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Mercury and Methyl Mercury in California Fish, Water and Sediment: the Importance of Ecosystem Factors

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Summary

Past anthropogenic activities in the state of California have led to an increase in levels of mercury found in many of the state's freshwater fish species. The Surface Water Ambient Monitoring Program- Bioaccumulation Oversight Group (SWAMP-BOG), funded by the California State Water Resources Control Board, conducted a study examining fish-tissue mercury concentrations in various lakes and reservoirs throughout the state. However no samples were analyzed for mercury or methyl mercury at any of the locations sampled. This study, funded by the State Water Resources Control Board for the development of methyl mercury bioaccumulation factors, served to supplement the SWAMP-BOG data by collecting water data to address the factors controlling mercury accumulation in fish. This included the calculation of methyl mercury bioaccumulation factors, collection of ancillary water measurements to help explain methyl mercury concentrations in water and fish, and developing correlations between the fish and methyl mercury water data.

Mercury lake concentrations varied considerably among lakes especially during stratified regimes where noticeable increases occurred in both near surface and bottom water methyl mercury concentrations. There is some evidence to suggest buildup of aqueous methyl mercury may be occurring in the thermocline in some lakes and which could be associated with lake oxygen levels. These lakes may benefit by the installation of pumps or bubblers to reduce methyl mercury concentrations in fish. There is also some evidence that increasing phytoplankton concentrations in lakes may reduce methyl mercury concentrations in fish as well. There were several factors that stand out as potential controlling factors that influence mercury concentrations in fish. These include methyl mercury in near surface waters and total mercury in sediments. To determine potential sources of methyl mercury in near surface waters however will require mass balance studies in each lake.

Introduction

California's historic gold and mercury (Hg) mining has led to a significant amount of mercury being released into the environment (Wiener and Suchanek 2008). As a result, many of California's lakes and rivers have become impaired due to high levels of mercury found in local populations of fish (Davis et al. 2009; Melwani et al. 2009). While most of the mercury in California exists as inorganic mercury (Hg^{II} and Hg^0), the organic and highly toxic form is methyl mercury (MeHg). Bacteria convert mercury to methyl mercury which is concentrated by microorganisms and subsequently biomagnified in food webs (Wiener et al. 2003). Nearly all of the mercury accumulated by fish and higher trophic levels is methyl mercury (Bloom 1992) which, when consumed, can adversely affect human health and wildlife.

Human consumption of fish species containing methyl mercury, even in low concentrations, can adversely affect the nervous, renal, immune, and reproductive systems in the adult, child, and developing fetus stages of human life (Zahir et al. 2005). Methyl mercury has also been shown to impair foraging efficiency, adversely affect endocrine systems, and reproduction in fish (Drevnick and Sandheinrich 2003; Hammerschmidt et al. 2002) and birds (Brasso and Cristol 2008; Schwarzbach et al. 2009). Considering the impact mercury can have on both humans and wildlife, addressing contaminant levels of mercury has been the focus of several studies in California.

Recently, the state of California's Surface Water Ambient Monitoring Program Bioaccumulation Oversight Group (SWAMP-BOG) conducted a study examining fish-tissue mercury concentrations in various lakes and reservoirs. Out of 152 lakes sampled, 74% were above the state's advisory tissue level (ATL) of 3 servings per week for mercury and 26% were above the no consumption range (>440 ppb; (Davis et al. 2009). However, it was unclear as to why some of these lakes had elevated levels of tissue mercury when past anthropogenic activities, such as mining did, not appear to be a factor.

Therefore, the objectives of our study were to (1) collect water methyl mercury data to adequately characterize the concentrations in a sub-set of lakes used in the SWAMP-BOG study, (2) collect ancillary parameter water data to help explain methyl mercury concentrations in water and fish, (3) develop correlations between the fish and mercury, and (4) calculate methyl mercury bioaccumulation factors (BAFs). Additional funding for the study was provided by the

Regional Water Quality Control Board (RWQCB) in Sacramento to supplement their ongoing Total Maximum Daily Load (TMDL) efforts. This study will also provide supplemental data to the Office of Environmental Health Hazard Assessment (OEHHA) for regulatory purposes to assist in developing fish consumption advisories . The use of the data allows OEHHA and RWQCB personnel to better address factors affecting methylation, suggest best management practices (BMPs), and implement control measures as necessary.

Methods

Lake Selection

Lakes were chosen based on their relative mercury concentrations in fish-tissue, primarily largemouth bass (data provided by SFEI, taken from the SWAMP-BOG study), and accessibility. Additional consideration was made to include lakes that were part of an ongoing RWQCB-TMDL effort. The final study design included 28 lakes (Table 1). Twenty-two of these lakes were sampled bi-monthly or monthly depending on RWQCB-TMDL programs from August 2008 through October 2009 and some of these lakes had, within in them, multiple stations were water and sediment was collected (See Table 1). The additional six lakes (Bass, Britton, Butt Valley, Rollins, New Melones, and Paradise) were sampled just once in September 2009, as part of RWQCB 5's TMDL effort. These lakes had associated fish mercury data as well.

Sample Collection

All water and sediment sampling was conducted by RWQCB and California Department of Fish and Game-Marine Pollution Studies Laboratory (CDFG-MPSL). A multi-parameter (probe)YSI 600 xL sonde measuring temperature, conductivity, pH, and oxygen was used to determine lake stratification prior to any water collections. Probe measurements were taken in 3-meter increments from the surface to near-bottom (50 ft. max in depth; RWQCB 3, 5, & 8) at all lakes and recorded. During the summer period, when most of the lakes were determined to be consistently stratified (Jun-Sept), water was collected in epilimnion (near surface) and hypolimnion (below thermocline; bottom) regions of each lake using a pre-cleaned (5% HCl)

Wildco Teflon Kemmerer sampler. During the winter period (Oct-Apr), when most of the lakes were determined to be well mixed, only a near surface sample was collected, with the exception of RWQCB 5 which sampled both near surface and bottom water throughout the study. All samples collected for aqueous mercury (total and methyl) were collected unfiltered and using a clean hands dirty hands techniques (Mpsl-Dfg_Fieldsop_V1.0 2007). The purpose of this study design was to characterize unfiltered aqueous mercury concentrations on a temporal scale and to examine any effects stratification may have on the distribution of unfiltered mercury in the water column.

