitoring project to-date.

Table 1. Summary of Biological Samples Analyzed for Mercury in This Six Month Period (Fall 2001 and Winter 2001/2002 Collections).

Site	Small Fish Composites	Aquatic Insect Composites	**Totals**
FALL 2001			
Cache Ck upstream of Preserve	7	9	**16**
Gordon Slough	9		**9**
Nature Preserve Wetlands	9		**9**
Cache Ck btw. Preserve & Gordon Sl.		9	**9**
Cache Ck downstream of Gordon Sl.	9	9	**18**
TOT. FALL 2001 SAMPLES (61 total):	**34**	**27**	**61**
WINTER 2001/2002			
Nature Preserve Wetlands	14		**14**
TOT. WINTER 2002 SAMPLES (14 total):	**14**		**14**
TOTAL SAMPLES FOR THg (75 total):	**48**	**27**	**75**
TOTAL SAMPLES FOR MeHg (75 total):	**48**	**27**	**75**

These 75 total mercury and 75 methylmercury samples were prepared and analyzed using research levels of QA/QC. Associated QA/QC data are presented in Table 2(a-b). No problems were encountered in the analyses and the associated data for the second two quarters of sampling, as those from the preceding quarters, can be treated as very reliable.

SITE TO SITE (SPATIAL) VARIATION IN MERCURY

Mercury in Small/Juvenile Fishes

The new multi-site fish mercury data from Fall 2001 are presented in Tables 3-6 and are shown graphically in Figures 1-4. In Year 2 fish sampling, we are focusing our efforts on non-native species that can be obtained in replicate composites from the maximum number of sites. While the composite samples were all powdered and analyzed on a dry weight basis for consistency, the values as presented have been converted to wet (fresh) weight concentrations so as to be comparable to various guidelines. Multiple tests of moisture percentage were averaged for each species to convert the consistent data from the dry, powdered samples to a fresh/wet weight basis. Replicate composite samples were generally similar in mercury concentration. The data are displayed so as to allow intercomparison of the sites and dates, for each sample type. The new methylmercury parameter will be additionally discussed in a following section, though it can be summarized as having virtually mirrored the total mercury data, at a consistent high percentage of corresponding total mercury. Identical mercury trends were described by both data sets and either would lead to the same conclusions. Below, we discuss the data trends relative to total mercury, corresponding to the previous two reports.

Red shiners (Table 3, Figure 1) were initially the most readily available of the fish species present at all of the fish sampling locations. They thus provided the strongest measures of inter-site variability in fish mercury bioaccumulation. Red shiners have remained abundant at the Gordon Slough and Cache Creek sites but, over the past year, shiners in the Nature Preserve itself have been largely displaced by fathead minnows as the new wetlands evolve. In the Fall 2001 sampling, it was possible to obtain multi-individual composite samples of the same 36-50 mm size class of red shiners at each of the creek and slough sites, each in triplicate, with a single composite from the Nature Preserve. Composites of the larger size class (51-65 mm) were taken in varying numbers of replicates, relative to availability. Fall 2001 data are shown in Table 3 and are plotted in Figure 1. Mercury concentrations ranged between 0.08 and 0.30 ppm among all 16 of the red shiner multi-individual composite samples. This was notably greater, by approximately three fold, than the results from Spring 2001. Within this range of concentrations, replication was generally good between replicate composites, providing useful statistical confidence intervals. The larger size class (51-65 mm, Class 3) exhibited higher concentrations than the mid-size class (36-50 mm, Class 2) at Gordon Slough and the two Cache Creek sites. Between sites, the Fall 2001 data set exhibits some statistical differences. Lowest mercury for both size classes was found in Gordon

Slough, with slightly greater levels in Cache Creek below Gordon Slough. The Class 2 shiners from the Nature Preserve were intermediate, while notably elevated concentrations were seen in both size classes at the upstream Cache Creek site. Among the size class with triplicate composite samples, the upstream Cache Creek shiners were statistically greater in mercury than those from both downstream Cache Creek and Gordon Slough, at the 95% level of confidence. Methylmercury spatial trends followed those seen for total mercury and were also statistically significant.

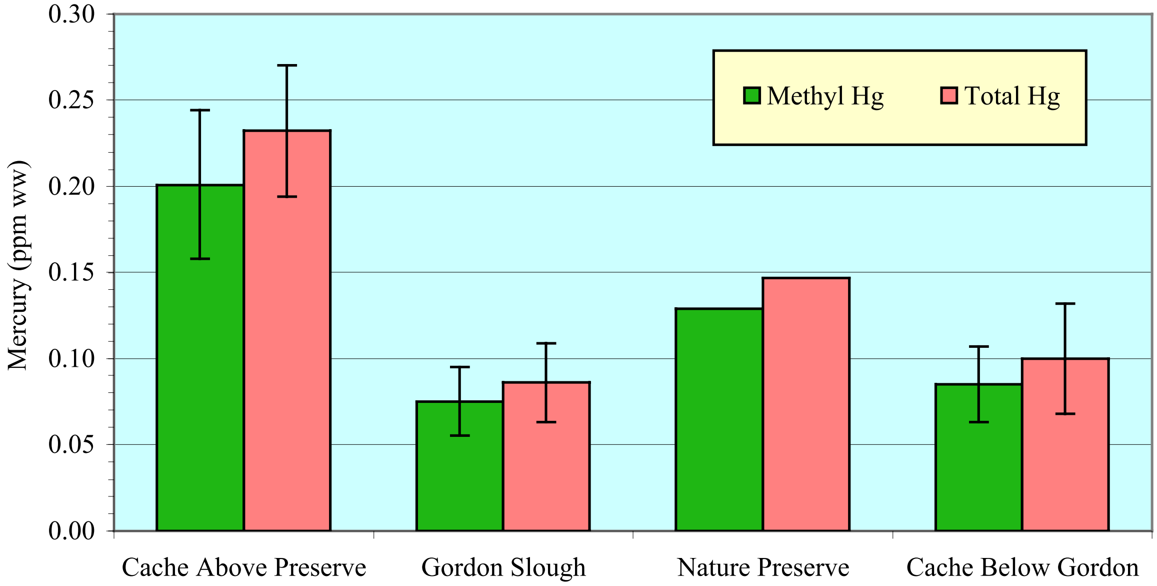
Fathead minnow data from the Fall 2001 collections are displayed in Table 4 and are shown graphically in Figure 2. This species was primarily available from the Nature Preserve wetlands, where it was possible to obtain triplicate composite samples for both mid and large size classes. Single composites of these size classes were also taken at Gordon Slough. The larger size class was somewhat higher in mercury concentration than the mid size class at the Nature Preserve, though in Gordon Slough the larger class was somewhat lower. In both size classes of fathead minnows, the Gordon Slough samples were notably lower in mercury than comparable fish from the Nature Preserve. However, as compared to red shiners of the same sizes, the fall fathead minnows at both sites were dramatically lower in overall mercury levels (0.02-0.07 vs. 0.08-0.30 ppm). The same trends were apparent in the methylmercury data.

Juvenile green sunfish (Table 5, Figure 3) were taken at all four of the fish sampling sites in the Fall 2001 sampling, though not in numbers sufficient to provide statistical confidence intervals. Green sunfish mercury concentrations from Fall 2001 ranged between 0.05 and 0.14 ppm. Similar mercury levels were found at upstream Cache Creek, Cache Creek below Gordon Slough, and the Nature Preserve, increasing slightly in concentration in that order. Comparable green sunfish from Gordon Slough were notably lower. Methylmercury trends followed.

Mosquitofish (Table 6, Figure 4) were collected successfully at all four fish sampling sites for the first time. While only single multi-individual composites were obtained from each site at this time, we believe that in the future we may be able to collect replicate composites for statistical comparison, using a new sampling strategy we recently developed. Concentrations in the Fall 2001 samplings ranged between 0.06 and 0.14 ppm across all four sites. Similar to the red shiners, lowest levels came from Gordon Slough, slightly higher levels from Cache Creek below Gordon Slough, slightly higher still from the Nature Preserve, and notably greatest concentrations from Cache Creek upstream of the Preserve. Methylmercury trends were identical.

Fig. 1. FISH Composite Hg (wet wt ppm) VS LOCATION
Red Shiner (*Notropis lutrensis*)
(mean values plotted for replicate composites)
(95% confidence intervals shown for samples with ≥3 replicates)

1(a). Red Shiner 36-50 mm size class.



1(b). Red Shiner 51-65 mm size class.

