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Key Points:
- Hypolimnetic hypoxia plays a critical role in methylmercury production and distribution in four seasonally stratified reservoirs
- Methylmercury is tightly coupled in water, zooplankton, and fish
- Pilot hypolimnetic oxygenation rapidly decreased methylmercury in bottom waters, but not in small fish

Supporting Information:
- Supporting Information S1

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Evaluation of mercury cycling and hypolimnetic oxygenation in mercury-impacted seasonally stratified reservoirs in the Guadalupe River watershed, California

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Abstract Surface water reservoirs trap inorganic mercury delivered from their watersheds, create conditions that convert inorganic mercury to highly toxic methylmercury (MeHg), and host sportfish in which MeHg bioaccumulates. The Santa Clara Valley Water District (District) actively manages and monitors four mercury-impaired reservoirs that help to serve communities in South San Francisco Bay, California. The Guadalupe River watershed, which contains three of those reservoirs, also includes the New Almaden mercury-mining district, the largest historic mercury producer in North America. Monthly vertical profiles of field measurements and grab samples in years 2011–2013 portray annual cycling of density stratification, dissolved oxygen (DO), and MeHg. Monitoring results highlight the role that hypolimnetic hypoxia plays in MeHg distribution in the water column, as well as the consistent, tight coupling between MeHg in ecological compartments (water, zooplankton, and bass) across the four reservoirs. Following the 2011–2013 monitoring period, the District designed and installed hypolimnetic oxygenation systems (HOS) in the four reservoirs in an effort to repress MeHg buildup in bottom waters and attain regulatory targets for MeHg in water and fish tissue. Initial HOS operation in Calero Reservoir in 2014 enhanced bottom water DO and depressed hypolimnetic buildup of MeHg, but did not substantially decrease mercury levels in zooplankton or small fish.

1. Introduction

Hypoxia is commonly defined as dissolved oxygen (DO) concentrations less than 2 mg/L [*Wyman and Stevenson*, 1991]. Hypolimnetic hypoxia in lakes is often related to degraded water quality [*Wetzel*, 2001] and enhanced bottom-water buildup of problematic compounds including phosphate, ammonia, iron, manganese, and methylmercury (MeHg) [*Beutel et al*., 2014a; *Davison*, 1993; *Golterman*, 2001; *Watras*, 2009]. Hypolimnetic hypoxia can further degrade cold-water fish habitat in and downstream of reservoirs, as cool bottom waters become devoid of DO and accumulate toxic compounds [*Beutel et al*., 2001; *Beutel and Horne*, 1999]. Diffusion, entrainment, and fall turnover can transfer compounds from the hypolimnion into the photic zone, where they can stimulate primary production, reduce DO, and biomagnify in the food web [*Welch and Cooke*, 1995; *Slotton et al*., 1995]. Internal loadings of nutrients can be particularly consequential, as they can impair water quality long after external sources have been controlled [*Welch and Jacoby*, 2001].

Concentrations of MeHg in water, sediments, and aquatic organisms depend upon numerous environmental factors, including type and abundance of microorganisms and organic matter, pH, temperature, redox potential, sulfate and sulfide concentration, and inorganic mercury concentration [*D'Itri*, 1990]. Fish MeHg concentrations are also influenced by their size, diet, sex, growth rate, and trophic position [*Wiener et al*., 2003]. MeHg in lake water can bioaccumulate to concentrations in predator fish over one million-fold higher than their ambient waters [*Davis et al*., 2010]. Plankton dynamics and trophic bioaccumulation pathways can also influence MeHg concentrations in top trophic-level fish [*Stewart et al*., 2008; *Karimi et al*., 2016]. Many studies have attempted to find correlations between fish MeHg concentrations and physical and chemical lake characteristics, and parameters such as lake morphology [*Mason and Sveinsdóttir*, 2003] and mercury levels in zooplankton [*Chen et al*., 2000] have been found to be of primary importance.

MeHg exposure causes developmental problems in fetuses and children and nervous system effects in adults (see review by the *United States Environmental Protection Agency (USEPA)* [2001]). Similar developmental and nervous system effects have been observed in wildlife [*Wiener et al*., 2003]. More than 100 reservoirs throughout California are known to have concentrations of MeHg in resident sportfish above USEPA's water quality criterion of 0.3 mg/kg wet fish muscle tissue for protection of human health [*USEPA*, 2001]. To address these impairments, the California *State Water Resources Control Board* [2015] is developing a statewide regulatory program to reduce MeHg in fish consumed by humans and wildlife.

Aeration and oxygenation techniques are commonly applied to maintain oxygenated conditions in drinking water reservoirs [*Wagner*, 2015]. Maintaining sufficient DO via engineered systems can complement watershed management for more effective long-term restoration of lakes [*Holdren et al*., 2001; *Davis et al*., 2012]. Hypolimnetic oxygenation systems (HOS) are a specific method of oxygenation in which the hypolimnion is oxygenated without disrupting the water column's overall stratification [*Beutel and Horne*, 1999]. One type of HOS, fine-pore diffusion, releases small pure-oxygen bubbles that quickly diffuse dissolved oxygen into the water as they rise upward through the water column. While the system does not induce destratification, the rising bubble plume enhances mixing in the hypolimnion and tends to erode the base of the metalimnion [*Gantzer et al*., 2009b].

The primary benefit of HOS in lakes is the maintenance of thermal stratification while improving bottom water DO content [*Beutel and Horne*, 1999; *Singleton and Little*, 2006; *Moore et al*., 2012]. Additional benefits of HOS include the decreased sediment release of a number of compounds, including nutrients (orthophosphate, ammonium) that exacerbate eutrophication, reduced metals (iron, manganese) that complicate potable water treatment, and toxic compounds that can harm aquatic biota (ammonium, hydrogen sulfide) [*Beutel and Horne*, 1999; *Gantzer et al*., 2009a]. HOS using pure oxygen avoids potential side-effects associated with other lake water column and sediment amendments such as aluminum toxicity associated with alum treatment [*Smeltzer et al*., 1999] and nitrogen supersaturation associated with aeration [*Colta and Westers*, 1982].

HOS is a promising in-lake strategy for addressing MeHg impairment. By maintaining oxic conditions, oxygenation may repress MeHg buildup in bottom waters through a number of mechanism, including: repressing growth of anaerobic microorganisms including sulfate-reducing bacteria that methylate ionic Hg [*Fleming et al*., 2006; *Gilmour et al*., 1992]; suppressing sulfide production, a key compound which at moderate levels can enhance bioavailability of ionic Hg for methylation [*Benoit et al*., 2003; *Regnell et al*., 2001] and MeHg for uptake into phytoplankton [*Benoit et al*., 1999]; maintaining iron and manganese oxides in surficial sediments which may act as a sorption barrier to upwardly diffusing MeHg [*Dent et al*., 2014; *Chadwick et al*., 2006]; and pushing the zone of methylation deeper into the sediment, thereby further impeding the upward diffusion on MeHg [*Gill et al*., 1999]. However, in some lake sediments, biogeochemical processes such as oxidative dissolution, which releases ionic mercury (Hg(II)) and sulfate from sediment, may lead to enhanced methylation under subsequent hypoxic conditions [*Beutel et al*., 2014b]. Oxygenated conditions and/or changes in mixing patterns in the water column, while lowering MeHg concentration in bottom waters, may also change patterns of bioaccumulation, potentially leading to higher levels of Hg in aquatic biota [*Beutel et al*., 2014a].

Reservoir operators need a better understanding of how DO affects MeHg production and bioaccumulation within the context of water quality conditions (e.g., DO and nutrient concentrations), food web effects (e.g., biodilution), changes in source loadings (e.g., upstream mine site cleanups), and other operational constraints (e.g., cold water flows for downstream fisheries). There are numerous applications of reservoir oxygenation and circulation throughout the United States, more than 60 of which were reviewed by *Wagner* [2015]. Of these, only the Santa Clara Valley Water District (District), located in San Jose, California actively oxygenates reservoir hypolimnia specifically for the reduction of MeHg. There are potentially many lakes, streams, bays, and sloughs where oxygenation could be applied to reduce MeHg production, sediment efflux, and subsequent bioaccumulation in fish. The objectives of this study of four mercury-impaired, seasonally stratified reservoirs managed by the District were to: (1) assess patterns of mercury concentration in water, zooplankton, and fish; (2) evaluate the impact of initial HOS operation on MeHg production and bioaccumulation; (3) identify HOS operation conditions that minimize MeHg bioaccumulation; and (4) identify key monitoring design elements.