Near surface water samples were analyzed for methyl mercury, Chlorophyll *a*, sulfates (SO4), and dissolved organic carbon (DOC) and deep water samples were only analyzed for methyl mercury. An additional water sample was collected for total mercury analysis on two separate sampling events (stratified and non-stratified lake type) coinciding with the regular sampling of lakes. One sediment sample was collected in the deepest depositional area of each lake using a Van Veen grab sampler (0.5 m^2). All sediment samples were analyzed for total mercury and total organic carbon (TOC).

Big Bear Lake, Lake Englebright, Thermalito Forebay, and Lake Hemet had no largemouth bass mercury data so an additional effort was put forth to collect fish at these lakes. CDFG-MPSL staff, using a Smith-Root Electrofishing boat, put forth an effort to collect fish at each of these lakes. As a result, largemouth bass were collected at Lake Hemet and Big Bear Lake while spotted bass were collected at Lake Englebright. However, no fish were collected from Thermalito Forebay.

Sample Custody

All samples were placed on ice or frozen and shipped overnight back to Moss Landing Marine Laboratories for analysis unless CDFG-MPSL personnel were able to drive them back to the laboratory. Standard two day hold times before acidification applied to all mercury water samples.

Analysis

The analytical and collecting techniques are identical to those used in current SWAMP programs. The investigators are involved in several SWAMP funded projects and quality assurance/quality control provisions of the study were identical to those in the SWAMP Quality Assurance Project Plan (QAPP). All protocols are available upon request.

All methyl mercury water samples were analyzed according to EPA 1630. They were distilled to separate methyl mercury from the water matrix (Horvat 1993). An ethylating agent was added to each sample to form a volatile methyl-ethyl mercury derivative, and then purged onto graphite carbon traps as a means of preconcentration and interference removal. The sample was then isothermally chromatographed, pyrolitically broken down to elemental mercury, and detected using a cold vapor fluorescence detector. Sample results are corrected for distillation efficiency.

Total mercury samples were analyzed using Modified EPA 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (Usepa 2002). Sediment samples were prepared by cold aqua-regia digestion (MPSL-107) and analyzed using a Flow Injection Mercury System (FIMS; MPSL-103). TOC in sediments were measured as percent loss on ignition (LOI).

Tissue-mercury samples were analyzed by USEPA method 7473 for the SWAMP-BOG program. Samples were dissected using standard clean procedures and analyzed on a Milestone Direct Mercury Analyzer (DMA-80). Briefly, the method involves a drying step followed by combustion, purging, trapping on gold, desorbtion, and AA detection. All fish samples used in this study were analyzed as individuals.

Statistical Analysis

Data were transformed to meet assumptions of statistical tests and all tests were performed using SPSS or SYSTAT software packages. Values that fell below detection limits were set to one half the reporting limit (R.L.). Anything less than 0.05 was considered to be statistically significant.

Bioaccumulation Factors

Methyl mercury BAFs were calculated for each lake using equation (1).

(1) $$BAF_T^t = \frac{C_t}{C_w}$$

C_t = *Total* concentration of chemical in fish tissue.
C_w= *Total* concentration of chemical in water.

All BAFs reported in this document were calculated using the above equation and are expressed in units of L•Kg^{-1}. BAF values were calculated using either the geometric mean or average of unfiltered aqueous methyl mercury concentrations (Sanborn 2006; USEPA 2003). Total mercury tissue concentrations were calculated using a length-tissue mercury regression and concentrations were normalized to 350 mm.

Results

Mercury in study lakes

Average near surface methyl mercury concentrations varied from < RL (Expressed as ½ the RL, 0.010 ng•L^{-1}) to 0.215 ng•L^{-1} and bottom methyl mercury varied from <RL to 0.351 ng•L^{-1}) among the stations in the study. Total mercury in sediments varied from <RL to 3.09 µg•g^{-1} , the highest being found at the Lake Nacimiento Las Tablas station. This was not surprising considering an abandoned mercury mine (Klau/Buena Vista), a designated EPA superfund site , discharges directly into Las Tablas Creek, which flows into Nacimiento. Table 2 summarizes the average, over the study period, of samples collected at each station.

Average methyl mercury concentrations within each lake and normalized (350 mm) mercury tissue concentrations were used for the purpose of calculating BAFs (Table 3). Calculations were made using data from the entire study period. Average mercury concentration in bass species varied considerably among lakes (91 – 1314 ng•g^{-1}) as well as average methyl mercury concentrations (<RL – 0.158 ng•g^{-1}).

Observed methyl mercury concentrations among study lakes varied more in stratified (summer) versus non-stratified (winter) regimes (Figure 1a). A large portion of the variability had to do with the distribution of aqueous methyl mercury concentrations in the water column during lake stratification (Figure 1b). Most notably, Lake San Antonio and Lake Hemet average bottom concentrations were around two orders of magnitude higher than their average near surface water concentrations during summer months (0.708 and 0.368 versus 0.051and 0.020 ng•L, respectively). However, largemouth bass tissue concentrations were among the lowest in the study for these two lakes (302 and 177 ppb) and below the no consumption limit of 440 ppb. Lake Pillsbury and Lake Nacimiento had the highest average near surface aqueous methyl mercury concentrations during summer months (0.163 and 0.089 ng•L) and the highest largemouth bass tissue concentrations in the study (1,314 and 1,236 ppb). The discrepancy between near surface and bottom water in Pillsbury and Nacimiento was not as large as in Lake San Antonio and Hemet. Lake Pillsbury's average near surface methyl mercury concentrations were only about one and a half times higher than the average bottom water concentrations (0.163 and 0.121 ng•L) and roughly a 2-fold difference between near surface and bottom water in Lake Nacimiento (0.089 and 0.043 ng•L).

Additional water samples were collected from Lake Nacimiento and Lake San Antonio in September 2009 to further profile the distribution of methyl mercury in the water column (Figure 2). The methyl mercury profile taken at Lake San Antonio was similar to the trend seen in the monthly summer collections: near surface concentrations were relatively low while bottom water concentrations were high. Lake Nacimiento however, had a rather large methyl mercury spike (3.73 ng•L^{-1}) near the oxygen minimum. We examined six additional profiles (see methods for the list of lakes) to ascertain whether this mid-water methyl mercury phenomena occurred in other lakes as well. Unfortunately, these lakes had either de-stratified by the time samples were collected or the methylmercury concentrations were too low (within 3x R.L.) to adequately assess whether the same phenomena had occurred.