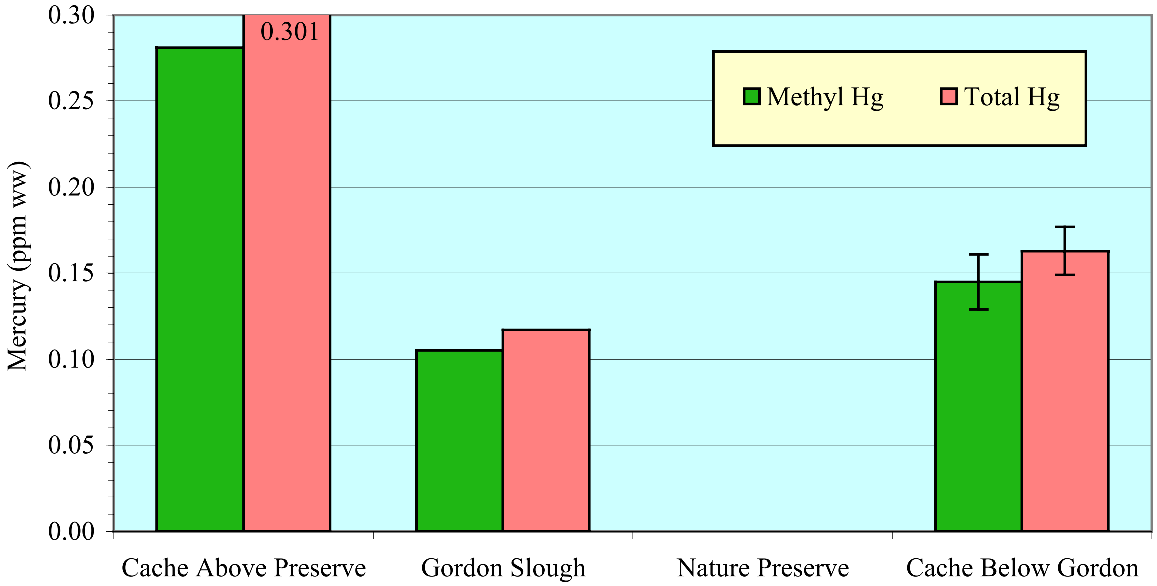
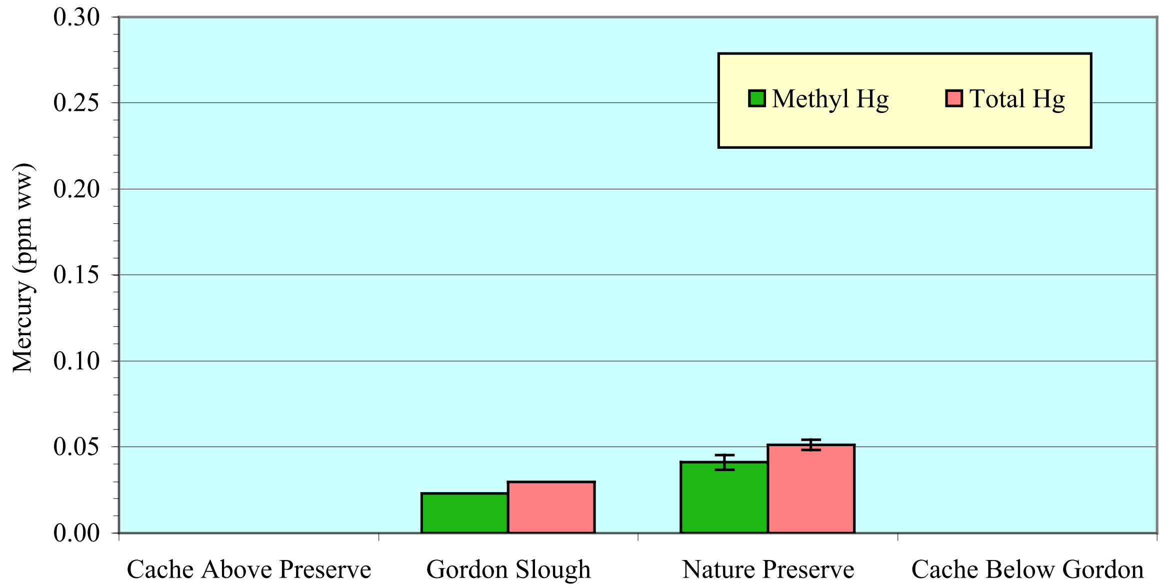


Fig. 2. FISH Composite Hg (wet wt ppm) VS LOCATION
<u>Fathead Minnow</u> (*Pimephales promelas*)
(mean values plotted for replicate composites)
(95% confidence intervals shown for samples with ≥3 replicates)

2(a). Fathead Minnow 36-50 mm size class.



2(b). Fathead Minnow 51-65 mm size class.

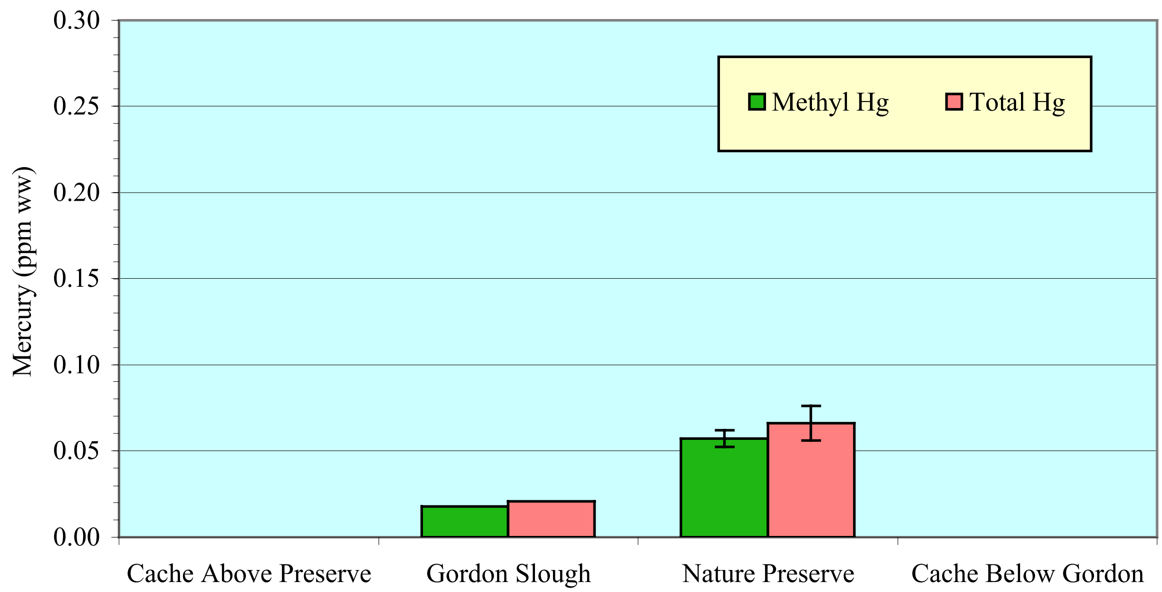
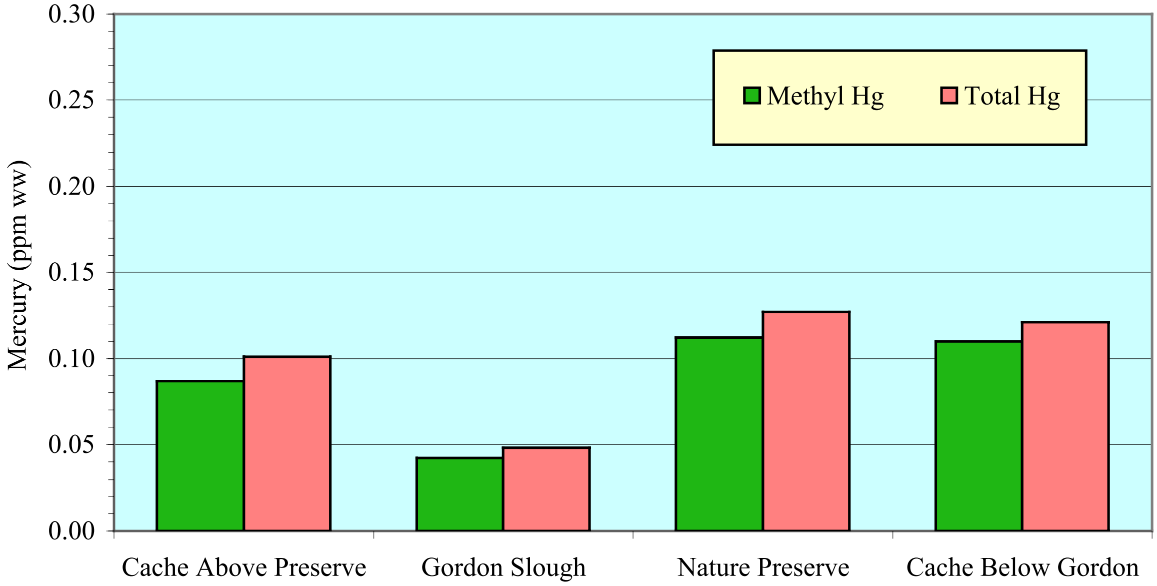


Fig. 3. FISH Composite Hg (wet wt ppm) VS LOCATION
<u>Green Sunfish</u> (*Lepomis cyanellus*)
(mean values plotted for replicate composites)
(95% confidence intervals shown for samples with ≥3 replicates)

3(a). Green Sunfish 25-50 mm size class.



3(b). Green Sunfish 51-80 mm size class.

