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Hypolimnetic Oxygenation 5. Copper, zinc, iron, and manganese declines in Camanche Reservoir downstream of an abandoned mine

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Abstract

An abandoned mine upstream of Camanche Reservoir in California had increased sediment copper (Cu) and Zinc (Zn) concentrations 10-fold. Regulators and environmentalists claimed that a hypolimnetic oxygenation system (HOS) on the reservoir bed would stir sediments and increase metal toxicity in the hypolimnetic water supplied to steelhead and Chinook salmon in the Mokelumne River and its large fish hatchery. On the contrary, after HOS, small decreases in the concentrations of Zn and Cu and large decreases in iron (Fe) and manganese (Mn) occurred. Before HOS, ΣCu concentrations were relatively low ($\bar{x}$ deep, 3.3 µg/L, surface, 2.4 µg/L) but in the soft water sometimes exceeded an aquatic life criterion of 3 µg/L. After HOS, the long-term mean ΣCu dropped 12% to 2.9 µg/L (deep); surface concentrations were unchanged. Before HOS, bottom water ΣZn ($\bar{x}$ = 17.7 µg/L) occasionally exceeded the criterion of 27 µg/L but after HOS the long-term mean fell 36% to 11.3 µg/L. In contrast, ΣFe dropped 40-fold, dissolved Fe dropped 150-fold, ΣMn dropped 30-fold and dissolved Mn dropped 400-fold. Fe and Mn declines were consistent with oxide precipitation. However, declines in Cu and Zn were due to homogenization of the deeper hypolimnion by mixing in the oxygenated HOS plume and not due to oxidation itself or the HOS-induced 79% reduction in algae. Important for reservoir management, HOS slightly reduced heavy metals in the reservoir outflows benefiting downstream river and fish hatchery. Similar results are predicted for mixing by aeration or propellers.

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Modern mines can be sanitary, but past mining's legacy has been hard on the aquatic environment (Da Rosa and Lyon 1997, Navarro et al. 2008). The Penn Mine ore body lies in the center of the 350 km long Foothill Copper-Zinc belt of California and was only a few km upstream of Camanche Reservoir (Fig. 1). Operated intermittently between 1861 and 1951, the mine was abandoned, but not rehabilitated, before the dam was constructed in 1964. Some pollution from the active mine operations would have been washed far downriver before Camanche Reservoir was filled but some accidental discharges continued. Through the 1980s, occasional overflows from the abandoned mine's holding ponds into the short river reach between the mine and Camanche Reservoir caused salmonid fish kills. These were attributed to increased Cu (Finlayson and Wilson 1997). Zinc is often associated with copper mines and was abundant in the Penn Mine. Whatever the historical details, the reservoir's sediments now contain up to 10 times the copper and zinc found in the granite rocks upstream, excluding the metal-rich sulfide body that was mined, and were considered above-background (Slotton and Reuter 1995, Lebo et al. 2000).

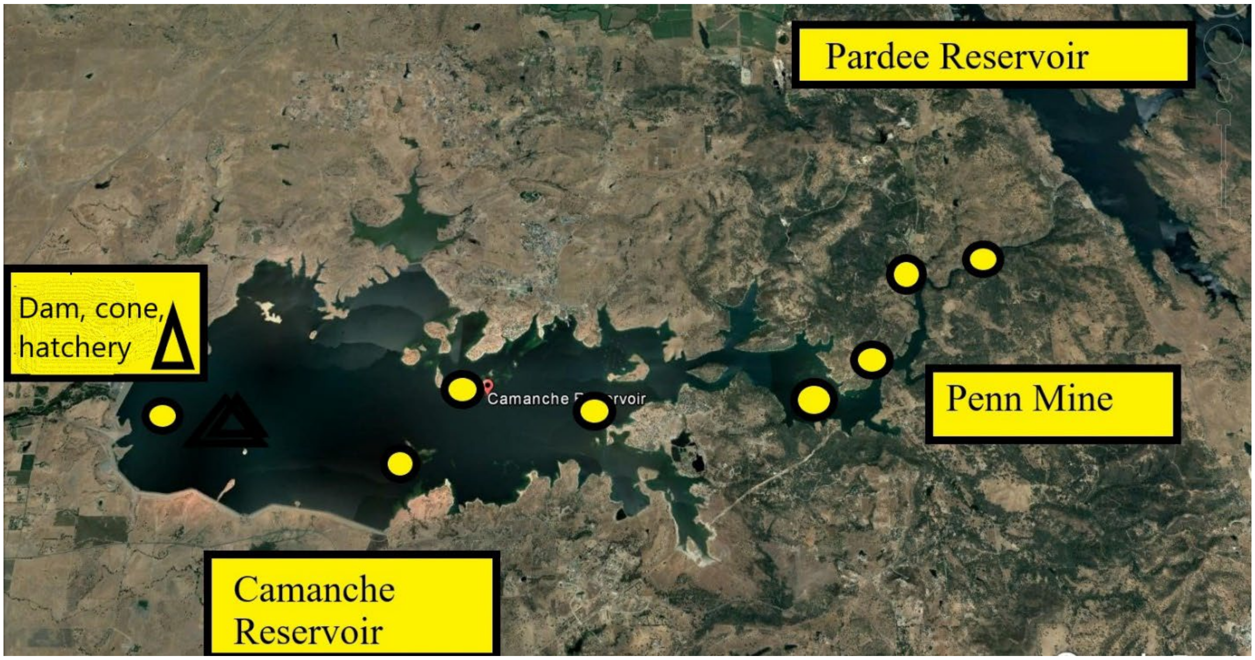

Fig. 1. Map of Camanche Reservoir with stations used in metal collections (circles), Speece cone (triangle, approx. location), the abandoned Penn Mine (copper and zinc), and upstream Pardee Reservoir. Bold face indicates most representative (longer term) results.

