OFF-CHANNEL GRAVEL PIT LAKES -- MERCURY CONSIDERATIONS

LOWER CACHE CREEK, YOLO COUNTY, CALIFORNIA

Preliminary Study, April 1996

prepared for

Yolo County, California

Study and Report by

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May 2, 1996

EXECUTIVE SUMMARY

Conditions of environmental mercury were investigated at existing off-channel gravel pit lakes near Cache Creek in Yolo County. Bottom sediments, water, aquatic invertebrates, and fishes were sampled for mercury levels at the existing lakes and in adjacent Cache Creek, to provide some indication of likely mercury conditions in proposed additional off-channel gravel pit lakes. Water concentrations of mercury at the time of this April 1996 sampling (2-4 ng/L) were lower and less variable than corresponding levels from adjacent Cache Creek, and were well below the water quality criterion for mercury (12 ng/L). Bottom sediments were somewhat elevated at 0.2-1.0 ppm, though this is typical for the region and is far lower than levels seen in highly contaminated sites. Fish collected from the existing gravel pit lakes were of some concern, in that they approached and in some cases even surpassed the 0.5 ppm consumption guideline for fish mercury. However, these fish muscle mercury concentrations were very similar to concentrations found in corresponding samples from adjacent Cache Creek. Similar levels are also routinely found from many locations throughout the mercury contaminated regions of northern California.

It is not clear at this point whether the existing pit lakes at Solano Gravel become anoxic in the bottom waters during the summer. We would recommend that this be investigated. The potential exists for new gravel pit lakes, if considerably deeper than the ones tested, to become anoxic. If this occurred, the possibility would exist for methyl mercury production and subsequent transfer of mercury into fish to be enhanced to some degree. However, the likelihood of dramatically increased mercury bioavailability occurring in off-channel pit lakes of any configuration along lower Cache Creek is not supported by the findings of this study of the existing lakes. Sediment bulk mercury levels are considerably lower than in highly contaminated sites and the water quality in these sytems may not be readily conducive to anoxia. However, we would strongly recommend that the issue of environmental mercury be monitored closely in conjunction with future operations.

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1. INTRODUCTION

In April 1996, our mercury biogeochemistry research group was approached by Yolo County and asked to provide input regarding the mercury related aspects of the currently proposed off-channel gravel mining operations near Cache Creek in Yolo County. The proposed expanded gravel operations will involve the formation of a number of fairly deep, temporary lakes adjacent to Cache Creek near Highway 505 and Highway 16. Concerns have been raised as to the potential for the resulting mining pit lakes to provide an environment in which mercury could conceivably become a problem, from a human health and environmental perspective. As Yolo County is known to naturally contain high levels of mercury in some areas, including the Cache Creek watershed, this concern was not unfounded. It is clear from our extensive work in the region that, under certain specific conditions, the naturally elevated levels of mercury in portions of the County may be readily transformed into the mercury species that has been demonstrated throughout the scientific literature to move into aquatic foodchains and result in unacceptably high mercury levels in edible fish. This mercury fraction is methyl mercury, an organic species.

Methyl mercury is produced as a biproduct of a select group of microorganisms, including sulfur reducing bacteria. Under conditions where an excess of inorganic mercury is present, together with a stable population of the key microorganisms, and the conditions to support them, methyl mercury can be produced at levels sufficient to raise the mercury levels in edible fish tissue above concentrations which have been deemed safe for consumption by governmental health agencies.

The approach taken in this short-term, preliminary study was to investigate the mercury conditions present in the most analagous off-channel, gravel pit lakes already in existence in Yolo County, i.e.--the two pit lakes present at Solano Gravel, north of Highway 16 and just east of Highway 505. These lakes have been in existence for approximately 8 years, are moderately deep (~40 ft, Fig. 1), and early in the lake's development were stocked with fish which can now be utilized as biological monitors of existing mercury availability.

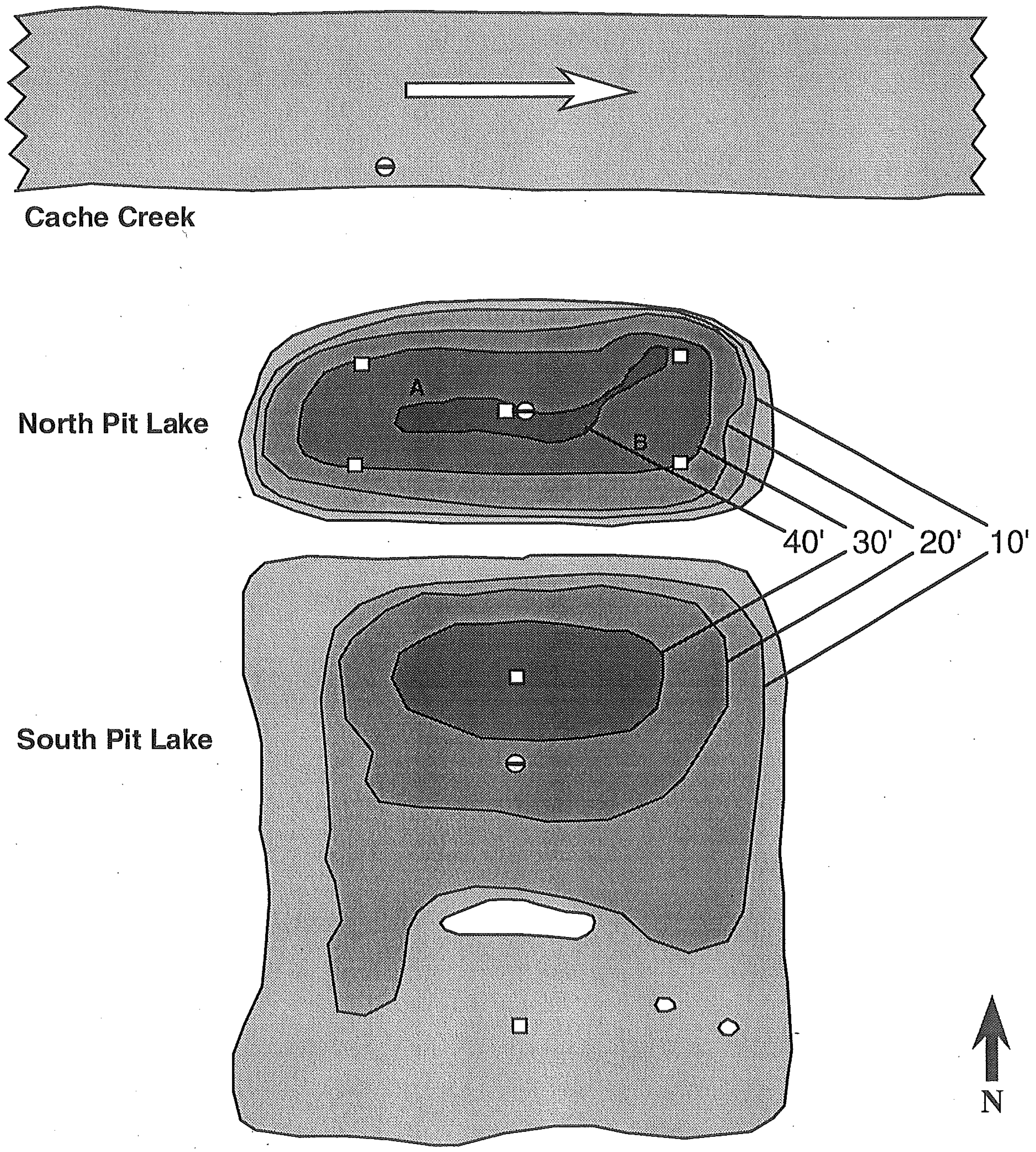
I thought there was just one.

Our plan for this preliminary study was to examine mercury levels in fish of the existing gravel pit lakes, together with aquatic invertebrates, bottom sediments, and water. These would be compared to corresponding levels in the adjacent Cache Creek, as well as levels in other water bodies in the County and in northern California in general. The initial plan was to focus on the North Lake, which was believed to be deeper. When fish collections proved difficult at this time in the North Lake, we extended the work into the adjacent South Lake, where fish were more populous and could be sampled effectively in a range of species and sizes.

The sampling sites utilized for this project at the Solano Gravel property are shown in Figure 1. We estimated depth contours of the existing lakes with the use of sonar. Comparative fish samples

Figure 1. Schematic Map of Solano Gravel Pit Lakes and Adjacent Cache Creek

☐ -- Sediment Sites
⊖ -- Water Mercury Sites
A, B -- Water Profiles



from Cache Creek were collected in October 1995 from lower Cache Creek between Road 102 and Highway 5.