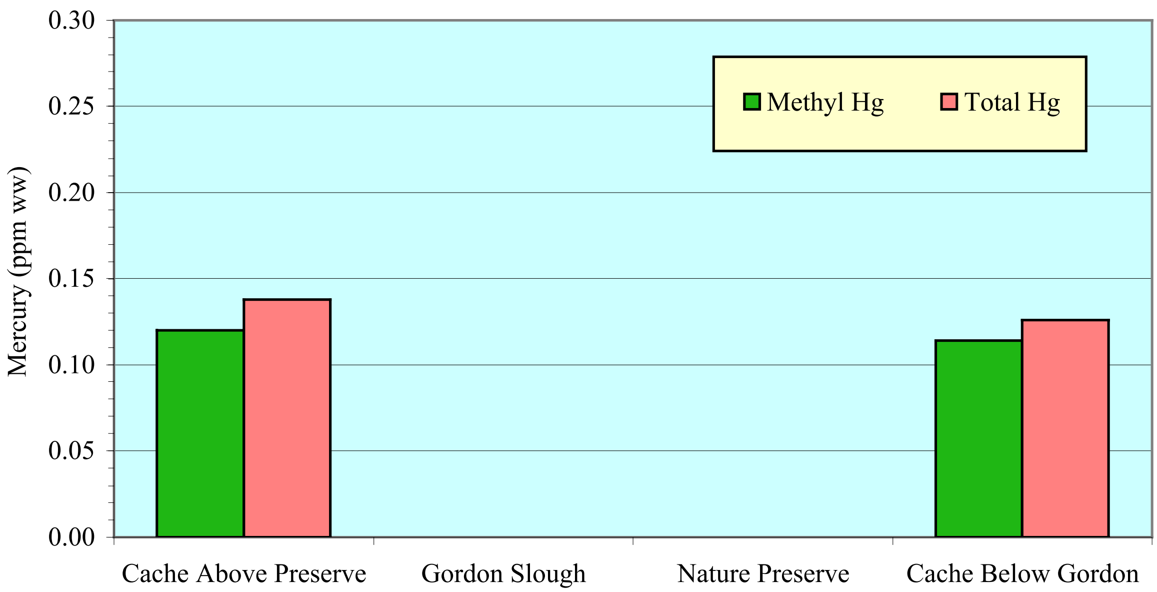
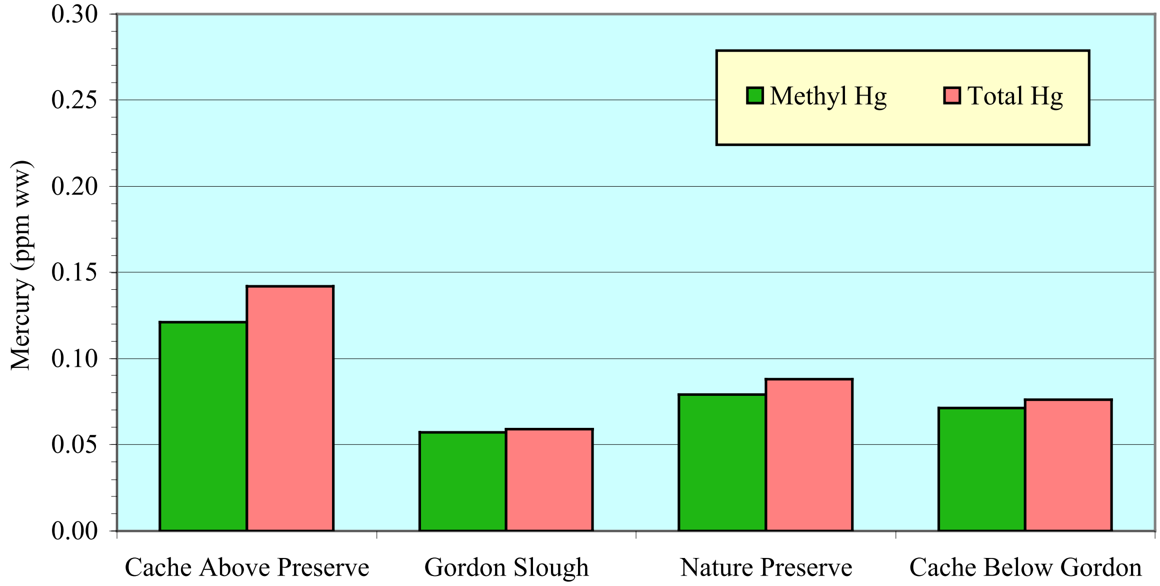


Fig. 4. FISH Composite Hg (wet wt ppm) VS LOCATION
<u>Mosquitofish</u> (*Gambusia affinis*)
(mean values plotted for replicate composites)
(95% confidence intervals shown for samples with ≥3 replicates)

4(a). Mosquitofish 20-30 mm size class.



Mercury in Aquatic Insects

Aquatic insect mercury data from the Fall 2001 collections are presented in Tables 7-9 and Figures 5(a-e). These data, for the first time, are displayed in units of *fresh/wet weight* parts per million total or methyl mercury, corresponding to the fish data. A sufficient data base of species-specific moisture percentage information was available, allowing the invertebrate mercury dry weight, powdered concentrations, as analyzed, to be converted to a wet weight basis, for comparability with the fish. Because of the generally lower range of mercury concentrations in the invertebrate samples relative to the fish, the invertebrate data are graphically plotted with 0.00-0.10 ppm axes rather than the 0.00-0.30 range used for the fish figures.

As in previous samplings, aquatic insects were not available from the Nature Preserve or Gordon Slough in sufficient numbers for meaningful comparative analysis. Fall 2001 aquatic insect data all come from the strategic series of Cache Creek sites including: Cache Creek above the Nature Preserve, Cache Creek between the Nature Preserve outlet and Gordon Slough, and Cache Creek below Gordon Slough.

<u>Hydropsychid caddisfly larvae</u> (Table 7, Figure 5a) were taken in triplicate composite samples of multiple individuals from each of the three Cache Creek sites. Fall 2001 caddisfly mercury ranged between 0.033 and 0.052 ppm among all 9 of the composites. Mean concentrations were somewhat greater at the Cache Creek site between the Nature Preserve and Gordon Slough (0.047 ppm), as compared to Cache Creek above the Preserve (0.040 ppm), though not at the 95% confidence level. Lowest concentrations were seen at the Cache Creek site below Gordon Slough (0.033 ppm). This was statistically lower than the data from the intermediate site, at the 95% confidence level, but was not statistically distinguishable from the upstream data. The caddisfly methylmercury data showed matching trends.

<u>Calopterygid damselfly nymphs</u> (Table 8, Figure 5b) were also taken from each of the three Cache Creek invertebrate sampling locations, with triplicate composites of multiple individuals available at each of the sites. Similar to the caddisflies, the calopterygid damselflies were not statistically different between the upstream Cache Creek site (0.040 ppm) and the intermediate site between the Preserve and Gordon Slough (0.037 ppm). In contrast to the caddisfly data, the damselfly data from the intermediate site showed a slight decline in total mercury relative to the upstream site. Methylmercury, however, exhibited an increase from 0.026 to 0.034 ppm, though this was not statistically distinguishable. Also similar to the caddisfly data, levels at the downstream site below Gordon Slough were the lowest of the set (0.021 ppm total Hg, 0.017 ppm methyl Hg). These levels were not statistically distinguishable from the upstream data. The downstream methylmercury concentration, though, was statistically lower than the corresponding methylmercury value from the intermediate site.

Data from <u>additional aquatic insect samples</u> (Table 9, Figures 5c-e) are consistent with those noted above. Because these less readily available invertebrate taxa each needed to be assembled into single multi-individual composites, statistical comparisons cannot be made. The overall trends, however, were quite similar. Comparisons among corresponding invertebrate composites again indicated lowest mercury bioaccumulation at the downstream site below Gordon Slough and higher concentrations at the intermediate and upstream sites. Corresponding concentrations between the intermediate and upstream sites were either very similar (Libellulidae and Naucoridae) or relatively elevated at the intermediate site (Coenagrionidae).

Organic (Methyl) Mercury vs. Total Mercury in Fall 2001 Biotic Samples

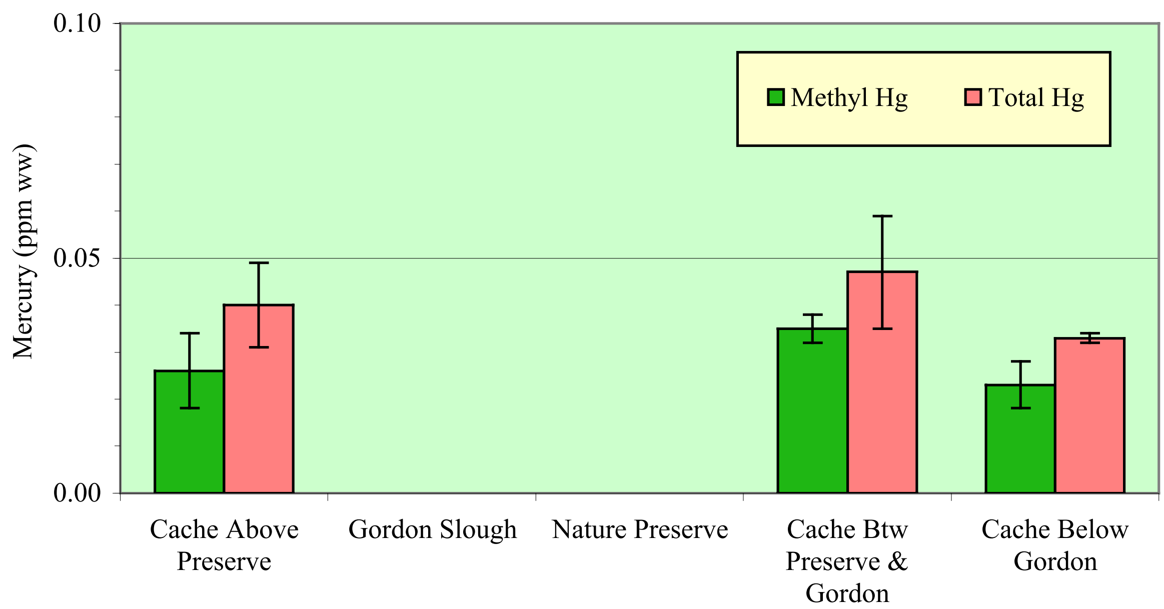
As already noted, the methylmercury data closely followed the corresponding total mercury values in nearly all paired comparisons, with the methylmercury concentration almost uniformly a high percentage proportion of the total mercury. Among the 48 fish samples analyzed for both parameters, methylmercury ranged from 77 to 97% of total mercury, with a mean of 88% ± 4% (standard deviation). The 27 invertebrate composites demonstrated methylmercury proportions that ranged from 60 to 104%, with a mean percentage of 79% ± 11%. Thus, the total mercury for these samples was primarily organic. As noted, the trends and conclusions to be drawn from them for these data would be very similar using either parameter as a monitoring tool.

