Summary Report on Metals and Metalloids in Clear Lake Based on Historical Data

A Report to the Blue Ribbon Committee for the Rehabilitation of Clear Lake

June 2022

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Contents

Executive Summary

This report addresses concerns raised about possible toxicity threats from metals in Clear Lake if the proposed Hypolimnetic Oxygenation (HO) pilot project in the Oaks Arm is executed. The HO comprises the addition of oxygen to the bottom waters of the lake when it falls to low levels (hypoxia), which typically occurs during the summer months. During the rest of the year, when the lake is actively mixing, Clear Lake has more than 5 mg/L in the bottom waters (oxic conditions). Thus, we can learn much about how the concentration of various metals respond to changes in dissolved oxygen (DO) concentrations by analyzing existing historic data. Here, we analyze the long-term data for metals and metalloids in Clear Lake collected monthly across the lake by the California Department of Water Resources (DWR) during the last 50 years to infer if oxic conditions result in the release of metals.

According to USEPA (2022), the metals and metalloids that commonly cause toxic effects include aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, and zinc. To evaluate seasonal trends for each of these metals, we plot monthly concentration data as boxplots, which identify median values and various percentiles (see Figs. 2-13). To put these values in context, we cite the numeric thresholds recommended to implement the California Toxics Rule (CTR) for aquatic life in freshwater and other criteria for metals published by the California State Water Resources Control Board.

To evaluate differences in metal concentrations under oxic and hypoxic conditions, we plot monthly DO concentrations as boxplots as done for the metals and define each month as being either 'oxic' or 'hypoxic' using the 5 mg/L threshold and median monthly values (Fig. 1). Monthly concentrations of metals were then binned according to these two categories of oxygen availability and a statistical test was used to determine if means between categories differed. Our results indicate (Fig. 0):

1. Dissolved oxygen concentrations had no significant effect on concentrations of aluminum, chromium, copper, iron, lead, mercury, selenium, and zinc; there was no statistical difference among their concentrations under oxic and hypoxic conditions.
2. There was a very small but significant positive effect of dissolved oxygen on nickel. Although median nickel concentrations were 0.5 microgram per liter higher under oxic conditions than under hypoxic conditions, the values were always well below nickel toxicity levels.
3. There was a significant negative effect of oxygen on arsenic and orthophosphate concentrations. Median arsenic concentrations were about 3 micrograms per liter higher under hypoxic conditions than under oxic conditions, but the values were always well below arsenic toxicity levels. Because lower concentrations of arsenic were measured during oxic conditions, the HO project should help to reduce arsenic concentrations during summer/hypoxic months.

Results from this report confirm that metal concentrations (except for nickel, at environmentally low levels) do not increase during oxic periods. This strongly supports the hypothesis that increasing summer DO concentrations using hypolimnetic oxygenation will improve lake water quality and pose no new threats.

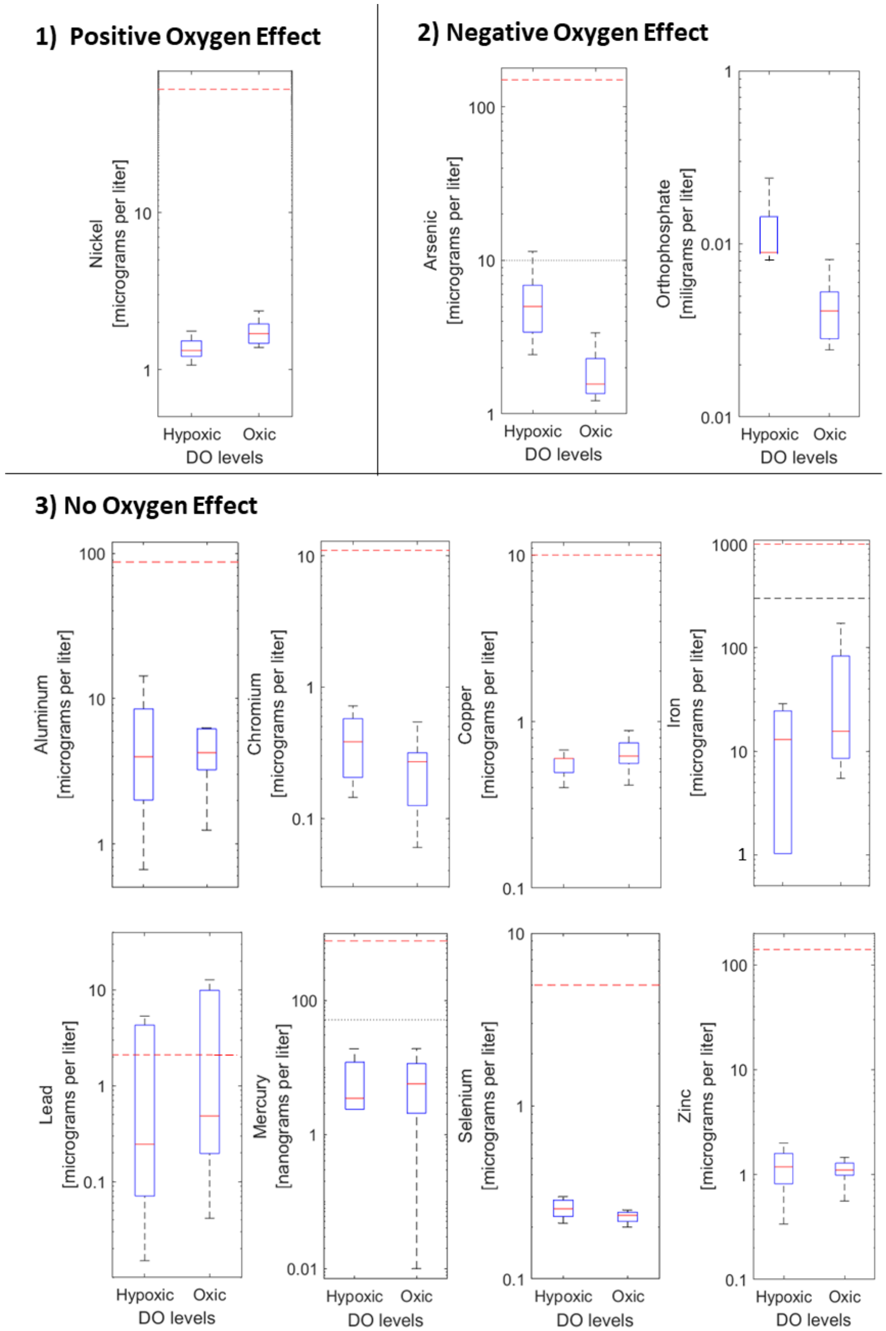

Figure 0. *Boxplots of monthly values of metal concentrations in the three Arms of Clear Lake grouped by oxic or hypoxic conditions of dissolved oxygen (i.e. equal and above 5 mg/L and below 5 mg/L, respectively). Oxic boxplots were computed using 21 data points (7 months in 3 arms), whereas hypoxic boxplots only had 15 data points (5 months in 3 arms). Each subplot shows a different metal. Note that y-axis is in log scale except for copper. The horizontal red line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample. Red dashed lines show the numeric thresholds recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Black dotted lines show the California goal for protection of human health from consumption of organisms for mercury and drinking water standard for arsenic.*

0 Introduction

At the Blue Ribbon Committee meeting on May 25, 2022, a question was raised concerning toxicity threats from metals in Clear Lake arising from a proposed hypolimnetic oxygenation (HO) project in the Oaks Arm. The process of HO adds oxygen to the bottom waters of the lake during the summer period when dissolved oxygen (DO) typically falls to much lower levels than are present in winter. These low oxygen (reducing) conditions are known to allow the release of nutrients and perhaps also some metals or metalloids from the sediments, and it is precisely the formation of these conditions that HO is intended to prevent.

