

2014 Harding Reservoir Report
Rivers and Reservoirs Monitoring Program



Field Operations Division
Environmental Indicators Section
Aquatic Assessment Unit
December 2017

Rivers and Reservoirs Monitoring Program

2014

Harding Reservoir

Chattahoochee River Basin

**Alabama Department of Environmental Management
Field Operations Division
Environmental Indicators Section
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LIST OF ACRONYMS

A&I	Agriculture and Industry water supply use classification
ADEM	Alabama Department of Environmental Management
AGPT	Algal Growth Potential Test
CHL <i>a</i>	Chlorophyll <i>a</i>
DO	Dissolved Oxygen
F&W	Fish and Wildlife
MAX	Maximum
MDL	Method Detection Limit
MIN	Minimum
MSC	Mean Standing Crop
NTU	Nephelometric Turbidity Units
OAW	Outstanding Alabama Waters
ONRW	Outstanding National Resource Water
PWS	Public Water Supply
QAPP	Quality Assurance Project Plan
RRMP	Rivers and Reservoirs Monitoring Program
S	Swimming and Other Whole Body Water-Contact Sports
SD	Standard Deviation
SOP	Standard Operating Procedures
TEMP	Temperature
TN	Total Nitrogen
TMDL	Total Maximum Daily Load
TP	Total Phosphorus
TSI	Trophic State Index
TSS	Total Suspended Solids
USACE	United States Army Corp of Engineers
USEPA	United States Environmental Protection Agency
USACE	United States Geological Survey

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INTRODUCTION

Originally constructed by Columbus Electric and Power Company in 1926, Harding Reservoir, also known as Bartlett's Ferry, was acquired by Georgia Power in 1930 and operated for hydropower ever since. The reservoir stretches from just north of Columbus, GA to Valley, AL and covers 5,850 acres along the Alabama/Georgia state line. Most of Harding's flow comes from upstream West Point Reservoir and three large tributaries, two in Alabama (Osanippa and Halawakee Creeks) and one in Georgia (Mountain Oak Creek).

The Alabama Department of Environmental Management (ADEM) monitored Harding Reservoir as part of the 2014 assessment of the Chattahoochee River Basin under the Rivers and Reservoirs Monitoring Program (RRMP). Implemented in 1990, the objectives of this program are to provide data that can be used to assess current water quality conditions, identify trends in water quality conditions, and to develop Total Maximum Daily Loads (TMDLs), and water quality criteria. Descriptions of all RRMP monitoring activities are available in ADEM's 2012 Monitoring Strategy.

In 2004, the ADEM implemented a specific water quality criterion for nutrient management at the forebay station of Harding Reservoir, which has been monitored by ADEM since 1990. This criterion represent the maximum growing season mean (April-October) chlorophyll *a* (chl *a*) concentration allowable while still fully supporting Harding Reservoir's Public Water Supply, Swimming, and Fish & Wildlife (PWS/S/F&W) use classifications.

The purpose of this report is to summarize data collected at four stations in Harding Reservoir during the 2014 growing season and to evaluate growing season trends in lake trophic status and nutrient concentrations using ADEM's historic dataset. Monthly and/or mean concentrations of nutrients [total nitrogen (TN); total phosphorus (TP)], algal biomass/productivity [chl *a*; algal growth potential testing (AGPT)], sediment [total suspended solids (TSS)], and trophic state [Carlson's trophic state index (TSI)] were compared to ADEM's historical data and established criteria.

METHODS

Sampling stations were selected using historical data and previous assessments ([Fig. 1](#)). Specific location information can be found in [Table 1](#). Harding Reservoir was sampled in the dam forebay and upper reservoir along with two tributary stations; Halawakee and Osanippa Creeks.

Water quality assessments were conducted at monthly intervals, April-October. All samples were collected, preserved, stored, and transported according to procedures in the ADEM Field Operations Division Standard Operating Procedures (ADEM 2014), Surface Water Quality Assurance Project Plan (ADEM 2012), and Quality Management Plan (ADEM 2013).

Mean growing season TN, TP, chl *a*, and TSS were calculated to evaluate water quality conditions at each site. Monthly concentrations of these parameters were graphed with the closest available USACE flow data and ADEM's previously collected data to help interpret the 2014 results.

Figure 1. Harding Reservoir with 2014 sampling locations.

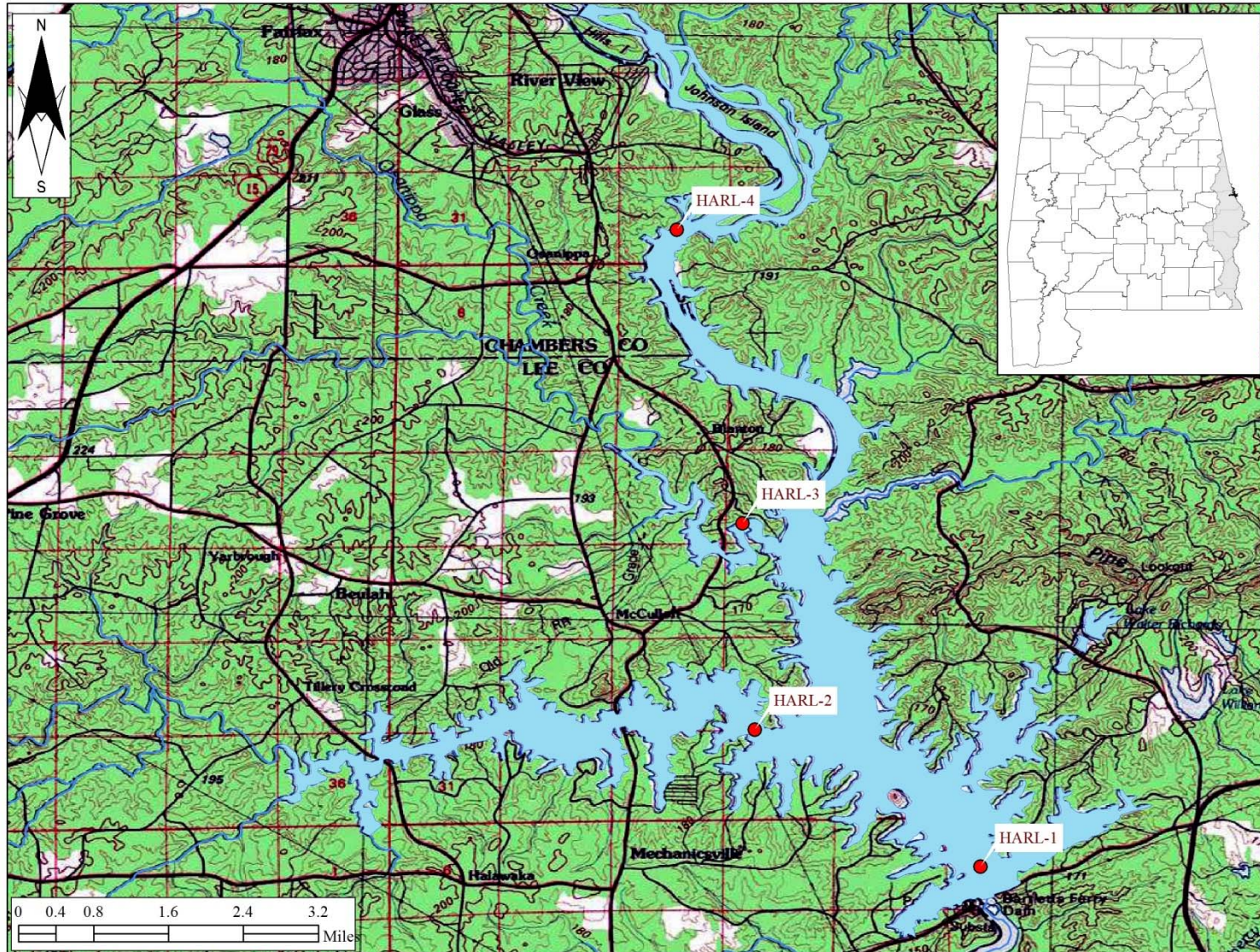


Table 1. Descriptions of the 2014 monitoring stations in Harding Reservoir.

HUC	County	Station Number	Report Designation	Waterbody Name	Station Description	Chl <i>a</i> Criteria	Latitude	Longitude
031300021109	Lee	HARL-1*	Lower	Chattahoochee R	Deepest point, main river channel, dam forebay.	15 µg/l	32.66763	-85.09190
031300021108	Lee	HARL-2	Halawakee Ck	Halawakee Ck	Deepest point, main channel, Halawakee Ck embayment.		32.68878	-85.12679
031300021105	Lee	HARL-3	Osanippa Ck	Osanippa Ck	Deepest point, main channel, Osanippa Ck embayment		32.72072	-85.12866
031300021109	Chambers	HARL-4	Upper	Chattahoochee R	Deepest point, main river channel, immediately downstream of Johnson Island.		32.76599	-85.13879

*Growing season mean chl *a* criteria implemented at this station in 2004.