The Camanche dam has a bottom release design, and a fish hatchery draws water from the river immediately downstream. Large fish kills in the hatchery below Camanche Dam were attributed to hydrogen sulfide (H_2S) during the 1986-92 droughts (Horne 2019a). Oxygenation in the form of HOS was installed in 1993 to prevent further fish kills due to H_2S generated in anoxic sediments in the reservoir. Three design parameters for the HOS were vital: (i) delivery of high levels of dissolved oxygen (DO) to the sediments, (ii) no change in thermal stratification and (iii) no increases in turbidity and heavy metals. The HOS consisted of a pure oxygen delivery system via a Speece cone (Horne et al. 2019a). It was located on the reservoir bed near the dam (Fig. 1) by the East Bay Municipal Utility District (EBMUD, Oakland, CA), the owner and operator of the reservoir. The idea was to oxygenate the sediments and suppress H_2S production, but other benefits occurred including oligotrophication (Horne and Beutel 2019). The water flow to the cone was taken from about 4 m above the bottom using a 0.9 m^3/s submersible water pump. The cool, dense 9 m thick plume of oxygenated water was delivered to the hypolimnion via a 45 m long manifold set 4.5 m above the bottom with a velocity that was designed to prevent sediment re-suspension. Nevertheless, in 1988, regulators worried that a HOS could stir up bottom sediments. If this were true for Camanche Reservoir, the HOS could increase the risk of metal toxicity to the threatened steelhead trout (*Oncorhynchus mykiss*) and economically important Chinook salmon (*O. tshawytscha*, Horne and Faisst. 2019). Other proposed solutions for the fish kills included mine

cleanup (Hood et al.1988) and more storage in the reservoir which would reduce flows to downstream fish, agriculture and drinking water supplies dam downstream.
It was not clear if there was a substantial metal toxicity problem in the reservoir as distinct from river upstream near the mine during spills. The quantification of the no-effect level of copper and zinc in receiving waters depends on many factors, including the variable chelating effect of natural substances (Millero 2001, Moore and Ramamoorthy 1984, Morel and Hering 1993, Hauri and Horne 2004, Adams and Chapman 2007, Woody 2007, USGS 1998, USEPA 2007, 2016). Metal toxicity from abandoned mines is worse if the river catchments are on hard acidic rocks that release few buffering calcium or carbonate anions or where natural metal chelating agents are low. Such is the situation above Camanche Reservoir which is located near the granite upthrust of the Sierra Nevada Mountains. The reservoir is fed by the soft waters of the Mokelumne River (hardness ~ 20 mg/L $CaCO_3$). For comparison, the hardness of Lake Michigan is ~130 mg/L $CaCO_3$. In addition, the upstream Pardee Reservoir (Fig. 1) retains much organic matter such as dead leaves that provide natural chelation potential (Boyle 1979, Hauri and Horne 1997, Perdue 1998). The hypolimnion water was sometimes acidic (pH 6.5) which is slightly favorable to production of ionic metal species.

Would oxygenating the sediments increase or decrease metal toxicity at the fish hatchery or in the Mokelumne River downstream? Because oxygenation of sediments increases redox potential, any soluble metals increased by anoxia should be precipitated back to the sediments (Mortimer 1941, 1942, Wetzel 2001), benefiting the fishery. The hypothesis was that no adverse effect due to heavy metals, measured as an increase in concentration, would follow HOS operations. Adverse here is in terms of the steelhead and Chinook fish hatchery and Mokelumne River biota, both below the dam. This paper presents the test of the validity of that assumption. Cu and Zn were chosen to show any effects of oxygenation. Iron (Fe) and manganese (Mn), of importance for fish hatcheries (slimes in egg trays) and drinking water (staining laundry and sinks), were also considered. However, a large decline in Fe and Mn was anticipated when oxygen was added as this is a common method to remove them from well water.

Methods

Samples were collected either weekly or monthly at the Index Station close to the dam and Speece cone HOS manifold and at 7 other sites (Fig. 1 and Horne et al, 2019 for other details). Collections were more frequent during the "legal phase" immediately following the lawsuits concerning salmon kills in the Mokelumne River fish hatchery (1989-95) than later. Several special studies were made that increased sample frequency for a metals plume study following an artificial flood (Horne, 1996) and during the mine cleanup from 1995-2005. Samples were collected using a plastic Kemmerer bottle at the surface and at 5, 10, 15, 20, 25 m and "near-bottom". For the long-term trends, this paper focused on collections made at the surface and the bottom water layer of "proto-sediments" also known as the nephelometric layer (Moore et al. 2012, Horne and Jung 2019) which is the higher turbidity layer about 0-2 m above the sediments. Except for very wet winters, the only outlet from Camanche Reservoir is at the bottom of the dam whose tailwaters pass directly and quickly to the fish hatchery and river spawning gravels both of which are close to the foot of the dam (Moore et al. 1996, Horne 2019a). Bottom samples were collected about 0.5 m above the sediments in the usual manner by "feeling" the bottom with the sample bottle, pulling it about 0.5 m up to flush out any sediment, then closing the bottle via the messenger. Twenty metals (Ag, Al, Ba, Ca, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sc, Se, Si, Sr, Ti, V, Na) were assayed using EPA methods 200.7 (Inductively Coupled Plasma, IPC) or 200.8 (Inductively Coupled Plasma-Atomic Spectrometry, ICPMS) by EBMUD's State-certified laboratory. QA/QC followed the EPA methods guidelines. Minimum detection levels for ΣCu ranged from 3 µg/L (1989-1992) and 1.5 µg/L (1994 onwards). Dissolved Cu was always below the detection limit of 3 µg/L. For ΣZn detection limits ranged from 3 to 5 µg/L for the period of record. Over 16 years (1988-2004), variation sometimes occurred between replicates using the two EPA methods for ΣCu. However, there was no consistent bias for one method versus the other. The values reported here are averages of the two methods. Zinc concentrations were higher and easier to measure but, especially for the period prior to HOS, the variance was high. Before HOS, the mean bottom water ΣZn was 17.7 µg/L which was almost equal to the standard deviation (sd) and thus the coefficient of variation (cv) was high (98% 1989-1992). For the post-HOS period (mean ΣZn = 11.3 µg/L µg/L), the sd was 6.0 µg/L, about half the mean so the cv was lower (53%, 1994-2004). A typical example of the variation was the stratified period (May-October 1995). Here the mean value for the six once-per month bottom water samples for ΣZn was 19.4 µg/L (range of individual replicate samples, 13.5 to 24.7 µg/L). Trends over time for the HOS were measured using Excel for the R^2 regression coefficient and means were compared using a t-test with paired monthly samples when possible, using 1-tailed test for equal variances and 2-tailed tests for the unequal variances found in the longer sample periods. Due to analytical problems no bottom ΣZn data was available for 1993 and the first half of 1994.