For much of the year, particularly in winter, Clear Lake is rich in oxygen. Thus, by examining the long-term data that have been collected for metals and metalloids in Clear Lake, it is possible to directly determine if highly oxygenated water results in the release of metals from lake sediments.

Metals and metalloids are electropositive elements that occur in all aquatic ecosystems. Some metals and metalloids occur as oxyanions in their more oxidized state, such as arsenic and chromium. Although trace concentrations of some metal(loid)s are essential as nutrients, all metal(loid)s can be toxic at some level. Deteriorated water quality results when metal(loid)s are available above certain concentrations affecting the survival, reproduction, and behavior of aquatic organisms or human health.

According to USEPA (2022), the metals and metalloids that commonly cause toxic effects include:

- Aluminum
- Arsenic
- Cadmium
- Chromium
- Copper
- Iron
- Lead
- Mercury
- Nickel
- Selenium
- Zinc

Previous work by USEPA (summarized by Aptim, 2018) indicates that "Aluminum, arsenic, total chromium, copper, iron, mercury, methyl mercury, and nickel concentrations in Clear Lake sediment exceeded conservative screening levels for the majority of samples". However, we have not found a synthesis of metal and metalloid concentrations in Clear Lake water.

National Recommended Water Quality Criteria are described in several USEPA documents:

- Water Quality Criteria, 1972 ("Blue Book")
- Quality Criteria for Water, 1976 ("Red Book")
- Quality Criteria for Water, 1986 ("Gold Book")

These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states and tribes to use the established water quality standards. National water quality criteria are grouped in aquatic life criteria, human health criteria and organoleptic effects criteria.

In May 2000, USEPA promulgated CWA 303(c) water quality criteria for priority toxic pollutants in California's inland surface waters and enclosed bays and estuaries in the "**California Toxics Rule**" (CTR), which was adopted by the California State Water Resources Control Board (SWRCB). The CTR filled the gap in California's water quality standards necessary to protect human health and aquatic life beneficial uses. The CTR criteria are similar to those published in the National Recommended Water Quality Criteria, mentioned above. In 2007, the SWRCB published an Assessment Thresholds Table with the numeric thresholds recommended to implement selected water quality goals.

Table 1. Numeric thresholds recommended to implement California Toxic Rule (CTR) for aquatic life in freshwater criterion, and drinking water maximum contaminant levels (MCLs) for the different metals published by the SWRCB.

	CTR Aquatic Life Criterion #	**Drinking Water Standards**	
Metal	**or National Recommended Water Quality Criterion**	**Primary MCL**	**Secondary MCL**
Aluminum	*87 µg/L	1,000 µg/L	200 µg/L
Arsenic	150 µg/L	10 µg/L	--
Cadmium	2.2 µg/L	5 µg/L	--
Chromium (total)	--	50 µg/L	--
Chromium (VI)	11 µg/L	10 µg/L	--
Copper	*10 µg/L	1,300 µg/L	1,000 µg/L
Iron	1,000 µg/L	--	300 µg/L
Lead	*2.1 µg/L	15 µg/L	--
Mercury (inorganic)	0.77 µg/L	2 µg/L	--
Nickel	*61 µg/L	100 µg/L	--
Selenium	5 µg/L	50 µg/L	--
Zinc	*140 µg/L	--	5,000 µg/L
	# Dissolved, continuous concentration, 4-day average	MCL, maximum contaminant level	
	*Assuming hardness of 120 mg/L as $CaCO_3$		

1 Data available for Clear Lake

The California Department of Water Resources (DWR) has measured metals and metalloids in Clear Lake since 1970 (https://wdl.water.ca.gov/waterdatalibrary/Map.aspx). For this report, we present data from the three main sampling stations located at the deepest site of the three basins in the lake (Upper Arm (UA), Oaks Arm (OA), and Lower Arm (LA)). Samples were taken monthly at discrete depths from the surface to the deepest depth of the station.

Data from the last 50 years in Clear Lake are presented using boxplots of monthly depth-averaged concentrations for each month (1 = January and 12 = December) for each of the three Arms. As a result, the trends of metal concentrations under different oxygenation conditions can be directly seen: (a) From January through May (months 1, 2, 3, 4, 5) and November-December (months 11 and 12) the lake is generally well mixed and oxygenated from top to bottom, whereas (b) from June through October (months 6-10) the lake episodically stratifies and develops low levels of dissolved oxygen below 5 mg/L (hypoxia) in the water adjacent to the sediment (Fig. 1).

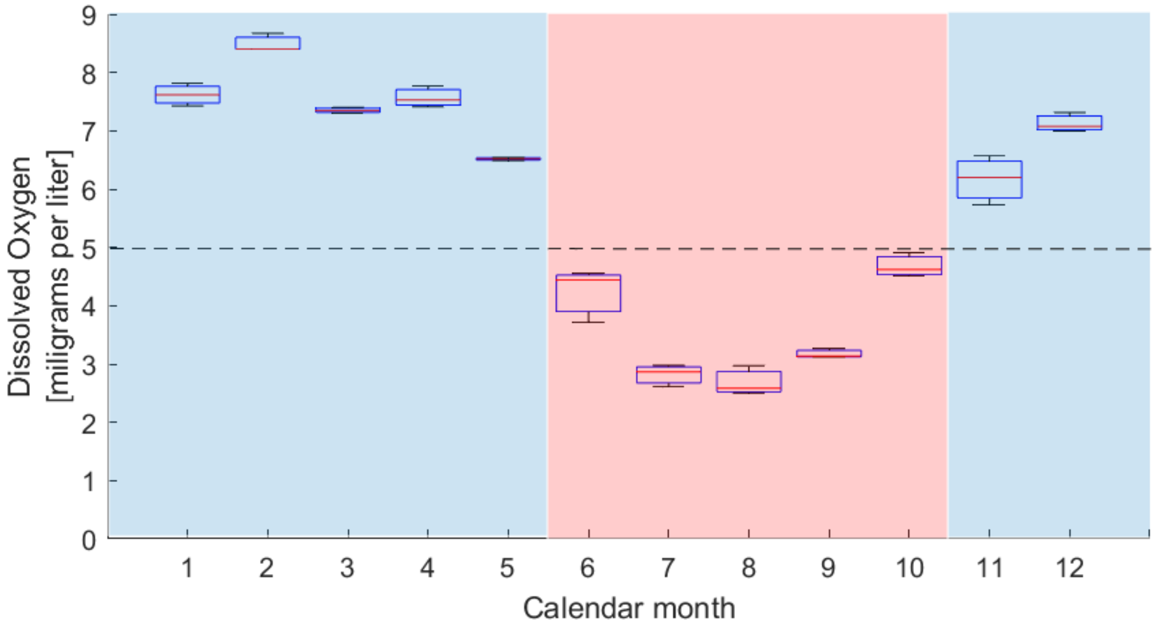

***Figure 1**. Dissolved Oxygen boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) in Clear Lake between 1970 and 2020. The horizontal red line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample. Red means hypoxic conditions and blue oxic conditions.*