RESULTS

Growing season mean graphs for TN, TP, chl *a*, and TSS are provided in this section ([Figs. 2 and 3](#)). Monthly graphs for TN, TP, chl *a*, TSS, DO, and TSI are also provided ([Figs. 4-8](#), and [11](#)), with mean monthly discharge included as an indicator of flow and retention time in the months sampled. AGPT results appear in [Table 2](#). Depth profile graphs of temperature, DO, and conductivity appear in [Figs. 9-10](#). Summary statistics of all data collected during 2014 are presented in [Appendix Table 1](#). The table contains the minimum, maximum, median, mean, and standard deviation of each parameter analyzed.

Stations with the highest concentrations of nutrients, chlorophyll, and TSS are noted in the paragraphs to follow. Though stations with lowest concentrations may not always be mentioned, review of the graphs that follow will indicate these stations that may be potential candidates for reference waterbodies and watersheds.

In 2014 the highest mean growing season TN value calculated among Harding Reservoir stations was in the upper station which is consistent with data collected 1999-2008 ([Fig. 2](#)). Mean TN values in the lower station have increased slightly while values in the upper station have remained steady since monitoring began. Mean TN values show no clear trends in the Halawakee Ck embayment while values in Osanippa Ck were lower in 2014 than 2004 and 2008. Monthly TN concentrations declined April through July then were generally higher through October in the lower, upper, and Halawakee Ck stations ([Fig. 4](#)). In the Osanippa Ck embayment TN concentrations fluctuated from their lowest point in April to their highest in October. Record high concentrations were measured in the upper station in August and September and in the Osanippa Ck station in May and October.

Mean growing season TP values in all Harding Reservoir monitoring locations increased from 1999 through 2004 then generally declined through 2014 ([Fig. 2](#)). Monthly TP concentrations in all Harding Reservoir monitoring locations were similar April-October, and were at or below historic means all months ([Fig. 5](#)).

A specific water quality criterion for nutrient management has been established for the lower station in Harding Reservoir. The growing season mean chl *a* concentration measured in

2014 was in compliance with the criteria limit ([Fig. 3](#)). In 2014 the highest mean growing season chl *a* value calculated among Harding Reservoir stations was in Osanippa Ck while the lowest value was in the upper station, which is consistent with data collected 1999-2014. Mean chl *a* values in the lower station were higher during 2014 than 2012, however the overall trend in this station, as well as the Halawakee Ck station, has declined from 2002-2014. Mean values in the upper and Osanippa Ck stations have varied little, 1999-2014. Monthly concentrations in August and October in Osanippa Ck were over double the other stations and the highest on record in October ([Fig. 6](#)). Monthly chl *a* concentrations in the riverine upper station were relatively low (near or <2.0 µg/l) most months monitored, however the highest concentrations on record were measured in May, August, and October. A historic high concentration was also measured in June in the lower station. Monthly concentrations in the Halawakee Ck station were near or below historic means all months with record low concentrations July-September.

The lowest mean TSS values on record were recorded in the upper and Osanippa Ck stations while slight increases, above 2012 values, were measured in the lower and Halawakee Ck stations. However, the overall trend in mean TSS values in all Harding Reservoir stations has declined 2003-2014 ([Fig. 3](#)). Monthly TSS concentrations measured in all stations were at or below historic means all months monitored ([Fig. 7](#)).

AGPT results at all stations in Harding Reservoir have remained phosphorus limited since testing began in 1999 ([Table 2](#)). MSC results in the lower station have remained below 5 mg/L MSC, the value that Raschke et al. (1996) defined as protective of reservoir and lake systems. The MSC value for Halawakee Ck however exceeded 5 mg/L in August 2014.

Measurements of dissolved oxygen (DO) at all stations met the ADEM Criteria (ADEM Admin. Code R. 335-6-10-.09) limit of 5.0 mg/L at 5.0 ft (1.5 m) ([Fig. 8](#)) though concentrations at the Halawakee Ck station were below 6 mg/L in September. Based on monthly DO profiles, thermal stratification was observed in the lower and in Halawakee Ck stations May-September. Anoxic conditions existed in the lower station from June through October at depths of 13m or greater, and in the Halawakee Ck station June through September at depths of 9m or greater ([Figs. 9 & 10](#)). Highest temperatures were measured in August.

Monthly TSI values were calculated using chl *a* concentrations and Carlson's Trophic State Index. TSI values calculated for the lower station ranged from oligotrophic in April and July to eutrophic in June and August while the upper station was oligotrophic most months and mesotrophic August and October (Fig. 11). In the Halawakee Ck station TSI values fluctuated between oligotrophic and mesotrophic throughout the sample season. Values in Osanippa Ck increased overall throughout the sample season from oligotrophic in April to high eutrophic in October.

Figure 2. Mean growing season TN and TP measured in Harding Reservoir, April-October, 1999-2014. Stations are illustrated from upstream to downstream as the graph is read from left to right.

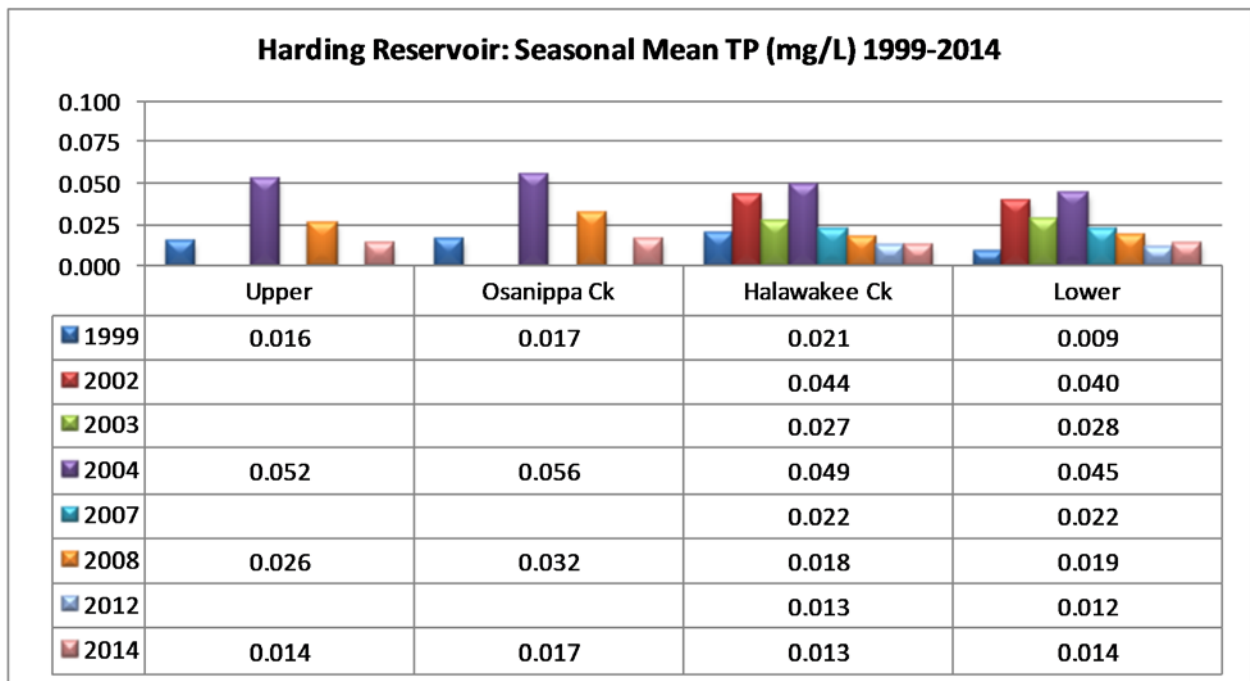
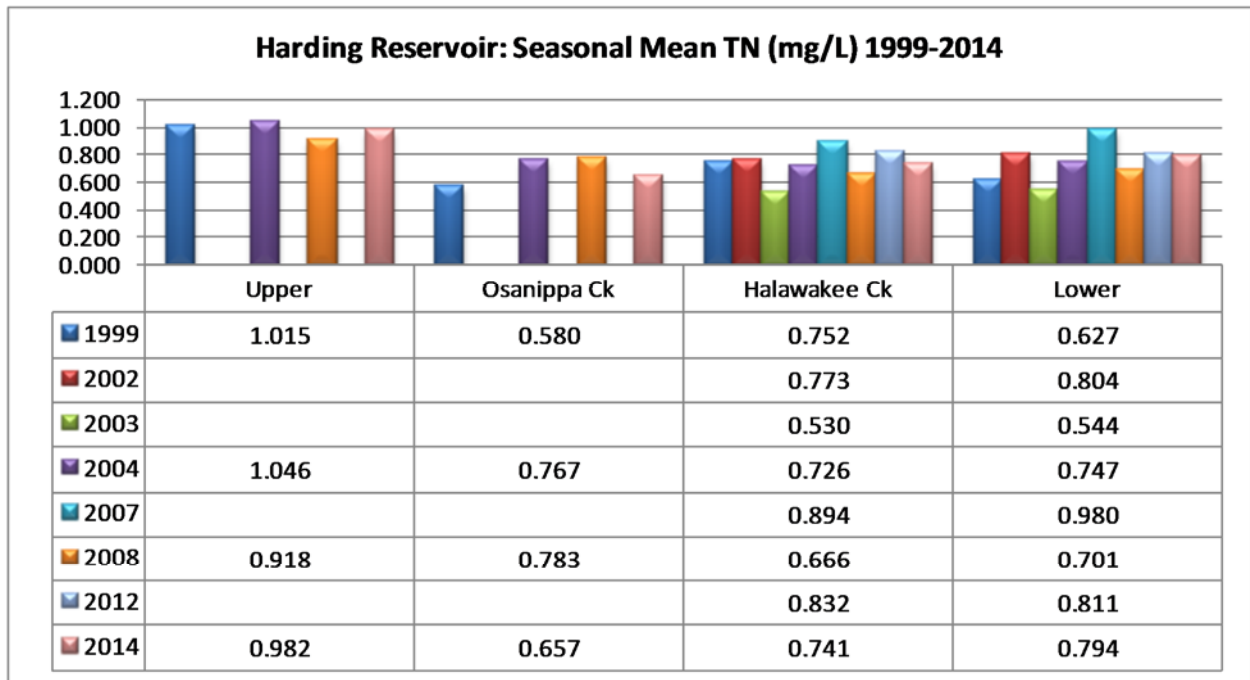