Results

Copper

In Camanche Reservoir the HOS was operated each year but only from about June or July through October, so averages from comparable periods (July-Nov from 1992 to 2002, Table 1) were used as well as all year data sets. In the years immediately before and after HOS, ΣCu in the deep hypolimnion (July-Nov) fell one-third from 3.8 µg/L (1992 prior to HOS) to 2.2 µg/L (1993) and 3.1 µg/L (1994) both after HOS giving an average of 2.7 µg/L. The average decline of 1.6 µg/L over three years is small in absolute terms and these yearly means were not statistically distinguishable at the 95% confidence level. However, this was primarily because the pre-HOS samples showed high variance so the small change may have been real. Supporting this, bottom water ΣCu dropped after HOS to concentrations close to the most conservative potential chronic toxicity effect concentration of ~ 3 µg/L (4-day average). Over a longer period of 9 years, bottom water ΣCu fell slightly (3.3 µg/L 1989-June 93) to 2.9 µg/L (July 1994 – May 2002, Fig. 2, Table 1). After almost 20 years of HOS, ΣCu in the deep layer in 2002 averaged 2.3 µg/L which was almost identical to the concentration soon after HOS (Table 1). As discussed later in the zinc section, all these small declines are attributable to homogenization of the bottom 9 m of water within the HOS plume and not metal precipitation by the oxygen in the HOS plume.

Table 1. Total copper concentrations in various periods before and after HOS installation in Camanche Reservoir. Oxygenation began in July 1993 and continued until turnover in early November. HOS was resumed in summer 1994. All values in µg/L. The deep-water layer was 0-2 m above the bottom sediments. sd = standard deviation. Underlined numbers are averages of the pre-HOS July-Nov years. Dissolved copper data (MDL = 3 µg/L) were unreliable.

Metal, depth	**Mean conc. before HOS**	**sd, (range)**	**Mean conc. after HOS**	**sd, (range)**	**Decrease or (increase) (µg/L)**
Total Cu bottom	3.8 (Jul-Nov 1992)	1.2 (2.5-5)	2.2 (Jul-Nov 1993)	1.5 (1-4.8)	1.6
			3.1 (Jul-Nov 1994)	1.4 (0.8-3.8)	0.7
			2.7 (Jul-Nov 1993-4)		1.1
	3.3 (1989-June 93)	2.1 (2-9)	**2.9 (Jul 1994-May 2002)**	2.5 (0.5-21.7)	**0.4**
			2.2 (2002 only)		*1.6*
Total Cu surface	1.7 (Jul-Nov 1992)	**0.9 (2.5-5)**	1.1 (Jul-Nov 1993)	0.7 (0.5-2)	0.6
			2.9 (July-Nov 1994)	1.4 (0.8-3.8)	(1.2)
			2.0 (Jul-Nov 1993-4)		(0.3)
	2.4 (1989-June 93)	**1.3 (2-7)**	**2.5 (July 1994 – May 2002)**	1.5 (0.5-11.2)	**(0.1)**
			2.3 (2002 only)		*0.1*
Diss. Cu bottom	Data unreliable		MDL = 2 to 3 µg/L		

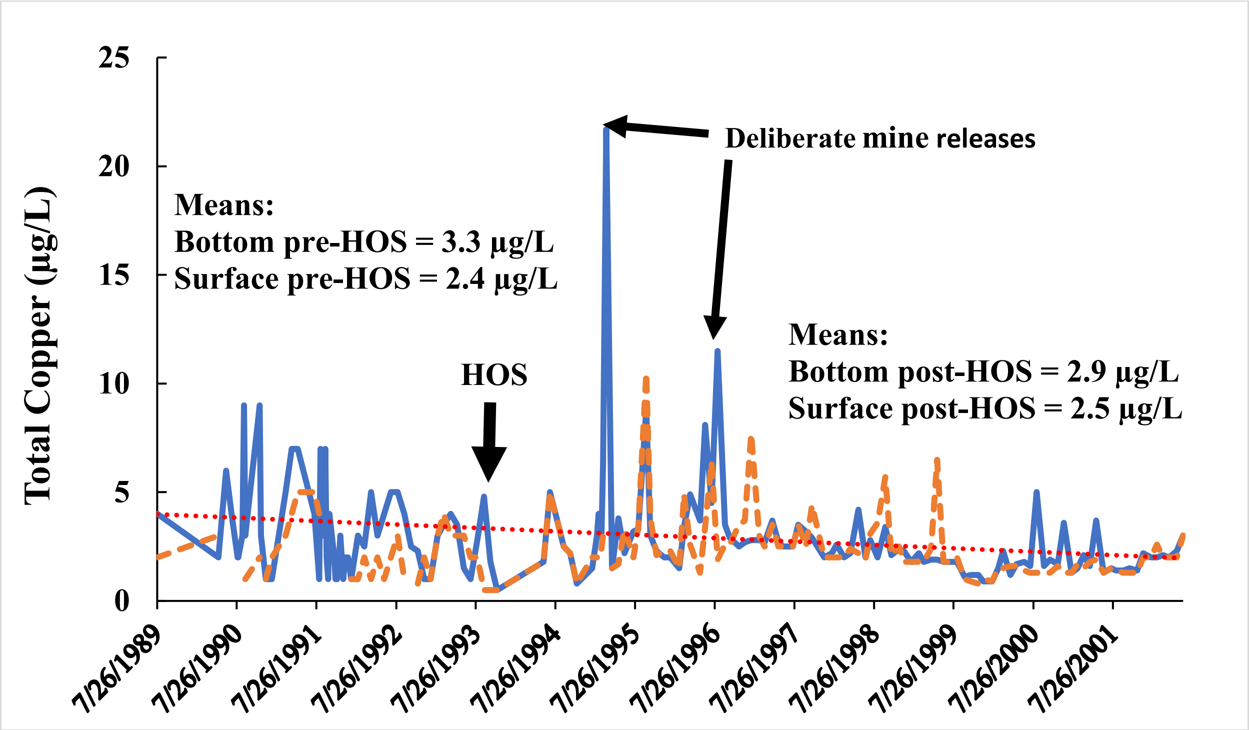

Fig. 2. Changes in ΣCu concentrations in bottom (solid line) and surface (dashes) water in Camanche Reservoir 1989- June 1993 (before HOS) and July 1993-June 2002 (after HOS). Slight downwards trend (dots) for surface ΣCu was not significant ($R^2 = 6\%$, $P = 0.024$ to 0.74, depending on the time periods compared). Bold face indicates most representative (longer term) results.