Table 1 summarizes the mercury analytical samples collected for this preliminary project. Aqueous mercury samples were taken on 4 different dates from the pit lakes, together with 4 corresponding samples from the adjacent creek. Each sample was fractionated into filtered (< 0.2 µm) and raw portions, each of which were analyzed for total mercury. In addition, methyl mercury was analyzed in all of the raw water samples and 6 of the 8 filtered samples. Total mercury was analyzed in 39 individual biotic and sediment samples, including 24 individual fish analyzed for muscle mercury from the Solano Gravel pit lakes. Additional analytical samples for the project included suspended solids samples from all 8 water collections, and moisture and organic percentage analyses in the 7 bottom sediment samples.

Table 1. Summary of all Samples Analyzed for Mercury in This Project

	Raw Water	Filtered
Aqueous Total Mercury:	8	8
Aqueous Methyl Mercury:	8	6
TOTAL AQUEOUS SAMPLES:	16	14

	Pit Lakes	Cache Creek
Invertebrate Composites:	8	2
Individual Fish Muscle Samples:	(24)	(16) ¥
Green Sunfish:	*7*	
Channel Catfish:	*10*	*4* ¥
Brown Bullhead:	*2*	*4* ¥
Smallmouth Bass:	*5*	
Carp:		*2* ¥
Sacramento Sucker:		*1* ¥
Bluegill Sunfish:		*2* ¥
White Crappie:		*3* ¥
Sediment:	7	1 ¥
TOTAL SOLID SAMPLES:	39	19

¥ - Samples collected earlier (10/95) by D. G. Slotton and S.M. Ayers

2. METHODS

2.1 Collection Techniques

2.1.1 Sediment

Surficial sediment was collected from the bottoms of the Solano Gravel pit lakes with an Ekman dredge. Resulting samples were spooned into pre-cleaned glass jars with teflon-lined caps. Sediment samples were maintained refrigerated but unfrozen (so as to not alter mineral structure) until they were analyzed for mercury within 18 days of collection.

2.1.2 Water

Water collections for mercury analysis were made in conjunction with Frontier Geosciences Laboratory, which is the most highly esteemed aqueous mercury laboratory in the world. Ultra-clean 1 L teflon collection bottles were shipped to us, individually packaged in double zip-lock bags. Two person clean collecting protocol was used, in which the actual sample bottle was touched only by one researcher, who handled nothing else and wore sterile gloves. Creek samples were taken in flowing water by standing in-stream and, facing upstream, submerging the bottle in the middle of the flow. Lake samples were taken by idling the boat slowly into the wind at midlake, with the sample taken from the front of the boat. In all collections, the bottle cap was removed underwater, allowing the bottle to fill without coming into contact with potential surface film material, and then resealed before bringing to the surface. The bottle was then placed into the waiting isolation bags, held by the co-worker. Bagged ice packs kept the bottles cool and samples were shipped by overnight mail to Frontier Geosciences. Water samples were filtered and preserved appropriately in a trace metal clean room within 24 hours of collection, and later analyzed within standard holding times.

In conjunction with each set of aqueous mercury samples, we collected identical water into 1 liter bottles for analysis of suspended solids. These bottles were held in a separate ice chest, on ice, and were returned to our laboratory in Davis for processing within 48 hours of collection.

2.1.3 Invertebrates

Aquatic invertebrates were taken from each of the sites, as available, with various nets and screens. Forceps were used to pick macro-invertebrates into prepared collection jars. This process was repeated at each site until a sufficient sample size of each taxon of interest was accumulated to permit analysis for mercury.

Samples were maintained in their collection jars on ice, and then cleaned in fresh water within 24 hours of collection. Cleaning was accomplished by suspending sample organisms in fresh water and, as necessary, shaking individuals in the water with teflon-coated forceps to remove any significant clinging surficial material. Gastropod samples (aquatic snails) taken from the two lakes were additionally purged of potentially high-sediment gut contents by maintaining them live for 4 days and changing the water repeatedly until clear. Cleaned organisms of all types were stored in pre-cleaned jars with teflon-lined caps, which were frozen and then dried at 50-60 °C. The dried sample was homogenized to a fine powder with teflon-coated instruments and a glass laboratory mortar and pestle. All of these techniques have been well established and tested in extensive prior mercury research work throughout California (Slotton et al. 1995a).

2.1.4 Fish

Fish were collected from the Solano Gravel pit lakes using a boat with a variety of experimental gillnets. Gill nets were also used in the Cache Creek collections, together with seines. Individual fish to be analyzed were weighed and measured on site. Stomach contents were assessed within an hour of collection. Muscle tissue samples for mercury analysis were excised in the laboratory within 24 hours, using clean technique, with stainless steel scalpels. Muscle samples were taken from the dorso-lateral ("shoulder") region, as done by the California Department of Fish and Game. Samples were placed directly into laboratory digestion tubes, which were capped with teflon liners. We have utilized these techniques with great success in similar work over the past 11 years (Reuter et al. 1989, Slotton 1991, Slotton et al. 1995a, Slotton et al. 1995b)

2.3 Analytical Methodology

2.3.1 Water

Total mercury in water was analyzed by dual amalgamation/cold vapor atomic fluorescence spectrometry, as developed by Bloom and Crecelius (1983). Methyl mercury was analyzed utilizing aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection, as developed by Bloom (1989). The detection levels for these extremely sensitive analyses are approximately 0.2 (total Hg) and 0.01 (methyl Hg) ng L^{-1} (parts per trillion), generally below most environmental aqueous mercury levels present throughout Northern California. It is notable that Nicolas Bloom, the developer of these techniques, is the director of the laboratory utilized for this work.

2.3.2 Suspended Solids

Suspended solids concentration at each site was determined by filtering a given volume of well mixed sample water through a pre-weighed glass fiber filter. The solids were retained on the filter, which was then dried at 105 °C for 24 hours. After cooling the filter in a dessicator, it was re-weighed to the nearest 0.0001 g. The weight of solids was obtained by subtracting the initial, clean weight of the filter from the weight with solids. This amount was divided by the volume of water filtered to derive the solids concentration on a milligram per liter basis.

2.3.3 Fish, Invertebrate, and Sediment Total Mercury

Solid samples for mercury were analyzed using homogeneous portions. Sediment was subsampled from homogenized, wet (liquefied) samples. Identical subsamples were used to determine moisture content for dry weight conversions. Fish tissue was also analyzed on wet (fresh) samples, as is the standard procedure used by governmental agencies. Mercury analyses of invertebrate samples were conducted with dried and powdered samples for uniformity, as described in Slotton et al. (1995a).

Solid samples of all types were processed by first digesting in concentrated sulfuric and nitric acids and potassium permanganate, under pressure, at 80-100 °C for three hours. They were subsequently analyzed for total mercury using a well-established modified cold vapor atomic absorption (CVAA) micro-technique, described in Slotton et al. (1995b). The level of detection for this technique is approximately 0.01 mg kg^{-1} (ppm), sufficient to provide above-detection results for nearly all aquatic sediment and biota samples in this region.

2.3.4 Sediment Water and Organic Content

Moisture content of sediment samples was determined by weight difference between fresh, homogenized sample (10-25 g) and the sample after drying at 105 °C to constant weight (generally 24 hours), subtracting out the weight of the weighing container. Weights were accurate to ± 0.001 g. To obtain the Loss On Ignition (LOI) estimate of organic content, the dried sample was subsequently placed in a 475 °C muffle furnace for 2 hours, to burn off any organic matter. After cooling, the mineral moisture of hydration was returned by re-wetting the sample. The sample was again dried at 105 °C to constant weight, cooled in a dessicator, and weighed again to ± 0.001 g. The loss in weight between the initial dry sample and the sample after the muffle furnace treatment is attributed to organic matter.

2.4 Quality Assurance/Quality Control (QA/QC)

2.4.1 Water

The water samples for mercury were analyzed at Frontier Geosciences Laboratory in a single analytical run for total mercury and another for methyl mercury. Each run was accompanied by QA/QC samples. QA/QC was excellent, as summarized below in Table 2.

Table 2. Frontier Geosciences Laboratory Aqueous Mercury QA/QC (from 2 analytical runs)

QC Data	Total Mercury (*ng/L*)	Methyl Mercury (*ng/L*)
Method Blanks	0.19 ± 0.06	0.013 ± 0.004
(n)	(3)	(3)
Estimated Detection Limit	0.18	0.012
NRCC Dogfish	4,733	4,465
Certified Concentration	4,640 ± 260	4,470 ± 370
Recovery (%)	102%	100%
Before Filter Blank (4/10/96)	0.45	
After Filter Blank (4/10/96)	0.28	
Before Filter Blank (4/16/96)	1.61	
After Filter Blank (4/16/96)	1.19	

2.4.2 Fish, Invertebrates, and Sediment

Extensive QA/QC accompanied our total mercury analyses of aquatic biota and sediment samples. For each sample batch of approximately 24 samples, a large number of QA/QC samples were included through all phases of the digestion and analysis procedures (16 total). These included 1 blank and 7 aqueous mercury standards, standard reference materials with known mercury concentrations, duplicates of analytical samples, and spiked analytical samples. These additional samples were used, as always, to ensure the reliability of the data generated. The QA/QC results for this portion of the work are summarized in Table 3.