Figure 3. Mean growing season chl *a* and TSS measured in Harding Reservoir, April-October, 1999-2014. Stations are illustrated from upstream to downstream as the graph is read from left to right. Chl *a* criteria applies to the growing season mean of the lower station only.

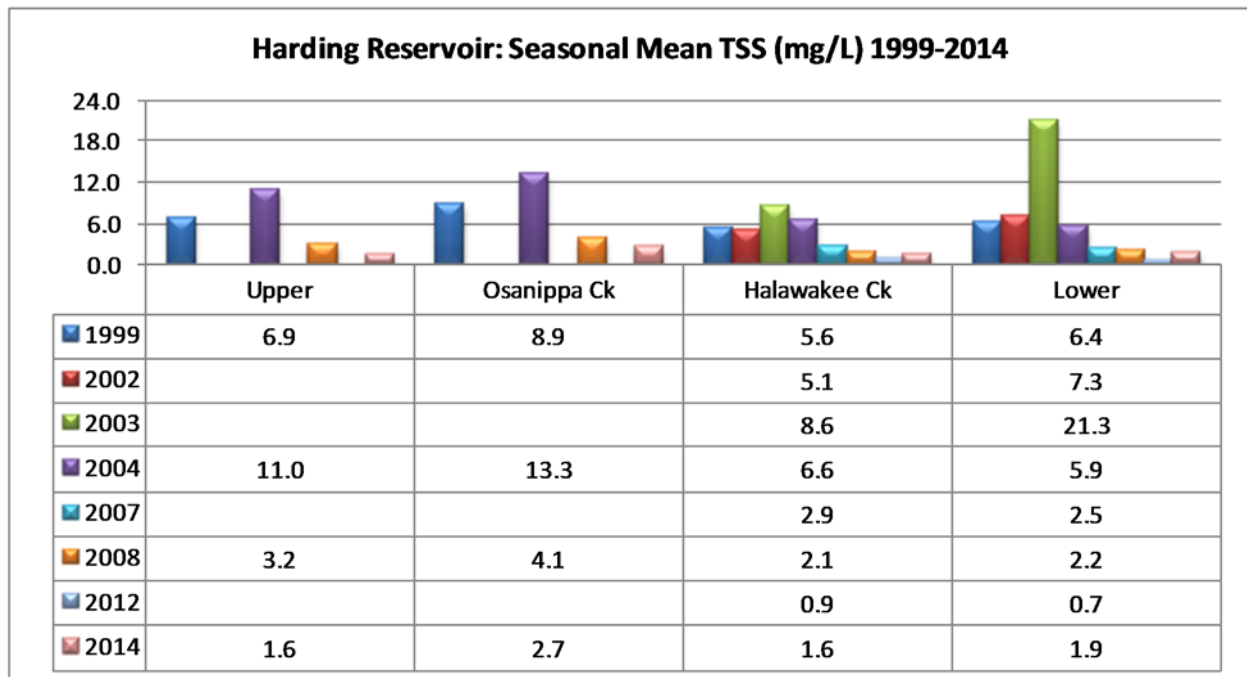
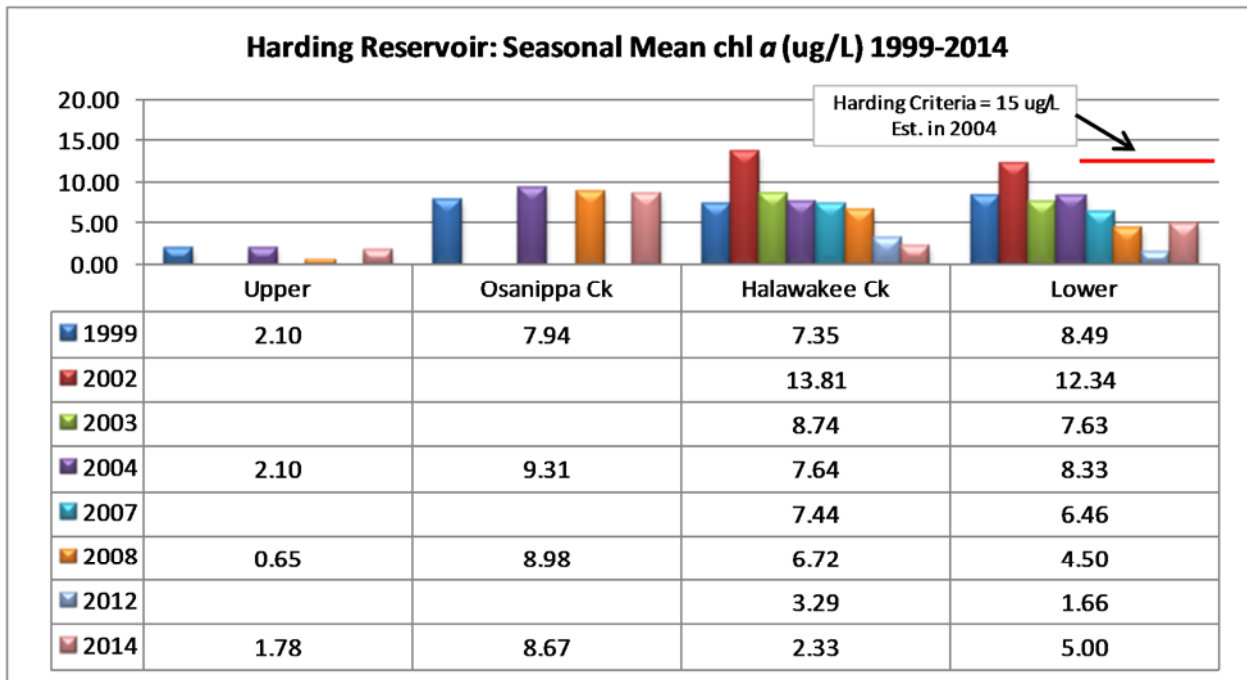


Figure 4. Monthly TN concentrations measured in Harding Reservoir, April-October 2014 vs. average monthly discharge. Monthly discharge acquired from USACE at West Point Dam. Each bar graph depicts monthly changes in each station. The historic mean (1990-2014) and min/max ranges are also displayed for comparison. The “n” value equals the number of datapoints included in the monthly historic calculations.