The seasonal pattern of concentrations of both metals in deep water for individual years before (1991-92) and after HOS (1993-94 and 1997) varied considerably after HOS (Figs. 3 a-b, Table 1). The two years following 1994 are not comparable to the pre-HOS data due to deliberate mine releases in 1995 and 1996. In addition, HOS was used only at the very end of the stratified period in 1996 so is atypical. Comparing 1991-92 (pre-HOS) with the most comparable post-HOS year

(1997), bottom water ΣCu, showed a small overall decrease after HOS (Fig 3a). For unknown reasons but possibly related to the 1986-92 drought, bottom water ΣCu showed a declining trend prior to HOS (990-June 1993) so that the lower concentrations and short-term trends (Aug 1993-95) cannot be ascribed to HOS. After 1998, an extensive mine cleanup begins to dominate a downward tread (Fig. 2).

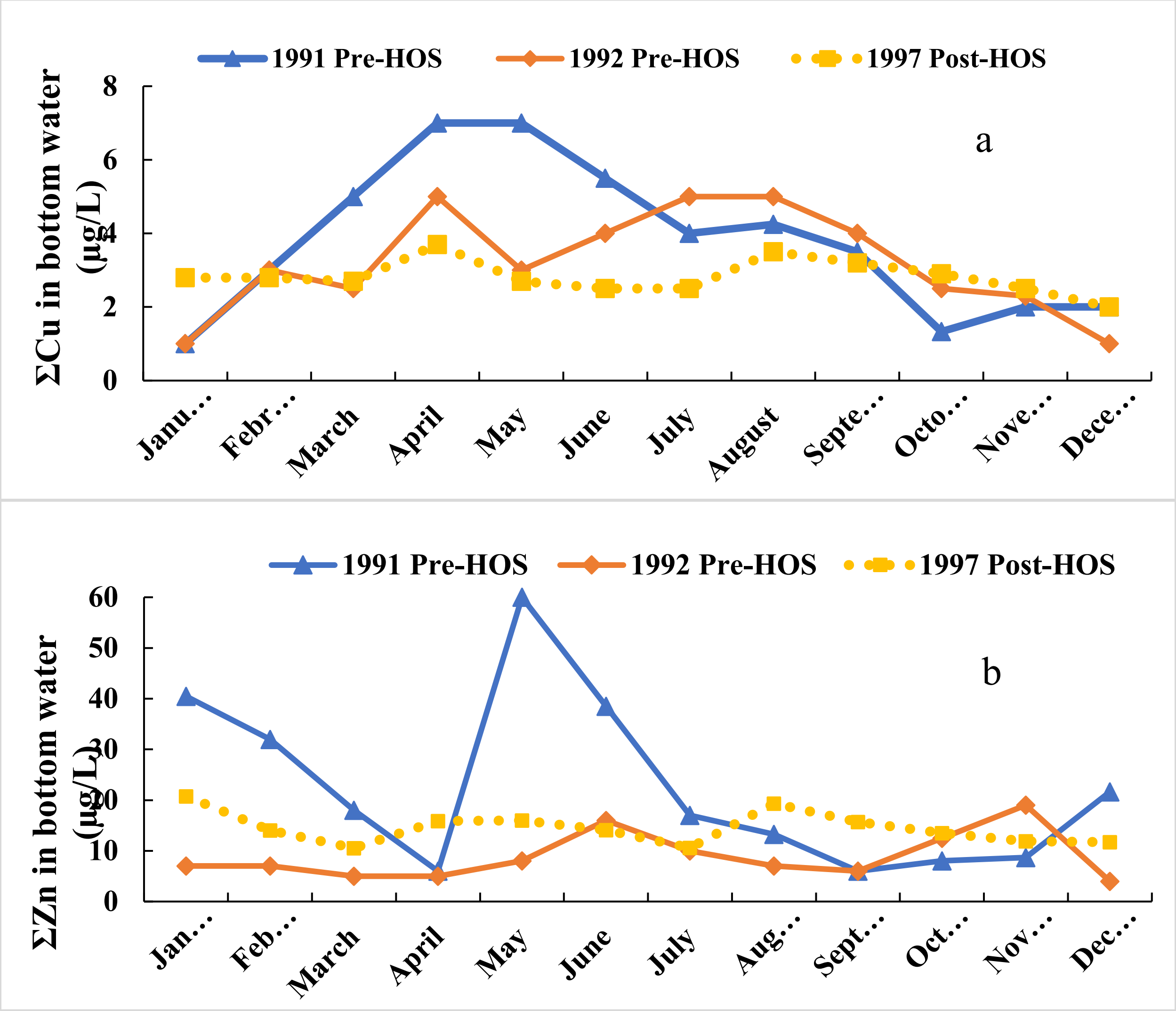

Fig. 3 a-b. Yearly changes in (a) ΣCu and (b) ΣZn bottom water for comparable years before HOS (1991 triangles, 1992, diamonds - both full lines), after HOS (1997, squares, dotted line). Small average annual declines (12% Cu and 30%, Zn from already low levels) before and after HOS are not easily discernable from the monthly values for either heavy metal.

Because the occasional higher concentrations of copper are the most troublesome for fishery managers, their frequency is important. The reduction in peak values of bottom water ΣCu after HOS is shown in Figs. 4 a-b. Exceedances at or above an arbitrary concentration of 5 µg/L prior to HOS were double (4/y) those after HOS (2/y, Fig. 4a). Bottom water ΣCu concentrations following HOS in July 1993 show five peaks in 1995-06 which were generally higher, though less prolonged, than before HOS (Fig. 4b). These peaks ranged from 6.3 to 21.7 ug/L (average 11.3

ug/L) and were due to a planned release from the abandoned mine's holding ponds at the end of a wet winter. The responsible agencies reasoned that the inevitable overflows from the flooded ponds would be most diluted, and thus least toxic, when the Mokelumne River was running at its spring maximum. No fish kills occurred in the river or reservoir during these short-lived peaks in ΣCu.