The extensive set of aqueous standards was used to construct an accurate curve of mercury concentration vs atomic absorbence for each analytical run. The standard curve R^2 values for the mercury runs utilized in this project fell between 0.999 and 1.000, well above the control range of ≥ 0.975. The standard reference material samples included two fish standards and a

Table 3. D.G. Slotton Laboratory Total Mercury QA/QC Summary (from 3 analytical runs)

	Std Curve R^2	Spike Recoveries	Duplicate RPD	NBS Tuna	IAEA Tuna	NBS Sediment
Certified Level (ppm)				0.95	4.70	1.47
Ideal Recovery	1.000	(100%)	(0%)	(100%)	(100%)	(100%)
Control Range (%)	≥0.975	75-125%	≤25%	75-125%	75-125%	75-125%
Control Range (ppm)				0.71-1.19	3.60-6.00	1.10-1.84
Recoveries (%)	0.999-1.000	94-111%	0.1-10.7%	95-110%	90-96%	101-107%
(ppm)				0.90-1.04	4.32-4.61	1.49-1.57
(n)	n=3	n=6	n=18	n=7	n=2	n=2
Mean Recoveries (%)	0.999	101%	4%	100%	93%	104%
Mean Recoveries (ppm)				0.95	4.47	1.53

sediment standard. All recoveries were within the 75% - 125% control levels, at 90-110%. Sample duplication was excellent, with relative % difference (RPD) having a mean value of 4% among 18 total paired samples. Spike recoveries were also consistently good, with recoveries of 94% - 111%, as compared to the 75% - 125% control levels.

3. RESULTS

3.1 General Limnological Survey

With sonar sweeps along transects, we were able to construct a rough bottom contour map of the Solano Gravel pit lakes (Fig. 1). The North Lake was found to have a fairly regular pit configuration, with relatively steep perimeter slopes and the majority of the bottom area deeper than 20 ft, reaching a maximum depth of approximately 43 ft. There was little area available for shallow accumulations of aquatic plants, which were confined largely to a narrow strip along the southern perimeter. The South Lake, 2-3 times larger in surface area, was considerably shallower on average, though it also contained a basin at its northern end that was similar to that in the North Lake. Here, depths reached approximately 35 ft. The majority of the South Lake, however, was shallower than 20 ft, with extensive areas at the southern end well under 10 ft. Here, plant growth was extensive, with beds of aquatic plants, macro-algae, and willows. This environment proved to be excellent fish habitat, with considerably greater collection success here as compared to deeper areas.

Adjacent Cache Creek, during the period of this April 1996 preliminary work, was quite variable, ranging from moderately high, turbid flow conditions soon after storms (4/4/96) to intermediate flow and turbidity levels (4/9/96), to relative baseline conditions (4/11/96, 4/15/96).

We collected information on a number of limnological parameters in the North Lake to provide some basic information as to the trophic status of the system and its potential to provide an environment suitable for mercury methylating microorganisms. At two sites in this basin (Fig. 1), we collected water column samples from surface, mid depth (5 m, 16 ft), and deep water 1 m above the bottom (11-12 m, ~38 ft). These samples were analyzed for pH, total suspended solids (TSS), and Chlorophyll A (a measure of algal density). Data are presented in Table 4. Additionally at these two sites, temperature and dissolved oxygen were profiled surface to bottom through the water column, at 1 m increments (Table 5, Fig. 2).

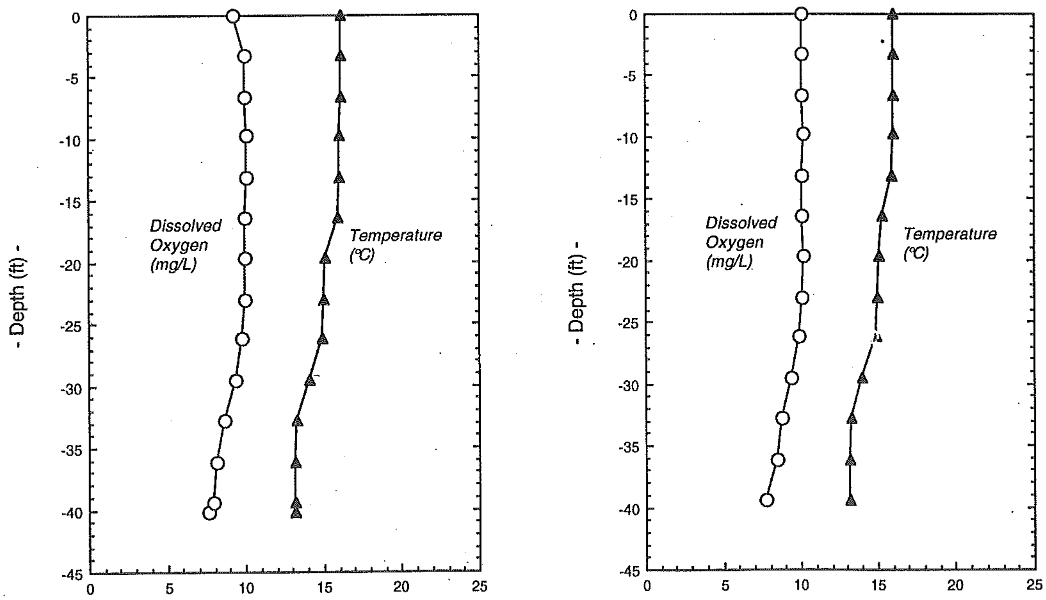
Table 4. Water Column pH, TSS, and Chlorophyll A; North Pit Lake, 4/4/96

Depth	pH		TSS (mg/L)		Chlorophyll A (µg/L)	
	Site A	Site B	Site A	Site B	Site A	Site B
Surface (0.3 m, 1 ft)	8.56	8.54	4.4	10.2	2.2	1.5
Mid (5 m, 16 ft)	8.57	8.54	4.1	4.4	2.0	1.9
Deep (11-12 m, ~38 ft)	8.40	8.39	6.2	7.8	1.8	1.8

Table 5. Water Column Profiles of Temperature and Dissolved Oxygen; North Pit Lake, 4/4/96

Depth		Temperature (°C)		Dissolved Oxygen (mg/L = ppm)	
(m)	*(ft)*	Site A	Site B	Site A	Site B
0.0	0.0	16.1	16.2	10.1	9.3
1.0	3.3	16.1	16.2	10.1	10.0
2.0	6.6	16.0	16.2	10.1	10.0
3.0	9.8	16.0	16.1	10.2	10.1
4.0	13.1	15.9	16.0	10.1	10.1
5.0	16.4	15.3	15.9	10.1	10.0
6.0	19.7	15.1	15.1	10.2	10.0
7.0	23.0	15.0	15.0	10.1	10.0
8.0	26.2	14.9	14.9	9.9	9.8
9.0	29.5	14.0	14.1	9.4	9.4
10.0	32.8	13.3	13.3	8.7	8.6
11.0	36.1	13.2	13.2	8.4	8.1
12.0	39.4	13.2	13.2	7.7	7.9
12.3	40.2		13.2		7.6

Figure 2. Water Column Profiles of Temperature and Dissolved Oxygen; North Pit Lake, 4/4/96


Site A (Northwest)

Site B (Southeast)

As expected, the water column was still relatively unstratified (fairly well mixed) on this April date, with only a slight difference in both temperature and dissolved oxygen between the surface and the bottom. Profiles were also essentially identical at the two sides of the lake. Temperature ranged from 13.2 °C (55.8 °F) in the deep water, gradually warming to 16.2 °C (61.1 °F) at the surface. Oxygen levels remained high throughout the water column at this time, at approximately 10 ppm in the top 25 ft, declining only to approximately 8 ppm at the bottom. With the onset of hot summer weather, the upper waters can be expected to become sufficiently warmer than the underlying cool bottom waters, so as to form a density stratification. In this circumstance, the upper waters remain mixed and in contact with the atmosphere, while the cooler, denser bottom waters become isolated from the upper water layer and the influence of the air. Under these normal conditions of warm season water column stratification, oxygen can become depleted in the bottom water. This occurs when there is sufficient organic matter and bacterial metabolism to use up the available oxygen.