Fig. 5. INVERTEBRATE Composite Hg (WET wt ppm) VS LOCATION

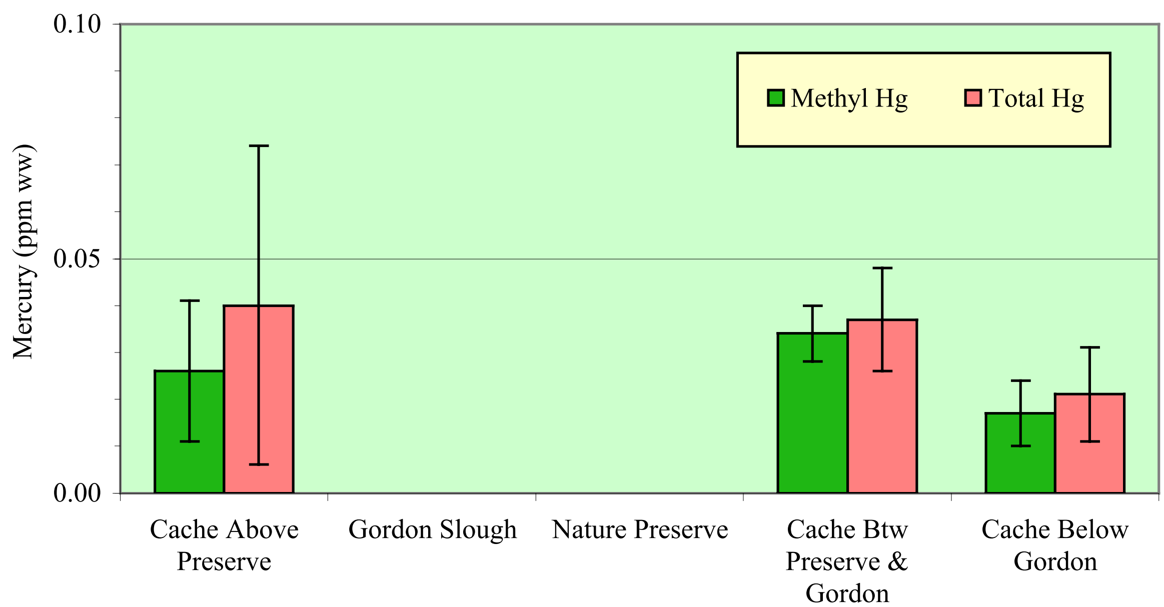
(mean values plotted for replicate composites)

(95% confidence intervals shown for samples with ≥3 replicates)

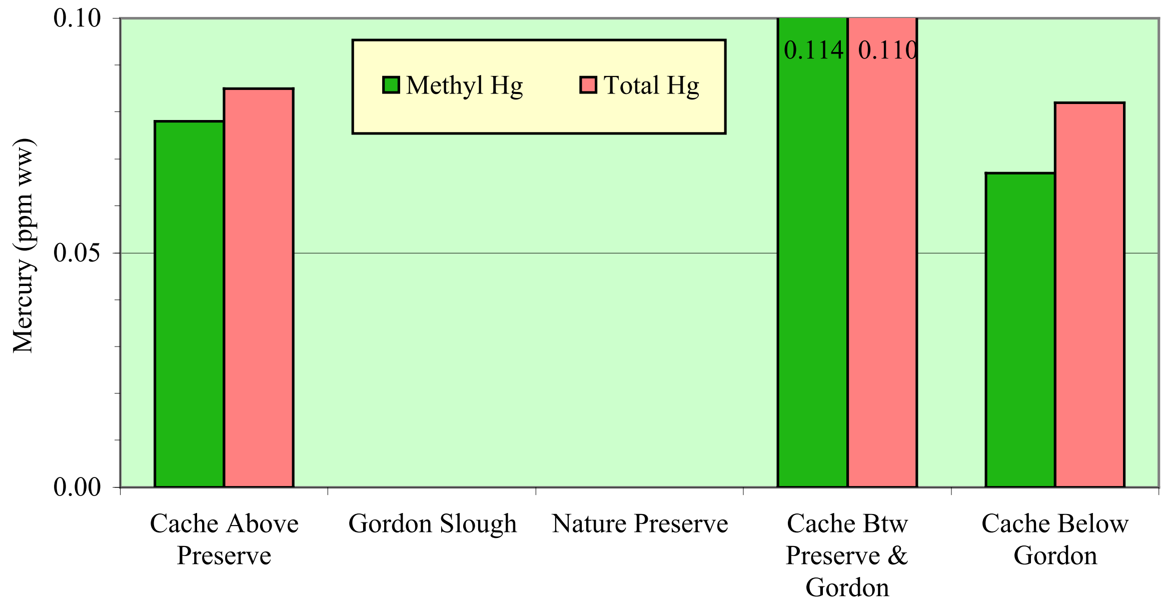
5(a). Hydropsychidae (caddisfly larvae, omnivores).



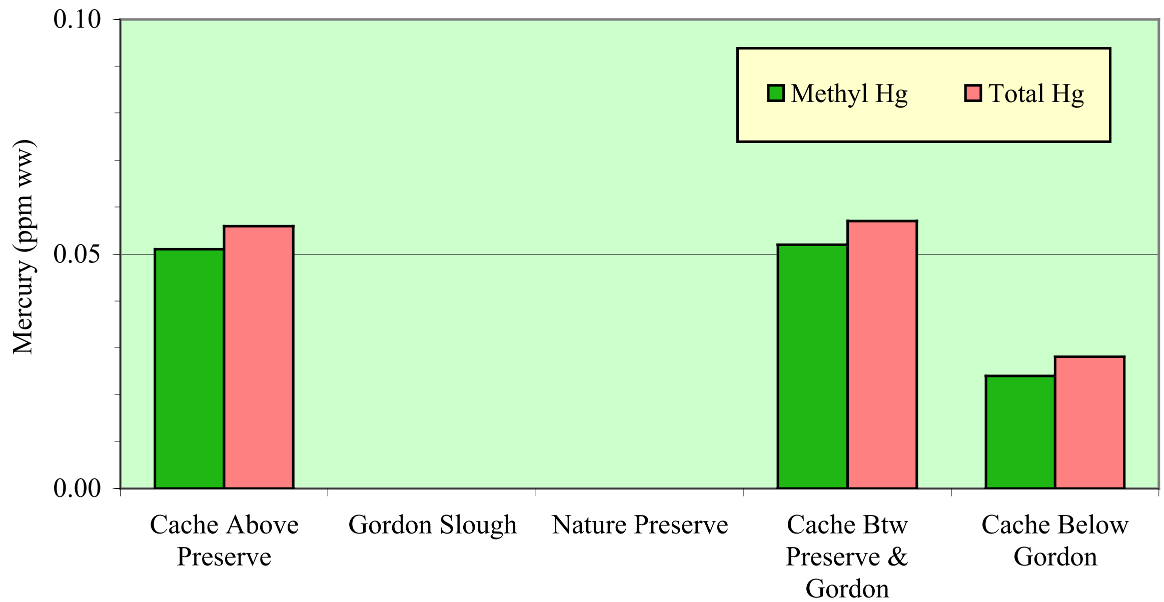
5(b). Calopterygidae (damselfly nymphs, omnivorous type).



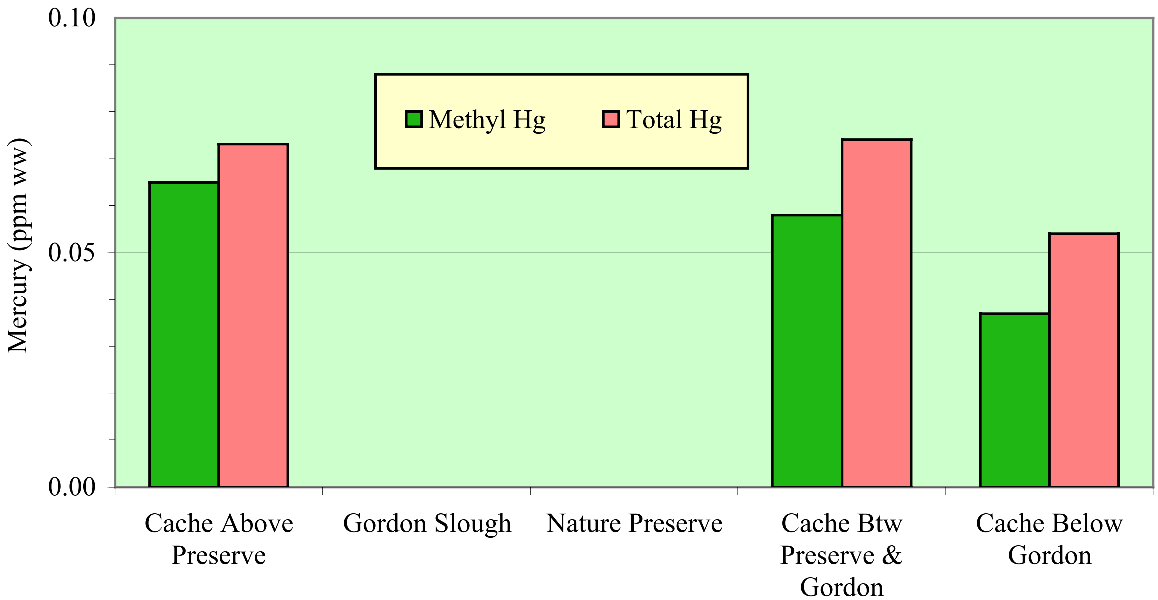
5(c). Coenagrionidae (predatory damselfly nymphs).



5(d). Libellulidae (predatory dragonfly nymphs).



5(e). Naucoridae (predaceous creeping water bugs).



SEASONAL VARIATION IN MERCURY LEVELS

In addition to the multi-site primary sampling of November 2001, a winter sampling of biota was made at the Nature Preserve wetlands site in early February 2002. Data from that sampling are presented in Table 10. At this point, midway through the project, we now have three semi-annual data sets from the Cache Creek and Gordon Slough sites (Fall 2000, Spring 2001, and Fall 2001) and six quarterly collections from the Nature Preserve (Fall 2000, Winter, Spring, Summer, and Fall 2001, and Winter 2002). Graphic comparisons of Fall 2000, Spring 2001, and Fall 2001 Cache Creek and Gordon Slough selected fish data are shown in Figures 6a, 6b, and 6e. Graphic comparisons of selected Nature Preserve fish data from all six seasonal samplings to date are displayed in Figures 6c and 6d. The seasonal trends for invertebrates from the series of Cache Creek sampling locations are plotted in Figures 7(a-c).