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2. Materials and Methods

2.1. Study Site

The Guadalupe River watershed is a complex hydrologic system covering 440 km^2, including six major reservoirs and over 129 km of waterways. The upper watershed includes dense forests at elevations over 1128 m above mean sea level, while the lower watershed includes the highly urbanized Silicon Valley. Guadalupe River discharges into South San Francisco Bay. The watershed contains the New Almaden mercury-mining district, the largest mercury producer in North America. From 1846 to 1975 (after which time production ceased), the mining district produced over 38 million kilograms of mercury, mostly to support the California gold rush [*Bailey and Everhart*, 1964]. Almaden and Guadalupe reservoirs, which receive runoff from the mining district, exhibit among the highest fish mercury concentrations in the state [*Davis et al*., 2010].

To protect against MeHg exposure problems, the Guadalupe River Watershed Mercury Total Maximum Daily Load (TMDL) regulates the District's Almaden, Calero, and Guadalupe reservoirs with a limit of 1.5 ng/L MeHg as a seasonal maximum in the hypolimnion. The TMDL also includes targets for biota: 0.05 mg/kg and 0.1 mg/kg MeHg wet weight in small and larger trophic level 3 fish, respectively [*Regional Water Quality Control Board-San Francisco Bay*, 2008]. The TMDL conceptual model is based on the premise that reducing hypolimnetic MeHg concentrations in bottom waters will reduce fish tissue concentrations in direct proportion. The District also owns and operates Stevens Creek Reservoir in an adjacent watershed, which is not subject to the TMDL.

All four reservoirs are managed principally for water supply to 12 local municipalities, private retailers, and others directly and through groundwater recharge, although each reservoir also provides some flood management capability and helps to maintain downstream fisheries during the dry season. Natural inflows occur almost entirely in winter, such that inflows during the typically stratified half of the year (April–October) represent around 10% of annual inflows. Calero Reservoir is unique among the four reservoirs in that it receives some water deliveries from the federal Central Valley Project and transfers from Almaden Reservoir. Calero and Guadalupe reservoirs are maintained below 50% capacity due to seismic concerns. Almaden, Calero, and Stevens Creek reservoirs are bottom drained (outlets are within 2 m of the original bottom),

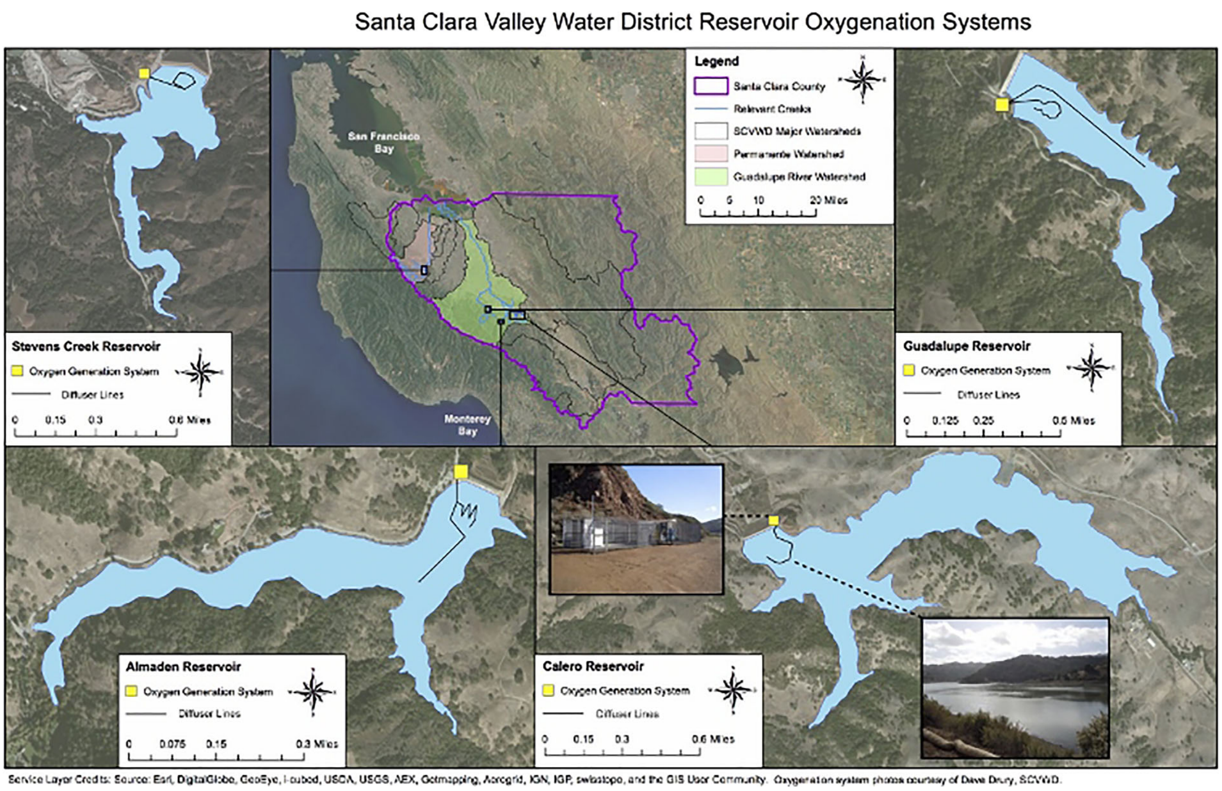

Figure 1. Site map for the four study reservoirs indicating HOS diffuser line layouts. See supporting information for detailed diffuser layouts.

Table 1. General Physical and Hydrological Characteristics of the Four Study Reservoirs

	Dimensions at Spillway Crest Elevation					Flows[a]	
Reservoir	Spillway Depth (m)	Area (km^2)	Vol. (km^3)	Length (km)	Width (km)	Avg. Inflow (km^3/yr)	Residence Time (days)
Almaden	22.2	0.23	0.002	1.25	0.12	0.017	42
Calero	26.2	1.42	0.012	2.74	0.44	0.012	370
Guadalupe	30.8	0.30	0.004	1.46	0.21	0.008	196
Stevens Creek	21.9	0.37	0.004	1.46	0.27	0.014	103

[a]Average inflows and residence times are based on calendar year 2011 data only. Inflows were more irregular during other years of this study.

while Guadalupe Reservoir's outlet is 4.9 m above the bottom. Allowed recreational uses include waterskiing, fishing, nonpower boating, and power boating. "Do Not Eat the Fish" signs are posted at major access points in an effort to limit human consumption of MeHg-contaminated fish from the reservoirs.

The four reservoirs are elongated in their former river channels (Figure 1), moderately deep and monomictic (Table 1), similar to numerous reservoirs throughout the temperate western U.S. Stratification typically sets up by April and fall turnover occurs by October. Once stratified, biochemical oxygen demand decreases hypolimnetic DO from near saturation to near zero within 1–2 months, where it remains so until fall turnover. Thermocline depths are typically 3–6 m. Water temperatures during stratification decrease with depth, and surface water temperatures increase over the summer from >10°C to >20°C. Nitrate ranges from <1 to 1.6 mg-N/L and total phosphorus ranges from <0.05 to 0.37 mg-P/L in Almaden, Guadalupe, and Calero (nutrients are not monitored in Stevens Creek). Most trophic status indicators per *Nürnberg* [1995, 1996] based on chlorophyll *a* concentration, Secchi depths, anoxic factors, and aerial hypolimnetic oxygen demand portray mesotrophic to eutrophic conditions.

2.2. HOS Design and Operation

The HOS at all four reservoirs utilize 95% pure oxygen gas generated on site by a pressure swing adsorption system that separates oxygen from a compressed air stream delivered by a 40 HP compressor on shore. The oxygen is delivered through a pressured high-density polyethylene pipe to a fine-bubble diffuser line suspended approximately 0.6 m above the sediment bed via a system of anchors and buoyancy piping [*Mobley et al.*, 2012]. The diffuser consists of two lines of porous hose along the full length of each diffuser. The hose is divided into independent 4.5 m-long sections. Oxygen flow to each porous hose is controlled by a flow-control orifice in the branch saddle connection to the supply pipe to equalize the flow along the length of the diffuser and to minimize losses in the event of a hose break. The HOS is designed to supply sufficient oxygen to counteract the oxygen depletion rate of the reservoir, with recovery capacity to increase the hypolimnetic oxygen content if operation is interrupted. The diffuser layout is designed to distribute oxygen directly within the reservoir's deepest, most anoxic regions.

The HOS was operated at Calero Reservoir periodically in the summer of 2013 and relatively continuously in the 2014 dry season at an oxygen flow rate of 0.47 kg/min (1490 lb/d) distributed over a diffuser length of 305 m (see surface photo in supporting information). The data period of record for Calero Reservoir includes 2 years prior to operation of HOS (2011–2012), intermittent operation in 2013, and sustained operation throughout most of the stratified period of 2014. Also during this period, HOS were operated intermittently for testing connections in 2013 at Guadalupe and Stevens Creek reservoirs, but not at all at Almaden Reservoir. The HOS were designed to maintain DO >5 mg/L in bottom waters while maintaining summer stratification to keep the cold-water pool for downstream fisheries [*Mobley Engineering*, 2014]. The overarching aim of oxygen addition is to reduce MeHg production in the hypolimnion and/or flux from the sediment bed into the hypolimnion and thereby to reduce MeHg bioaccumulation in fish.