Total mercury in water was measured twice (1 summer /1 winter) at each study lake with the exception of Pillsbury, Nacimiento, and San Antonio where only one summer collection was made. Aqueous total mercury concentrations were similar to the pattern observed in the aqueous methyl mercury data (Figure 1). Lake Nacimiento and Camp Far West were outliers among study lakes with respect to total mercury concentrations. Furthermore, Camp Far West had the third highest largemouth bass tissue concentrations in the study (843 ppb) behind Pillsbury and Nacimiento.

Ancillary measurements and correlations with fish tissue mercury

Variables measured in the study were examined using a Pearson correlation to ascertain which factors may potentially be important in driving bioaccumulation in largemouth bass (LMB) only. Averaged summer datasets were compared against averaged winter datasets to determine if there were any temporal trends among the mercury variables relative to LMB mercury concentrations ($n = 17$; Table 4).

Overall, total mercury in sediment had the highest correlation to LMB tissue mercury concentrations ($r = 0.709$; $p < 0.01$) and explained roughly 50% of the variability in LMB mercury concentrations ($R^2 = 0.503$; $p < 0.01$; Figure 3). Averaged summer near surface methyl mercury concentrations were moderately correlated to LMB ($r = 0.473$; $p = 0.055$) while winter concentrations were weakly correlated at best($r = 0.235$; $p = 0.363$). Total mercury concentrations were moderately correlated to LMB in the winter ($r = 0.433$; $p = 0.094$) and summer near surface/bottom concentrations weakly correlated ($r < 0.400$; $p > 0.10$).

Summer DOC, SO4, chl-*a*, and specific conductivity ancillary measurements had a significant and moderate correlation (negative) with LMB mercury concentrations ($r > -0.500$; $p < 0.05$). The same results held true in the winter, with the exception of DOC, which had no significant correlation with largemouth bass during this period. All of these variables, regardless of summer or winter periods, typically had a strong correlation among each other ($r > 0.700$; $p < 0.01$).

Among the mercury variables, total mercury in sediments was the only variable that had a significantly negative correlation with both chl-*a* and SO4 ($r = -0.547$, -0.493 respectively; $p < 0.05$) in the summer period and only with chl-*a* during the winter period. Near surface methyl mercury concentrations were moderately correlated with DOC ($r = 0.533$; $p = 0.028$) and pH ($r = 0.563$; $p = 0.563$) in the winter period and had no significant correlations with any of the other ancillary measurements.

We also examined the relationship between mercury in lakes and all bass species collected with respect to general areas of the state (Table 5). In general, Coast Range lakes (RWQBs 1and 3) were high in LMB, methyl, and total mercury in surface waters. Additionally these lakes were high in sediment total mercury and had a high degree of stratification. The Sierra Nevada Lakes (RWQB 5) were medium to high in LMB mercury (for the most part) and low to medium in the degree of stratification. The southern California lakes (RWQCB 8) were low in LMB mercury, low to medium in methyl and total mercury surface waters and variable in stratification. In general, mercury concentrations were highest in Coast Range lakes, medium in the Sierra's, and lowest in southern California. However, there were exceptions in each, which illustrates the complexity of the lakes and supports the concept that there are multiple processes occurring at each lake that control the concentration of mercury in bass species.

Discussion

Oxygen and stratification

Although there was no significant correlation between the degree of stratification and LMB mercury among all study lakes, there was however a significant correlation between the degree of stratification and LMB mercury concentration in the Sierra Nevada Lakes (r^2= 0.68, $p < 0.01$; Figure 4). We are currently examining possible reasons attributed to why this only seen in the Sierra Nevada lakes.

Two of our study lakes, San Antonio and Hemet, had significant levels of hypolimnetic methyl mercury associated with low dissolved oxygen and six of the lakes had > 65% change in oxygen concentrations between surface and bottom waters but little evidence of a buildup of hypolimnetic methyl mercury. Studies have shown methyl mercury formation in anoxic bottom water can be attributed to in situ processes and may not necessarily be controlled by source inputs (Eckley et al. 2005). Methyl mercury in fish has also been attributed to methyl mercury in bottom water in other areas such as Davis Creek Reservoir (Slotton et al. 1995) and lakes in the Guadalupe Watershed near San Jose California. Both San Antonio and Hemet had elevated surface methyl mercury concentrations in mid to late summer months when stratification was the greatest. This suggests that in situ processes may be controlling bottom water methyl mercury concentrations in these lakes. However, at neither of these lakes were mercury tissue concentrations elevated.

Near surface water methyl and total mercury concentrations

There was a moderate correlation between methyl mercury in surface waters and LMB in the summer (r =0.47) and a lesser correlation between total mercury in surface waters and LMB in the summer and winter (r =0.36-0.43 respectively). In the two study lakes that did have the highest tissue mercury concentrations , Pillsbury and Nacimiento, near surface methyl mercury concentrations were also the highest among lakes indicating in these two lakes epilimnetic methyl mercury may be causing high tissue levels. Others have found methyl mercury and total mercury in surface waters to be an important factor for influencing the bioaccumulation of mercury in fish (Wiener et al. 2006).

Total mercury in sediments

Total mercury in sediments was correlated to LMB mercury (r =0 .71) and total mercury in surface waters in summer and winter periods (r = 0.48-0.51). Total mercury in sediments was used as a proxy for the presence of mercury in the watershed due to mining activities or natural deposits of cinnabar. The total mercury in sediments was also correlated to methyl mercury in surface waters indicating the methyl mercury may be formed in the sediments and fluxed up into the surface waters or alternatively methyl and total mercury could be co-occurring in water brought into the lakes via tributaries. To determine whether methyl mercury in water is coming from in place sediments or the tributaries is not possible with this data set and would need follow-up mass balance studies to make this assessment. In one study at Folsom Reservoir, the Sacramento Regional Water Quality Control Board determined the methyl mercury concentrations could not be accounted for by tributary inputs alone and there must be some within lake production (Chris Foe, personal communication).

Conclusion

The concentrations of mercury in LMB are correlated (for the most part) to methyl mercury and total mercury in surface waters, and total mercury in sediments. In the Sierra Nevada Range the concentration of mercury in LMB was also correlated to degree of lake stratification. There were four lakes that exhibited a high degree (>65%) of stratification and high levels of mercury in LMB and would be candidates for destratification using pumps or bubblers. These include Lakes Pillsbury, Mendicino , Nacimiento, and Camp Far West. Destratification best management practices have been used successfully in lakes in the Guadalupe Watershed near San Jose California to lower the concentrations of mercury in fish.