At this time, the water of the North Lake appeared to be relatively sterile, as compared to more eutrophic ponds and lakes in the region. Chlorophyll A was similar in the various samples, at 1.5-2.2 µg/L (ppb), which is quite low. The corresponding Secchi disk measure of water column visibility was 2.2 m (7.2 ft) which is fairly clear for these types of systems. The sediment data (below) also indicates that organic matter in the lake is relatively low, integrated across the seasonal accumulations sampled at the bottom.

Water column pH was very similar throughout and well above neutrality at 8.39-8.57. This is typical for the region. Suspended solids were in the range of 4-5 mg/L (ppm) in most surface and midwater samples, with a somewhat higher level at the bottom (6-8 mg/L), as is typical. The Site B surface sample was higher at this time (10.2 mg/L), consistent with the surface cloud of suspended sediment noted at this site on this windy collection date.

3.2 Bottom Sediments

Bottom sediments were taken from 5 locations distributed across the deep portion of the North Lake and from a deep and shallow site in the South Lake (Fig. 1). Most of the deep sediments were composed of fine-grained silts and clays, as is typical. While a variety of grain sizes enter lakes, the smaller particles are particularly susceptible to resuspension from wave action. They are repeatedly resuspended into the water column until they randomly deposit in deeper water, beyond the reach of continued wave action. Thus, deepwater sediments will ultimately be of finer grain size (clays and silts) than the sands and gravels remaining in the shallower areas.

Analytical data from the sediment samples are presented in Table 6. Moisture percentage was similar among the samples, at 52% - 68%. Organic percentage was relatively low in the North Lake sediments (1.1% - 2.4%), a function of the relatively low presence of aquatic plants and water column algae. South Lake sediments were somewhat higher, at 3.2% - 4.5% organic fraction. The South Lake was characterized by containing shallower regions with extensive plant growth.

Table 6. Sediment Analytical Data; Solano Gravel Lakes, April 1996

Sediment I.D.	Depth *(m)*	Depth *(ft)*	Description	ppm Hg *(dry wt)*	Percent Moisture	Percent Organic
NORTH LAKE						
Northwest	11.6	38.1	Silts and fine sands	0.38	58.6%	2.4%
Northeast	11.9	39.0	Fine silts, clays	0.77	54.2%	1.9%
Southeast	10.0	32.8	Fine silts, clays	0.65	67.5%	1.1%
Southwest	10.5	34.4	Fine silts, clays	0.60	52.0%	1.4%
Center	13.0	42.7	Finest clays	1.00	60.3%	2.3%
SOUTH LAKE						
North Side (deep)	11.0	36.1	Fine silts, clays	0.15	56.9%	3.2%
South Side (shallow)	2.7	8.9	Silts and fine sands	0.22	53.2%	4.5%

Mercury concentrations were lower in the South Lake sediments (0.15 - 0.22 ppm) than in the samples from the North Lake (0.38 - 1.00 ppm). The highest concentration (1.00 ppm) came from the deepest sample taken from the center of the North Lake, where the finest grain sizes were present. The lowest mercury sample from the North lake (0.38 ppm) was found in conjunction with larger grain size material, including sands. Among the North Lake samples with similar grain size, mercury was similar at 0.60 - 0.77 ppm. These data are consistent with other regional research, in which metals, including mercury, have been found to be more concentrated in a given weight of fine grained particles than in coarser material (Slotton and Reuter 1995). This is a function of the larger surface area for adsorption afforded by the smaller particles.

These sediment mercury concentrations are elevated as compared to global averages, but are considerably lower than levels seen in many mercury contaminated regions of California, where levels in the 10s and 100s of ppm have been reported. In our October 1995 collections of fish from lower Cache Creek, we took a single sample of creek sediment for mercury. This sample was quite coarse, dominated by fine sands and silts, with a mercury concentration of 0.51 ppm. Depending on the flow regime and consistency of the bottom sediment, sediment mercury from the creek can be expected to be highly variable.

3.3 Aqueous Mercury Concentrations

Aqueous mercury concentrations, in units of nanograms per liter (ng L^{-1}, = parts per trillion), are presented in Table 7. Concentrations from the North Lake were quite consistent across the 11 day period of sampling. This period encompassed a variety of climatic conditions including post-rain, high winds, and warm/calm. Total mercury ranged from 2.89 to 3.45 ng/L in raw water samples, with a mean of 3.22 ng/L. Total mercury in the filtered fraction was also quite consistent at 1.12-1.47 ng/L, with a mean of 1.27 ng/L and a mean filtered fraction representing 40% of raw concentrations. These concentrations appear to be relatively characteristic of the lake, and can be compared to the water quality criterion for mercury of 12 ng/L. These raw water total mercury concentrations are approximately 27% of the criterion level.

Table 7. Mercury Concentrations in Water; Solano Gravel Lakes and Cache Creek, April 1996

	Date	Total Hg (ng/L)		Methyl Hg (ng/L)	
		(raw)	*(≤0.2 μm)*	*(raw)*	*(≤0.2 μm)*
NORTH LAKE					
	4/4/96	3.45	1.12	0.032	(not done)
	4/9/96	2.89	1.47	0.031	0.007
	4/15/96	3.31	1.23	0.022	0.011
SOUTH LAKE					
	4/11/96	2.25	0.88	0.044	0.010
CACHE CREEK AT SOLANO GRAVEL					
	4/4/96	52.50	1.14	0.329	(not done)
	4/9/96	7.46	1.53	0.116	0.039
	4/11/96	3.60	1.16	0.114	0.038
	4/15/96	3.81	1.30	0.114	0.043

A sample was taken from the South Lake when it became clear that we would need to utilize the other basin in our fish collections. While a single point is not enough to form statistical conclusions, it is notable that this sample was somewhat lower in total mercury than those taken from the North Lake, with 2.25 ng/L in raw water and 0.88 ng/L (39%) in the filtered fraction.

The corresponding samples taken across this time period from adjacent Cache Creek ranged from concentrations very similar to the pit lake samples to considerably higher levels, clearly associated with high flow suspended sediment loads. A high concentration of 52.50 ng/L was found in the turbid, high flow raw water sample from April 4. In related work by the Central

Valley Regional Water Quality Control Board, raw water concentrations of total mercury in lower Cache Creek have ranged as high as 1,500 ng/L during peak storm flow conditions (Chris Foe, Central Valley Regional Water Quality Control Board, personal communication).

By April 9 in the present study, flows had receded considerably and a much reduced intermediate concentration of 7.46 ng/L total mercury was found in raw water from the creek. Flows and, apparently, mercury levels had stabilized relative to storm flows on the April 11 and 15 collection dates, with similar raw water total mercury concentrations of 3.60 and 3.81 ng/L. These levels were approximately 15% higher than the corresponding levels from the North Lake and 65% higher than the single concentration measured in the South Lake.

When the suspended particulate contribution to the creek total mercury concentrations was factored out by filtering the samples, levels were quite similar across the range of flow conditions (1.14-1.53 ng/L). This was nearly identical to filtered concentrations from the North Lake samples.

Methyl mercury was measured at 0.329 ng/L in Cache Creek raw water during the high flow date (4/4/96), and then at approximately 1/3 of that concentration in further collections, with nearly identical levels of 0.114, 0.114, and 0.116 ng/L. Methyl mercury in the creek water filtered fraction was also very consistent at 0.038-0.043 ng/L (~35% of the raw water methyl mercury).

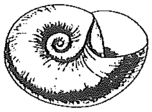
In contrast, methyl mercury in the pit lake samples was significantly lower in both raw and filtered samples. Levels of 0.022-0.032 ng/L were found in raw water from the North Lake. These methyl mercury concentrations were approximately 25% of the levels found in corresponding lower flow Cache Creek samples. Raw water methyl mercury from the South Lake sample was somewhat higher at 0.044 ng/L (~38% of creek levels). Filtered samples of methyl mercury from both pit lakes were very similar, at 0.007-0.011 ng/L. These levels were also approximately 25% of the corresponding levels seen at this time in the adjacent creek.

3.4 Aquatic Invertebrates

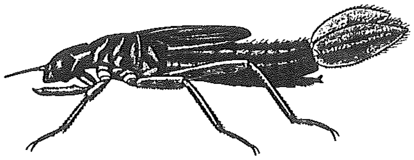
Aquatic invertebrates that were analyzed for this project are illustrated in Figure 3. We were able to collect extensive samples of Coenagrionid damselfly nymphs from each of the pit lakes, together with aquatic snails, which were an important food item for the fish. Additional invertebrate samples included predaceous giant water bugs (Belostomatidae) from the North Lake, predaceous creeping water bugs (Naucoridae) from Cache Creek, and dragonfly nymphs (Aeschnidae, Libellulidae) from the North Lake and Cache Creek. The mercury data for the invertebrate samples are presented in Table 8.