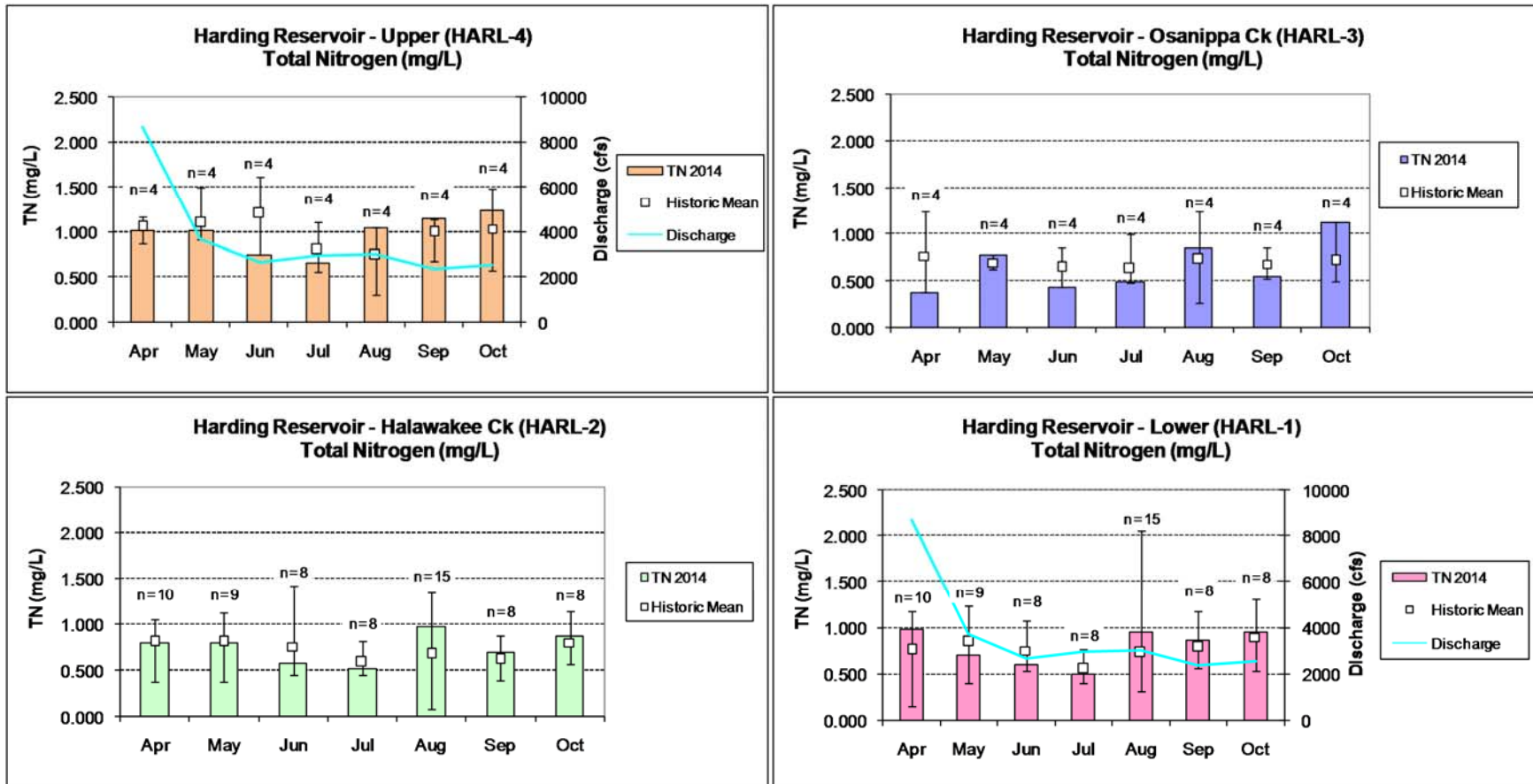


Figure 5. Monthly TP concentrations measured in Harding Reservoir, April-October 2014 vs. average monthly discharge. Monthly discharge acquired from USACE at West Point Dam. Each bar graph depicts monthly changes in each station. The historic mean (1990-2014) and min/max ranges are also displayed for comparison. The “n” value equals the number of datapoints included in the monthly historic calculations.

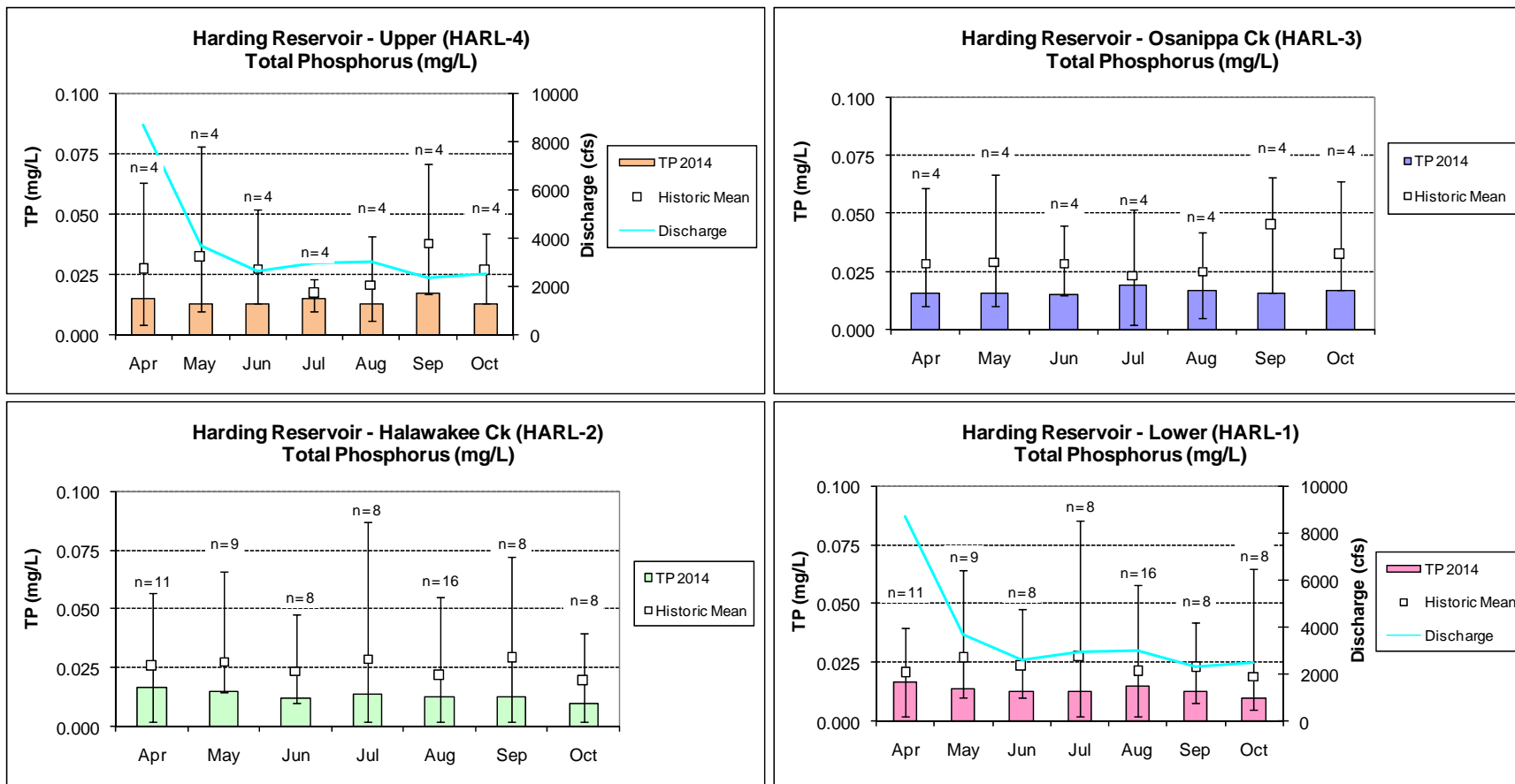


Figure 6. Monthly chl *a* concentrations measured in Harding Reservoir, April-October 2014 vs. average monthly discharge. Monthly discharge acquired from USACE at West Point Dam. Each bar graph depicts monthly changes in each station. The historic mean (1990-2014) and min/max ranges are also displayed for comparison. The “n” value equals the number of datapoints included in the monthly historic calculations. The scale of the vertical axis of the upper station is smaller than the other two stations to allow visibility of the results.