1.1 Aluminum

Aluminum concentrations typically remained below toxic levels for aquatic life in freshwater (87 µg/L) year-round in Clear Lake. Median values ranged between 0.8 and 9 µg/L, with the low median values observed in August and the high median values measured in March (Fig. 2). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

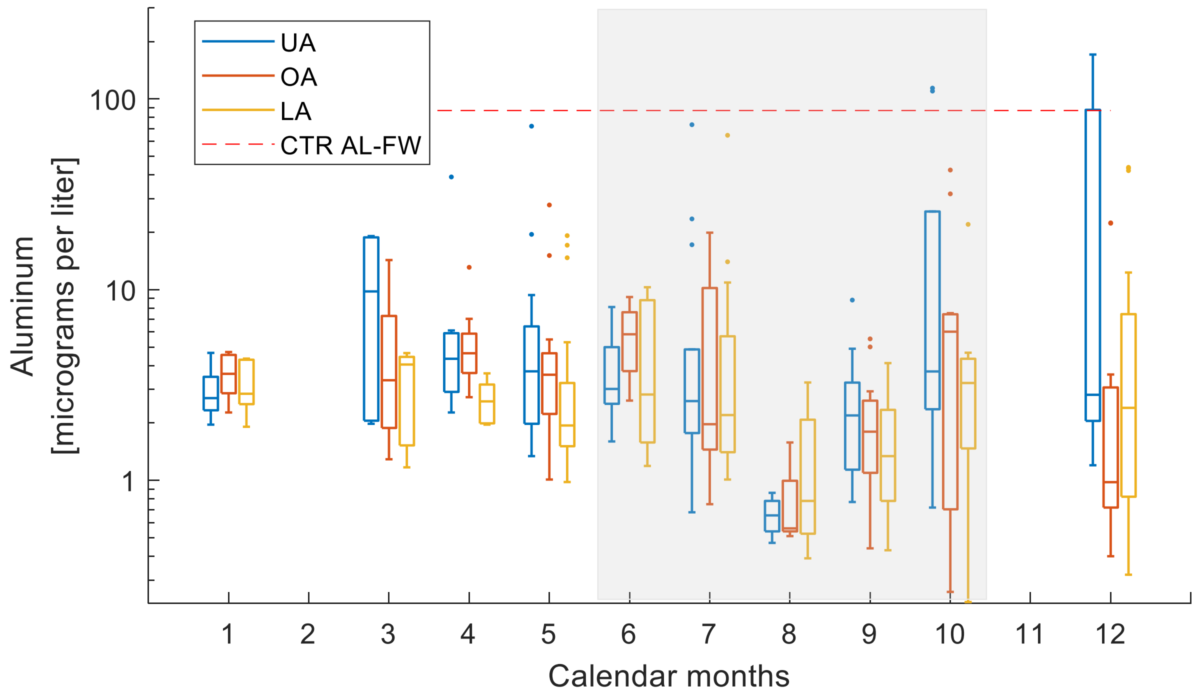

***Figure 2**. Dissolved Aluminum boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.2 Arsenic

Arsenic concentrations remained below toxic levels for aquatic life in freshwater (150 µg/L) year-round in Clear Lake. Also, median arsenic concentrations remained below the numeric threshold for the California public health goal for drinking water (10 µg/L), although 75th percentile values exceeded 10 µg/L during August and September. Higher concentrations occurred during summer months (median values typically about 7.5 µg/L) when low dissolved oxygen would have existed for at least part of the time, whereas base level values (about 2.5 µg/L) have been measured during winter when the water column was typically well mixed and fully oxygenated (Fig. 3). Similar trends of arsenic concentrations were observed when comparing values at the lake surface and next to the sediments (not shown). Note that the arsenic concentrations in the Oaks Arm are not consistently higher than the other two arms. Hence, it is not clear whether or not the source of arsenic is the mine waste from the Sulphur Bank Mercury Mine. Interestingly, seasonal variability of arsenic is very similar to orthophosphate (Fig. 4), which suggests that the same geochemical mechanisms apply to both constituents, which typically occur as the oxyanions AsO_4^{3-} and PO_4^{3-}.