Native invertebrate species have proven to be excellent monitors of mercury bioavailability in California water bodies (Slotton et al. 1995a). Because they incorporate mercury into their bodies

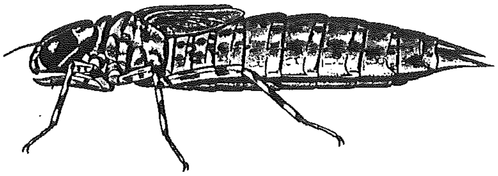
Figure 3. Aquatic Invertebrates Sampled in This Project
(illustrations taken from McCafferty 1981)



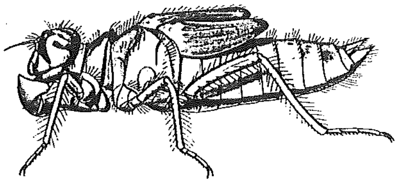
Aquatic Snails (Gastropoda)



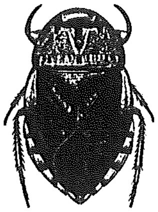
Damselflies (Zygoptera)
Coenagrionidae



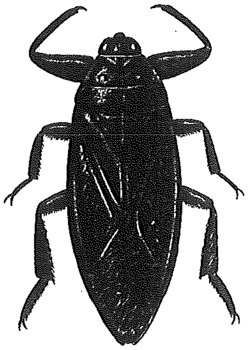
Dragonflies (Anisoptera)
Aeschnidae



Dragonflies (Anisoptera)
Libellulidae



Creeping Water Bugs (Hemiptera)
Naucoridae



Giant Water Bugs (Hemiptera)
Belostomatidae

throughout their lives, they can provide a time-integrated measure of mercury availability, as compared to standard "point-in-time" grab sampling for water. The mercury incorporated into local aquatic biota is, by definition, specifically the bioavailable fraction, which can be of paramount importance for management considerations. Additionally, many of these species are ideal indicators of highly localized conditions. They thus function as relatively static biological probes of the fraction of mercury in the water that is bioavailable.

Table 8. Invertebrate Mercury Concentrations; Solano Gravel Lakes and Cache Creek, April 1996
(Dry weight mg/kg mercury, =ppm; Multiple individual composites)

Invertebrates	North Pit Lake	South Pit Lake	Cache Creek at Solano Gravel
Snails	0.16 (n=23)	0.11 (n=29)	
Damselfly Nymphs A	0.22 (n=48)	0.17 (n=47)	
Damselfly Nymphs B	0.21 (n=36)	0.17 (n=37)	
Dragonfly Nymphs	0.27 (n=3)		0.32 (n=4)
Naucoridae (Creeping water bugs)			0.29 (n=14)
Belostomatidae (Giant water bugs)	0.51 (n=5)		

It was not possible to collect identical types of samples from each of the sites, though there was some overlap. Aquatic snails and damselfly nymphs were taken from each of the pit lakes. Dry weight mercury levels were somewhat higher from the North Lake (0.16 ppm in snails vs 0.11 ppm in the South Lake, and 0.21 ppm in damselfly nymphs vs 0.17 ppm in the South Lake). The field duplicate composites of both sets of damselfly nymphs were essentially identical, suggesting that the difference seen between basins in this parameter reflected actual environmental differences rather than general variability.

Mercury in dragonfly nymphs and Naucorid bugs (predaceous "creeping" water bugs) from the Creek samples was similar (0.32 and 0.29 ppm), reflecting their very similar diet of small to medium invertebrates. The majority of biotic mercury is typically accumulated through the food chain in the diet, particularly in the higher trophic levels (Lindberg et al. 1987, Gill and Bruland 1990). Mercury levels among invertebrate species with similar foods are typically similar (Slotton et al 1995a). Concentrations generally increase, moving up through the food chain. That was the case in the samples taken in this project, which are arranged in order of ascending trophic food level in Table 8.

Dragonfly nymphs from the North Lake were similar in mercury, though somewhat lower, as compared to dragonflies from the creek (0.27 ppm vs 0.32). The Belostomatid ("giant") water bugs from the North Lake were considerably higher in mercury than any of the other invertebrate samples, at 0.51 ppm. This reflects the considerably higher mercury levels in their preferred food item, juvenile fish. The utility of this preliminary invertebrate mercury data could be increased with expanded collections.

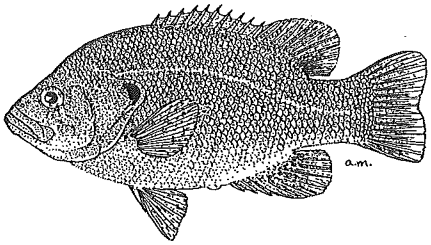
3.5 Fish

Fish sampling for mercury was a very important component of this preliminary study. Throughout their lifetimes, fish accumulate mercury almost exclusively of the methyl fraction in their tissues, primarily in the edible fillet muscle, and thus provide time-integrated information on mercury bioavailability, which can be compared to fish data from other systems. Regulatory considerations are often driven by fish mercury levels, largely because fish muscle mercury represents the major exposure pathway of significance, both for people and fish-eating wildlife.

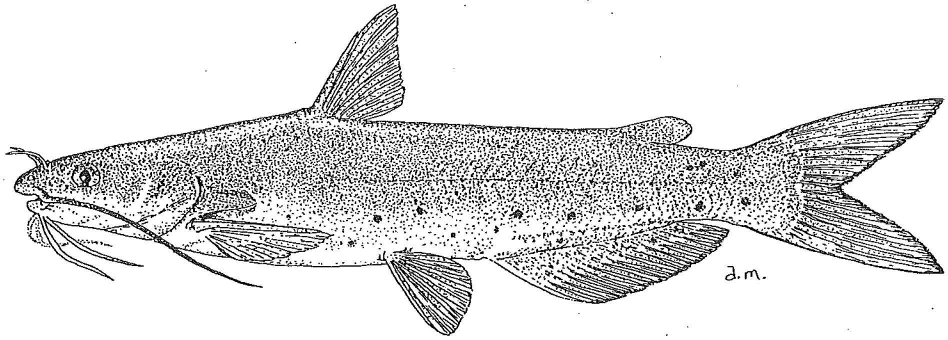
The fish species sampled in this project are illustrated in Figures 4 and 5. The gravel pit lakes contained green sunfish, channel catfish, brown bullhead, and smallmouth bass. The Cache Creek samples also included channel catfish and brown bullhead, together with carp, Sacramento sucker, bluegill sunfish, and white crappie. In order to obtain sufficiently diverse samples from the gravel pit lakes, we had to utilize the South Lake as well as the North Lake. At this time of year (April), only smaller individuals were collectable from the North Lake. However, when muscle mercury concentrations are plotted against fish size, the trends are generally consistent between lakes (Fig. 6). The fish muscle mercury data collected in this project are shown in Tables 9 and 10 and are plotted graphically in Figures 6 and 7.

Mercury concentrations generally varied with size/age of individual and with trophic feeding level of the species, as is typical. Small green sunfish, which eat small invertebrates, contained the lowest muscle mercury levels (0.16-0.30 ppm in 5-6 " fish), while the highest levels were found in the larger predatory species. Channel catfish contained muscle mercury of 0.27-0.67 ppm in 11-23" fish, smallmouth bass of 10-15" had 0.30-0.90 ppm, and 11-12" brown bullhead were relatively quite high at 0.72-0.92 ppm. These levels can be compared to the 0.5 ppm Health Guidelines of the California Department of Health Services, the U.S. Academy of Sciences, and most nations (TSMP 1990). The U.S. federal guideline (FDA) for mercury in edible fish is 1.0 ppm. None of these pit lake fish were above the 1.0 ppm guideline, though several were above the 0.5 ppm level, including the largest channel catfish (23 inches, 6 lbs, 0.67 ppm), the larger smallmouth bass (13-15 inches, 1.5-2 lbs, 0.79-0.90 ppm), and the brown bullheads (~12 inches,

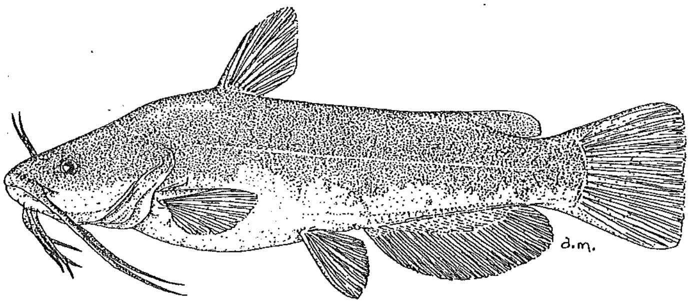
Figure 4. Fish Species Sampled From Solano Gravel Pit Lakes
(illustrations taken from Moyle 1976)