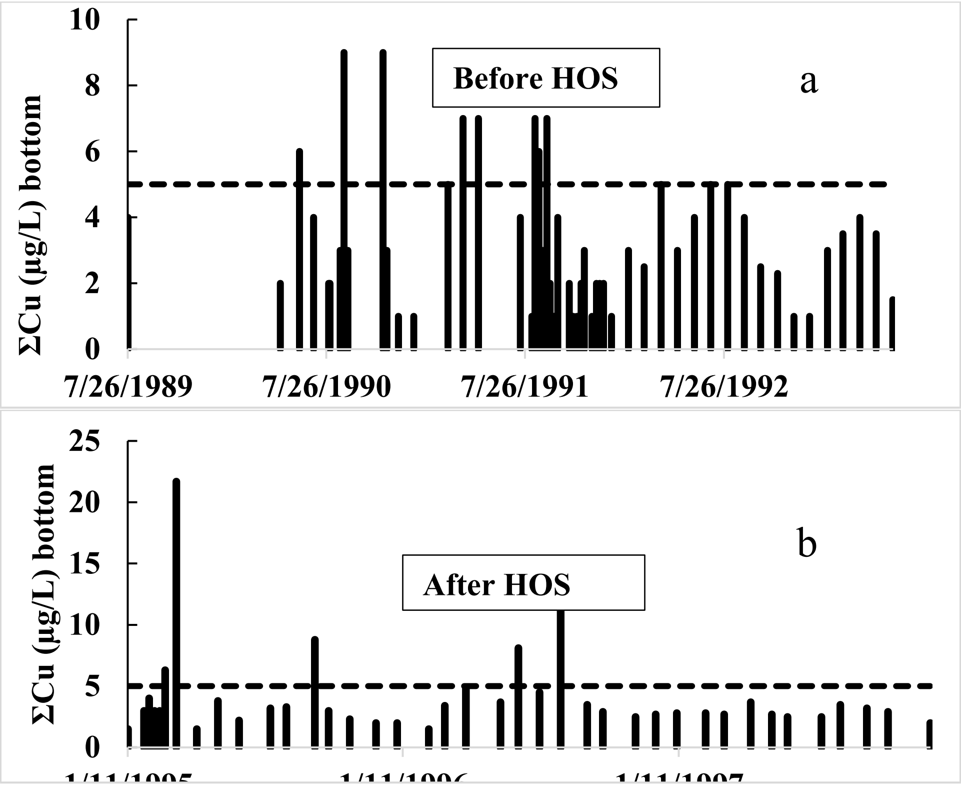

Fig. 4 a-b. Higher concentrations of ΣCu (> 5 µg/L) in bottom waters comparing (a) pre-HOS and (b) post-HOS periods. Occasional high values can be more important than averages for fish toxicity

Surface water Cu does not reach the hatchery directly but is experienced by most of the reservoir biota. The epilimnion is not greatly affected by HOS, which is confined to the deeper hypolimnion with a deliberate gap of several meters between the top of the HOS plume and the bottom of the thermocline to prevent any early destratification (Horne et al. 2019). However, interaction occurs from hypolimnion to epilimnion via leakage around the thermocline edges, breaking internal waves (Horne & Goldman, 1994, Mortimer, 2004), and as the thermocline lowers in the autumn incorporating deeper water. Each winter the lake mixes top to bottom, so changes in the hypolimnion metals in summer will be reflected in the next year's epilimnion. The trends of average ΣCu in the surface water were like that found for the deep-water ΣCu before and after oxygenation, though changes were smaller. Comparing similar periods (July-Nov) immediately before and after oxygenation, there was slightly more ΣCu in surface waters following HOS operation in 1993 ($\bar{x}$ = 2.0 µg/L) than before oxygenation in 1992 ($\bar{x}$ = 1.7 µg/L, Table 1). Further declines as well as increases occurred over time (Fig. 2, Table 1), but the main effect of HOS can only be demonstrated over the first three years after HOS. Increases due to deliberate but intermittent release of mine water (3/8/95 to 1/11/96 and 3/6/96 to 9/11/96) and reductions due to a major $10 million cleanup in summer-fall 1999 are beyond the scope of this paper. None of the changes for ΣCu at the bottom or surface water near the dam were statistically significant.

Zinc

The mean concentration of bottom water ΣZn for four years prior to oxygenation (1989-92) was 17.7. µg/L (Fig. 5, Table 2;). After HOS (July 1994-Dec 1995), mean ΣZn in deep water fell by about one-third to 12.1 µg/L (Fig. 3b). Over a longer period (1994- 2004), ΣZn fell only slightly further to 11.3 µg/L. Surface water ΣZn followed a similar pattern to that in deep water and fell from 11.2 µg/L before HOS to 7.7 µg/L (1994-95) and over a longer period to 8.3 µg/L (Fig. 5. Table 2). Soluble or filtered Zn, which contains the potentially toxic un-chelated ion fraction (Zn^{++}), was only measured in the bottom water layer and on fewer occasions prior to HOS (n = 9). Nonetheless, the overall pattern was like ΣZn in both deep and shallow water. Soluble Zn in the bottom water fell from 11 µg/L to 4.4 µg/L (1994-95).

Table 2. Zinc concentrations in various periods before and after HOS installation in Camanche Reservoir. Oxygenation began in summer 1993 until turnover in early November and was resumed in summer 1994. All values in µg/L. The deep-water layer was 0-2 m above the bottom sediments. sd = standard deviation.