The fish data from all of the sites now clearly demonstrate what appears to be a consistent seasonal pattern. This apparent cycle includes a maximum in the fall, and a distinctive minimum level of fish mercury concentrations in the spring samplings. Where sufficient numbers of replicate composites have been available for statistical comparison, this fall high vs. spring low phenomenon was significant at the 95% confidence level. The single exception was the fathead minnow data, which exhibited the smallest relative seasonal changes. But among the other species, the seasonal fluctuation in mercury content was relatively enormous, with fall levels typically ranging from 50% to over 400% greater than corresponding concentrations measured in the spring. Both fall samplings to date (2000 and 2001) exhibited this distinctive elevation over the spring data. The higher resolution quarterly data from the Nature Preserve wetlands provide additional information, also describing an annual pattern of minimal fish mercury concentrations in spring, increasing toward maximal concentrations in fall, with transitions between the spring low and fall high levels generally present in the winter and summer.

As fish mercury accumulates over time, it is likely that these peaks and lows exhibited in their concentrations are not precisely matched with the seasonal underlying patterns in methylmercury production and bioavailability. It is likely that those processes somewhat precede their appearance in the fish tissue record; i.e. lowest in the winter and highest in the summer. This would be consistent with the small but evolving data set we have for methylmercury in water.

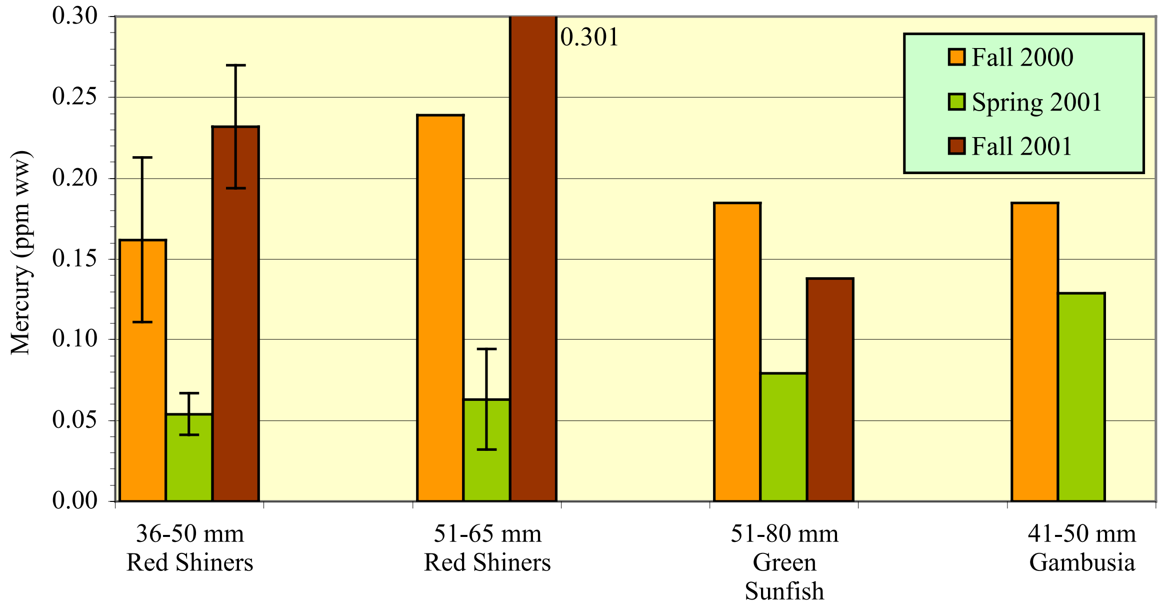
In contrast to the dramatic seasonal trends noted nearly uniformly for fish, the invertebrate seasonal data (Figures 7a-c) exhibited no consistent seasonal trend of any kind. For some sites and/or organisms, spring data were lower than corresponding fall values. For others, spring levels were higher. In the case of Hydropsychidae (caddisfly larvae) at the upstream Cache Creek site, this apparent spring increase was statistically significant. The invertebrate data were generally far more consistent than the fish across seasons. This is nearly the reverse of what we would intuitively expect. The apparent lack of a seasonal pattern in the Cache Creek invertebrate data may be due to a different invertebrate response to changes in localized methylmercury exposure, relative to the small fishes. This difference, if real, could be related to either a slower or a more rapid invertebrate mercury concentration response to changing exposure conditions. Some of our other current research in the watershed (for CALFED) indicates that the latter possibility may be the case. Under this scenario, methylmercury production and exposure may indeed be maximal in the summer and at lowest levels in the winter. The fish may be taking a period of one to several months for their accumulated mercury burdens to reflect recent conditions, while the invertebrates may be able to change more rapidly. This could be due to greater relative growth rates in the seasonal invertebrates as compared to the fish. Exposure and quick uptake may be fairly similar for the invertebrates in the beginning of the warm season in the spring and the end of the warm season in the fall.

Fig. 6 (a-e). FISH Composite Hg VS SEASON

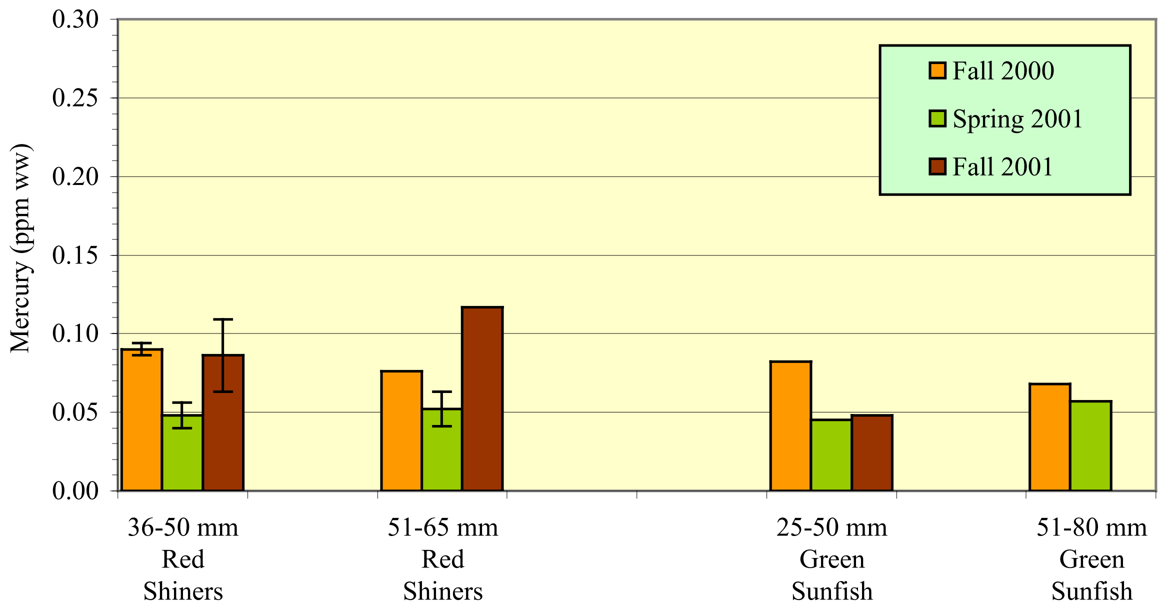
(mean values plotted for replicate composites)

(95% confidence intervals shown for samples with ≥3 replicates)

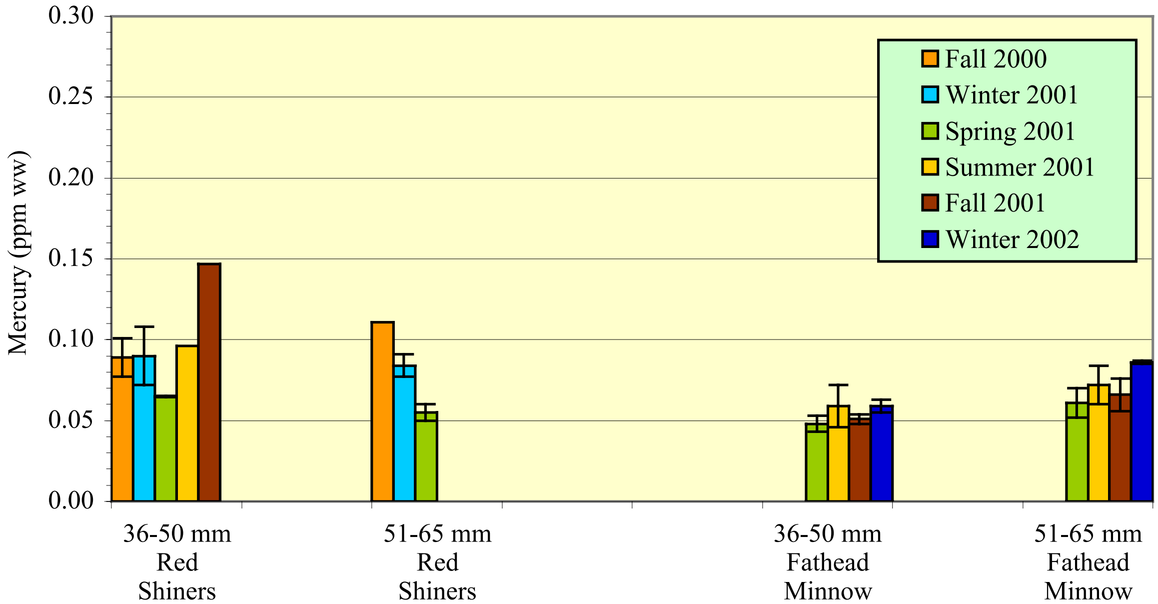
6(a). Cache Creek above Nature Preserve.