2.3. Water Quality Monitoring

District field crews were professional staff trained in ultraclean sampling methods. Vertical profiles within the reservoirs were taken with a Hydro-Lab DS5 sonde for pH, temperature, redox potential, specific conductivity, dissolved oxygen, chlorophyll *a*, and phycocyanin. Profile data were normally logged at 0.25 m intervals to a depth of 1 m, at 1 m intervals through the epilimnion, at 0.25 m intervals through the thermocline ($\Delta T > 1°C/m$), and at 1 m intervals through the hypolimnion. Secchi depth measurements were hand-recorded during each sampling event. Samples were collecting at discrete depths using a Wildco Beta Plus Btl-2.2L H Horizontal Van Dorn style sampler. In the epilimnion, water samples were collected at a depth of 2 m. In the hypolimnion, water samples were typically collected 1 m or less above the bottom and at a mid-depth between the epilimnion and hypolimnion sample depths. During April–October, additional samples were collected midway between the normal sample depths. Single vertical profiles over the deepest region of each reservoir were conducted approximately monthly in years 2011–2013, and twice-monthly during HOS operation at Calero Reservoir in 2014.

Consistent with U.S. Environmental Protection Agency Method 1669 for ultraclean sampling [*USEPA*, 1996], all containers were acid cleaned, and field crews followed "clean hands—dirty hands" procedures. Samples were stored in 250 mL poly and double-bagged. MeHg samples were preserved with HCl. All samples were stored in dark coolers at 4°C and tracked by standard chain-of-custody procedures. During the study period, a total of 58 vertical profiles of field measurements were measured and recorded, and 302 samples were collected and analyzed for constituent concentrations.

2.4. Aqueous Mercury Analyses

All aqueous mercury samples were unfiltered. Total mercury (THg) and MeHg samples were analyzed according to Methods 1631 [*USEPA*, 2002] and 1630 [*USEPA*, 1998], respectively, at Brooks Rand Labs (Seattle, WA) in 2011–2013 and TestAmerica (Pleasanton, CA) in 2014. Method detection limits for THg and MeHg were 0.5 and 0.05 ng/L, respectively. Standard laboratory quality control procedures included calibration blanks, matrix spikes, and precision recovery samples [*Drury*, 2011].

2.5. Biota Monitoring

2.5.1. Zooplankton

Zooplankton samples were collected via vertical tows of 120 cm length, towing a 125 mesh zooplankton net. Tows were combined until at least 100 mg of biomass were obtained. Samples were collected in 1 L Teflon jars by rinsing off the mesh. Sufficient head space was kept in the bottles to avoid asphyxiation. Each bottle was labeled and placed in plastic bags, stored at 4°C in closed coolers, and delivered to analytical labs following chain-of-custody protocols. Zooplankton mercury contents were analyzed in October 2011 and July and October 2012 by Tri-Dent Aquatic Resource Solutions and reported as dry weight. Zooplankton mercury content was measured in April–May 2013 and July and October 2014 by Brooks Rand Lab. Samples were processed and analyzed according to the U.S. Environmental Protection Agency Methods 1630 [*USEPA*, 1998] for MeHg and 1631 [*USEPA*, 2002] for THg. Results represent water column-average content in large-body zooplankton ($>243\ \mu m$ in length). Phytoplankton represented up to 74% of the total mass of the samples collected in July 2012. Because zooplankton could not be physically isolated from filamentous blue-greens, a small amount of pure filamentous phytoplankton was extracted to determine the phytoplankton contents of both MeHg and THg, which was then subtracted from the content of the mixture. The results reported are zooplankton MeHg and THg contents. Samples in 2013–2014 were analyzed and reported as wet weight and converted to dry weight using 0.1 as the conversion factor per U.S. Environmental Protection Agency standard procedures [*USEPA*, 2003].

2.5.2. Trophic Level 3 Fish

Small (trophic level 3) fish were sampled by staff in years 2011–2013, plus 2014 for Calero only, to document fish assemblages present, relative changes in fish populations, and MeHg body burden in target fish species over time as HOS were implemented. Target species included black bluegill, crappie, golden shiner, and largemouth bass. Fish were captured using a Smith-Root Model H electrofishing boat. Four stations were sampled at each reservoir. Sampling was initiated at night shortly after dusk. Stations were located along the shoreline following the lake margin with sampling proceeding in a clockwise direction. Station distances were defined by the amount of shoreline sampled in 15 min spans with positioning recorded on a Lowrance Global Positioning System. At the end of each sampling station, the boat was stopped and anchored away from the shoreline. Fish were then identified to species, measured, and counted. Fork length was taken for the first 25 of each species measured at a station. Fork length was measured from the tip of the jaw/snout with closed mouth to the center of the fork in the tail. Lengths of small fish collected and analyzed were all 50–150 mm. All small fish were analyzed as whole body for THg via U.S. Environmental Protection Agency Method 1631 [*USEPA*, 2002] by Brooks Rand Labs (Seattle, WA).

2.6. Data Analyses

2.6.1. Volumetric Average Concentrations of MeHg and DO

Concentrations of MeHg and DO at 0.5 m intervals were linearly interpolated from available vertical profile data. Concentrations at depths above and below the highest and lowest measurements, respectively, were assumed equivalent to their nearest measurements. Upper and lower extents of the metalimnion were approximated visually at the breakpoints in vertical profiles for temperature. Bathymetric survey data available in 0.04 m elevation increments were used to estimate lakebed sediment areas, total volumes for each lake layer (epilimnion, metalimnion, and hypolimnion) and incremental volumes associated with each interpolated concentration, for each profile at each reservoir. Hypoxia-exposed area was calculated as the total horizontal surface area below the minimum depth of hypoxia. Volumetric average concentrations were