Metal, depth	**Mean before HOS**	**sd, (range)**	**Mean conc. after HOS**	**sd, (range)**	**Decrease (µg/L)**
Total Zn	**17.7** (1989-Dec 92)	17, (2-83)	**12.1** (July 1994-Dec 1995)	6.5, (1-30.1)	**5.6**
bottom			**11.3** (July 1994-Dec 2004)	6.0 (2-33.6)	**6.4**
Total Zn	**11.2** (1989-July 93)	13.6, (2-63)	**7.7**(July 1994-Dec1995)	5.9 (2.25.1)	3.5
surface			**8.3** (July 1994-Dec 2004)	5.3 (2-25.8)	**2.9**
Diss. Zn	**11** (1991-91)	12.1 (7-44)	**4.4** (July 1994-Dec 1995)	5.1 (3-27)	**6.6**
bottom			**4.9** (July 1994-Dec 2004)	3.5 (3-27)	**6.1**

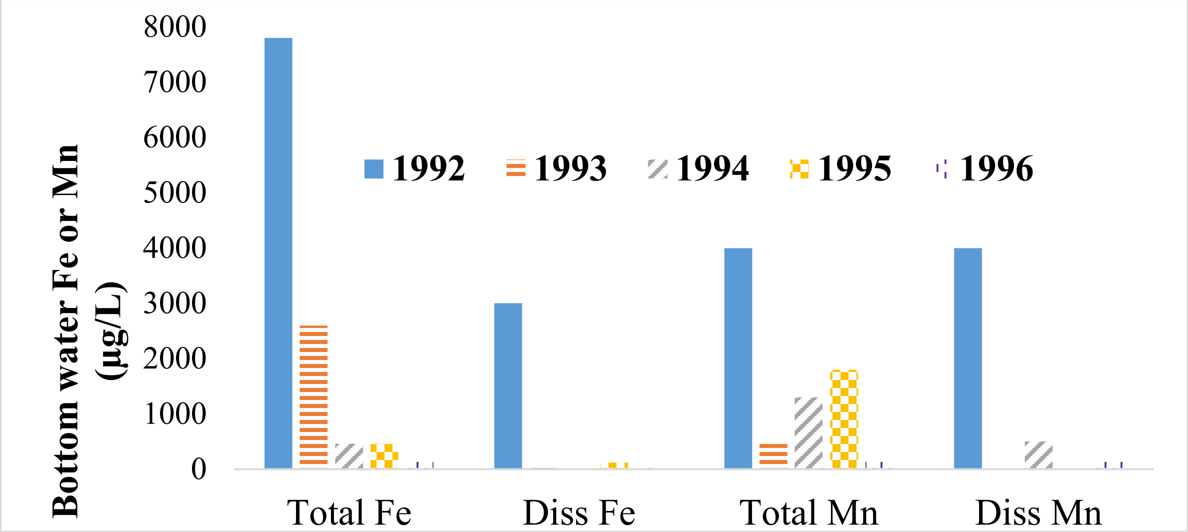

Fig. 5. Changes in ΣZn in the bottom (solid line), and surface waters (dashes) of Camanche Reservoir 1989- June 1993 (before HOS) and July 1993-June 2002 (after HOS). The decline trend line (dots) is more pronounced than for Cu and, although not large (R^2 = 13%) due high variance, the long-term trend is probably real since P = 0.00015 for the 1989-92 (before HOS) versus 1994-

2004 (long period after HOS including mine cleanup). Shorter period comparisons were not significantly different.

As with ΣCu, further declines as well as increases in ΣZn occurred over time but the main effect of HOS can only be observed over the first three years. In this time comparisons were not significantly different even using paired monthly samples. Only the long-term decline in bottom water ΣZn showed a statistically significant decline [means, 17.5 µg/L (1989-1992), 8.3 µg/L (1994-2004), $P<0.05$)]. Most of the decline is likely due to the upstream mine cleanup which began in 1998 and not due to direct effects of the oxygen in HOS.

Depth profiles of zinc. The changes, or lack of them, in the concentrations of ΣZn with depth before and after HOS are shown in Table 3. In two of the years prior to HOS (1990 and 1992), the ΣZn stratification mimicked the turbidity pattern described in a previous paper (Horne 2019b), with higher values at the bottom. In two years after HOS, there was no (1997) or small (2000) indication of Zn vertical stratification after HOS. For turbidity, there was a moderate overall water column increase for the first year of HOS (1993) which did not persist into the following years. The temporary turbidity increase was ascribed to re-suspension of small (~ 2 µm calcite particles) produced by "lake whiting" caused by the previous dense cyanobacteria blooms which were eliminated by HOS in the years following 1993. Since calcite ($CaCO_3$) contains no Cu or Zn it would not affect the distribution of these metals as shown in Table 3. The measured homogenization of Zn (and Cu) was probably due to mixing in the turbulent bottom water oxygenated plume which was about 9 m thick (Horne et al. 2019).

Table 3. Depth profiles of total zinc before and after HOS. There was stratification of zinc with depth prior to HOS but not after HOS probably due to homogenization within the oxygenated Speece Cone plume (the reservoir was shallower during the drought in 1992 than in later years so bottom was at a shallower depth ~ 22 m). nd = no data collected at these depths in 2000.

Depth (m)	Zinc (µg/L)	Zinc (µg/L)
	Before HOS	After HOS
	5/2/1990	*7/16/1997*
0	7	6.3
5	4	6.6
10	4	6
15	13	7.8
20		6.9
25		6.9
Average	**7**	**6.8**
	8/5/1992	*8/9/2000*
0	4	4.5
5	4	5.3
10	4	nd
15	4	nd
20	7	nd
25-30	nd	6.3
Bottom	nd	6.1
Average	**4.6**	**5.4**

Iron and manganese

After HOS, bottom water ΣFe dropped forty-fold from 7,800 to 200 µg/L and dissolved Fe fell by a factor of 150 from 3,000 to 200 µg/L (Fig. 6). Similarly, bottom water ΣMn dropped thirty-fold from 4,000 to 130 µg/L and dissolved Mn fell over 400 times from 4,000 to 5-13 µg/L (Fig. 6). Fe and Mn did not rise in 1995 when HOS was only briefly operational in late October and early November because overturn had begun, and oxygen naturally reached the sediments. There was a slight rise in ΣMn (from 1,300 to 1,800 µg/L, Fig. 6). Since this was not accompanied by a rise in dissolved Mn it is likely due to stirring of bottom waters during overturn.