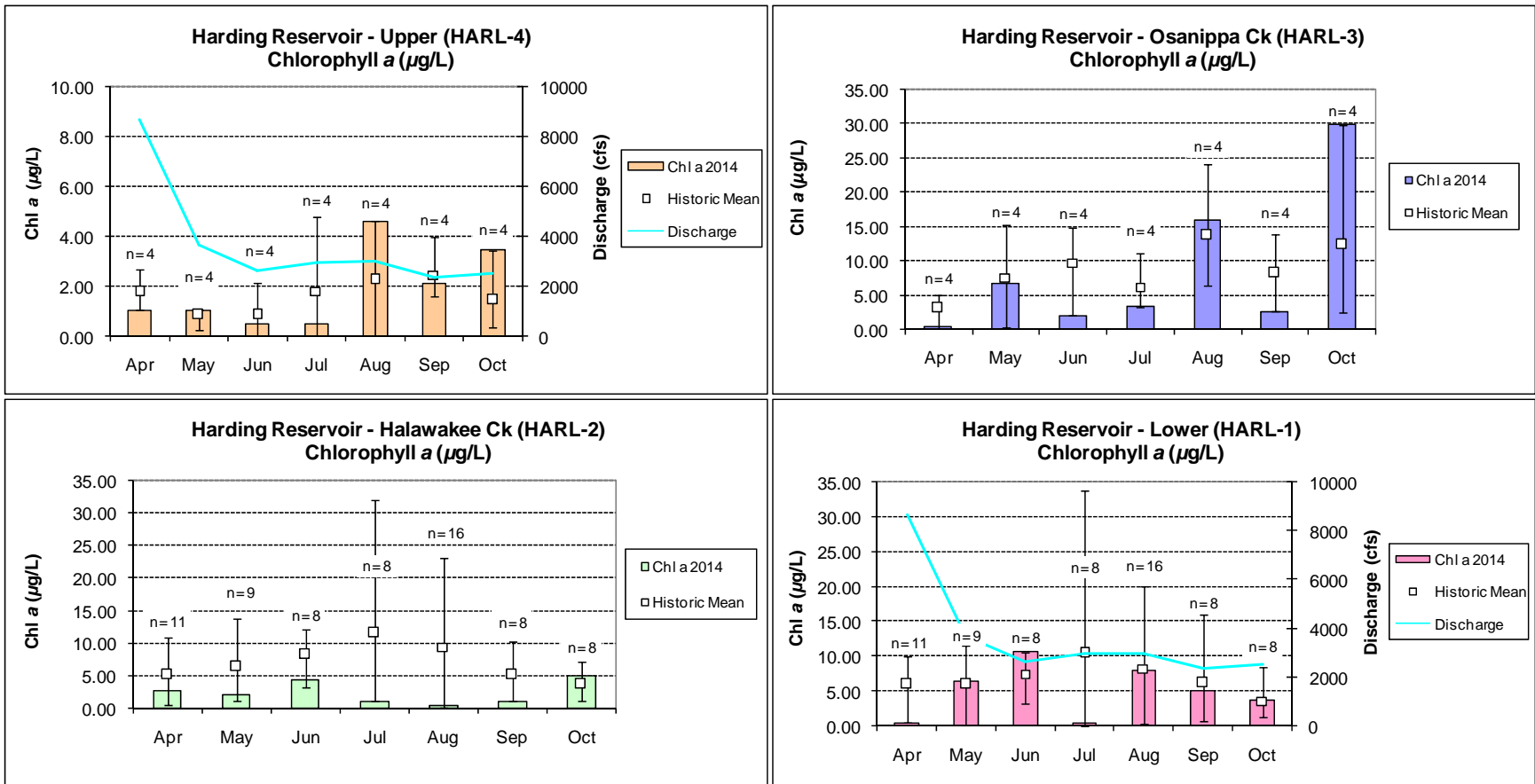


Figure 7. Monthly TSS concentrations measured in Harding Reservoir, April-October 2014 vs. average monthly discharge. Monthly discharge acquired from USACE at West Point Dam. Each bar graph depicts monthly changes in each station. The historic mean (1990-2014) and min/max range are also displayed for comparison. The “n” value equals the number of datapoints included in the monthly historic calculations.

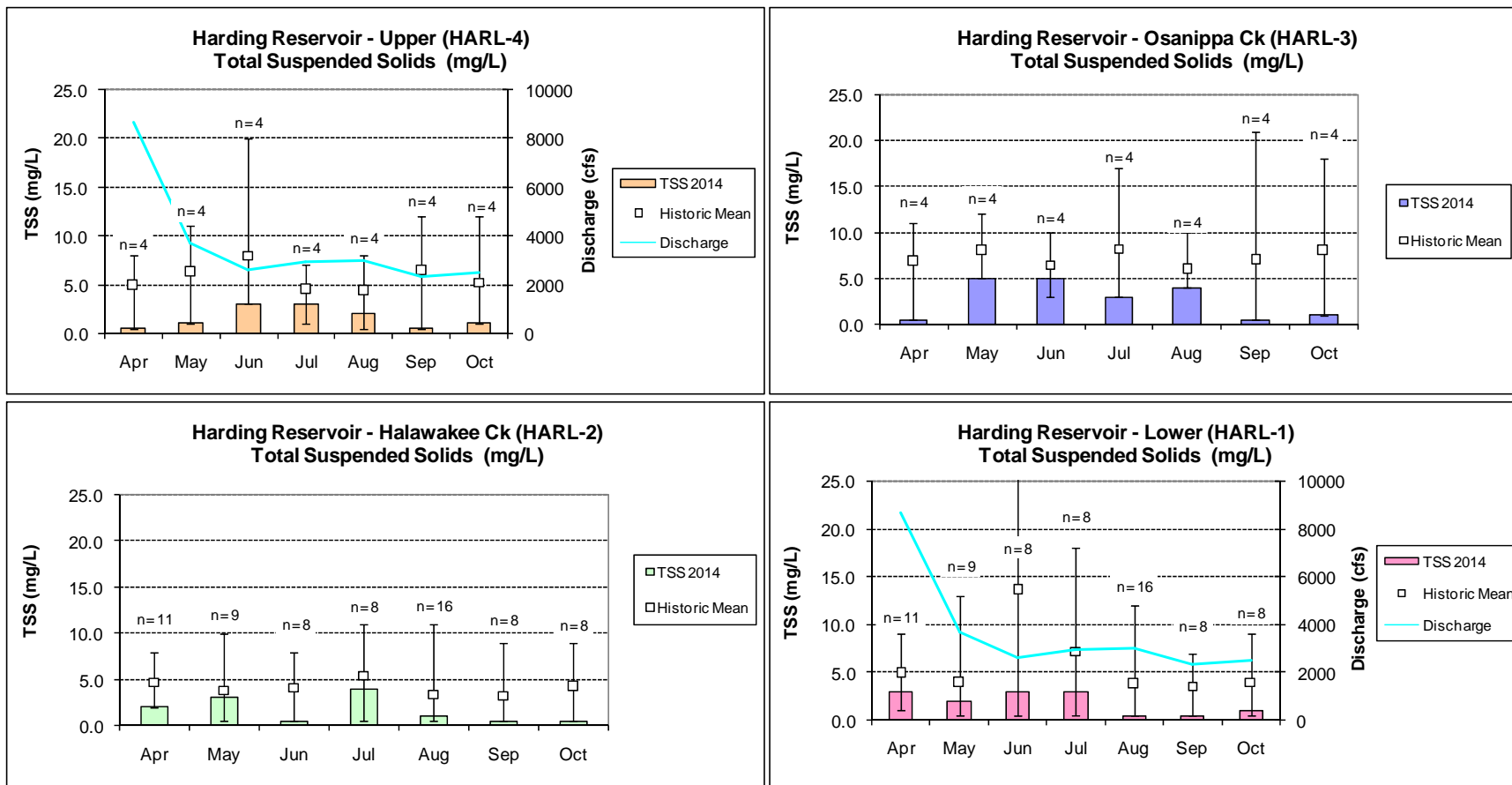


Table 2. Algal growth potential test results, Harding Reservoir, 1999-2014 (expressed as mean Maximum Standing Crop (MSC) dry weights of *Selenastrum capricornutum* in mg/L) and limiting nutrient status. MSC values below 5 mg/L are considered to be protective in reservoirs and lakes; values below 20 mg/L MSC are considered protective of flowing streams and rivers (Raschke and Schultz 1987).

	Upper		Osanippa Ck		Halawakee Cr		Lower	
June 1999	5.18	Phosphorus	6.99	Phosphorus	1.57	Phosphorus	1.34	Phosphorus
July 1999	6.14	Phosphorus	2.74	Phosphorus	3.43	Phosphorus	2.48	Phosphorus
August 1999	2.62	Phosphorus	1.74	Phosphorus	1.51	Phosphorus	1.84	Phosphorus
August 2004	5.27	Phosphorus	---	---	2.47	Phosphorus	2.36	Phosphorus
August 2008	---	---	---	---	3.93	Phosphorus	3.59	Phosphorus
August 2014	---	---	---	---	5.53	Phosphorus	4.39	Phosphorus

Figure 8. Monthly DO concentrations at 1.5 m (5 ft) for Harding Reservoir stations collected April-October 2014. ADEM Water Quality Criteria pertaining to reservoir waters require a DO concentration of 5.0 mg/L at this depth (ADEM 2010).