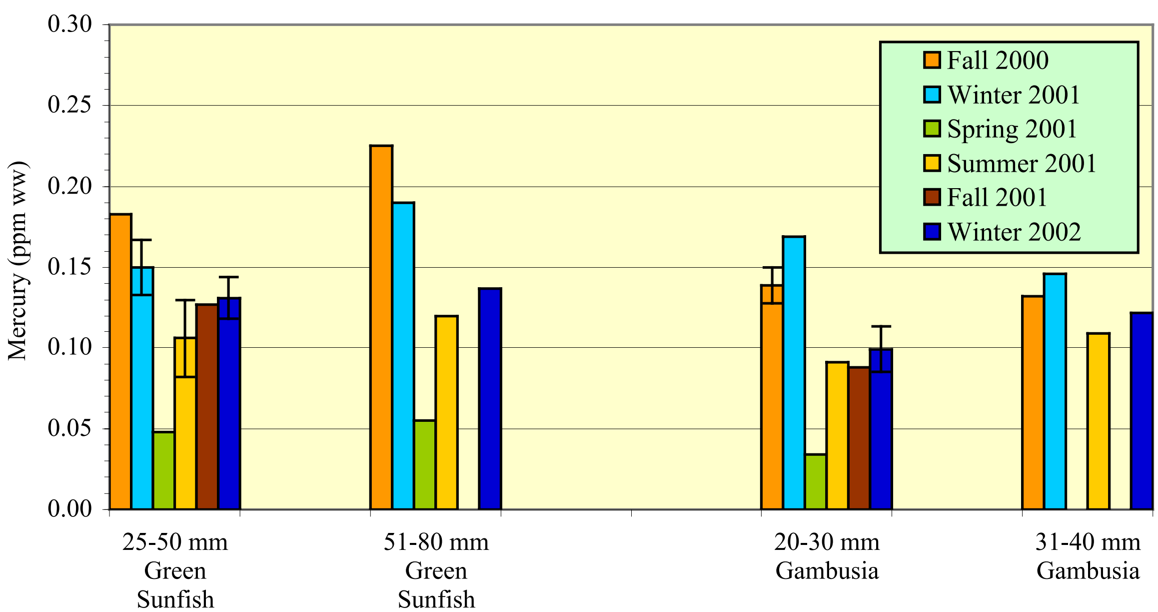
6(b). Gordon Slough.



6(c). Nature Preserve: Red Shiners and Fathead Minnows.



6(d). Nature Preserve: Green Sunfish and Mosquitofish.



6(e). Cache Creek below Gordon Slough.

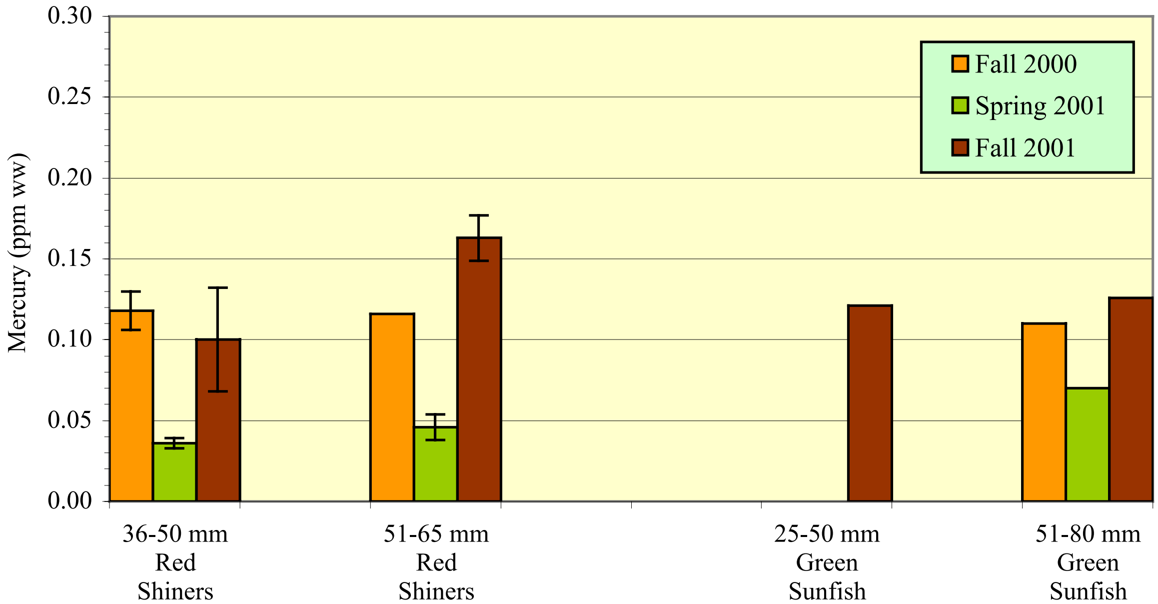
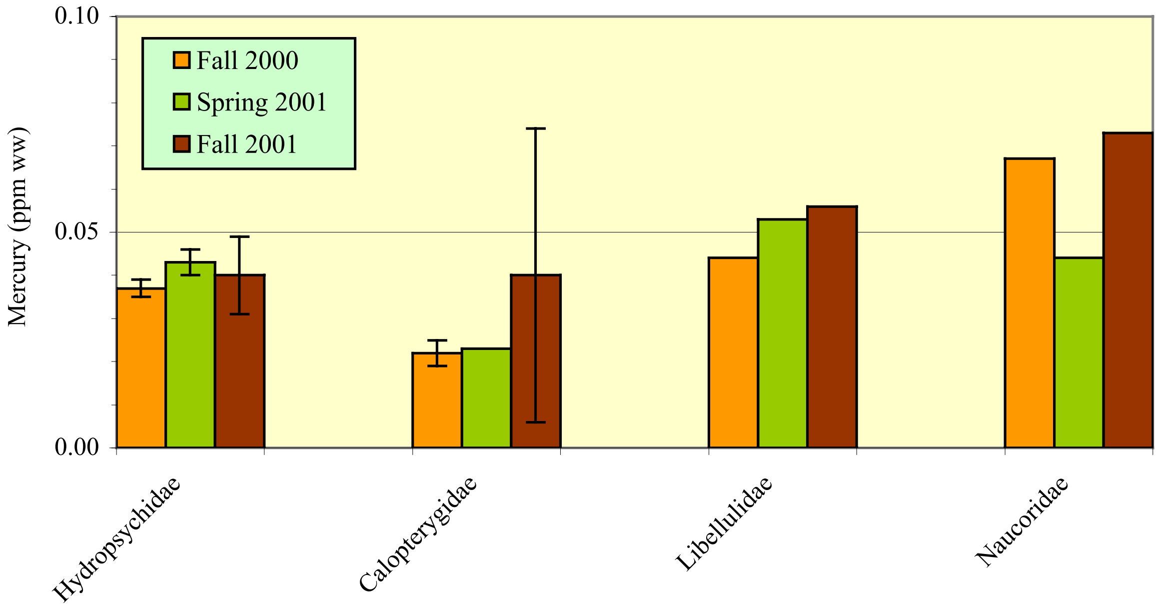
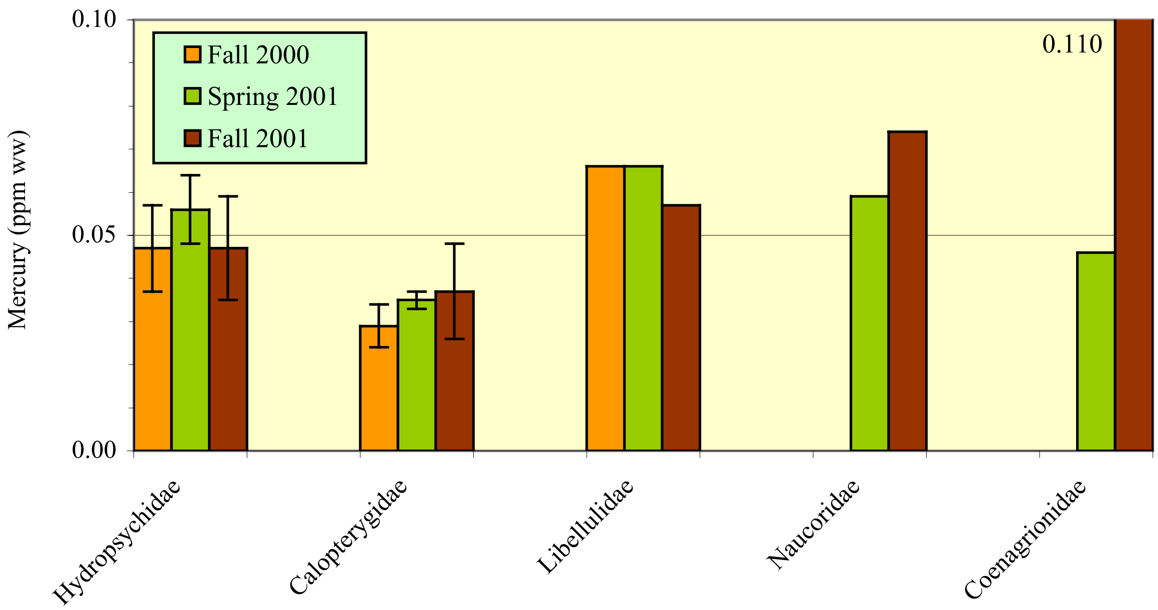


Fig. 7 (a-c). INVERTEBRATE Composite Hg VS SEASON
(mean values plotted for replicate composites)
(95% confidence intervals shown for samples with ≥3 replicates)

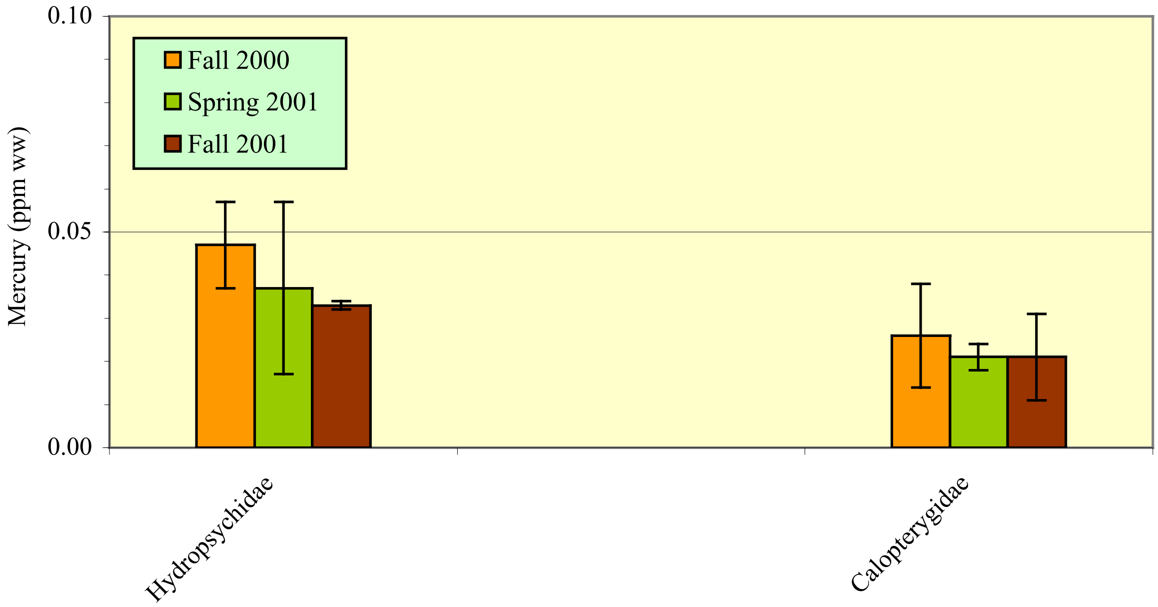
7(a). Cache Creek above Nature Preserve.