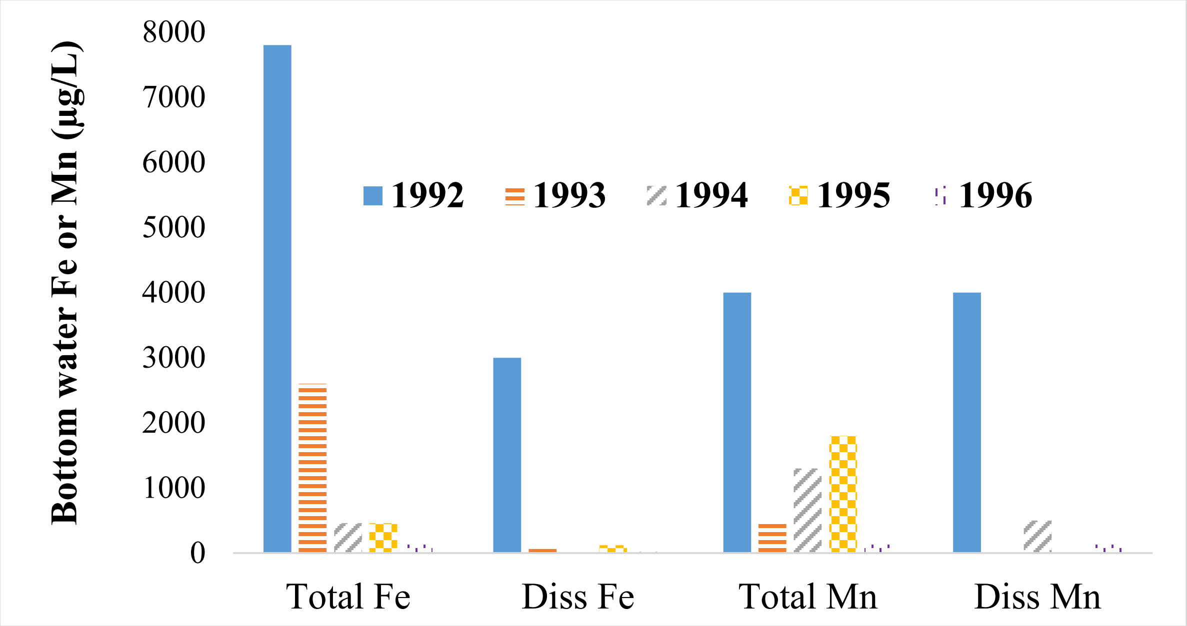

Fig.6. Annual average total and soluble Fe and Mn concentrations in the bottom water of Camanche Reservoir before and after HOS which began in July 1993. Diss = dissolved metal fraction. Both metals showed large declines following HOS.

Metals in suspended particles

In November 1993 following a period of HOS, the dry weight concentrations of Cu (0.006 ppm) and Zn (0.02 ppm) in the deep-water nephelometric particles were much lower than in granite rock that underlies the main part of the drainage (Cu, 13 ppm; Zn, 60-130 ppm; Table 4). Similar findings were found for Fe, Al, and Si. The low Si indicates that, although silica diatom frustules were microscopically visible in the nephelometric layer (Horne 2019b), they were a small fraction of the total particles. The metals analysis supports a nephelometric layer comprised primarily of small particles and a few dead algae.

Table 4. Chemical analysis (in ppm) of copper, zinc, iron, aluminum, and silica in the nephelometric layer (proto-sediments) from the two sites in deep water (0-2 m from bottom) in the central section of Camanche Reservoir and near the Speece Cone, the influent to the downstream

hatchery fish hatchery, and detritus in the hatchery egg trays. Collected in early Nov 1993 towards the end of an oxygenation period.

	Main reservoir	**300 m from HOS**	**Hatchery influent**	**Egg tray**	**Earth's crust**
Cu	0.006	0.006	<0.005	0.038	13 ppm - granite 24 crust
Zn	0.02	0.02	<0.02	0.1	130 ppm - basic rock; 60 ppm acid rock
Fe	0.41	0.49	0.54	14	5
Al	0.31	0.38	0.4	18	8.1
Si	5.1	5.2	5.2	38	28

Discussion

The water quality of the deepest layer of water in Camanche Reservoir is important since it is the source of downstream discharge to the fish hatchery and Mokelumne River fishery. The Speece cone HOS intake was also close to this bottom water layer. Heavy metals are such a concern for salmonid fisheries in soft water that even small long-term trends are important.

Metals and reservoir management with HOS

Although Camanche Reservoir lies only about 5 km downstream of the abandoned Penn Copper mine and the sediments contained 5-10 times background (Bond. 1988, Martin et al. 1980), the concentrations of Cu and Zn in the reservoir water were relatively low (3.2-3.5 μg/L for ΣCu). These concentrations are minute compared with mine leaks which can range from 100 to 69,000 μg/L in the arid Southwest USA (Rösner 1998). Camanche Reservoir ΣCu levels were also at the lower end of typical lake levels of 4-10 μg/L in the USA (ATS 2012). Because of the already low pre-HOS concentrations, substantial reductions were not possible with any method including HOS. In addition, the effect of anoxia (low redox potential) solubility for the Cu and Zn likely to be present in the Camanche Sediments (insoluble silicates and sulfides) is slight, especially compared with Fe or Mn species. Long-term average yearly ΣCu concentrations in the bottom water that flows to the salmon hatchery and river did decrease, if only slightly, after HOS from 3.3 μg/L (1989-92) to 2.9 μg/L (1994-2002).

The toxicity of copper is due to the unchelated soluble form. In Camanche Reservoir soluble copper was almost always below detection levels (2-3 μg/L) in the entire water column. The unchelated fraction of soluble Cu was not measured. However, studies in creeks influenced by abandoned mines in Berkeley (the campus has a mine as do nearby hills) show <20% of soluble Cu to be in the toxic, labile form (Hauri and Horne 1997) and maybe much less in eutrophic lakes (Xue and Sigg. 1993). Thus, the actual copper toxicity in the reservoir water was probably minimal. The lowest threshold toxicity values for fish vary, especially with hardness, but one comprehensive survey gives an average of 2.6 μg/L as the threshold chronic effect for 10 fish species at a hardness of 30 mg/L $CaCO_3$ and for algae at 16 μg/L (Australian Government Initiative 2000). The USEPA freshwater criteria (USEPA 2007 revision) also gives a lowest chronic value for Chinook salmon of 5.9 μg/L (Chapman 1978) for a low hardness range (20-45 mg/L $CaCO_3$) that just overlaps with that at Camanche Reservoir (~ 17-20 mg/L $CaCO_3$). A lower value for cyanobacterial processes such as N_2-fixation (5 µg/L, Horne and Goldman 1974) is still above many of the concentrations found at Camanche Reservoir. These laboratory toxicity values were made using unchelated water. Concentrations of total zinc (ΣZn) in surface waters are higher than those for ΣCu (Martin et al. 1980) but zinc toxicity also occurs at higher levels. Like ΣCu, and for the same reason of bottom water homogenization by the HOS plume, the ΣZn levels declined substantially (~ 30%) after HOS.