The concentrations of mercury in LMB were also negatively correlated with chlorophyll a in surface waters indicating stimulating growth of phytoplankton may reduce mercury in fish. Chlorophyll a has been shown in other studies to be negatively correlated to LMB and Clams in the Delta (Foe, personal communication). Others have found algal blooms reduce the uptake of methyl mercury in freshwater food webs (Pickhardt et al., 2002).

Both methyl mercury in surface waters and total mercury in sediment are correlated to mercury in LMB. To determine whether control measures to reduce methyl mercury loadings to the lake by reducing inputs from the tributaries would be successful mass balance studies would be necessary to determine the relative amounts of methyl mercury coming from the tributaries and within lake sources.

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RWQCB	Lake	Station	Latitude	Longitude
1	Sonoma	Smith Creek	38.7398	-123.0722
1	Sonoma	Dam	38.7205	-123.0205
1	Mendocino	Dam	39.2009	-123.1754
3	Mendocino	Russian River	39.2327	-123.1739
3	Pillsbury	Dam	39.4229	-122.9547
5	Pillsbury	Eel River	39.4126	-122.9242
5	Naciemento	Dam	35.7629	-120.9030
5	Naciemento	Las Tablas	35.7088	-120.9514
5	San Antonio	Marina	35.8702	-121.0101
5	San Antonio	Delta	35.8912	-121.0598
5	Lake Engelbright		39.2519	-121.2705
5	Thermalito Afterbay		39.4897	-121.6801
5	Thermalito Forebay		39.5169	-121.6204
5	Lake Oroville		39.5482	-121.4764
5	Folsom Lake		38.7199	-121.1466
5	Lake Natomas		38.6370	-121.2178
5	Don Pedro		37.7144	-120.3942
5	Lake McClure		37.5924	-120.2632
5	Lake McSwain		37.5187	-120.2992
5	San Luis Resrvoir		37.0609	-121.1024
5	Oneil Forebay		37.0814	-121.0526
5	Camp Far West		39.0339	-121.2831
8	Big Bear		34.2476	-116.9567
8	Irvine	Dam	33.7824	-117.7247
8	Irvine	Santiago Flats	33.7755	-117.7045
8	Perris	Dam	33.8556	-117.1815
8	Perris	Allesandro	33.8648	-117.1714
8	Hemet		33.6648	-116.7036
8	Elsinore		33.6562	-117.3518
Additional Lakes sampled one time in September 2009				
5	Bass Lake*		37.3139	-119.5474
5	Lake Britton*		41.0276	-121.6426
5	Butt Valley Reservoir*		40.1459	-121.1739
5	Rollins Reservoir*		39.1529	-120.9374
5	New Melones*		37.9917	-120.5337
5	Paradise Lake*		39.8555	-121.5748

Table 1. Study Lakes by Water Quality Control Board (RWQCB).

RWQCB	Lake	Station	Chlorophyl-*a* (mg/L)	DOC (mg/L)	SO4 (mg/L)	Epilimnion MeHg (ng/L)	Hypolimnion MeHg (ng/L)	THg in water (ng/L)	THg in sediment (Dry, ug/g)
1	Sonoma	Smith Creek	1.36	9.03	7.39	0.033	0.040	0.920	0.171
1	Sonoma	Dam	0.82	9.81	7.39	0.032	0.035	1.666	0.254
1	Mendocino	Dam	1.79	10.14	8.13	0.052	0.049	1.213	0.100
1	Mendocino	Russian River	2.02	8.88	8.14	0.047	0.043	1.231	0.045
1	Pillsbury		1.92	11.60	5.85	0.158	0.135	1.032	0.195
3	Naciemento	Dam	1.66	8.27	38.29	0.043	0.116	1.012	0.048
3	Naciemento	Las Tablas	5.41	12.85	40.57	0.215	NA	14.708	3.090
3	San Antonio	Marina	7.02	18.97	67.43	0.045	0.351	0.971	0.067
3	San Antonio	Delta	13.86	17.15	68.29	0.046	NA	1.342	0.076
5	Lake Engelbright		0.44	1.92	4.45	0.042	0.045	0.850	0.214
5	Thermalito Afterbay		1.38	2.03	3.90	0.025	NA	0.683	0.012
5	Thermalito Forebay		1.80	1.93	3.75	0.022	0.010	0.792	0.051
5	Lake Oroville		1.58	1.91	3.85	<RL	0.026	0.506	0.066
5	Folsom Lake		1.17	2.02	3.00	0.043	0.034	0.644	0.126
5	Lake Natomas		1.18	1.94	3.03	0.033	0.035	0.919	0.055
5	Don Pedro		0.91	1.47	2.10	0.032	0.026	0.266	0.128
5	Lake McClure		1.33	1.77	3.00	0.041	0.025	0.354	0.081
5	Lake McSwain		1.63	2.08	2.72	0.033	0.029	1.552	0.115
5	San Luis Resrvoir		6.01	11.66	43.17	0.043	0.032	0.442	0.071
5	Oneil Forebay		1.98	8.62	47.80	0.043	0.042	0.803	0.105
5	Camp Far West		2.04	3.97	7.85	0.067	0.069	2.580	0.599
5	Bass Lake*		NC	NC	NC	<RL	<RL	NC	<RL
5	Lake Britton*		NC	NC	NC	<RL	<RL	NC	0.030
5	Butt Valley Reservoir*		NC	NC	NC	<RL	<RL	NC	0.120
5	Rollins Reservoir*		NC	NC	NC	0.042	0.037	NC	0.804
5	New Melones*		NC	NC	NC	<RL	<RL	NC	0.098
5	Paradise Lake*		NC	NC	NC	<RL	<RL	NC	0.147
8	Big Bear		3.80	13.73	20.83	0.032	<RL	0.432	0.066
8	Irvine	Dam	5.79	44.66	235.00	0.090	0.322	0.767	0.192
8	Irvine	Santiago Flats	5.87	45.14	229.00	0.141	0.166	1.671	0.186
8	Perris	Dam	5.06	14.22	51.67	0.039	0.031	0.234	0.061
8	Perris	Allesandro	5.58	14.25	52.67	0.036	NC	0.272	0.045
8	Hemet		4.87	10.89	15.80	0.030	0.196	0.278	0.037
8	Elsinore		42.64	65.35	220.00	0.042	0.076	1.098	0.029

Table 2. Average of anlytes collected at each study station. *Sampled only once. NC = No Collection and <RL = below reporting limit.