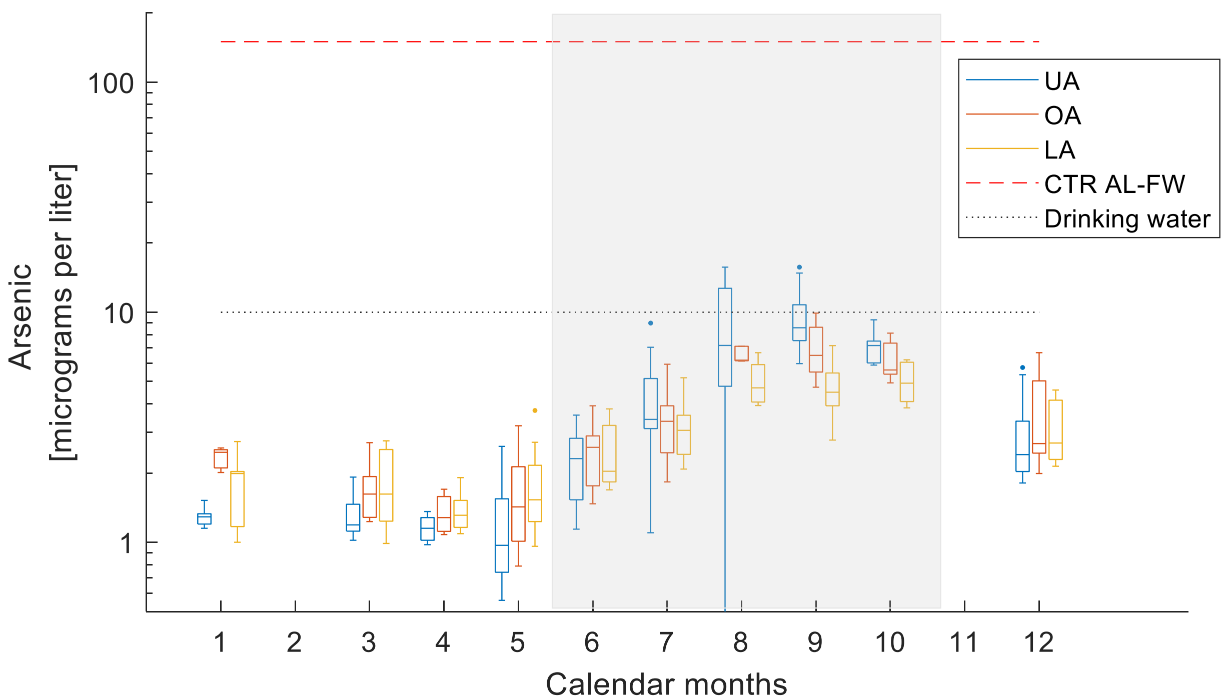

***Figure 3**. Dissolved Arsenic boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Black dotted line shows the California public health goal for drinking water. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

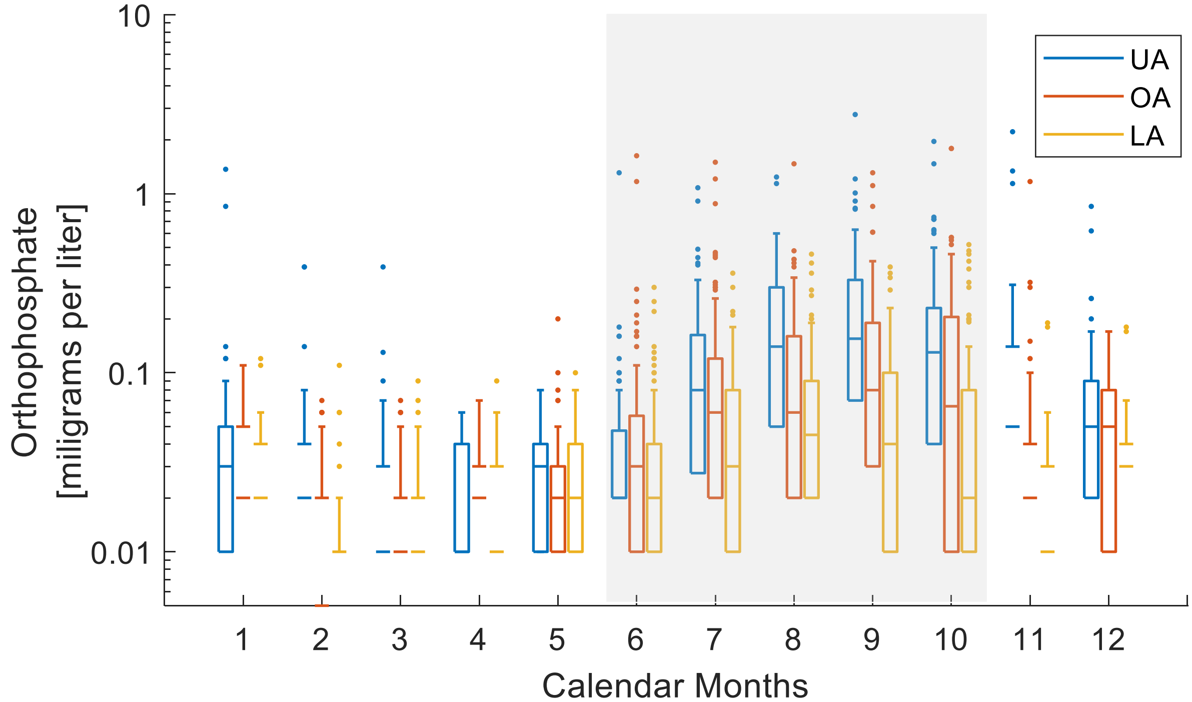

***Figure 4**. Dissolved Orthophosphate boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. Some horizontal lines may not have box. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Limit of detection is 0.01 mg/L. Gray shading indicates months when the lake was hypoxic.*

1.3 Cadmium

Cadmium concentrations remained below toxic levels for aquatic life in freshwater (2.2 µg/L) year-round in Clear Lake. Given the large proportion of analyses below the reporting limit, there is no discernable seasonal trend for this metal in Clear Lake (Fig. 5). The small number of data points in this graph are because most measurements were below detection levels.

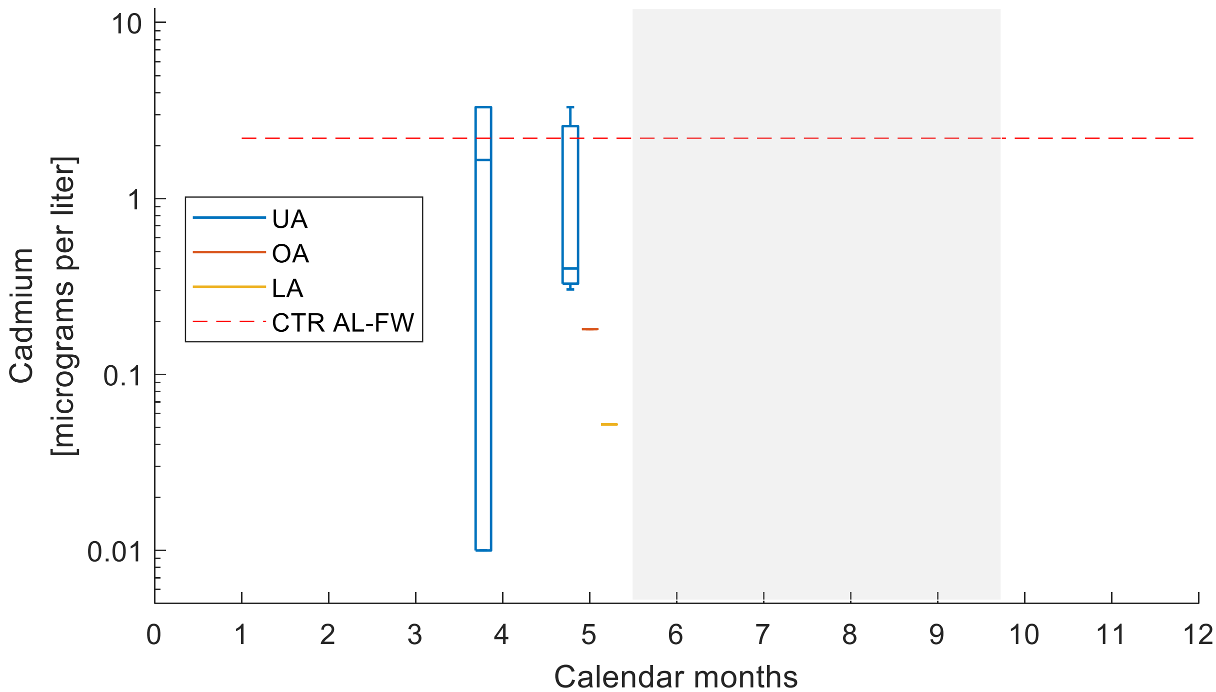

***Figure 5**. Dissolved Cadmium boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The small data points in this graph are because most measurements were below detection levels. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.4 Chromium