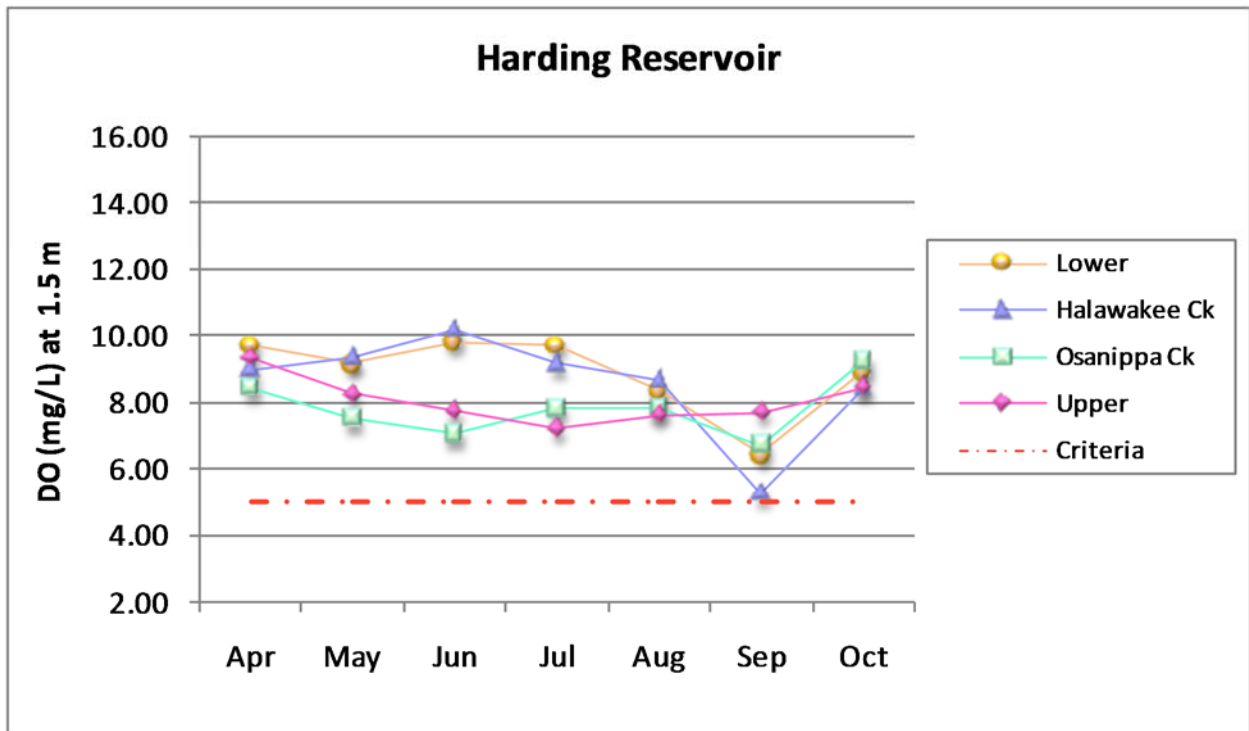


Figure 9. Monthly depth profiles of dissolved oxygen, temperature, and conductivity in the lower Harding Reservoir station, April-October 2014.

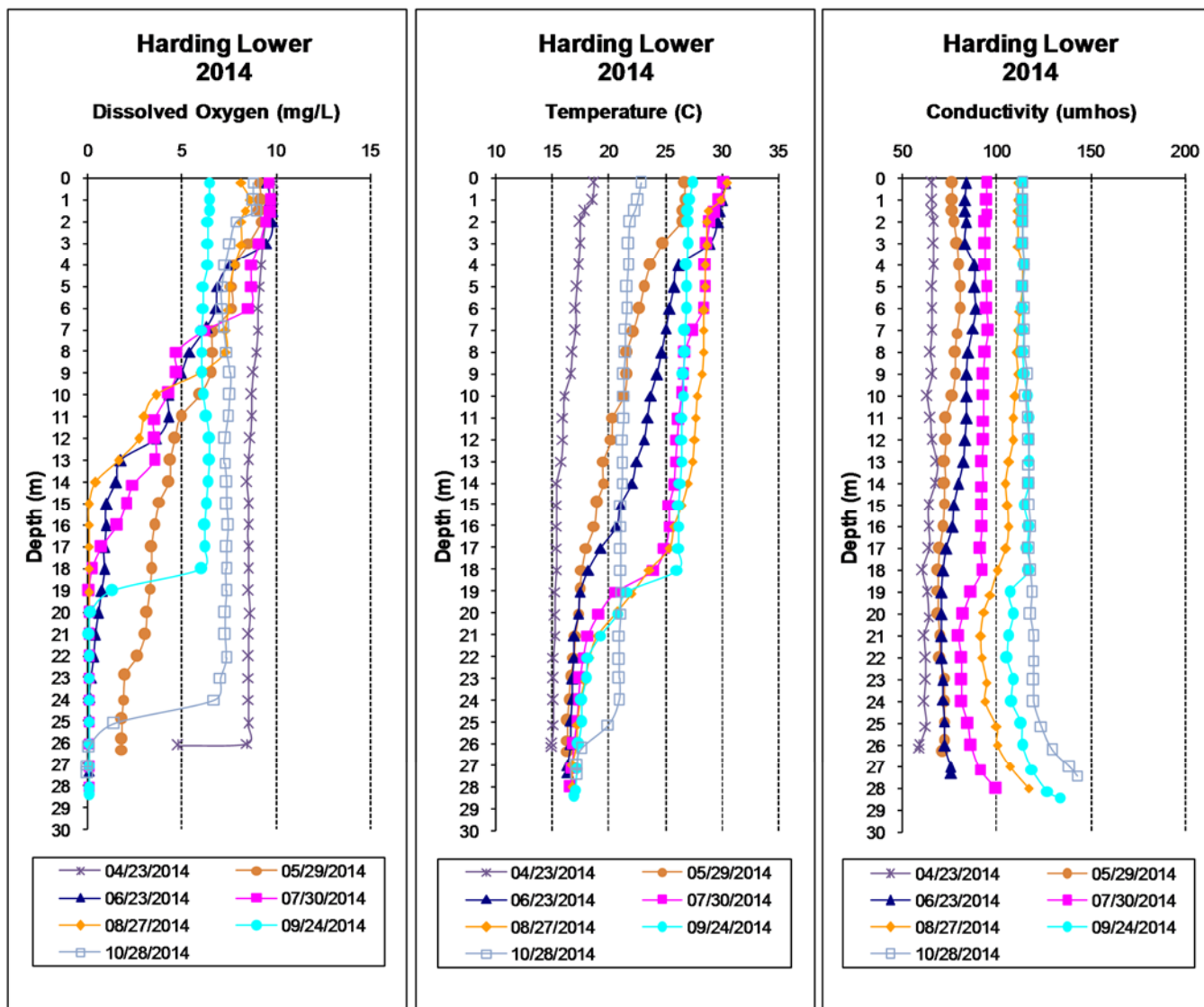


Figure 10. Monthly depth profiles of dissolved oxygen, temperature, and conductivity in the Halawakee Ck station, April-October 2014.