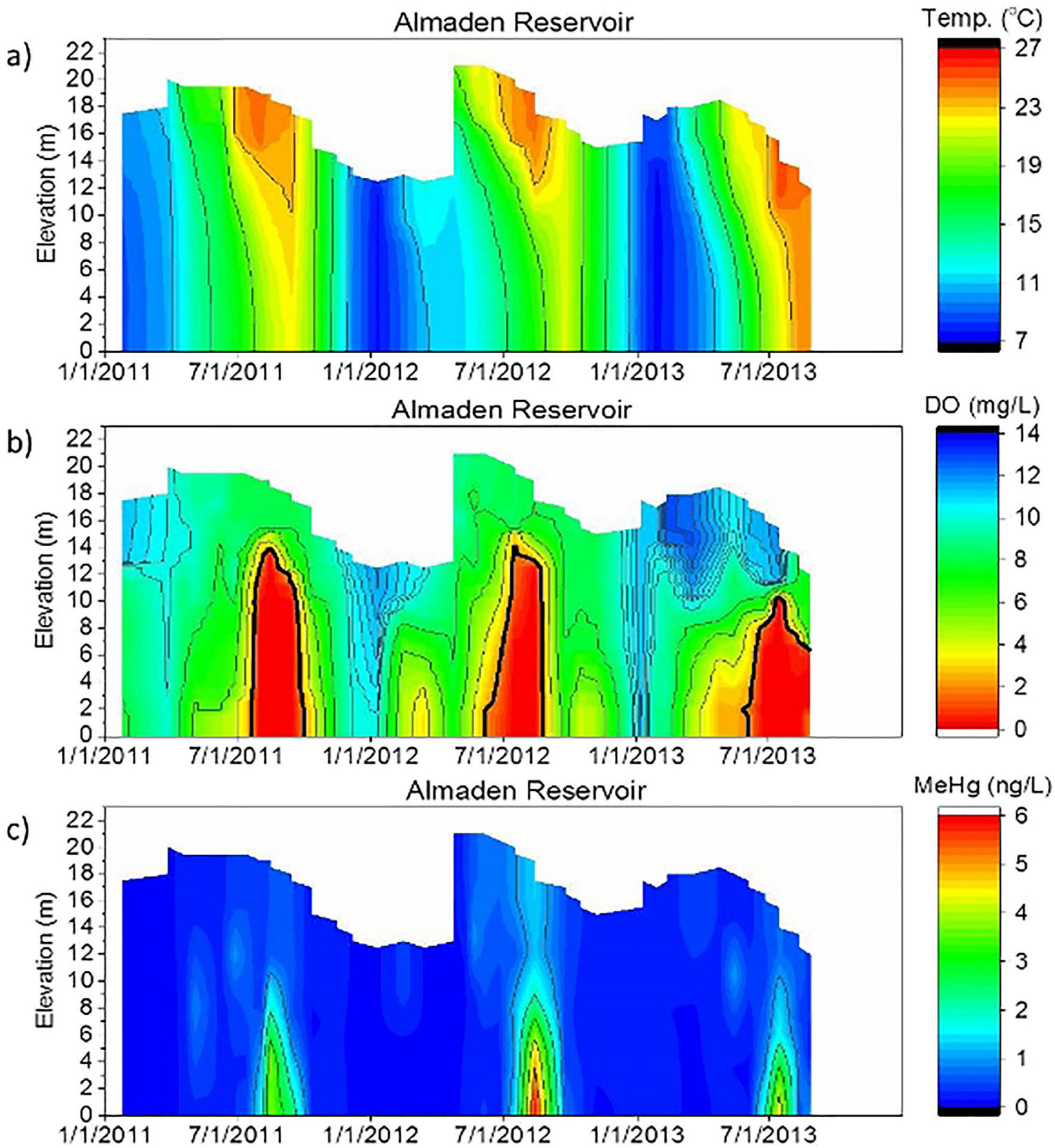

Figure 2. Isopleths in Almaden Reservoir, 2011–2013, for (a) temperature, (b) DO, and (c) MeHg. Contour lines are in increments of 4°C temperature, 1 mg/L DO (DO = 2 mg/L is bolded), and 1 ng/L MeHg. Water surface elevation is indicated by the upper bounds of the isopleths. Monitoring data set ends after August 2013.

calculated by summing each incremental depth's mass (concentration multiplied by its incremental volume) and dividing by the total layer volume.

2.6.2. Normalized Fish Tissue Concentrations

Data for individual fish were length-normalized to a standard 100 mm fork length based on a power regression of all fish in the size class (50–150 mm for small fish) for each reservoir [*Scudder Eikenberry et al.*, 2015]. Seasons and years were not separated for annual regressions because the low numbers of sampling events relative to the spread in the available data precluded statistical assessment of temporal variation.

2.6.3. MeHg Bioaccumulation Factors

Site-specific biota mercury (Hg_{biota}) bioaccumulation factors (BAF) were calculated as:

$$\mathrm{BAF} = \mathrm{Hg_{biota}} / \left[\mathrm{MeHg_{aq}}\right] \quad (1)$$

where BAF is in L/kg, Hg_{biota} is in mg/kg wet weight for fish and mg/kg dry weight for zooplankton, and [$MeHg_{aq}$] is the whole-lake average water column MeHg concentration in mg/L [*USEPA*, 2010]. Each [$MeHg_{aq}$] value used to calculate BAF is the volumetrically averaged concentration calculated at the time most nearly preceding its corresponding biota sampling event.

3. Results

3.1. MeHg Production During Stratification and Hypoxia

All four reservoirs displayed typical annual cycles of temperature and DO (see Figure 2 for Almaden, Figure 9 for Calero, and supporting information for Guadalupe and Stevens Creek). The isopleth figures combine several years of once or twice-monthly vertical profiles into a single time series. Summer stratification was generally followed within 4 weeks by hypoxia extending from the bottom upward. Hypoxia was followed within 2–4 weeks by MeHg concentrations increasing from the bottom upward. MeHg concentrations were always near the analytical method detection limit (0.02 ng/L) in epilimnion samples, but increased to as high as 2.8 ng/L (Stevens Creek), 4.4 ng/L (Calero), 5.9 ng/L (Almaden), and 25.1 ng/L (Guadalupe) in near-bottom samples. Peak concentrations typically occurred in July–September for all four reservoirs. As paired hypolimnion-averaged values, none exceeded the MeHg concentration regulatory threshold of 1.5 ng/L while DO $>$ 2 mg/L (Figure 3).

3.2. Largemouth Bass Monitoring

Largemouth bass (fish) is the only fish species sampled and analyzed for tissue mercury concentrations in all four reservoirs in sufficient numbers for interlake comparisons. The numbers of individuals, their size ranges, and their mercury concentrations varied greatly within each reservoir and over an order of magnitude among the reservoirs (Table 2). All lengths were within the targeted 50–150 mm juvenile size class (age $<$ 1 year), and averaged within 20% of the normalized length of 100 mm. Total length (mm) and weight (g) of fish reveal a consistent, significant positive correlation (Figure 4), indicating that their foraging patterns do not vary during the portion of their life cycle represented by their 50–150 mm size range and Trophic Level 3 status, and that fish growth patterns are similar among the four reservoirs being compared [*Verta*, 1990].

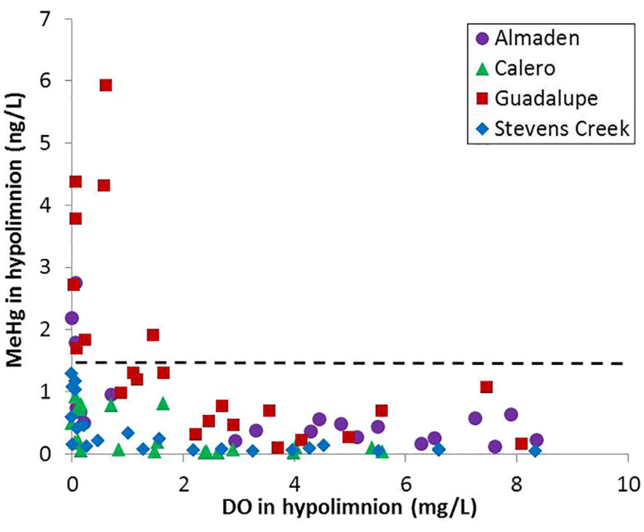

Figure 3. Hypolimnetic average concentrations of MeHg versus DO, 2011–2013, for all four study reservoirs. Dashed line indicates the regulatory target of 1.5 ng/L for seasonal maximum MeHg concentrations in the hypolimnion.

Seasons and years were not separated because of the low numbers of sampling events relative to the spread in

Table 2. Fish Monitoring Data Summary for All Four Study Reservoirs, 2011–2013 (Plus 2014 for Calero)[a]

Reservoir	# Fish	Weight (g)	Length (mm)	THg Conc. (ng/g ww at 100 mm)
Almaden	61	2.3, 8.5 ± 6.3, 25.9	60, 80.9 ± 18.9, 122	507, 946 ± 286, 1750
Calero	128	1, 19.3 ± 31.3, 203	50, 97.4 ± 36.4, 244	23, 231 ± 342, 3349
Guadalupe	28	1.6, 14.1 ± 13.8, 41.4	51, 91.9 ± 34, 149	358, 1156 ± 793, 3222
Stevens Creek	32	2.0, 16 ± 12.7, 43	51, 100 ± 28.5, 148	34, 112 ± 48, 267

[a]Values are presented as minimum, averages ± one standard deviation, maximum.

the available data, which precluded statistical assessment of temporal variation. But at this stage, there is no apparent change over time in either the average fish body burdens or their BAFs for each reservoir, including in Calero during the first season of continuous HOS operation (Figure 5).

3.3. Water-Zooplankton-Fish Relationships

In this section, water column MeHg concentrations ([$MeHg_{aq}$]) are as described previously for equation (1). Correlations between trophic level compartments showed a consistent, linear relationship between zooplankton THg and water column MeHg (Figure 6) and between fish THg and zooplankton THg (Figure 7). Linear correlations for both relationships aggregating paired data from all four reservoirs were statistically significant ($p < 0.05$). THg in fish also correlated positively with water column MeHg (Figure 8). The four-lake geometric mean BAFs for water and biota were 8.2×10^5 L/kg for zooplankton and 9.6×10^5 L/kg for fish, indicating a relatively small biomagnification from zooplankton to fish. BAF measured in our lakes were somewhat lower than the U.S. Environmental Protection Agency's estimated national geometric mean BAF for small fish in freshwater lentic systems of 1.26×10^6 L/kg. Every annual average THg concentration in fish in all four reservoirs exceeded the regulatory MeHg threshold of 50 ng/g wet weight for small fish. In Figures 6–8, results during pilot HOS operation in 2014 at Calero are also shown, but are not used in the regressions.