Chromium concentrations remained below toxic levels for aquatic life in freshwater year-round in Clear Lake (11 µg/L). Median values were very low during the first half of the year (0.1 µg/L), whereas median values were up to 0.8 µg/L for the second half of the year (Fig. 6). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

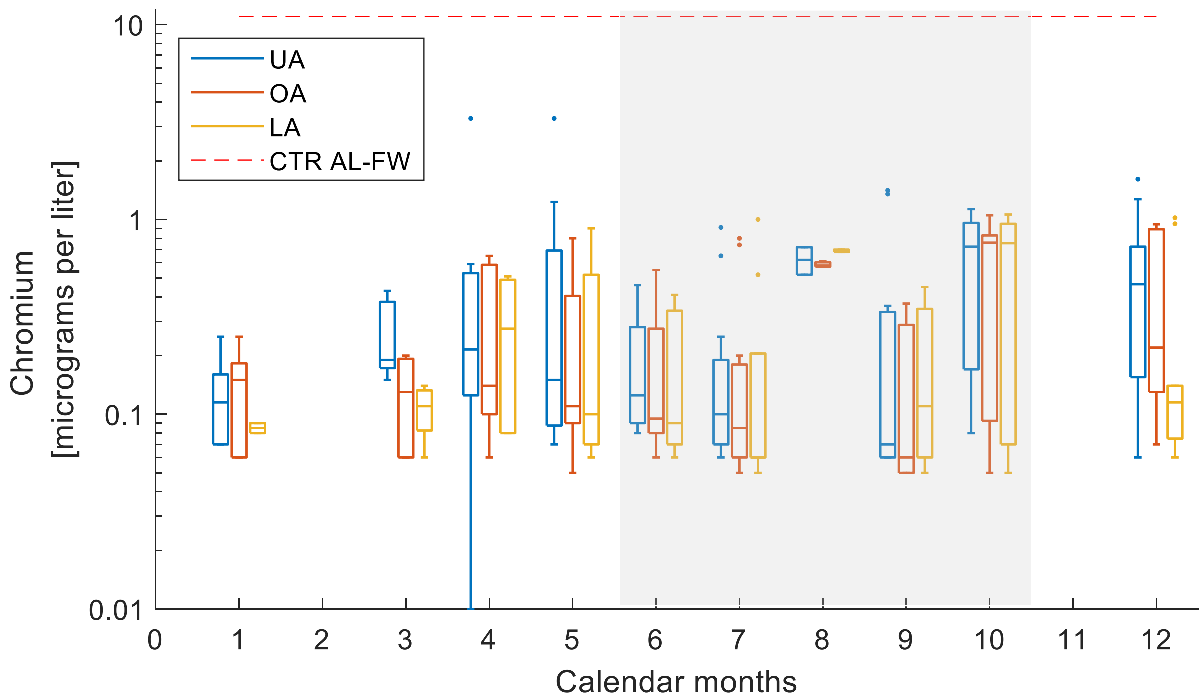

***Figure 6**. Dissolved Chromium boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.5 Copper

Copper concentrations remained below toxic levels for aquatic life in freshwater (10 µg/L) year-round in Clear Lake. Median values were below 1 µg/L for most of the year (Fig. 7). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

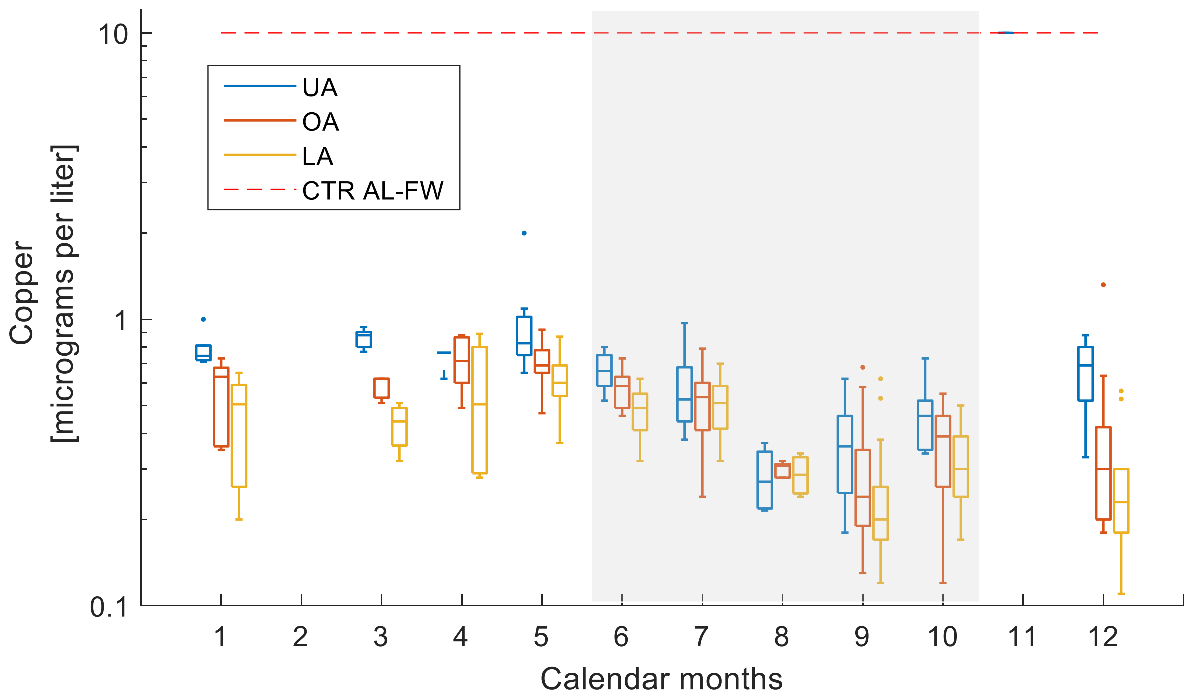

Figure 7. *Dissolved Copper boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.6 Iron

Aluminum concentrations remained below toxic levels for aquatic life in freshwater (1,000 µg/L) year-round in Clear Lake. Median values ranged between 2 and 20 µg/L, except for November when concentrations were close to 100 µg/L (Fig. 8). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