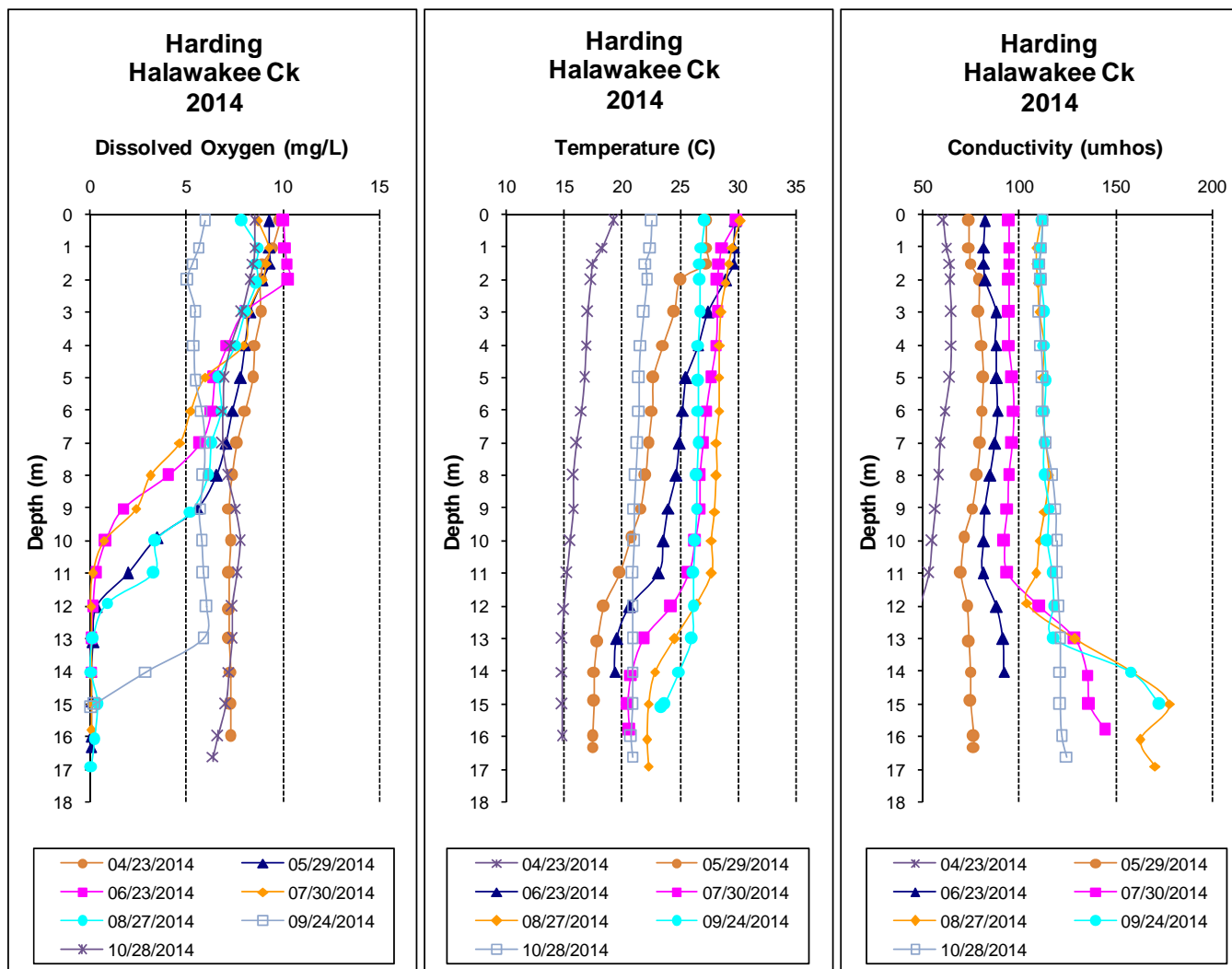
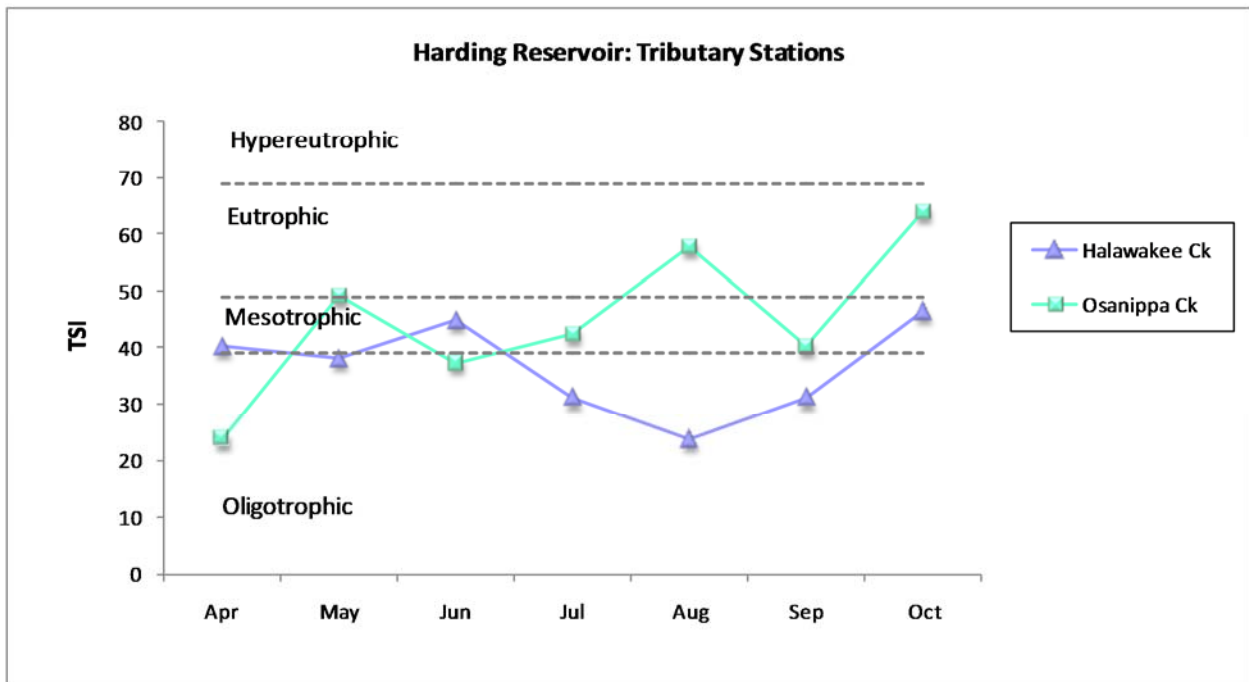
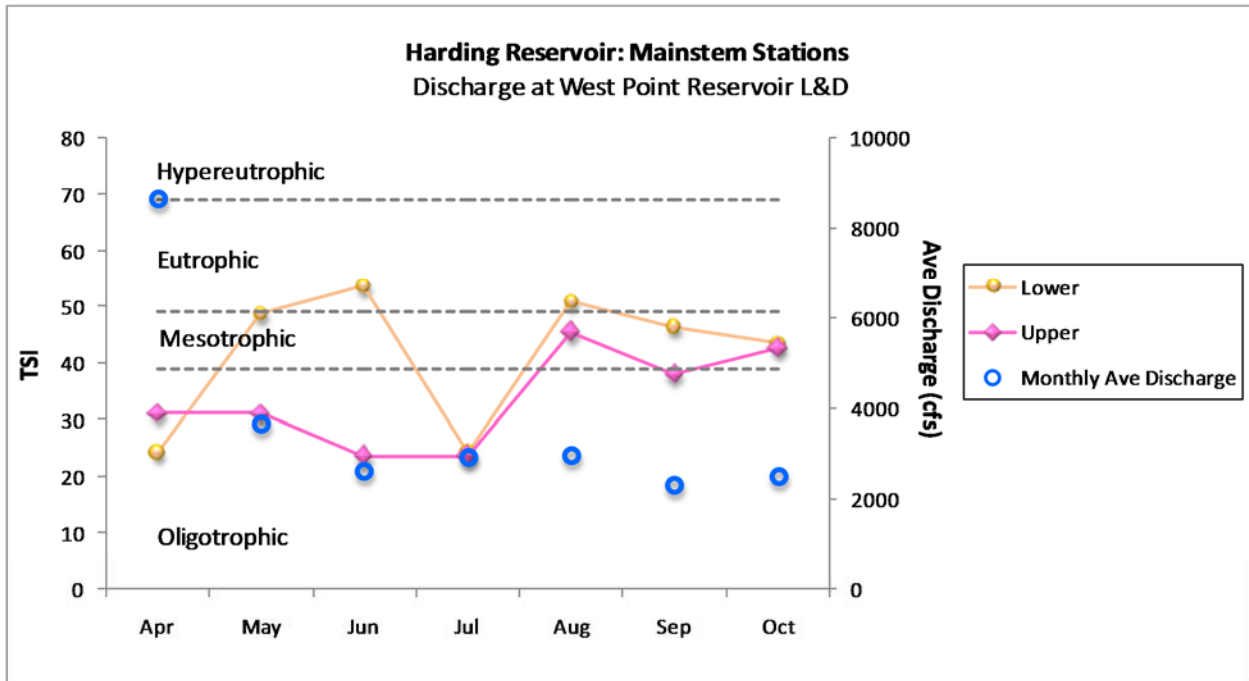


Figure 11. Monthly TSI values, April-October 2014, calculated for mainstem and tributary Harding Reservoir stations using chl *a* concentrations and Carlson's Trophic State Index calculation. Monthly discharge acquired from USACE at West Point Lock and Dam.