7(b). Cache Creek between Nature Preserve and Gordon Slough.



7(c). Cache Creek below Gordon Slough.



MID-PROJECT CONCLUSIONS

With the completion of half of the seasonal samplings in this three-year mercury monitoring program, we are beginning to accumulate a sizeable database of inter-comparable mercury bioaccumulation information from the Cache Creek Nature Preserve and related adjacent sites. With some difficulty, it has been possible to collect a series of closely corresponding fish samples from the Preserve and three additional fish locations. No corresponding aquatic insects were obtainable among all of the sites, although two types (Hydropsychid caddisfly larvae and Calopterygid damselfly nymphs) were taken in excellent numbers at a series of three Cache Creek locations, and three additional invertebrate taxa were obtainable in lower numbers from all three of these creek sites.

The following points can be made about the data collected in the past semi-annual period:

- Of the sites sampled throughout the project area, Gordon Slough continued to exhibit the lowest levels of mercury bioaccumulation in fish.

- The Cache Creek site located downstream of Gordon Slough and the Nature Preserve demonstrated higher fish mercury levels than Gordon Slough and lower or similar levels to those seen at the upstream Cache Creek site above the Preserve.

- Fish taken within the Nature Preserve generally contained mercury at levels intermediate between those seen at the upstream and downstream Cache Creek sites. These levels, while similar to those from the Creek, represented a substantial increase over conditions in Gordon Slough, which provides the source water for the Nature Preserve.

- Fall season invertebrates collected at the intermediate Cache Creek site, located between the Nature Preserve outflow and Gordon Slough, did not demonstrate as strong a trend in localized mercury elevation as seen in Spring 2001. A localized mercury elevation was seen at this location relative to upstream in three of five fall 2001 comparisons, with a single data pair (caddisfly methylmercury) demonstrating a statistically significant elevation. The fall 2001 data thus provide mixed evidence that the Nature Preserve outflow may be contributing to an elevation in mercury bioaccumulation in this localized area. It is curious, however, that this apparent localized effect was more muted in the fall collections, following the irrigation season when Preserve through-flows occurred, than in the spring collections which were made after less than ten days of Preserve through-flow immediately following six months of no outflows. This apparent conflict might be consistent, however, with a rapid invertebrate mercury response to changing mercury exposure, as discussed for the seasonal trends.

- Throughout the project to date, Cache Creek below Gordon Slough contained biotic mercury at levels similar to and in most cases lower than corresponding samples from Cache Creek above the Preserve.

- Mercury in small fish bioindicators exhibited what appears to be a strong seasonal pattern, resulting in minimum concentrations in the spring and maximum concentrations in the fall. We believe that this may represent a delayed measure of underlying cycles of mercury methylation and methylmercury bioavailability, which likely peak in the summer and decline in the winter. Invertebrate bioindicators, as sampled, did not demonstrate this pattern; related data from other research suggests that this may be due to different accumulation dynamics in the invertebrates (more rapid equilibration) and not to a different underlying trend in seasonal biological mercury exposure.

- With the addition of organic (methyl) mercury analyses during this project year, the recent data indicate that methylmercury constituted the majority of the mercury measured in fish (88±4%) and invertebrates (79±11%) from the project region. The methylmercury data generally mirrored the total mercury results, at a high proportion of the corresponding total mercury levels. At this point in the analytical cross-comparison, identical or very similar trends and conclusions would be supported by either parameter.

LITERATURE CITED

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Table 2a. Laboratory QA/QC Summary for UC Davis Total Mercury Analyses Used in This Data Report.
Method Detection Limit (MDL) = 0.005 µg THg/g (ppm)

	Std Curve R^2	Lab Split RPD	Field Dup. RPD	Spike Recoveries	Lab Cont. Std. Recoveries	Cont. Calibration Validation
Ideal Recovery	1.000	(0%)	(0%)	(100%)	(100%)	(100%)
Control Range (%)	≥0.975	≤25%	≤25%	75-125%	75-125%	75-125%
Tracking Method		Control Chart		Control Chart	Control Chart	Control Chart
Recoveries (%)	0.9996-0.9998	0.4%-11.2%	0.1%-69.3% *(higher near MDL)*	85%-101%	101%-107%	99%-101%
(n)	n=4	n=6	n=49	n=12	n=12	n=15
Mean Recoveries (%)	0.9997	5.6%	15.0%	95.4%	104.2%	99.8%

Standard Reference Materials

	TORT-2 Lobster	DOLT-2 Dogfish	NIST 2976 Mussel
Certified Level (ppm THg)	0.27±0.02	2.14±0.28	0.061±0.004
Ideal Recovery	(100%)	(100%)	(100%)
Control Range (%)	75-125%	75-125%	75-125%
Tracking Method	Control Chart	Control Chart	Control Chart
Control Range (ppm)	0.20-0.34	1.61-2.68	0.046-0.076
Recoveries (%)	94%-107%	99%-100%	101%-107%
Recoveries (ppm)	0.25-0.29	2.12-2.14	0.061-0.064
(n)	n=11	n=2	n=2
Mean Recoveries (%)	100.7%	99.6%	102.5%
Mean Recoveries (ppm)	0.27	2.13	0.063

Table 2b. Laboratory QA/QC Summary for UC Davis Methyl Mercury Analyses Used in This Data Report.
Method Detection Limit (MDL) = 0.005 µg MeHg/g (ppm)

	Std Curve R^2	Lab Split RPD	Field Dup. RPD	Spike Recoveries	Lab Cont. Std. Recoveries	Cont. Calibration Validation
Ideal Recovery	1.000	(0%)	(0%)	(100%)	(100%)	(100%)
Control Range (%) Tracking Method	≥0.975	≤25% Control Chart	≤25%	75-125% Control Chart	75-125% Control Chart	75-125% Control Chart
Recoveries (%)	0.9996-0.9998	0.1%-7.4%	0.4%-83.6% *(higher near MDL)*	94%-115%	101%-107%	99%-103%
(n)	n=4	n=6	n=49	n=12	n=12	n=15
Mean Recoveries (%)	0.9997	2.0%	16.0%	104.6%	104.2%	101.1%

Standard Reference Materials

	TORT-2 Lobster	DOLT-2 Dogfish	NIST 2976 Mussel
Certified Level (ppm MeHg) Ideal Recovery	0.152±0.013 (100%)	0.693±0.053 (100%)	0.0278±0.0011 (100%)
Control Range (%) Tracking Method Control Range (ppm)	75-125% Control Chart 0.114-0.190	75-125% Control Chart 0.520-0.866	75-125% Control Chart 0.021-0.035
Recoveries (%) Recoveries (ppm) (n)	97%-107% 0.148-0.162 n=11	101%-103% 0.702-0.711 n=2	90%-94% 0.025-0.026 n=2
Mean Recoveries (%) Mean Recoveries (ppm)	102.5% 0.156	101.9% 0.707	91.7% 0.026

Table 3. Fall 2001 Fish Mercury:
RED SHINER (*Notropis lutrensis*).
(composite samples of multiple (n) whole individuals)
(wet weight = fresh weight, µg mercury per gram = parts per million)

Size Class	(n)	Mean Fish Size wt (g)	Mean Fish Size lgth (mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
			Cache Creek Above Preserve			
2 (36-50 mm)	(12)	0.8	44	0.184	0.215	86%
2 (36-50 mm)	(12)	0.8	44	0.218	0.244	89%
2 (36-50 mm)	(12)	0.8	44	0.200	0.237	85%
			Means:	**0.201**	**0.232**	**87%**
			95% Conf. Intervals:	*± 0.043*	*± 0.038*	*± 6%*
3 (51-65 mm)	(15)	1.3	55	0.281	0.301	93%
			Gordon Slough			
2 (36-50 mm)	(20)	0.9	44	0.079	0.090	88%
2 (36-50 mm)	(20)	0.9	44	0.065	0.076	86%
2 (36-50 mm)	(20)	0.9	44	0.079	0.093	85%
			Means:	**0.075**	**0.086**	**86%**
			95% Conf. Intervals:	*± 0.020*	*± 0.023*	*± 5%*
3 (51-65 mm)	(11)	1.6	56	0.096	0.112	85%
3 (51-65 mm)	(11)	1.7	56	0.114	0.121	94%
			Means:	**0.105**	**0.117**	**90%**
			Nature Preserve Wetlands			
2 (36-50 mm)	(10)	0.8	40	**0.129**	**0.147**	**88%**
			Cache Creek Below Gordon Slough			
2 (36-50 mm)	(25)	0.9	44	0.085	0.105	80%
2 (36-50 mm)	(25)	0.9	44	0.076	0.085	89%
2 (36-50 mm)	(25)	0.9	44	0.094	0.108	87%
			Means:	**0.085**	**0.100**	**86%**
			95% Conf. Intervals:	*± 0.022*	*± 0.032*	*± 12%*
3 (51-65 mm)	(12)	1.9	60	0.140	0.165	85%
3 (51-65 mm)	(12)	1.9	60	0.152	0.168	90%
3 (51-65 mm)	(12)	2.0	60	0.142	0.157	90%
			Means:	**0.145**	**0.163**	**89%**
			95% Conf. Intervals:	*± 0.016*	*± 0.014*	*± 7%*