3.4. Pilot HOS Operation at Calero Reservoir

Oxygen addition had a substantial impact on patterns of DO and MeHg in Calero Reservoir (Figure 9). Seasonal (summer) stratification occurred in 2011 and 2012, prior to any HOS operation. Hypolimnetic DO loss rates during initial April–June stratification periods were on the order of 50 kg/d each year. The HOS delivers approximately 600 kg/d of oxygen to the diffuser line, providing a sufficient factor of safety for incomplete DO transfer, intermittent shutdowns, induced sediment oxygen demand, and the greater capacity needed in years with greater storage volumes. Intermittent HOS operation in 2013 had minimal effect on temperature profiles and produced only a transient increase in hypolimnetic DO. In 2014, hypoxia that had already commenced before startup of the HOS remained below the diffuser (bottom-most ~4 m) and in the metalimnion. Nearly continuous HOS operation in summer 2014 maintained DO > 5 mg/L in the majority of the hypolimnion volume. Nonetheless, various short-term shutdowns for maintenance, compressor over-heating, and electrical failures led to hypolimnetic DO slowly decreasing to <4 mg/L by early September before fall turnover.

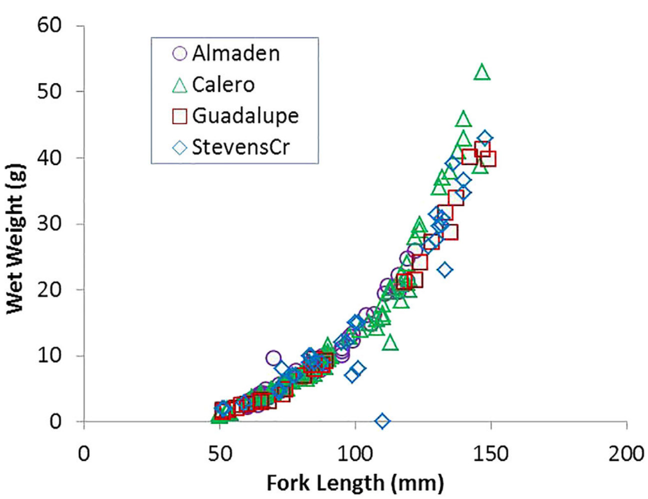

Figure 4. Fork length to wet weight for fish, 2011–2013, for all four study reservoirs.

Hypolimnetic MeHg concentrations increased from the bottom upward within weeks of the onset of hypoxia, but decreased during intermittent HOS operation in 2013. During continuous (albeit delayed start-up) HOS operation in 2014, MeHg buildup was suppressed in the hypolimnion. Importantly, hypolimnetic MeHg changed from exceeding the regulatory threshold of 1.5 ng/L to peaking at 0.5 ng/L. MeHg in bottom waters corresponded closely with

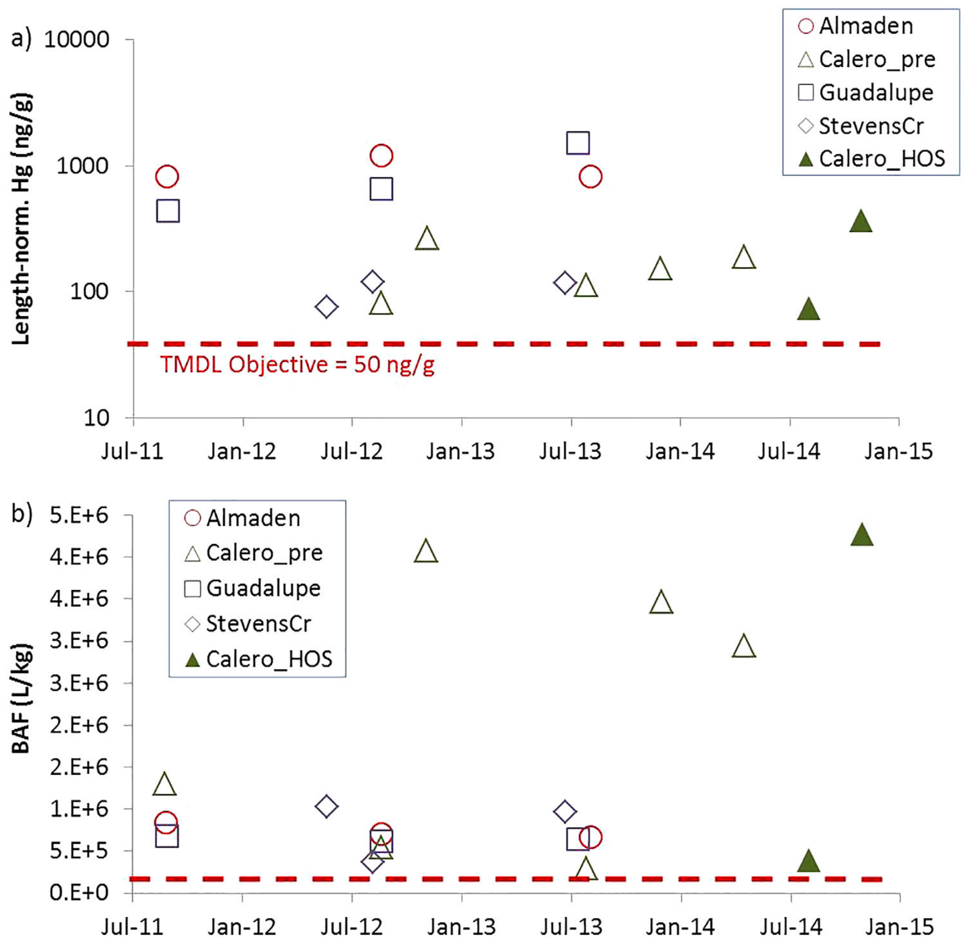

Figure 5. (a) Average length-normalized THg concentrations in fish and (b) fish bioaccumulation factors (BAFs) for each sampling event, for all four study reservoirs.

hypoxic sediment area (DO < 2 mg/L) (Figures 10a and 10b). In 2011 and 2012, 15–20 ha of sediments were exposed to hypoxia for 2–3 months. In 2013, the year of intermittent oxygenation, hypoxia-exposed sediment area was not decreased. In 2014, the year of nearly continuous HOS operation, the area and time of hypoxia exposure were both reduced by more than half.

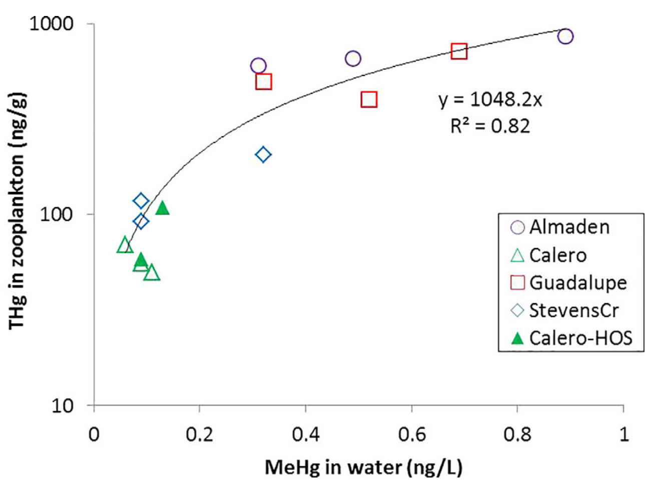

Figure 6. Correlation between whole-lake average MeHg concentrations in water to THg concentrations in zooplankton, 2011–2013, for all four study reservoirs, plus 2014 data for Calero during pilot HOS operation. Line is linear regression ($p < 0.05$).

The impacts of HOS operation on MeHg buildup in the epilimnion and consequently on a whole-lake average basis (because the hypolimnion volume is only one-quarter of the whole-lake volume) are less evident (Figures 10c and 10d, respectively, which are at one-tenth the concentration scale of Figure 10b), although the duration and magnitude of the peak epilimnetic MeHg concentration was reduced compared to two of the previous three years. Mean water column MeHg concentration, which is akin to the total mass of MeHg in the system because mean concentration multiplied by lake

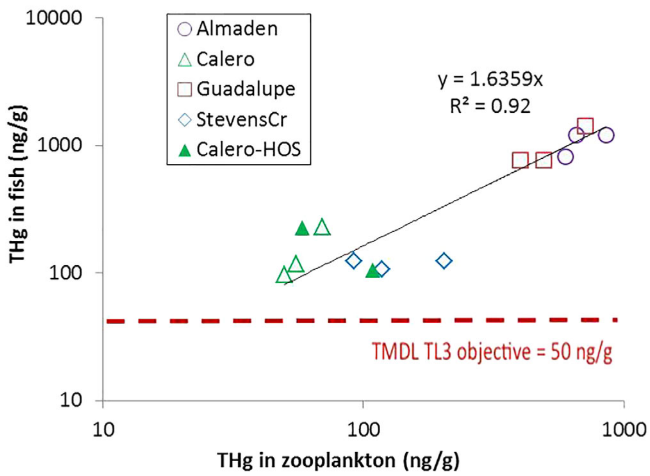

Figure 7. Zooplankton (dry weight) compared to fish (wet weight) THg concentrations, 2011–2013, for all four study reservoirs, plus 2014 data for Calero during pilot HOS operation. The horizontal red-dashed line indicates the regulatory target of 0.05 mg/kg (50 ng/g) wet weight in small (50–150 mm fork length) fish. Solid line is linear regression ($p < 0.05$).

volume effectively normalizes the MeHg mass, during oxygenation in 2014 peaked at 0.2 ng/L, compared to peaks 0.4 ng/L in 2011 and 2013. This analysis, based on one season of continuous HOS operation, suggests that while peak concentration of MeHg in the hypolimnion were much lower, there was still a substantial mass of MeHg distributed in the lake during oxygenation in 2014.