RWQCB	Lake	Spp. Collected	Normalized Tissue Hg (ng•g^{-1})	Average Aqueous MeHg (ng•L^{-1})	Geomtric Mean Aqueous MeHg (ng•L^{-1})	Average BAF	Geometric Mean BAF
1	Sonoma**	Largemouth Bass	677	0.030 ± 0.014	0.027	2.25×10^{7}	2.55×10^{7}
1	Mendocino**	Largemouth Bass	543	0.032 ± 0.025	0.023	1.71×10^{7}	2.33×10^{7}
1	Pillsbury**	Largemouth Bass	1314	0.158 ± 0.072	0.143	8.31×10^{6}	9.21×10^{6}
3	Naciemento**	Smallmouth Bass	1236	0.120 ± 0.099	0.079	1.03×10^{7}	1.57×10^{7}
3	San Antonio**	Largemouth Bass	302	0.146 ± 0.267	0.058	2.07×10^{6}	5.23×10^{6}
5	Camp Far West	Spotted Bass	843	0.068 ± 0.009	0.067	1.25×10^{7}	1.26×10^{7}
5	Lake Engelbright	Spotted Bass	521	0.036 ± 0.021	0.029	1.45×10^{7}	1.82×10^{7}
5	Thermalito Afterbay	Largemouth Bass	211	0.010 ± 0.009	0.010	1.22×10^{7}	1.35×10^{7}
5	Thermalito Forebay	--	NC	0.010 ± 0.005	0.010		
5	Lake Oroville	Smallmouth Bass	513	0.010 ± 0.005	0.010	4.53×10^{7}	4.74×10^{7}
5	Folsom Lake	Largemouth Bass	471	0.036 ± 0.024	0.031	1.3×10^{7}	1.53×10^{7}
5	Lake Natomas	Largemouth Bass	542	0.024 ± 0.013	0.020	2.27×10^{7}	2.7×10^{7}
5	Don Pedro Reservoir	Largemouth Bass	442	0.010 ± 0.008	0.010	3.36×10^{7}	3.7×10^{7}
5	Lake McClure	Largemouth Bass	769	0.023 ± 0.014	0.010	3.31×10^{7}	5.9×10^{7}
5	Lake McSwain	Largemouth Bass	535	0.025 ± 0.010	0.025	2.1×10^{7}	2.12×10^{7}
5	San Luis Resrvoir	Largemouth Bass	564	0.030 ± 0.016	0.026	1.87×10^{7}	2.2×10^{7}
5	Oneil Forebay	Largemouth Bass	234	0.040 ± 0.015	0.036	5.91×10^{6}	6.54×10^{6}
5	Bass Lake*	Largemouth Bass	91	0.021	0.010	4.46×10^{6}	5.75×10^{6}
5	Lake Britton*	Smallmouth Bass	248	0.010	0.010	2.48×10^{7}	2.48×10^{7}
5	Butt Valley Reservoir*	Smallmouth Bass	180	0.010	0.010	1.8×10^{7}	1.8×10^{7}
5	Rollins Reservoir*	Smallmouth Bass	762	0.039	0.038	1.96×10^{7}	2.01×10^{7}
5	New Melones*	Largemouth Bass	1125	0.010	0.010	7.6×10^{7}	8.81×10^{7}
5	Paradise Lake*	Largemouth Bass	161	0.010	0.010	1.61×10^{7}	1.61×10^{7}
8	Big Bear	Largemouth Bass	178	0.010 ± 0.012	0.010	9.2×10^{6}	1.09×10^{7}
8	Irvine**	Largemouth Bass	479	0.161 ± 0.162	0.115	2.98×10^{6}	4.18×10^{6}
8	Perris**	Largemouth Bass	98	0.023 ± 0.015	0.010	4.25×10^{6}	5.19×10^{6}
8	Hemet	Largemouth Bass	166	0.087 ± 0.202	0.032	1.91×10^{6}	5.18×10^{6}
8	Elsinore	Largemouth Bass	121	0.054 ± 0.035	0.047	2.23×10^{6}	2.56×10^{6}

Table 3. *Lakes were sampled once in September 2009 as part of RWQCB 5's TMDL program. ** Multiple stations within lake sampled for water and sediment. (NC= No calculation) No fish were collected at Thermalito Forebay. Values below the reporting limit (RL) were set to 1/2 the RL (0.010 ng/L). Data presented here are lake-wide averages of methylmercury in water (Value ± S.D.). Tissue tissue mercury values are normalized (350 mm) and represent the lake-wide average.