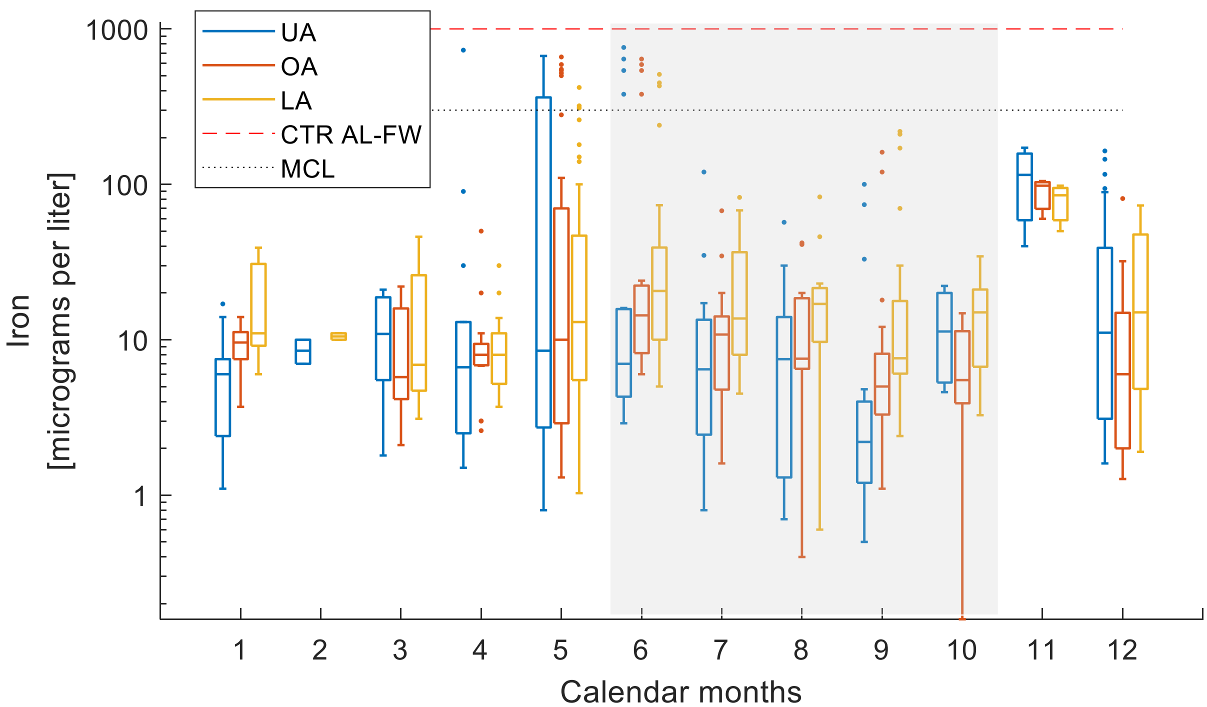

Figure 8. *Dissolved Iron boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. The black dashed line is the secondary MCL for iron in drinking water. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.7 Lead

On average, median lead concentrations remained below toxic levels for aquatic life in freshwater year-round in Clear Lake (2.1 µg/L). Median values were less than 1 µg/L for most of the year (Fig. 9). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

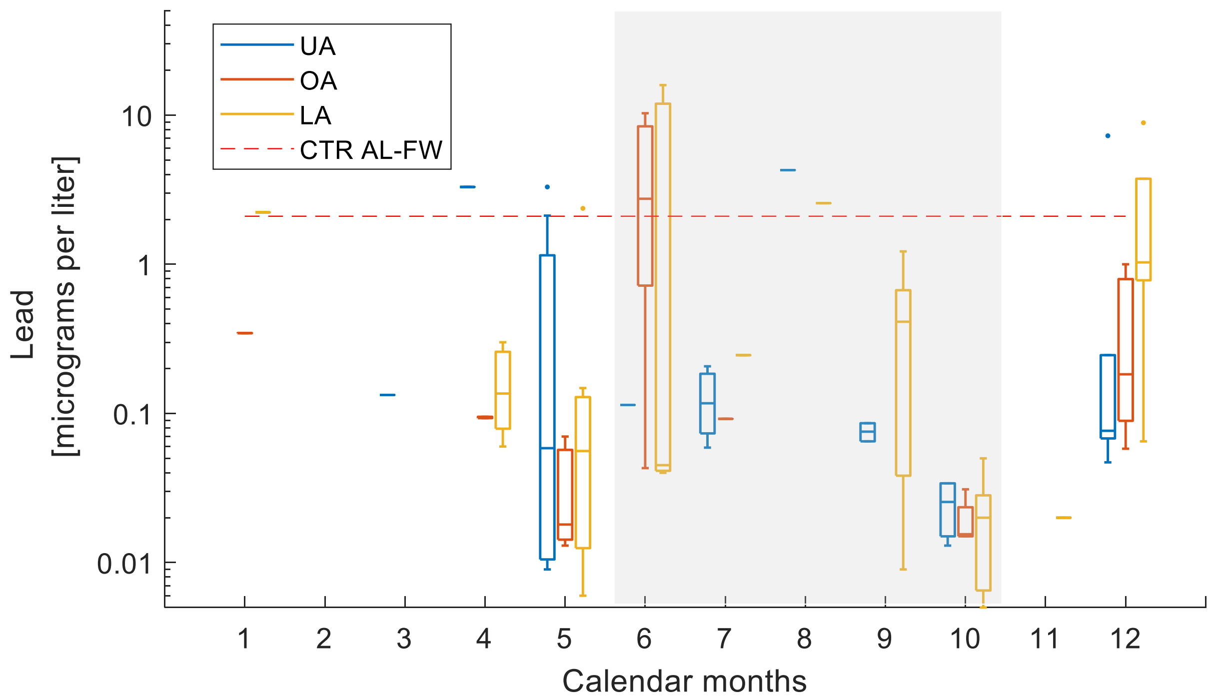

Figure 9. *Dissolved Lead boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.8 Mercury

Mercury concentrations typically do not exceed the toxic levels for aquatic life in freshwater in Clear Lake (770 ng/L) nor the California goal for protection of human health from consumption of organisms (i.e. eating fish) (51 ng/L). Median values ranged between 1 and 10 ng/L (Fig. 10). Similar trends of mercury concentrations were observed when comparing values at the lake surface and next to the sediments. Mercury concentrations were highest in the Oaks Arm, consistent with the hypothesis that Sulphur Bank Mercury Mine is the predominant source. There was no statistically significant difference in total mercury concentrations between periods that were oxic and hypoxic.