4. Discussion

4.1. Patterns of Mercury Concentration in Water, Zooplankton, and Fish

An exceptional value of this data set is that MeHg concentrations in water and biota vary widely across the four reservoirs, even while they all greatly exceed those found in unimpacted freshwater lakes [*Watras*, 2009]. Combined, values for MeHg in water samples range over three orders of magnitude (0.02–25 ng/L) whereas values for THg in fish range 15-fold (76–1500 ng/L ww). While MeHg in water and mercury in zooplankton and fish do not portray clear correlations for any individual reservoir, the ensemble data set does (see Figures 6–8). In effect, while relatively small changes in MeHg concentrations in pelagic waters do not indicate corresponding shifts in mercury concentrations in small fish, the ensemble data set indicates that larger, sustained reductions in water column MeHg should reduce THg concentrations in small fish. Likewise, even though the water-zooplankton relationships for each reservoir individually are not significant, the pattern observed in the ensemble data set indicates that there are similar bioaccumulation dynamics in all four reservoirs. While mercury cycling in pelagic freshwater ecosystems is complex, one generally accepted relationship supported by our study is that higher MeHg levels in water correspond with higher mercury levels in biota [*Watras et al*., 1998].

There was a one million-fold increase in mercury bioaccumulation in zooplankton over the MeHg concentrations in water but less than a twofold increase in mercury from zooplankton to fish. These factors are similar to observations of others nationally [*Wiener et al*., 2003], although *Kuwabara et al*. [2005] found approximately fivefold increases in the study reservoirs. The four-lake geometric mean BAF is 25% lower than the national average BAF determined by *USEPA* [2001] for small fish. While appreciating that the national average BAF reported is based on few data and is thus not necessarily representative, plausible explanations for the lower BAF at the four reservoirs compared to that national average include: the whole-lake volumetric average MeHg may be greater than the concentration to which the fish (and their prey) were actually exposed; MeHg monitored over each lake's deepest point may underestimate concentrations to which

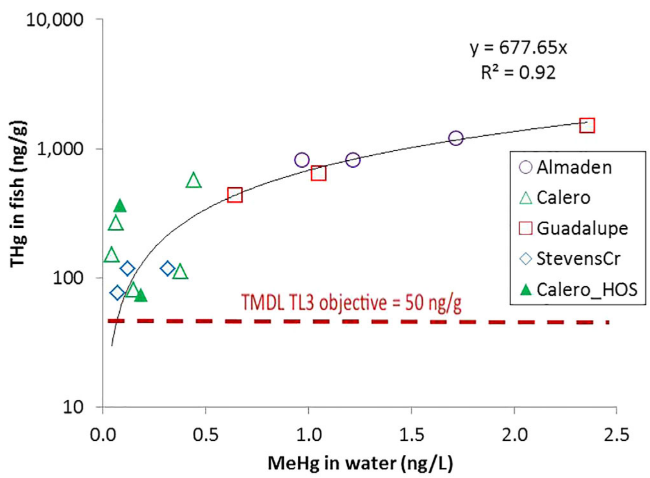

Figure 8. Comparison between concurrent water column-average MeHg concentrations and 100 mm length-normalized fish THg concentrations in each study reservoir, for monitoring events in years 2011–2013, plus 2014 data for Calero during pilot HOS operation. The horizontal red-dashed line indicates the regulatory target of 0.05 mg/kg (50 ng/g) wet weight in small (50–150 mm fork length) fish.

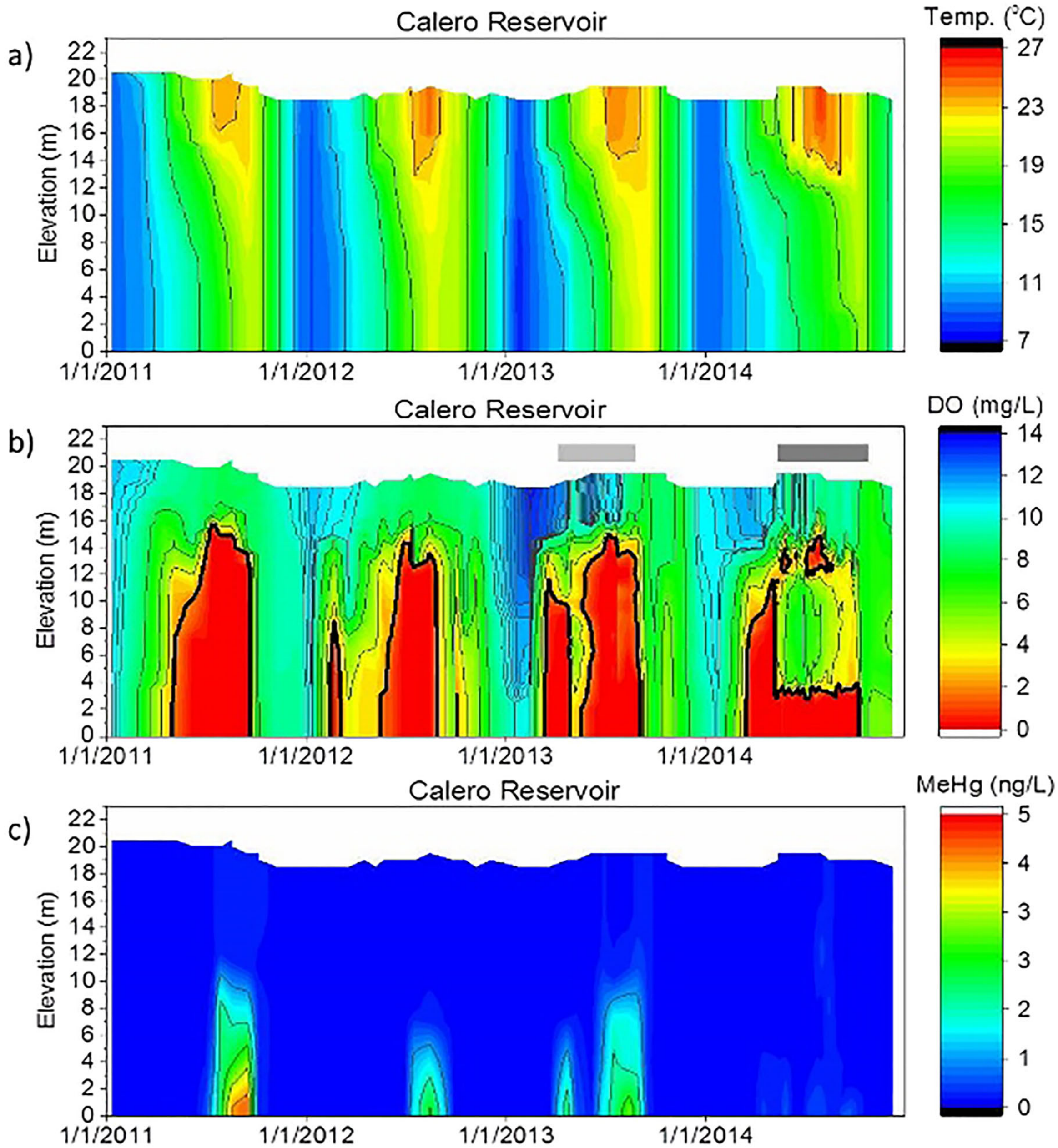

Figure 9. Isopleths in Calero Reservoir, 2011–2014, with pilot HOS operational periods indicated as relatively intermittent (lighter bar) and continuous (darker bar) for (a) temperature, (b) DO, and (c) MeHg. The HOS diffuser line was at 4 m elevation. Contour lines are in increments of 4°C temperature, 1 mg/L DO (DO = 2 mg/L is bolded), and 1 ng/L MeHg. Water surface elevation is indicated by the upper bounds of the isopleths.

the littoral fish monitored were exposed; and the relatively more eutrophic status of these reservoirs may have provided a biodilution effect [*Wiener et al*., 2003].