REFERENCES

- ADEM. 2014. Standard Operating Procedures Series #2000, Alabama Department of Environmental Management (ADEM), Montgomery, AL.
- ADEM. 2013. Quality Management Plan (QMP) for the Alabama Department of Environmental Management (ADEM), Montgomery, AL. 58 pp.
- ADEM. 2012. Quality Assurance Project Plan (QAPP) for Surface Water Quality Monitoring in Alabama. Alabama Department of Environmental Management (ADEM), Montgomery, AL. 78 pp.
- ADEM. 2012. State of Alabama Water Quality Monitoring Strategy June 19, 2012. Alabama Department of Environmental Management (ADEM), Montgomery, AL. 88 pp. <http://www.adem.alabama.gov/programs/water/wqsurvey/2012WQMonitoringStrategy>
- Alabama Department of Environmental Management Water Division (ADEM Admin. Code R. 335-6-10-.09). 2010. Specific Water Quality Criteria. Water Quality Program. Chapter 10. Volume 1. Division 335-6.
- Alabama Department of Environmental Management Water Division (ADEM Admin. Code R. 335-6-10-.11). 2010. Water Quality Criteria Applicable to Specific Lakes. Water Quality Program. Chapter 10. Volume 1. Division 335-6.
- Carlson, R.E. 1977. A trophic state index. *Limnology and Oceanography*. 22(2):361-369.
- Raschke, R.L. and D.A. Schultz. 1987. The use of the algal growth potential test for data assessment. *Journal of Water Pollution Control Federation* 59(4):222-227.

APPENDIX

Appendix Table 1. Summary of Harding Reservoir water quality data collected April-October, 2014. Minimum (min) and maximum (max) values calculated using minimum detection limits when results were less than this value. Median (med), mean, and standard deviation (SD) values were calculated by multiplying the MDL by 0.5 when results were less than this value.

Station	Parameter	N	Min	Max	Med	Mean	SD
HARL-1	Physical						
	Turbidity (NTU)	7	1.7	13.6	2.7	4.3	4.2
	Total Dissolved Solids (mg/L)	7	38.0	95.0	60.0	60.6	19.4
	Total Suspended Solids (mg/L)	7	< 1.0	3.0	2.0	1.9	1.2
	Hardness (mg/L)	4	16.6	27.4	24.0	23.0	5.0
	Alkalinity (mg/L)	7	15.8	29.0	27.1	25.1	4.8
	Photic Zone (m)	7	2.44	6.81	5.47	5.01	1.43
	Secchi (m)	7	0.86	2.26	1.90	1.78	0.45
	Bottom Depth (m)	7	26.00	28.40	27.40	27.36	0.88
	Chemical						
	Ammonia Nitrogen (mg/L)	7	< 0.006	0.010	0.003	0.004	0.001
	Nitrate+Nitrite Nitrogen (mg/L)	7	0.266	0.708	0.502	0.495	0.130
	Total Kjeldahl Nitrogen (mg/L)	7	0.156	0.454	0.248	0.299	0.120
	Total Nitrogen (mg/L)	7	0.493	0.978	0.869	0.794	0.195
	Dissolved Reactive Phosphorus (mg/L) ^j	7	0.003	0.007	0.004	0.004	0.001
	Total Phosphorus (mg/L)	7	0.010	0.017	0.013	0.014	0.002
	CBOD-5 (mg/L)	7	< 2.0	2.0	1.0	1.0	0.0
	Chlorides (mg/L)	7	5.0	10.8	7.8	8.0	2.2
	Biological						
	Chlorophyll a (ug/L)	7	0.53	10.68	5.07	5.00	3.76
E. coli (col/100mL) ^j	3	1	5	1	2	2	
HARL-2	Physical						
	Turbidity (NTU)	7	1.8	17.2	3.0	4.8	5.5
	Total Dissolved Solids (mg/L)	7	32.0	93.0	67.0	61.6	22.9
	Total Suspended Solids (mg/L)	7	< 1.0	4.0	1.0	1.6	1.4
	Hardness (mg/L)	4	15.4	27.6	25.0	23.3	5.6
	Alkalinity (mg/L)	7	15.6	30.0	27.7	25.3	5.0
	Photic Zone (m)	7	2.27	6.62	5.00	4.70	1.47
	Secchi (m)	7	0.93	2.68	1.97	1.84	0.58
	Bottom Depth (m)	7	14.00	16.90	16.00	15.81	0.99
	Chemical						
	Ammonia Nitrogen (mg/L)	7	< 0.006	0.033	0.003	0.008	0.011
	Nitrate+Nitrite Nitrogen (mg/L)	7	0.275	0.625	0.455	0.437	0.108
	Total Kjeldahl Nitrogen (mg/L)	7	0.162	0.495	0.323	0.303	0.106
	Total Nitrogen (mg/L)	7	0.508	0.964	0.787	0.741	0.160
	Dissolved Reactive Phosphorus (mg/L) ^j	7	0.003	0.005	0.003	0.004	0.001
	Total Phosphorus (mg/L)	7	0.010	0.017	0.013	0.013	0.002
	CBOD-5 (mg/L)	7	< 2.0	2.0	1.0	1.0	0.0
	Chlorides (mg/L)	7	4.6	10.4	7.8	7.7	2.2
	Biological						
	Chlorophyll a (ug/L)	7	< 0.10	5.07	2.14	2.33	1.82
E. coli (col/100mL) ^j	3	< 1	2	1	1	1	

Station	Parameter	N	Min	Max	Med	Mean	SD
HARL-3	Physical						
	Turbidity (NTU)	7	4.4	20.5	7.3	8.8	5.4
	Total Dissolved Solids (mg/L)	7	8.0	91.0	60.0	56.6	26.3
	Total Suspended Solids (mg/L)	7	< 1.0	5.0	3.0	2.7	2.0
	Hardness (mg/L)	4	14.3	28.1	24.8	23.0	6.0
	Alkalinity (mg/L)	7	16.2	30.4	28.3	26.5	4.9
	Photic Zone (m)	7	2.06	4.11	2.50	2.63	0.67
	Secchi (m)	7	0.75	1.74	0.95	1.00	0.34
	Bottom Depth (m)	7	4.90	5.50	5.30	5.19	0.37
	Chemical						
	Ammonia Nitrogen (mg/L)	7	< 0.006	0.010	0.003	0.004	0.001
	Nitrate+Nitrite Nitrogen (mg/L)	7	0.113	0.824	0.307	0.341	0.226
	Total Kjeldahl Nitrogen (mg/L)	7	0.128	0.531	0.280	0.315	0.133
	Total Nitrogen (mg/L)	7	0.378	1.124	0.541	0.657	0.270
	Dissolved Reactive Phosphorus (mg/L) ^J	7	0.003	0.005	0.005	0.004	0.001
	Total Phosphorus (mg/L)	7	0.015	0.019	0.016	0.017	0.001
	CBOD-5 (mg/L)	7	< 2.0	2.0	1.0	1.0	0.0
	Chlorides (mg/L)	7	2.0	11.2	6.6	6.3	3.0
	Biological						
	Chlorophyll a (ug/L)	7	< 0.10	29.90	3.34	8.67	10.74
E. coli (col/100mL) ^J	3	8	15	11	11	3	
HARL-4	Physical						
	Turbidity (NTU)	7	2.5	9.0	3.4	4.0	2.2
	Total Dissolved Solids (mg/L)	7	40.0	89.0	64.0	60.6	16.3
	Total Suspended Solids (mg/L)	7	< 1.0	3.0	1.0	1.6	1.1
	Hardness (mg/L)	4	16.9	29.4	23.9	23.5	5.6
	Alkalinity (mg/L)	7	16.9	29.8	27.6	25.7	4.7
	Photic Zone (m)	7	2.60	3.60	3.10	3.10	0.37
	Secchi (m)	7	1.20	2.33	2.03	1.87	0.42
	Bottom Depth (m)	7	2.90	3.60	3.10	3.10	0.37
	Chemical						
	Ammonia Nitrogen (mg/L)	7	< 0.006	0.063	0.005	0.023	0.027
	Nitrate+Nitrite Nitrogen (mg/L)	7	0.369	1.027	0.598	0.629	0.199
	Total Kjeldahl Nitrogen (mg/L)	7	0.154	0.605	0.362	0.353	0.153
	Total Nitrogen (mg/L)	7	0.659	1.238	1.019	0.982	0.206
	Dissolved Reactive Phosphorus (mg/L) ^J	7	< 0.003	0.006	0.004	0.004	0.002
	Total Phosphorus (mg/L)	7	0.013	0.017	0.013	0.014	0.002
	CBOD-5 (mg/L)	7	< 2.0	2.0	1.0	1.0	0.0
	Chlorides (mg/L)	7	6.4	12.4	8.7	8.8	2.4
	Biological						
	Chlorophyll a (ug/L)	7	< 0.10	4.63	1.07	1.78	1.74
E. coli (col/100mL) ^J	3	22	47	25	31	14	

J=one or more of the values provided are estimated; < = Actual value is less than the detection limit