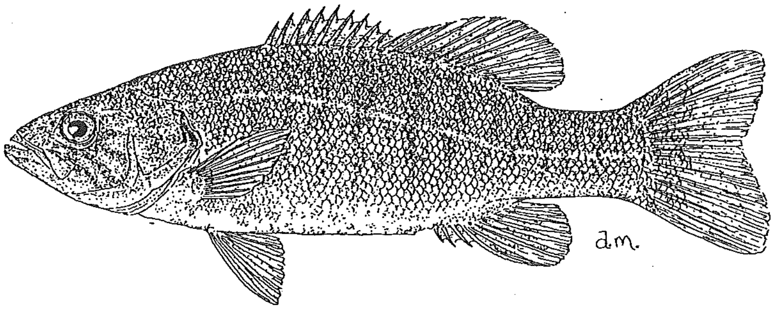
Green Sunfish
Lepomis cyanellus



Channel Catfish
Ictalurus punctatus

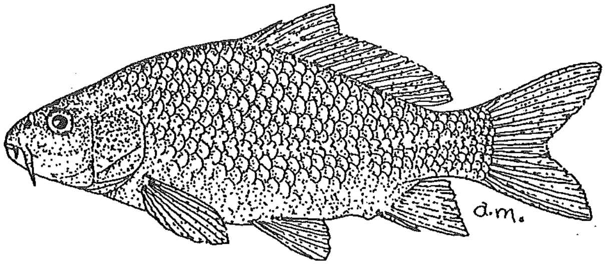


Brown Bullhead
Ictalurus nebulosus

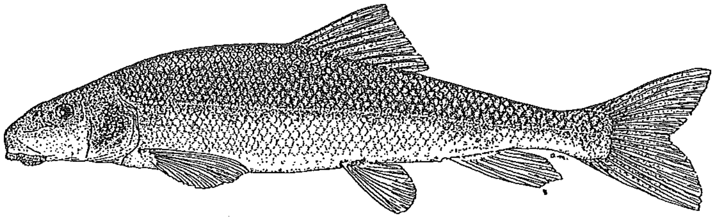


Smallmouth Black Bass
Micropterus dolomieui

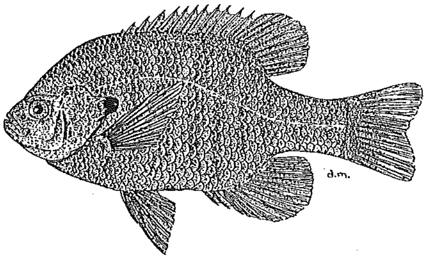
Figure 5. Additional Fish Species Sampled From Cache Creek
(illustrations taken from Moyle 1976)



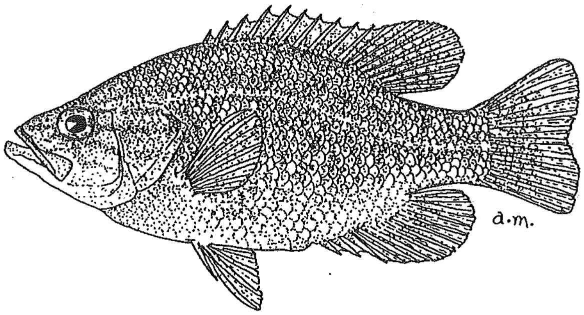
Carp
Cyprinus carpio



Sacramento Sucker
Catostomus occidentalis



Bluegill Sunfish
Lepomis macrochirus



White Crappie
Pomoxis annularis

Table 9. Fish Muscle Mercury Concentrations *(wet wt ppm)*; Solano Gravel Lakes, April 1996

Identification	Length		Weight		ppm Hg
	(mm)	*(inches)*	*(grams)*	*(pounds)*	*(wet wt)*
NORTH LAKE (4/96)					
Green Sunfish	135	5.3	45	0.1	0.21
Green Sunfish	132	5.2	48	0.1	0.21
Green Sunfish	153	6.0	67	0.1	0.30
Green Sunfish	152	6.0	70	0.2	0.16
Green Sunfish	154	6.1	74	0.2	0.21
Channel Catfish	192	7.6	82	0.2	0.24
Channel Catfish	210	8.3	95	0.2	0.13
Channel Catfish	238	9.4	163	0.4	0.23
Smallmouth Bass	223	8.8	135	0.3	0.19
SOUTH LAKE (4/96)					
Green Sunfish	135	5.3	65	0.1	0.25
Green Sunfish	160	6.3	73	0.2	0.29
Channel Catfish	279	11.0	250	0.6	0.35
Channel Catfish	375	14.8	600	1.3	0.44
Channel Catfish	400	15.7	770	1.7	0.27
Channel Catfish	400	15.7	860	1.9	0.30
Channel Catfish	432	17.0	950	2.1	0.39
Channel Catfish	467	18.4	1,375	3.0	0.47
Channel Catfish	584	23.0	2,630	5.8	0.67
Brown Bullhead	298	11.7	435	1.0	0.72
Brown Bullhead	305	12.0	463	1.0	0.92
Smallmouth Bass	267	10.5	300	0.7	0.45
Smallmouth Bass	273	10.7	305	0.7	0.30
Smallmouth Bass	337	13.3	640	1.4	0.79
Smallmouth Bass	371	14.6	850	1.9	0.90

Table 10. Fish Muscle Mercury Concentrations *(wet wt ppm)*; Lower Cache Creek, October 1995

Identification	Length *(mm)*	*(inches)*	Weight *(grams)*	*(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

Figure 6. Fish Muscle Mercury From Solano Gravel Pit Lakes, April 1996

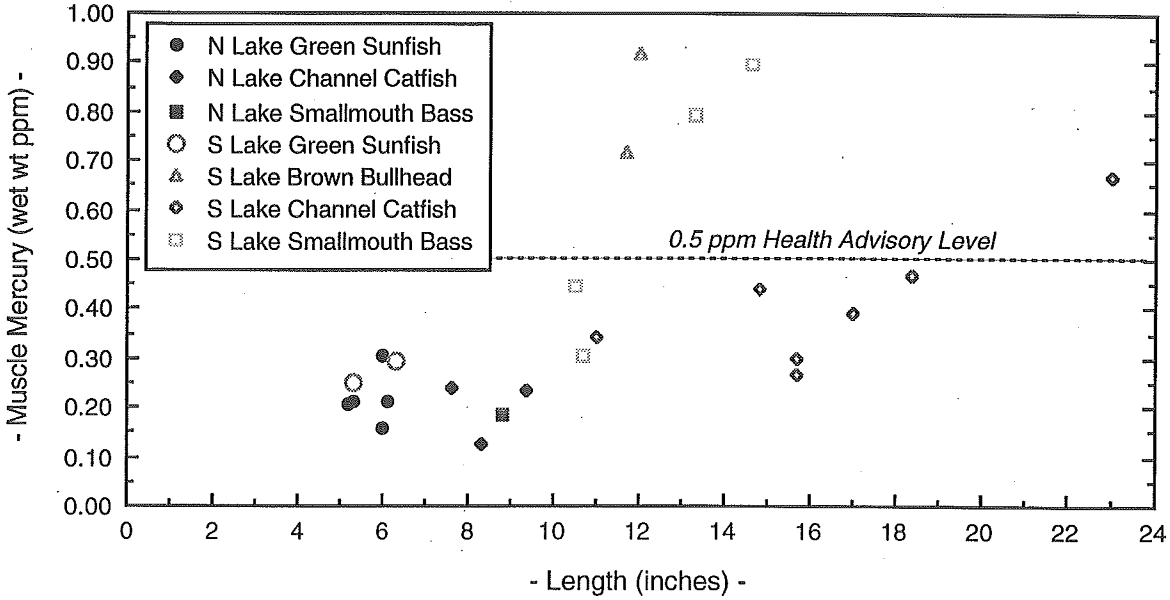
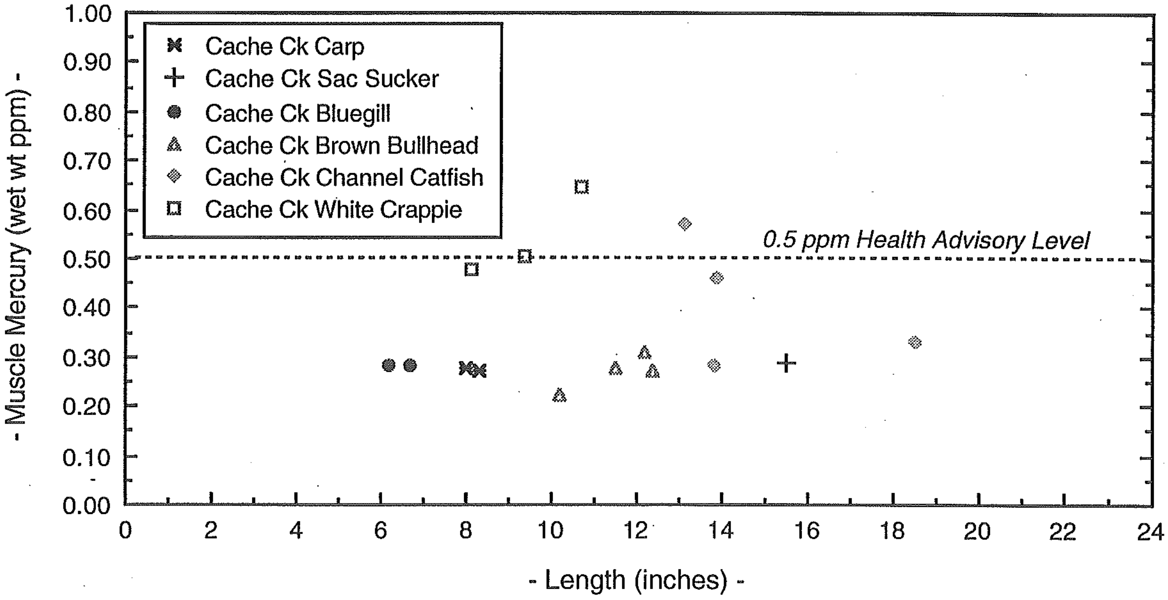