Biological factors such as growth rate, age, physiology, and diet may have influenced bioaccumulation rates and mercury concentrations in fish. Year-to-year abundance and size distribution of fish varied within and among the four reservoirs. In particular, the catch per unit effort for fish in Stevens Creek and Guadalupe reservoirs was much lower in 2013 when compared with 2012 [*Drury*, 2013]. Slight changes in sampling dates relative to young-of-year population dynamics also may have impacted results. *Kuwabara et al*. [2005] found that neither zooplankton densities nor biomass correlated with

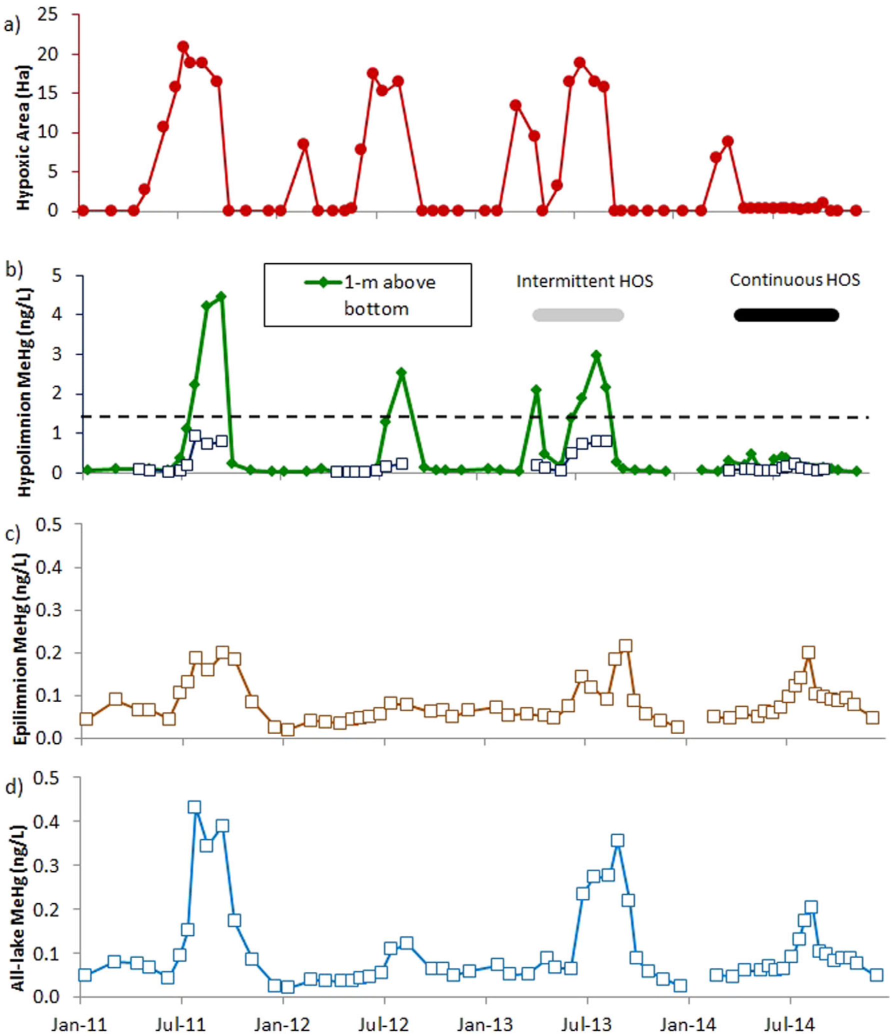

Figure 10. Time series of hypoxia-exposed area and MeHg concentrations in Calero Reservoir, 2011–2014 for (a) hypoxia-exposed area; (b) discrete and hypolimnetic average MeHg concentrations with dashed line indicating the regulatory target for seasonal maximum MeHg concentration; (c) epilimnion average (upper 6 m for each sampling event) MeHg concentration; and (d) water column-average MeHg concentrations.

phytoplankton densities or biovolumes in the study reservoirs, suggesting that the communities were not in equilibrium and thus that bioaccumulation factors should be measured at finer temporal and spatial scales.

For calculating BAFs, the whole-lake, vertically averaged MeHg concentration assumes a wide vertical distribution of zooplankton. The depth of mercury exposure will depend on the species. *Chaoborus*, for example, can grab an air bubble and swim deep into the anoxic zone to avoid predation during the day, and then migrate back up at night [*Gäde*, 1985]. Other zooplankton groups such as copepods and daphnia also migrate diurnally to avoid predation, but they are limited to oxygenated zones [*Stich*, 1981]. Estimating exposure-average MeHg concentrations is hindered by greater diurnal variability in MeHg photodemethylation and zooplankton migration.

4.2. Impact of Initial HOS Operation on MeHg Production and Bioaccumulation

HOS operation in Calero Reservoir resulted in lower concentrations of MeHg in hypolimnetic waters, both during short-term oxygen addition in 2013 and long-term oxygen addition in 2014. Significantly, oxygen addition in 2014 resulted in MeHg concentrations in bottom waters that were below the TMDL objectives of 1.5 ng/L. Oxygenated conditions are generally recognized to correspond with lower MeHg concentrations in the profundal zone of lakes. Hypoxic hypolimnia typically have MeHg concentrations that are 10 to 100-fold higher than oxic hypolimnia [*Watras*, 2009]. The presence of oxidized conditions at the sediment-water interface supports key biogeochemical processes that minimize or repress MeHg efflux from sediment including repression of sulfate reducing bacteria in surfacial sediments [*Gilmour et al.*, 1992] and sorption of upward diffusing MeHg to metal oxides of iron and manganese in surfacial sediments [*Chadwick et al.*, 2006]. A handful of studies have shown that oxidized surficial sediments have been found elsewhere to effectively inhibit MeHg diffusion from sediments into their overlying waters [*Gagnon et al.*, 1996; *Gill et al.*, 1999; *Merritt and Amirbahman*, 2008]. In addition, a few studies have documented how whole-lake manipulations that enhance the redox conditions of bottom waters can repress MeHg accumulation in bottom waters [*Austin et al.*, 2016; *Perron et al.*, 2014; *Beutel et al.*, 2014a; *Matthews et al.*, 2013].

While HOS operation at Calero Reservoir in 2014 lowered MeHg concentrations in bottom waters, there was no signal of lower Hg levels in zooplankton (Figures 6 and 7) or in juvenile fish (Figures 7 and 8). One process that may have counteracted anticipated decreases in MeHg bioaccumulation under oxygenated conditions in Calero Reservoir is expanded bottom water habitat for zooplankton during HOS operation. DO is an important environmental control on the vertical distribution of zooplankton in lakes [*Klumb et al.*, 2004]. Zooplankton likely utilized profundal waters, once no longer hypoxic in 2014, as a daytime refuge from predation. If these profundal waters still harbored higher levels of MeHg than that to which they were previously exposed, bioaccumulation may still have increased. A similar mechanism was proposed for oxygenation-enhanced mercury uptake into zooplankton in Twin Lakes, WA [*Beutel et al.*, 2014a]. A number of studies have also implicated MeHg production in littoral sediments as an important source Hg to aquatic food webs [*Krabbenhoft et al.*, 1998; *Stewart et al.*, 2008]. Stable isotope work by *Stewart et al.* [2008] in mercury-impacted Camp Far West Reservoir, California, found that MeHg contribution to predatory fish was significantly higher for pelagic carbon sources relative to benthic sources, some of which appear to have been collected in the littoral zone of the reservoir. This suggests in the case of Camp Far West Reservoir that managing MeHg in the profundal/pelagic zone, as is achieved via hypolimnetic oxygenation, should reduce levels of bioaccumulation in predatory fish.

Last, eddy diffusion across the thermocline can be a significance source of MeHg to the epilimnion [*Todorova et al.*, 2014]. It is possible that HOS operation enhanced the transfer of MeHg across thermocline, thereby promoting its uptake into biota in the epilimnion. We assessed this contention by calculating the mean eddy summer/fall diffusion coefficient across the thermocline for 2012, before HOS operation, and 2014, during HOS operation, based on the thermocline heat exchange method outlined by *Chapra* [1997]. The calculations did not reveal a dramatic change in the diffusion coefficient, suggesting that HOS operation did not enhance diffusion at the whole-lake scale. A coupled hydrodynamic-water quality model may be employed in the future to quantify more discretely the effects of HOS operation on vertical mixing processes.