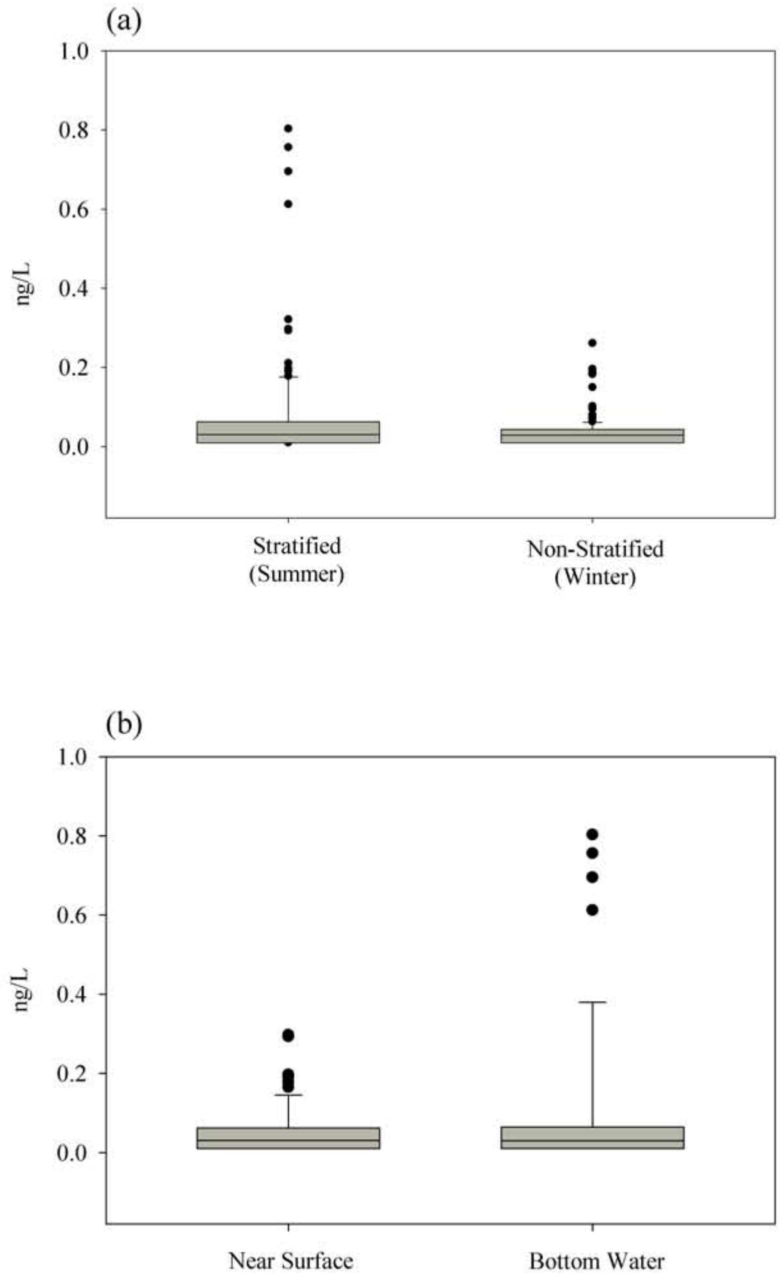

Figure 1. Median, upper and lower quartiles (25th and 75th percentile), standard deviation, and outliers (90th percentile) for the 21 study lakes.Observed aqueous methylmercury (MeHg) concentrations in stratified and non-stratified lake regimes (a) and the distribution of MeHg in stratified (summer) lakes (b). Stratified regimes were more variable due to the larger number of outliers (spikes in MeHg) especially in bottom water MeHg concentrations.

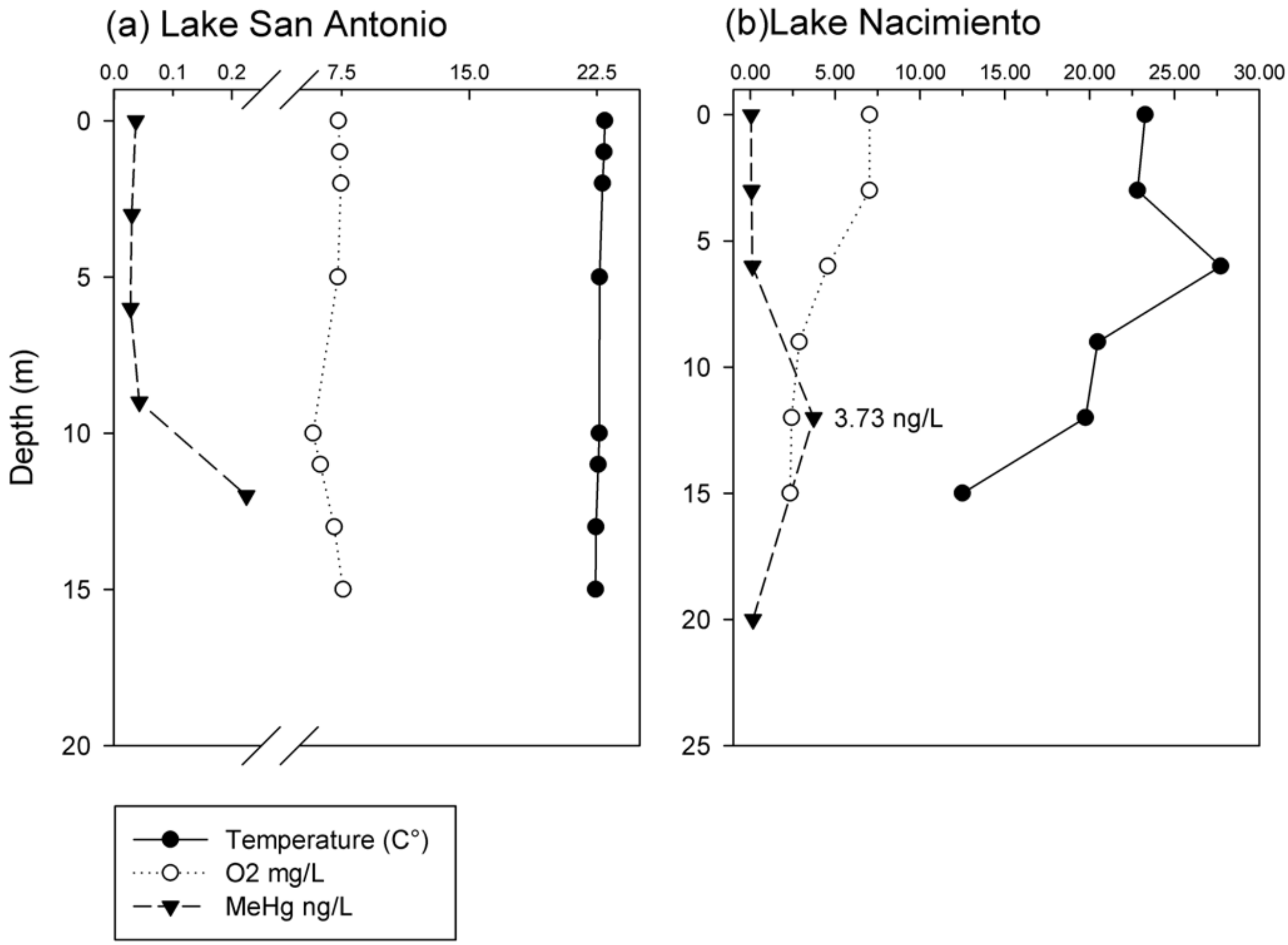

Figure 2. MeHg profiles of Lake San Antonio(a) and Lake Nacimiento(b) collected in September 2009. Lake San Antonio had relatively low aqueous MeHg concentrations in near surface and elevated values in bottom water that was a typical and consistent observation throughout the study period. Lake Nacimiento was relatively consistent in both near surface and bottom water and consistent with the observed data from the study (Not illustrated here). However, there was a large concentration of aqueous MeHg was around 12 m and was considered to be associated with either the thermocline or oxycline or both.