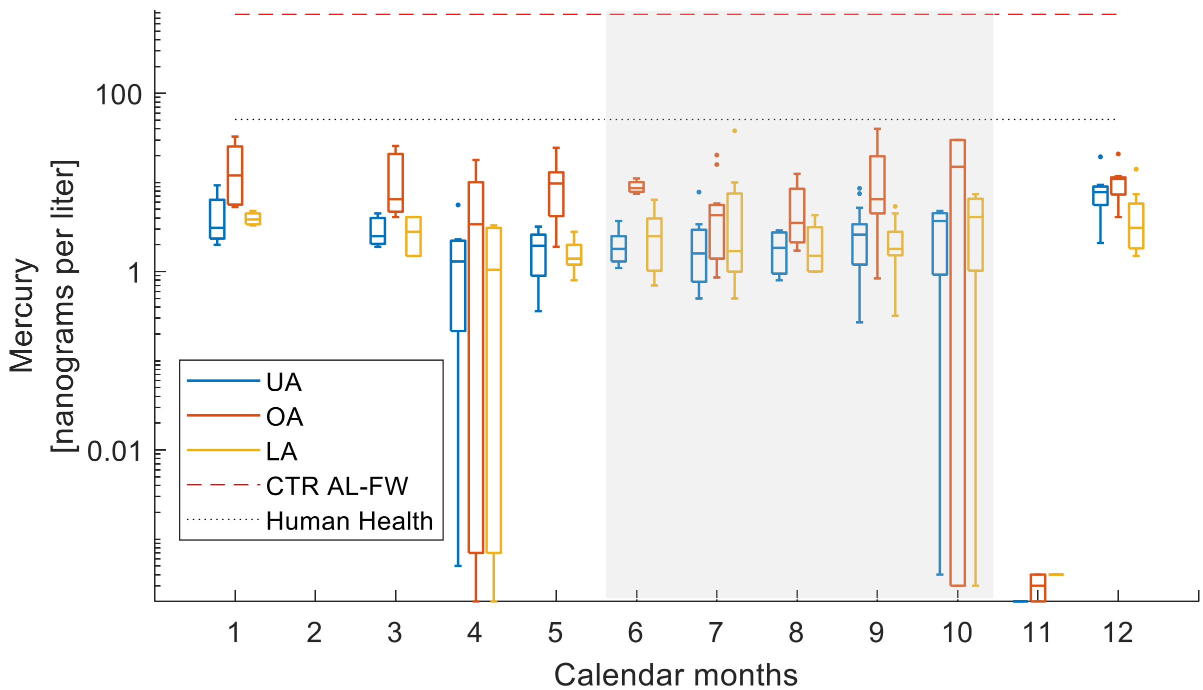

***Figure 10**. Total Mercury boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Black dotted line shows the human health goal. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.9 Nickel

Nickel concentrations remained below aquatic life criterion (61 µg/L) year-round in Clear Lake. Median values were lower during the summer (average of 1.3 µg/L) and higher during the winter (average of 1.8 µg/L) (Fig. 11). Concentrations are highest in the Upper Arm, which may be a function of geology of the watershed surrounding this arm. There was a small but statistically significant difference between oxic and hypoxic periods.

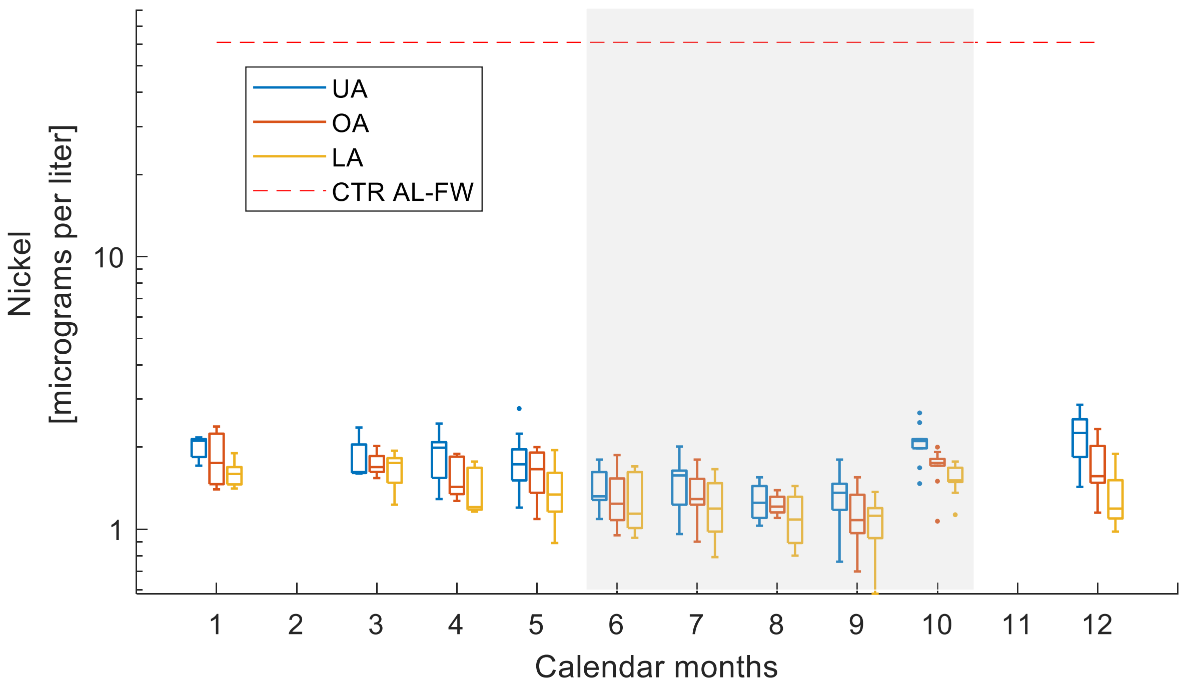

***Figure 11**. Dissolved Nickel boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.10 Selenium

Selenium concentrations remained far below toxic levels (5 µg/L) year-round in Clear Lake. Median values were always below 0.3 µg/L (Fig. 12). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