In conclusion, there was little positive or negative effect of the oxygen from HOS on bottom water bottom water Zn or Cu over short periods whether these be for entire years or during the stratified period when the Speece cone was switched on. Based on the principle of Cu and Zn mobility in anoxic and oxygenated conditions, it could have been concluded in the late 1980s that HOS would have had little or no direct effect on ΣCu. Nonetheless, direct proof based on the pre- and post-HOS data was needed to convince the state and local agencies and the environmental groups who brought the lawsuit that initiated a Speece cone installation (Horne 2019a). This paper provides that assurance.

In contrast, a decline was expected for Fe and Mn when oxygenated water replaced anoxia. Fish hatchery operators were concerned about a "brown slime or foam" in the egg trays and raceways because it is difficult to wash off any solids or slime buildups on the delicate fish eggs (Horne 2019a). Obvious candidates for such brown slimes were iron and/or manganese oxy-hydroxides such as non-crystalline goethite, FeO(OH). The latter is the first oxidation product of anoxic reservoir outflows although the brown color may be exaggerated by a covering of golden-brown diatoms once exposed to sunlight. Following HOS, Mn and Fe fell more (73% and 96%, respectively) than Cu or Zn and also declined more rapidly. All reductions occurred during the first summer-fall HOS in 1993 and persisted over the 13 years of measurements. The post-HOS concentrations of ΣFe was about 200 µg/L which can be compared to other lakes such as the Great Lakes (120 µg/L, GLWQB 1976) or 15-30 µg/L in Clear Lake, a eutrophic lake about 50 km from Camanche Reservoir where dense *Aphanizomenon* blooms use iron for N_2-fixation and associated processes (Wurtsbaugh and Horne 1983).

In Camanche Reservoir, the horizontal, bubble-free plume HOS operation resulted in a decrease in bottom water ΣMn from 4,000 to 130 µg/L. This is similar to results found for a rising bubble plume HOS in Carvins Cove Reservoir, Virginia where ΣMn in the hypolimnion declined from >2,000 µg/L to <50 µg/L (Gantzer et al. 2008). Although Mn is more slowly oxidized than Fe in streams emerging from bogs or when in aerated water, this difference was not seen for Camanche Reservoir where both metals declined soon after oxygenation. Iron precipitation in the presence of oxygen is well-known but Mn is usually much slower since the oxidized forms may remain suspended. Reservoir Mn is best suppressed by maintaining oxygenated sediments year-round.

Deep-water homogenization "reduces" bottom water Cu and Zn

The relatively small absolute reductions of Cu and Zn following HOS (~ 30% from already low concentrations) can be explained by the mixing of the bottom water into the entire 9-m thick oxygenation HOS plume. The very bottom water (0.2 m) contained higher metal levels than the rest of the plume. Cu and Zn declines were not likely due to precipitation of metal-rich particles back to the sediments. It is unlikely that oxygen at 0.5% by volume equivalent in water would change aquatic sediment Cu or Zn binding (biotic ligand model, USEPA, 2016). From the viewpoint of fish toxicity, the mechanism is not important because the modest reduction in Cu and Zn delivered to the hatchery would be reduced by either process. In contrast, the large reduction of Fe and Mn was attributable to oxygen in the HOS plume and was a clear benefit to the hatchery and river fishery. For Camanche Reservoir at least, oxidation of Fe and Mn and homogenization in the HOS plume for Cu and Zn provide a unique protection against heavy metal toxicity. If the reservoir were to reach a trophic state where sediment anoxia was eliminated and HOS and concomitant bottom water mixing was no longer required, the tailwater levels of Cu and Zn would rise slightly.

Changes in phytoplankton biomass cannot account for the decline in the four heavy metals following HOS. Although chl-*a* levels dropped ~ 79% and algal biomass by a similar amount. (Horne and Beutel 2019), phytoplankton in Camanche Reservoir contributed only small amounts of trace metals before and after HOS. The maximum chl-*a* change was from 50 to 5 μg/L which reflects a drop in Cu of only 0.0025% [assuming algae cell Cu = 4.5 mg Cu/kg dw (USGS 1998) and chl-*a* = 1% of dw]. Similar conclusions were drawn for Zn, Fe, and Mn.

Lessons for management

Uneasiness about novel solutions such as HOS is common among reservoir and fishery managers alike and is not without basis considering some dubious lake management methods (Beaty, 1995). Although there was a leaking mine upstream and there were high metal concentrations in the sediments, this study showed that Cu and Zn levels in the deep hypolimnion water of Camanche Reservoir prior to HOS were generally lower than feared. But that was cold comfort for hatchery managers when the exceptionally soft water occasionally caused small amounts of ΣCu present prior to HOS potentially exceeded the lowest 4-day chronic toxicity threshold.

However, with hindsight, the feared unknowns in hypolimnetic oxygenation can provide some comfort to hatchery mangers if HOS is considered in relation to the natural annual cycle of a reservoir or lake. Many temperate zone waters are holomictic and fully mixed top to bottom in winter, fully or partially satisfying any biological oxygen demand built up during thermal stratification. Flocculent particles in the nephelometric layer at the base of the hypolimnion as well as any products of anoxic conditions at the sediment-water microzone interface are swirled up and oxidized. No fish kills were ever associated with metals at overturn in Camanche Reservoir prior to HOS; oxygenation merely extended the oxygenated part of the natural cycle to all year. From a management viewpoint, the important fact is that in summer and fall average concentrations of Cu and Zn delivered to the hatchery did not show a substantial change.

Conclusions

- Oxygenation due to HOS had no direct effect on copper and zinc concentrations. This was expected based on the chemistry of these two metals.
- A small (12-30%) decline in bottom water copper and zinc, respectively, from already low concentrations did occur after HOS. The decrease was due to homogenization of the very bottom water (higher metal concentration) with the rest of the 9 m high HOS plume (lower metal levels) and not an effect of oxygen itself.

- Large declines in iron and manganese can be attributed directly to precipitation caused by HOS. This was expected based on chemistry of these two metals.
- HOS began in July 1993 but the cleanup of the upstream Penn Mine after 1998 dominated reservoir copper and zinc concentrations thereafter.

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