4.3. HOS Operation Conditions That Minimize MeHg Bioaccumulation

A number of operational factors may account for the fact that pilot HOS operation at Calero in 2014 did not clearly reduce MeHg bioaccumulation in zooplankton or small fish. First, the HOS was started after the onset of hypoxia below the epilimnion. The 4 week delay allowed MeHg to accumulate in the hypolimnion and metalimnion (perceptible in Figure 9c), which subsequently may have mixed upward—diluting it but also increasing MeHg in the epilimnion where it was available for uptake by phytoplankton [*Morel et al.*, 1998; *Pickhardt and Fisher*, 2007; *Rolfhus et al.*, 2011]. In future years, HOS start-up should occur before the onset of hypolimnetic hypoxia, as commonly recommended in the lake oxygenation literature [*Wagner*, 2015]. Second, HOS did not oxygenate profundal waters underlying the diffuser. The vertical gap between the diffuser line and the deepest sediments left a small hypoxic zone which represented an ongoing source of MeHg to bottom waters. Once diffused into the mixing zone of the HOS, that MeHg would have been distributed throughout the water column by the diffuse bubble plume. Alternative systems developed with the aim of maintaining an oxidized sediment-water interface in lakes include horizontal discharge of superoxygenated water near the sediment [*Speece*, 1994] and release of a nitrate-rich density plume that settles over the sediment-water interface [*Matthews et al.*, 2013]. Third, HOS did not overcome hypoxia in the metalimnion, which may have provided the late-summer MeHg spike to the epilimnion (see Figure 9c) as others have observed [*Todorova et al*., 2014; *Bernhardt et al*., 2014].

HOS design and operation must balance oxygen delivery and induced turbulence. While greater gas flow provides more oxygen input into bottom waters, it also induces hypolimnetic oxygen demand at the sediment-water interface and mixes bottom waters farther up the water column. *Bryant et al*. [2011] and *Gantzer et al*. [2009b] both documented enhanced oxygen demand as a result of HOS operation in reservoirs. *Bryant et al*. [2011] also found that diffusive manganese flux out of a lake sediment was enhanced by HOS due to increased turbulence at the sediment-water interface. Similarly, *Deemer et al*. [2015] observed how the motion of internal waves at the "internal shoreline" (where the thermocline contacts the lakebed) can create periodic fluctuating redox conditions and turbulence that could enhance sediment flux of MeHg in that middepth region. To maximize the probability of success in maintaining sufficient DO, *Wagner* [2015] recommended that HOS be designed to overcome at least twice the background (i.e., quiescent) oxygen demand to counter oxygen demand induced by gas addition and related water movement near the sediment-water interface. Initiating HOS operation prior to hypoxia and aiming to maintain DO $>$ 5 mg/L in most of the hypolimnion may minimize effects of oxygen demand from reduced compounds which can be released from sediments during hypoxia.

4.4. Key Monitoring Design Elements

To optimize available monitoring budgets, monitoring designs associated with mercury management should focus on key elements and increase monitoring frequency and the number of water column sampling depths and profile locations during the period of stratification. In the present study, single profiles at the deepest location in each reservoir may not be sufficient to represent conditions laterally throughout each reservoir during HOS operation, and additional years of HOS operation and affects monitoring are warranted. When assessing HOS, additional vertical profiles should be measured laterally away from the diffuser to confirm that the vertical patterns in DO and MeHg are consistent. A compensatory reduction in monitoring locations and events is acceptable between fall turnover and late winter, when the HOS may even be turned off because MeHg concentrations are much lower, show no vertical gradient, and are less ecologically relevant. Because MeHg buildup in the hypolimnion appears to be predominantly from sediment flux during hypoxia, tracking redox-sensitive metals iron and manganese concurrently with MeHg may provide a lower-cost monitoring surrogate [*Beutel et al*., 2014a]. Similarly, total and dissolved organic carbon may help to interpret chlorophyll *a* field measurements, to explain variations in MeHg bioaccumulation [*Luengen et al*., 2012], and to provide another MeHg surrogate [*Bergamaschi et al*., 2011].

To characterize sources, monitoring designs should measure surficial bed sediment THg content once every ~5 years. If strongly correlated to fish tissue MeHg, this factor would encourage watershed mercury load reduction projects as a management tool over in-lake controls. Sediment MeHg production potential could also be measured by quantifying the percent MeHg of THg at depth in the sediment [*Hollweg et al*., 2009]. If HOS maintains an oxic sediment-water interface, then peak methylation potential should be depressed into deeper sediments. Additionally, inflows should be monitored for suspended sediment, THg and MeHg concentrations in times when such volumes represent significant contributions to the overall mass balance. In Calero, for example, transfers from Almaden Reservoir in 2012 were one-quarter to one-half the previous and next years' totals, respectively, and all-lake average MeHg concentrations followed a similar pattern.

For biota, the monitoring design should focus on the most ubiquitous fish species and optimize the number of fish sampled to obtain coefficients of variation in bioaccumulation factors $<$20% [*Scudder Eikenberry et al*., 2015]. In addition, fish monitoring should focus on juvenile fish because they should respond more rapidly to changes in MeHg at the base of the food web than older large fish. Carbon (^{13}C) and nitrogen (^{15}N) isotopic composition in fish can be measured and fish gut content analyzed to distinguish littoral, benthic, and pelagic food webs which vary in MeHg exposure [*Stewart et al*., 2008]. The concern is that HOS may be targeting pelagic fish while monitoring (and the majority of fish caught and consumed) focuses on fish that thrive primarily in littoral or benthic food webs. More frequent monitoring (e.g., monthly) of zooplankton is also an effective approach to assessing Hg uptake into the profundal food web, and is an important compliment to fish monitoring. However, unlike fish which accumulate predominantly MeHg, zooplankton accumulates both ionic Hg and MeHg. So zooplankton must be analyzed for MeHg to clearly assess trends in Hg bioaccumulation. Zooplankton monitoring also can help assess food web interactions. The monitoring design should identify zooplankton species and record total length of plankton net tows to estimate volumetric concentrations. Seasonal shifts in zooplankton species composition and density could be overlaid on time series of water column MeHg to evaluate how various species (each with characteristic exposure and predation) drive MeHg biomagnification in fish.

5. Conclusions

With an increased regulatory focus on Hg in reservoir fish, there is growing interest in the use of in situ management strategies to reduce Hg bioaccumulation in managed reservoirs. This study evaluated Hg cycling in four mercury-impaired seasonally stratified reservoirs in California, the effect of hypolimnetic hypoxia on MeHg production, and HOS operation at one of the study sites. Monitoring showed that across reservoirs, MeHg in water tightly correlated with Hg levels in zooplankton and juvenile bass. In addition, Hg levels in zooplankton and juvenile bass covaried. The pooled geometric mean BAF for the four study reservoirs (9.6×10^6 L/kg) was similar in magnitude to the national average BAF used by the U.S. Environmental Protection Agency (1.26×10^5 L/kg). Because of the multiple and interrelated biogeochemical processes that promote MeHg production and mobility at the sediment-water interface under reduced conditions, high MeHg concentrations in bottom waters corresponded with hypoxic conditions. Results support the contention that water column MeHg concentration is an important predictor of MeHg concentrations in biota, which bioaccumulate mercury to concentrations one million-fold that of water. Based on these observations, management strategies that enhance the oxidative capacity of hypolimnetic waters should lower MeHg concentrations in water and its bioaccumulation in zooplankton and fish.

One potential in situ management strategy that merits study is hypolimnetic oxygen addition—the use of pure oxygen to enhance oxic conditions in the bottom of lakes and reservoirs while maintaining thermal stratification. In Calero Reservoir, HOS operation in 2014 caused a dramatic decrease in bottom water MeHg concentration that resulted in meeting the TMDL objectives of a peak hypolimnetic concentration of 1.5 ng/L. But during oxygenation, a substantial mass of MeHg was still observed in the reservoir's water column on a whole-lake basis. This finding may have been the result of starting the HOS weeks after the onset of hypoxic conditions, by which time the mass of MeHg already present appears to have been mixed upward. In addition, subsequent HOS operation did not overcome anoxic conditions both at the sediment-water interface below the oxygen line diffuser and in the metalimnion. Both sites may have been ongoing sources of MeHg to the reservoir's biota.

Results of this study encourage several operational and monitoring strategies aimed at repressing and assessing MeHg bioaccumulation in reservoirs using HOS. To be most effective, HOS systems must be started before the onset of hypoxia. HOS systems are designed to meet oxygen demand and are not effective at making up an oxygen deficit, partly because of a feedback in which elevated turbulence and oxygen concentration associated with high oxygen delivery rates tend to enhance oxygen consumption rates. Because many of the biogeochemical processes that control MeHg production in reservoirs are associated with surficial sediments, HOS systems should also aim to deliver oxygen to the sediment-water interface, in addition to maintaining a well-oxygenated water column. Results from this study suggest that DO $>$ 2 mg/L near the sediment-water interface may effectively repress MeHg accumulation in hypolimnetic waters. Water quality monitoring of HOS operational impacts on MeHg bioaccumulation should include multiple vertical profiles measured laterally away from the diffuser to fully assess spatial patterns of DO and MeHg. Water quality monitoring should also include the redox-sensitive metals iron and manganese, which are good indicators of the redox status of surficial profundal sediment. Biota monitoring should focus on THg in a meaningful number ($>$24 each) of juvenile fish annually and monthly quarterly monitoring of MeHg in zooplankton.

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