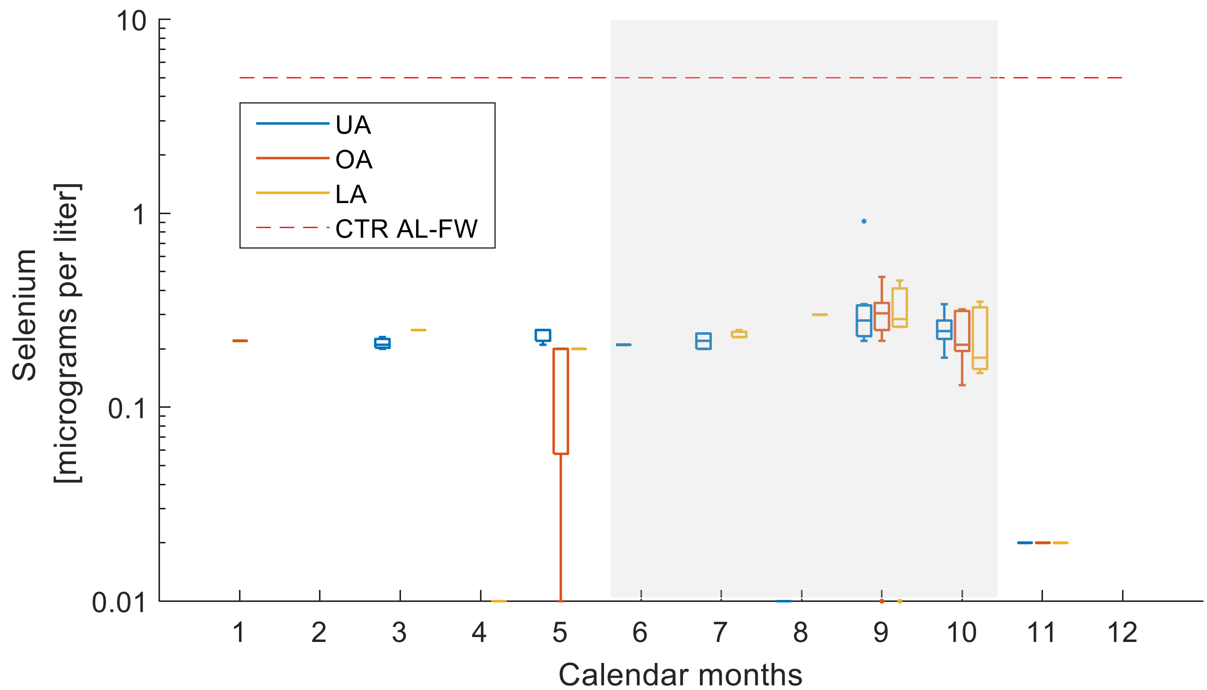

Figure 12. *Dissolved Selenium boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The small data points in this graph are because measurements were below detection levels. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

1.11 Zinc

Zinc concentrations remained below toxic levels (140 µg/L) year-round in Clear Lake. Median values of monthly averages ranged between 0.2 and 2 µg/L (Fig. 13). There was no statistically significant difference in concentrations between periods that were oxic and hypoxic.

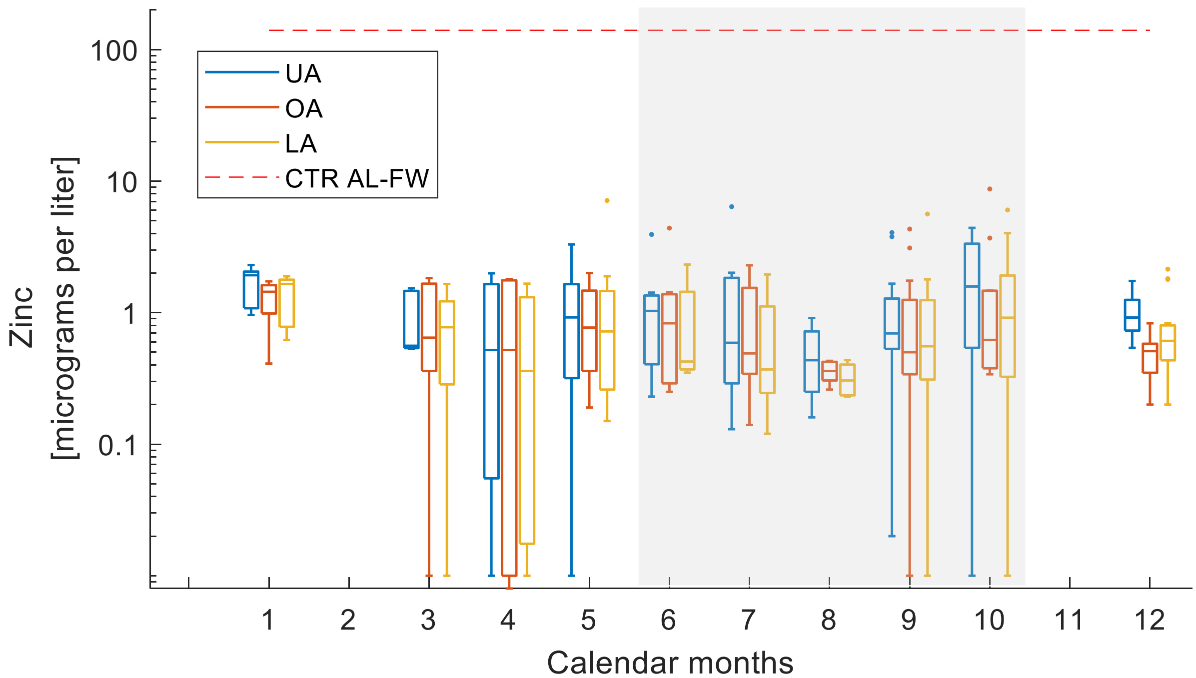

Figure 13. *Total Zinc boxplots of monthly-averaged concentrations for each month (1 = January and 12 = December) for the three arms in Clear Lake between 1970 and 2020. Red dashed line shows the Numeric threshold recommended to implement California Toxic Rule (CTR) for Aquatic Life in Freshwater (AL-FW) criterion. Note that y-axis is in log scale. The horizontal line in each box represents the median of all values. The bottom and top of each box are the 25th and 75th percentiles of the sample, respectively. The extent of the whiskers shows the 5th and 95th percentiles of the sample, and individual points indicate outliers. Gray shading indicates months when the lake was hypoxic.*

2 Conclusions

A review of 50 years of monitoring data indicates that metal and metalloid concentrations typically remained below regulatory criteria for protection of aquatic life and human health year-round in Clear Lake.

For nickel, the mean values were lower during the summer and larger during the winter when more oxygen was present (Fig. 11). Nonetheless, the values were always well below aquatic life criteria indicating potential toxicity. Nickel concentrations were highest in the Upper Arm, which may be a function of the geology of the watershed surrounding this arm. Other metals including aluminum, chromium, copper, iron, lead, selenium, and zinc did not show a clear seasonal pattern.

For arsenic and orthophosphate, higher concentrations were present during the summer months when low oxygen concentrations were occurring. At all times, the values were well below arsenic aquatic life criteria; however, arsenic concentrations occasionally exceeded the drinking water standard (10 ug/L) during August and September. Lower concentrations of arsenic and orthophosphate were measured during fully oxygenated winter months (Fig. 3). This suggests that the HO project should result in lower concentrations of arsenic and orthophosphate in bottom water.

Examination of 50 years of data from Clear Lake indicates that metal concentrations (with the exception of nickel, at environmentally low levels) do not increase during periods of oxygenation. This strongly supports the hypothesis that increasing summer DO concentrations using hypolimnetic oxygenation will improve lake water quality in multiple ways, including lowering the existing concentrations of both arsenic and phosphorus, and pose no additional risks to humans or wildlife.

3 References

Aptim Federal Services, LLC (2018) Sampling and Analysis Plan for Human Health Risk Assessment Data Gap Sampling, Sulphur Bank Mercury Mine Superfund Site Clearlake Oaks, California. Prepared for the U.S. Environmental Protection Agency, in coordination with E2 Consulting Engineers, Contract number EP-S9-13-02, task order 0045, October, 2018, 637 p.

USEPA (U.S. Environmental Protection Agency) (2022) Metals, in Causal Analysis/Diagnosis Decision Information System (CADDIS), volume 2: Sources Stressors, and Responses. https://www.epa.gov/caddis-vol2/metals (accessed June 8, 2022).