(a)

	LMB_t	AVG_T	AVG_O2	AVG_pH	AVG_spC	Chl-a	DOC	SO4	THg_tw	TMMHg_tw	THg_bw	TMMHg_bw	THg_s	TOC%
Tissue	1													
AVG_T	0.18528	1												
AVG_O2	0.06041	-0.39525	1											
AVG_pH	-0.36265	0.09405	-0.25662	1										
AVG_spC	**-0.61586**	0.23645	-0.37226	0.78898	1									
Chl-a	**-0.61251**	0.27231	-0.4296	0.47082	0.81025	1								
DOC	**-0.53898**	0.34632	-0.45328	0.79274	0.97301	0.83751	1							
SO4	**-0.69512**	0.15617	-0.38392	0.67829	0.96627	0.89434	0.94588	1						
THg_tw	0.36848	0.09893	-0.49394	0.23302	0.11339	0.08815	0.23553	0.0962	1					
TMMHg_tw	0.47314	0.39861	-0.31803	0.25632	0.12485	-0.02341	0.18591	0.02414	0.58108	1				
THg_Bw	0.36526	-0.33559	-0.2199	-0.04951	-0.122	-0.09084	-0.10915	-0.11006	0.62041	0.38467	1			
TMMHg_bw	-0.02954	0.30264	-0.32969	0.28866	0.33369	0.38897	0.4299	0.37585	0.33498	0.52807	0.22737	1		
THg_s	**0.70944**	-0.14146	0.0953	-0.30631	-0.46092	-0.54687	-0.415	-0.49307	0.48343	0.42004	0.61269	0.01337	1	
TOC%	-0.43652	-0.32276	0.15484	0.02693	0.29186	0.36856	0.18224	0.35519	-0.24156	-0.36333	0.1654	-0.05446	-0.07641	1

(b)

	LMB_tis	AVG_T	AVG_O2	AVG_pH	AVG_spC	Chl-a	DOC	SO4	THg	TMMHg	THg_s	TOC%
Tissue	1											
AVG_T	0.19466	1										
AVG_O2	0.01918	-0.53182	1									
AVG_pH	-0.36265	0.05279	-0.25427	1								
AVG_spC	**-0.62083**	0.16736	-0.22832	0.7961	1							
Chl-a	**-0.60778**	0.24611	-0.21666	0.66613	0.85019	1						
DOC	-0.31898	0.18126	-0.63398	0.78951	0.74344	0.67287	1					
SO4	**-0.56732**	0.23578	-0.2041	0.66279	0.95235	0.8269	0.67147	1				
THg	0.43282	-0.1706	0.46104	-0.13293	-0.22685	-0.12763	-0.12397	-0.17853	1			
TMMHg	0.23537	0.27531	-0.16781	0.563	0.39568	0.44563	0.53257	0.37381	0.30731	1		
THg_s	**0.70944**	-0.13096	0.21929	-0.30631	-0.45621	-0.52197	-0.23493	-0.36488	0.51263	0.31606	1	
TOC%	-0.43652	-0.33809	-0.09741	0.02693	0.26883	0.23883	0.23352	0.18961	-0.30104	-0.07813	-0.07641	1

Table 4. (a)Correlation matrix of summer variables (r). (b)Winter variables. Values highlighetd in bold are significant ($p<0.05$; LMB only)