Table 4. Fall 2001 Fish Mercury:
FATHEAD MINNOW (*Pimephales promelas*).
(composite samples of multiple (n) whole individuals)
(wet weight = fresh weight, µg mercury per gram = parts per million)

Size Class	(n)	Mean Fish Size wt (g)	Mean Fish Size lgth (mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
			Gordon Slough			
2 (36-50 mm)	(19)	1.0	44	**0.023**	**0.030**	**77%**
3 (51-70 mm)	(10)	2.2	60	**0.018**	**0.021**	**86%**
			Nature Preserve Wetlands			
2 (36-50 mm)	(26)	0.8	44	0.039	0.051	77%
2 (36-50 mm)	(26)	0.8	44	0.042	0.052	82%
2 (36-50 mm)	(26)	0.8	44	0.041	0.049	84%
			Means:	**0.041**	**0.051**	**81%**
		95% Conf. Intervals:		*± 0.004*	*± 0.003*	*± 9%*
3 (51-70 mm)	(9)	1.9	60	0.055	0.062	89%
3 (51-70 mm)	(9)	1.9	60	0.059	0.070	85%
3 (51-70 mm)	(9)	1.8	60	0.057	0.066	85%
			Means:	**0.057**	**0.066**	**86%**
		95% Conf. Intervals:		*± 0.005*	*± 0.010*	*± 6%*

Table 5. Fall 2001 Fish Mercury:
GREEN SUNFISH (*Lepomis cyanellus*).
(composite samples of multiple (n) whole individuals)
(wet weight = fresh weight, µg mercury per gram = parts per million)

Size Class	(n)	Mean Fish Size wt (g)	Mean Fish Size lgth (mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
			Cache Creek Above Preserve			
1 (25-50 mm)	(10)	1.3	41	**0.087**	**0.101**	**86%**
2 (51-80 mm)	(6)	4.0	60	**0.120**	**0.138**	**87%**
			Gordon Slough			
1 (25-50 mm)	(12)	1.4	42	**0.042**	**0.048**	**87%**
			Nature Preserve Wetlands			
1 (25-50 mm)	(10)	1.1	42	**0.112**	**0.127**	**88%**
			Cache Creek Below Gordon Slough			
1 (25-50 mm)	(7)	1.2	40	**0.110**	**0.121**	**91%**
2 (51-80 mm)	(8)	6.2	67	**0.114**	**0.126**	**90%**

Table 6. Fall 2001 Fish Mercury:
MOSQUITOFISH (*Gambusia affinis*).
(composite samples of multiple (n) whole individuals)
(wet weight = fresh weight, µg mercury per gram = parts per million)

Size Class	(n)	Mean Fish Size wt (g)	Mean Fish Size lgth (mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
			Cache Creek Above Preserve			
1 (20-30 mm)	(61)	0.2	25	**0.121**	**0.142**	**86%**
			Gordon Slough			
1 (20-30 mm)	(17)	0.2	26	**0.057**	**0.059**	**97%**
			Nature Preserve Wetlands			
1 (20-30 mm)	(66)	0.2	26	**0.079**	**0.088**	**89%**
			Cache Creek Below Gordon Slough			
1 (20-30 mm)	(60)	0.2	25	**0.071**	**0.076**	**94%**

Table 7. Fall 2001 Invertebrate Mercury:
Primary Indicator Samples From Cache Creek Transect;
HYDROPSYCHIDAE (Caddisfly Larvae, Omnivores).
(composite samples of multiple (n) whole individuals)
(WET weight µg mercury per gram = parts per million; comparable to fish)

(n)	Size (mean mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
		Cache Creek Above Preserve		
(75)	11	0.030	0.044	69%
(75)	11	0.025	0.041	60%
(75)	11	0.024	0.037	65%
	Means:	**0.026**	**0.040**	**65%**
	95% Conf. Intervals:	*± 0.008*	*± 0.009*	*± 10%*
		Cache Creek Between Nature Preserve and Gordon Slough		
(60)	11	0.034	0.042	79%
(60)	11	0.034	0.052	66%
(60)	11	0.036	0.046	78%
	Means:	**0.035**	**0.047**	**75%**
	95% Conf. Intervals:	*± 0.003*	*± 0.012*	*± 18%*
		Cache Creek Below Gordon Slough		
(72)	11	0.025	0.034	74%
(72)	11	0.021	0.033	64%
(72)	11	0.022	0.033	67%
	Means:	**0.023**	**0.033**	**69%**
	95% Conf. Intervals:	*± 0.005*	*± 0.001*	*± 13%*

Table 8. Fall 2001 Invertebrate Mercury:
Primary Indicator Samples From Cache Creek Transect;
CALOPTERYGIDAE (Damselfly Nymphs, Omnivorous Type).
(composite samples of multiple (n) whole individuals)
(WET weight µg mercury per gram = parts per million; comparable to fish)

(n)	Size (mean mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
		Cache Creek Above Preserve		
(13)	21	0.031	0.052	60%
(13)	21	0.019	0.025	77%
(13)	21	0.028	0.043	66%
	Means:	**0.026**	**0.040**	**67%**
	95% Conf. Intervals:	*± 0.015*	*± 0.034*	*± 21%*
		Cache Creek Between Nature Preserve and Gordon Slough		
(13)	24	0.033	0.037	91%
(13)	24	0.032	0.033	95%
(13)	24	0.036	0.042	87%
	Means:	**0.034**	**0.037**	**91%**
	95% Conf. Intervals:	*± 0.006*	*± 0.011*	*± 10%*
		Cache Creek Below Gordon Slough		
(16)	24	0.019	0.023	81%
(16)	24	0.018	0.023	76%
(16)	24	0.014	0.016	83%
	Means:	**0.017**	**0.021**	**80%**
	95% Conf. Intervals:	*± 0.007*	*± 0.010*	*± 8%*

Table 9. Fall 2001 Invertebrate Mercury:
Additional Samples from Cache Creek Sites.
(composite samples of multiple (n) whole individuals)
(WET weight µg mercury per gram = parts per million; comparable to fish)

Insect Family	Description	Trophic Level	(n)	Size (mm)	Wet ppm Hg METHYL	Wet ppm Hg TOTAL	Percent Methyl
			Cache Creek Above Preserve				
Coenagrionidae	damselfly nymph	predator	(5)	16	**0.078**	**0.085**	92%
Libellulidae	dragonfly nymph	lg predator	(16)	15	**0.051**	**0.056**	90%
Naucoridae	water bug	lg predator	(36)	11	**0.065**	**0.073**	88%
			Cache Creek Between Nature Preserve and Gordon Slough				
Coenagrionidae	damselfly nymph	predator	(10)	17	**0.114**	**0.110**	104%
Libellulidae	dragonfly nymph	lg predator	(4)	16	**0.052**	**0.057**	91%
Naucoridae	water bug	lg predator	(16)	11	**0.058**	**0.074**	77%
			Cache Creek Below Gordon Slough				
Coenagrionidae	damselfly nymph	predator	(9)	16	**0.067**	**0.082**	81%
Libellulidae	dragonfly nymph	lg predator	(5)	16	**0.024**	**0.028**	86%
Naucoridae	water bug	lg predator	(24)	11	**0.037**	**0.054**	68%

Table 10. Winter 2001/2002 Fish Mercury:
Nature Preserve Wetlands Only
(composite samples of multiple (n) whole individuals)
(wet weight = fresh weight, µg mercury per gram = parts per million)

Size Class	(n)	Mean Fish Size wt (g)	Mean Fish Size lgth (mm)	µg/g METHYL Hg in WET Sample	µg/g TOTAL Hg in WET Sample	% Methyl Hg of Total Hg
FATHEAD MINNOW (*Pimephales promelas*)						
2 (36-50 mm)	32	0.8	44	0.055	0.061	90%
2 (36-50 mm)	32	0.7	44	0.049	0.058	84%
2 (36-50 mm)	32	0.7	44	0.051	0.058	88%
			Means:	**0.052**	**0.059**	**88%**
		95% Conf. Intervals:		*± 0.007*	*± 0.004*	*± 7%*
3 (51-70 mm)	20	1.8	59	0.071	0.086	83%
3 (51-70 mm)	20	1.6	59	0.080	0.086	92%
3 (51-70 mm)	20	1.7	59	0.076	0.087	87%
			Means:	**0.076**	**0.086**	**87%**
		95% Conf. Intervals:		*± 0.010*	*± 0.001*	*± 12%*
GREEN SUNFISH (*Lepomis cyanellus*)						
1 (25-50 mm)	30	0.9	38	0.105	0.126	84%
1 (25-50 mm)	30	0.8	38	0.118	0.137	86%
1 (25-50 mm)	30	0.9	38	0.124	0.132	94%
			Means:	**0.116**	**0.131**	**88%**
		95% Conf. Intervals:		*± 0.024*	*± 0.013*	*± 14%*
2 (51-80 mm)	9	2.6	57	**0.127**	**0.137**	**93%**
MOSQUITOFISH (*Gambusia affinis*)						
1 (20-30 mm)	40	0.2	25	0.086	0.093	93%
1 (20-30 mm)	40	0.2	25	0.092	0.099	94%
1 (20-30 mm)	40	0.2	25	0.097	0.104	93%
			Means:	**0.092**	**0.099**	**93%**
		95% Conf. Intervals:		*± 0.013*	*± 0.014*	*± 1%*
2 (31-40 mm)	7	0.4	34	**0.114**	**0.122**	**93%**