Figure 7. Fish Muscle Mercury From Lower Cache Creek, April 1996



1 lb, 0.72-0.92 ppm). In Figure 6, the data for the pit lake fish are displayed in conjunction with the 0.5 ppm guideline.

We collected comparable fish from lower Cache Creek in October of 1995. These data appear in Table 10 and Figure 7. Similar symbols are utilized in the plot for same or similar species, as compared to the pit lake samples. It was not possible to obtain bass or very large catfish in the creek sampling, but there was considerable overlap. The species which feed lower in the food web (carp, Sacramento sucker, and bluegill sunfish) were quite similar to each other in mercury content (0.27-0.29 ppm), and also very similar to the levels seen in the pit lakes green sunfish (0.16-0.30 ppm). Channel catfish in the range of 11-19" had 0.28-0.57 ppm muscle mercury from Cache Creek (mean = 0.41 ppm) and 0.27-0.47 ppm in the gravel pit lakes (mean = 0.37 ppm). These levels for comparable fish between pit lakes and Cache Creek are very similar and not differentiable statistically.

Additional Cache Creek fish samples included white crappie and brown bullhead. The crappie from Cache Creek were also consistent with the pit lake data. These fish are piscivorous (fish eaters) and thus correspond closest to the smallmouth bass. Crappie of 8-11" and 0.3-0.6 lbs from the creek had elevated mercury levels of 0.48-0.65 ppm. While sizes are not directly comparable, the diets of crappie in this size range would be similar to those of small to medium smallmouth bass, which demonstrated similar mercury concentrations in the pit lakes.

Only the brown bullhead showed a difference between pit lakes and Cache Creek. The four creek bullhead, of a similar size to those taken in the pit lakes, were considerably lower in mercury (0.22-0.31 ppm), similar to the carp, sucker, and bluegill samples from the creek. The relatively high mercury levels seen in the two 12" bullhead taken from the South Lake (0.72-0.92 ppm) are anomalous, as compared to all of the other fish data. We have no clear explanation at this time. The digestive tracts of these two fish were full of aquatic snails, a relatively low mercury food source. At this time we would not place too much significance on the two anomalous samples.

4. DISCUSSION AND CONCLUSIONS

At the time of this survey, water column mercury in the existing off-channel gravel pit lakes at Solano Gravel (2.2-3.5 ng/L) was well below the 12 ng/L water quality criterion and was lower than concentrations seen in the adjacent section of Cache Creek (3.6-52 ng/L). Levels in the filtered fraction (≤ 0.2 μm) were similar across dates and sites (0.9-1.5 ng/L for lake and creek samples), indicating that the variation seen in raw water total mercury was mainly a function of mercury in suspended sediment. The total mercury levels in raw and filtered water from the pit lakes were consistent across a variety of climatic conditions and are probably relatively characteristic for these lakes.

Methyl mercury was found at orders of magnitude lower levels (0.02-0.04 ng/L) and was also considerably lower in the pit lake samples than in the corresponding creek samples (~0.11 ng/L). However, this fraction of the aqueous mercury could change significantly under different conditions. Thermal stratification of the water column had not developed at the time of this work and oxygen was present at moderate to high levels throughout. As methyl mercury is produced from inorganic mercury mainly as a metabolic bi-product of certain microorganisms, its relative concentrations are dependent on (1) presence of inorganic mercury, (2) presence of mercury methylating organisms, and (3) presence of conditions favorable for the methylating organisms.

In our mercury research work in the region, we have found that the rate of methyl mercury production--and the corresponding transfer of mercury into fish--is enhanced by anaerobic (no oxygen) conditions. At Davis Creek Reservoir in northwestern Yolo County, the water column stratifies thermally each warm season and the entire hypolimnion (lower water layer) goes anaerobic by mid to late summer. The bottom water goes anaerobic because the system is sufficiently rich in organic matter for normal bacterial metabolism to use up the existing store of dissolved oxygen, which cannot be replaced until later in the year when the thermal stratification breaks down and the water column mixes top to bottom. Large concentrations of methyl mercury accumulate in the anaerobic water and are delivered into surface waters, available for biological uptake, at fall turnover each year (Slotton et al 1995b). This system also has a much larger source of inorganic mercury than the lower Cache Creek region, as it is located in the heart of the historic mercury mining district of the California Coast Range.

Fish accumulations are probably the most dependable indicators of methyl mercury production and availability, as averaged across time. Despite the variation we found on these dates in water column mercury between the gravel pit lakes and the adjacent creek, fish accumulations were very similar, suggesting that, on average, the fish in both environments have similar overall exposures to bioavailable mercury.

At Davis Creek Reservoir, levels of mercury in fish are far higher than those found in this project (Table 11, Figs. 8 and 9). During the initial flush of bacterial activity associated with the formation of the reservoir and the flooding of formerly terrestrial soils, extremely high levels (to over 4.0 ppm) were seen in 1987 largemouth bass and bluegill. In recent years, levels have stabilized, though they are still quite high, as indicated by the 1995 data, with most "keeper" sized bass and bluegill well above the 0.5 ppm guideline at 1.0-2.0 ppm. Clearly, that system provides a much greater exposure to methyl mercury than do the existing gravel pit lakes and lower Cache Creek. The levels seen in the gravel pit lakes are of some concern, in that they approach and in some cases even surpass the 0.5 ppm consumption guideline for fish. However, these fish muscle mercury concentrations were very similar to concentrations found in adjacent Cache Creek. Similar levels are also routinely found from many locations throughout the mercury contaminated regions of northern California, including Clear Lake, Lake Berryessa, the American River, Lake Herman, Lake Nacimiento, Folsom Lake, and Bullards Bar Reservoir (TSMP 1990, 1991, 1992, 1993).

It is not clear at this point whether the existing pit lakes at Solano Gravel become anoxic in the bottom waters during the summer. We would recommend that this be investigated. The potential exists for new gravel pit lakes, if considerably deeper than the ones tested, to become anoxic. If this occurred, the possibility would exist for methyl mercury production and subsequent transfer of mercury into fish to be enhanced to some degree. However, the likelihood of conditions similar to Davis Creek Reservoir occurring in off-channel pits of any configuration along lower Cache Creek is not supported by the findings of this study of the existing gravel pit lakes. Sediment bulk mercury levels are considerably lower and the water quality in these sytems may not be readily conducive to anoxia. However, we would strongly recommend that the issue of environmental mercury be monitored closely in conjunction with future operations.