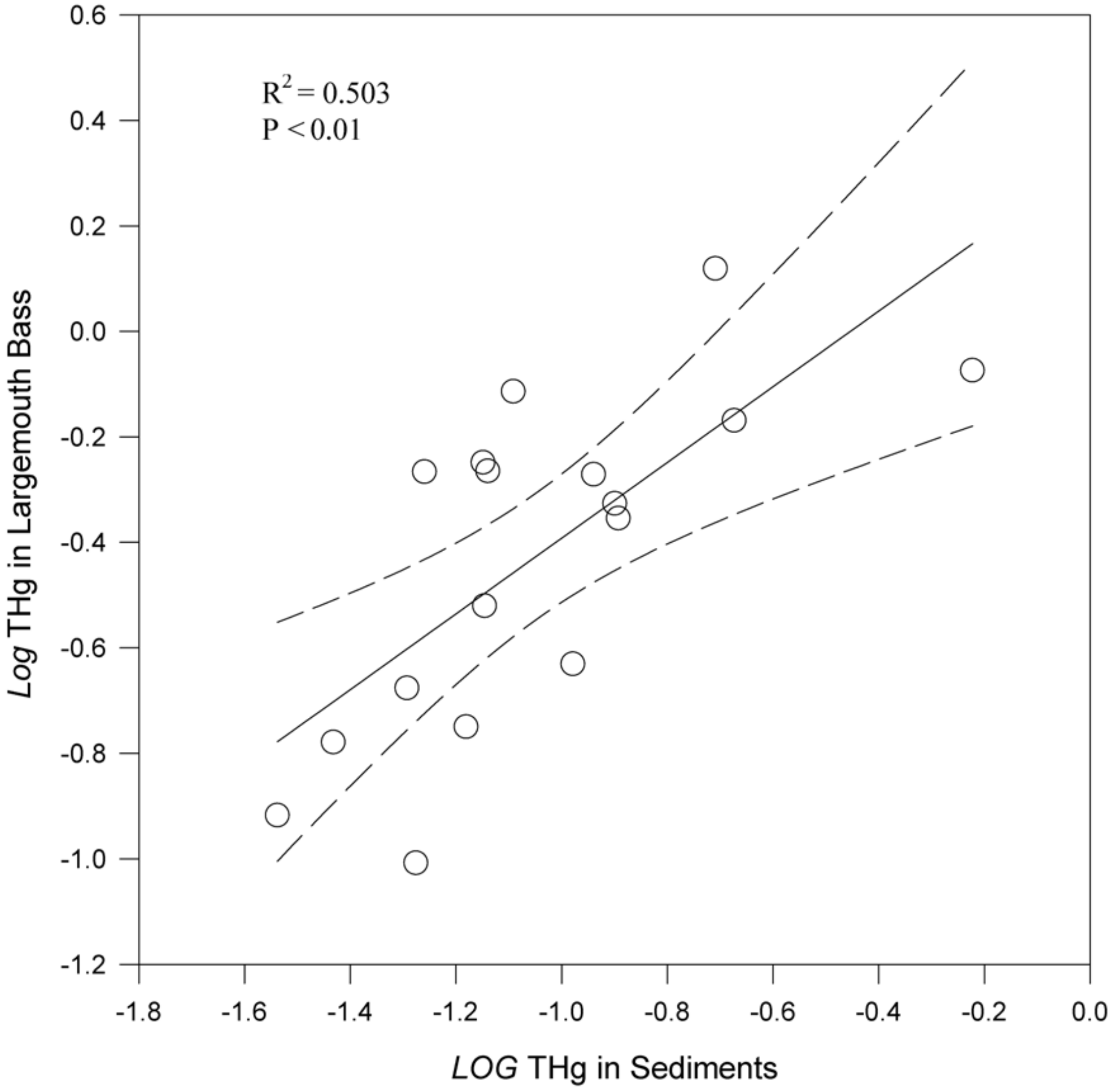

Figure 3. Logarithmic function of total mercury in largemouth bass expressed as a logarithmic function of total mercury in sediments.

RWQCB	StatName	Avg-LMB Hg (normalized -350mm)	Avg-MeHg_(Near surface)	AVG THg in water	THg Sediment	ΔO2-summer
1	Lake Mendocino					
1	Lake Pillsbury					
1	Lake Sonoma					
3	Lake Nacimento					
3	Lake San Antonio					
5	Camp far West					
5	Lake McClure					
5	San Luis Reservoir					
5	Folsom Lake					
5	Lake McSwain					
5	Oneil Forebay					
5	Don Pedro Reservior					
5	Lake Natomas					
5	Lake Oroville					
5	Thermalito Afterbay					
5	Lake Engelbright					
8	Lake Elsinore					
8	Perris Reservoir					
8	Lake Hemet					
8	Big Bear Lake					

Table 2. The table is sorted ascending on RWQCB. Darker shades represent higher average concentrations during the summer period relative to the rest of the study lakes. ΔO2 represents a percent change over time of the oxycline. In general, the longer a lake maintains an oxycline, coupled with the difference between O2 max and min, the greater the percent change. General areas of lakes: RWQCB 1 = Coast Range, RWQCB 5 = Sierra Nevada, RWQCB 8 = Southern California

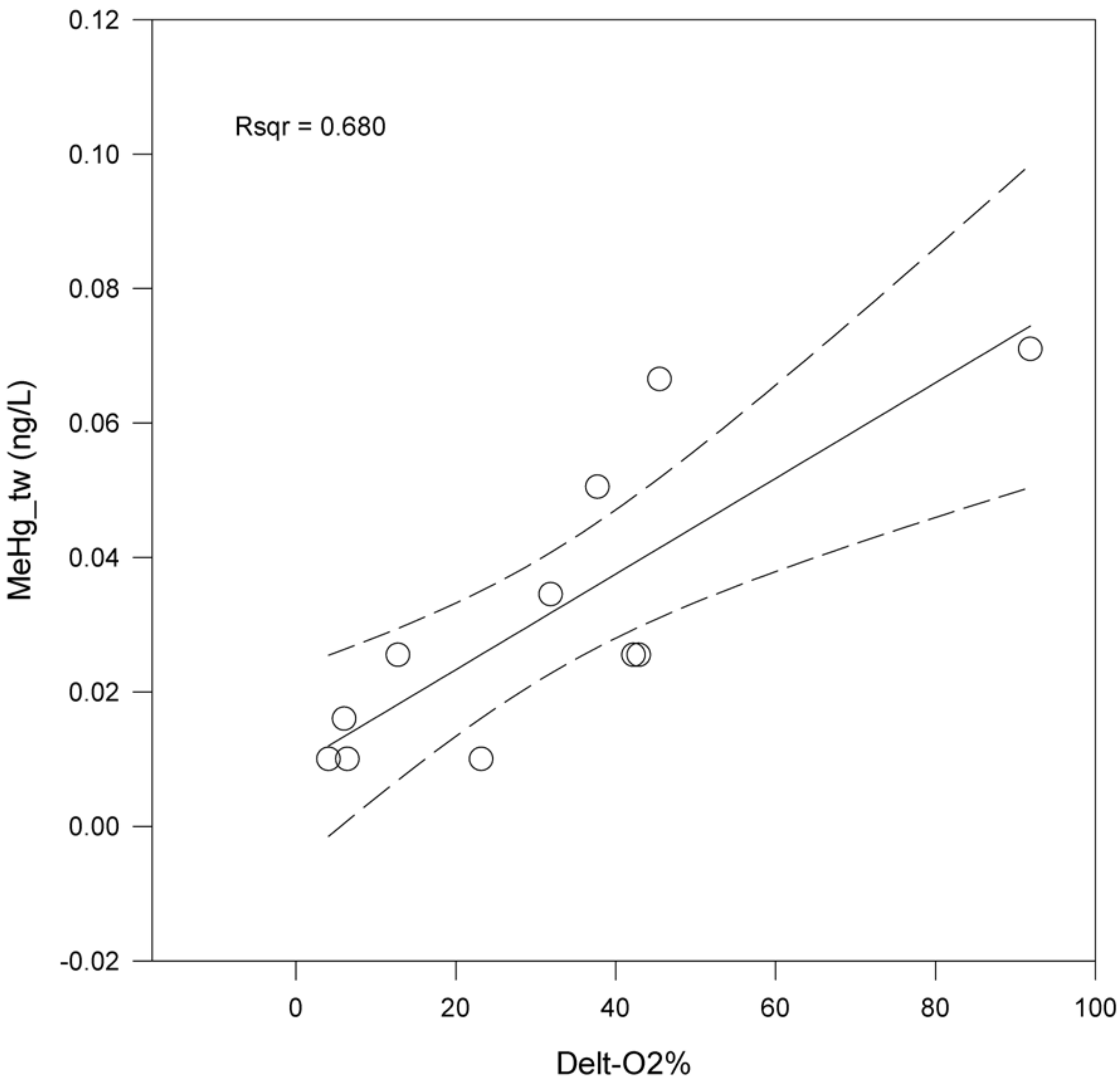

Figure 4. Delta O2 over time versus mercury in near surface water for RWQB 5 lakes (Sierra Nevada Region).