Table 11. Selected Fish Muscle Mercury Concentrations *(wet wt ppm)*; Davis Creek Reservoir

Identification	Length		Weight		ppm Hg
	(mm)	*(inches)*	*(grams)*	*(pounds)*	*(wet wt)*
DAVIS CREEK RESERVOIR (9/87, = new impoundment Hg surge)					
Largemouth Bass	169	6.7	63	0.1	2.79
Largemouth Bass	188	7.4	83	0.2	3.14
Largemouth Bass	206	8.1	121	0.3	3.15
Largemouth Bass	215	8.5	136	0.3	3.85
Largemouth Bass	233	9.2	160	0.4	3.50
Largemouth Bass	239	9.4	195	0.4	3.31
Largemouth Bass	253	10.0	230	0.5	4.50
Bluegill Sunfish	152	6.0	91	0.2	2.22
Bluegill Sunfish	163	6.4	117	0.3	2.23
Bluegill Sunfish	166	6.5	124	0.3	2.81
Bluegill Sunfish	168	6.6	130	0.3	2.51
Bluegill Sunfish	203	8.0	227	0.5	2.60
Bluegill Sunfish	205	8.1	270	0.6	2.67
DAVIS CREEK RESERVOIR (11/95, = equilibrium levels)					
Largemouth Bass	165	6.5	52	0.1	0.79
Largemouth Bass	232	9.1	185	0.4	1.07
Largemouth Bass	266	10.5	285	0.6	1.43
Largemouth Bass	300	11.8	375	0.8	1.21
Largemouth Bass	352	13.9	625	1.4	1.45
Largemouth Bass	375	14.8	870	1.9	1.61
Largemouth Bass	437	17.2	1,275	2.8	1.87
Bluegill Sunfish	142	5.6	65	0.1	0.67
Bluegill Sunfish	149	5.9	72	0.2	0.74
Bluegill Sunfish	193	7.6	203	0.4	0.98
Bluegill Sunfish	211	8.3	272	0.6	1.01
Bluegill Sunfish	221	8.7	302	0.7	1.18
Bluegill Sunfish	250	9.8	440	1.0	1.51

Figure 8. Comparative Fish Muscle Mercury From Davis Creek Reservoir (1987, 1995)

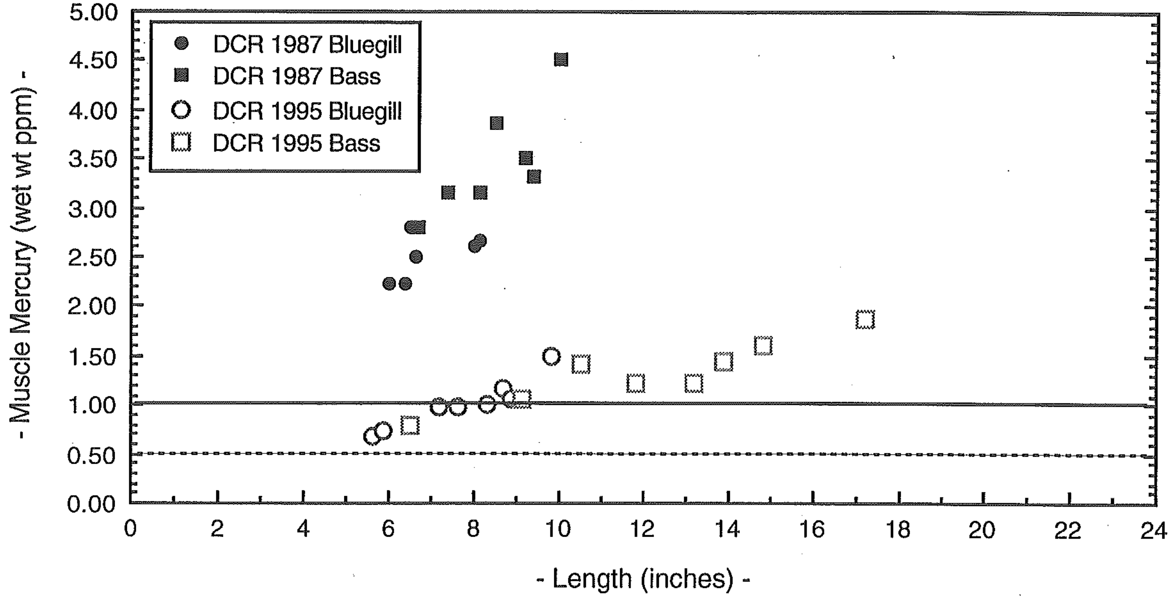
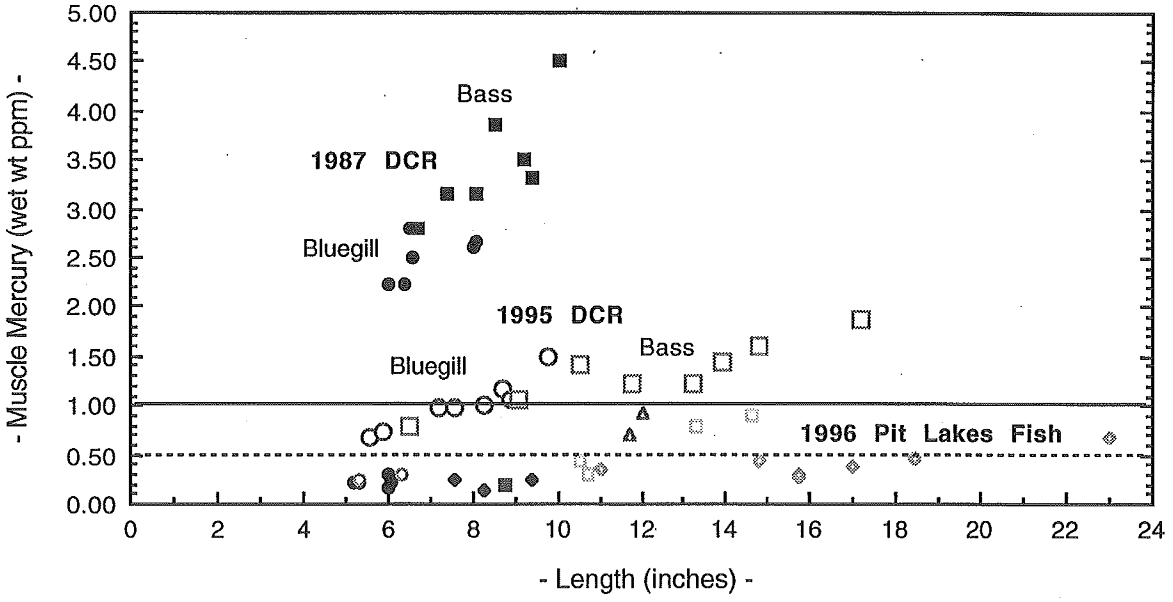


Figure 9. Davis Creek Reservoir Fish vs Fish From Solano Gravel Pit Lakes



5. LITERATURE CITED

Bloom, N.S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Canadian Journal of Fisheries and Aquatic Sciences*, 46:1131-1140.

Bloom, N.S. and E.A. Crecelius. 1983. Determination of mercury in seawater at sub nanogram per liter levels. *Marine Chemistry*, 14:49-59

Gill, G.A. and K.W. Bruland. 1990. Mercury speciation in surface freshwater systems in California and other areas. *Environmental Science and Technology*, 24(9):1302-1400.

Lindberg, S., P.M. Stokes, and E. Goldberg. 1987. Group report: Mercury. Chapter 2 in *Lead, Mercury, Cadmium, and Arsenic in the Environment.* T.C. Hutchinson and K.M. Meema, eds. John Wiley and Sons Ltd, 17-33.

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

Moyle, P.B. 1976. *Inland fishes of California.* University of California Press, Berkeley, Los Angeles, London. 405 pp.

Reuter, J.E., D.G. Slotton, R.P. Axler, and C.R. Goldman. 1989. Analysis of the Long-Term Environmental Monitoring Program for Davis Creek Watershed Surface Waters--January 1, 1982 - June 30, 1989. *Report for Yolo County.* 268 pp.

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. and J.E. Reuter. 1995. Considerations of heavy metal bioavailability in intact and resuspended sediments of Camanche Reservoir, California, USA. *Marine and Freshwater Research*, 46:257-265.

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

TSMP 1990. Toxic Substances Monitoring Program: Ten year summary report, 1978-1987. *State of California Water Resources Control Board publication* 90-1WQ, August 1990. Prepared by Del Rasmussen and Heidi Blethrow, Division of Water Quality.

TSMP 1991. Toxic Substances Monitoring Program: 1988-1989. *State of California Water Resources Control Board publication* 91-1WQ, June 1991. Prepared by Del Rasmussen, Division of Water Quality.

TSMP 1992. Toxic Substances Monitoring Program: 1990 Data Report. *State of California Water Resources Control Board publication* 92-1WQ, May 1992. Prepared by Del Rasmussen, Division of Water Quality.

TSMP 1993. Toxic Substances Monitoring Program: 1991 Data Report. *State of California Water Resources Control Board publication* 93-1WQ, June 1993. Prepared by Del Rasmussen, Division of Water Quality.